Dimensionality reduction of the many-body problem using coupled-cluster subsystem flow equations: Classical and quantum computing perspective

Karol Kowalski*

Physical Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99354, USA

(Received 26 April 2021; revised 15 August 2021; accepted 16 August 2021; published 7 September 2021)

We discuss reduced-scaling strategies employing the recently introduced subsystem embedding subalgebra (SES) coupled-cluster (CC) formalism to describe quantum many-body systems. These strategies utilize properties of the SES CC formulations where the equations describing certain classes of subsystems can be integrated into computational flows composed of coupled eigenvalue problems of reduced dimensionality. Additionally, these flows can be determined at the level of the CC ansatz by the inclusion of selected classes of cluster amplitudes, which define the wave-function "memory" of possible partitioning of the many-body system into constituent subsystems. One of the possible ways of solving these coupled problems is through implementing procedures where the information is passed between the subsystems in a self-consistent manner. As a special case we consider local flow formulations where the local character of correlation effects can be closely related to the properties of subsystem embedding subalgebras employing a localized molecular basis. We also generalize flow equations to the time domain and to downfolding methods utilizing a double-exponential unitary CC ansatz, where the reduced dimensionality of constituent subproblems offers a possibility of efficient utilization of limited quantum resources in modeling realistic systems.

DOI: 10.1103/PhysRevA.104.032804

I. INTRODUCTION

Over the past few decades, the coupled-cluster (CC) theory [1–12] has evolved into one of the most accurate and dominant theories to describe various quantum systems across spatial scales, hence addressing fundamental problems in many-body physics [6,13–22] (for an excellent review of these developments see Ref. [23]), quantum field theory [24–28], quantum hydrodynamics [29,30], nuclear structure theory [31–33], quantum chemistry [34–41], and material sciences [42–52]. Many strengths of the single-reference (SR) CC formalism or coupled-cluster methods originate in the exponential parametrization of the ground-state wave function $|\Psi\rangle$,

$$|\Psi\rangle = e^{T}|\Phi\rangle, \tag{1}$$

where T and $|\Phi\rangle$ correspond to the cluster operator and reference function. For example, one can define a hierarchy of CC approximations by increasing the rank of excitations included in the cluster operator. Another important feature of CC theory stems from the linked cluster theorem [53,54], which allows one to build efficient noniterative algorithms for higher-order excitations. When both approximation techniques are combined, one can define efficient and accurate methodologies that can deliver a high level of accuracy in simulations of chemical systems [55–70]. More recently, CC methodologies have been integrated with stochastic Monte Carlo methods probing configurational space and leading to near full-configuration-interaction accuracy of calculated energies [41,71,72]. However, the applicability of canonical formulations of these theories (especially to large molecular systems) may be limited by their steep (polynomial) numerical scaling. Unfortunately, even with rapid progress in computational technologies, problems with data locality, data movement, and polynomial scaling of high-rank canonical CC methods lead to insurmountable numerical problems in modeling large systems. Although impressive progress has been achieved in the development of local approaches for CC pair theories [73–84], extension of these methods to include higher-rank excitations may still requires significant theoretical effort. Some of these problems may be addressed by using the mature form of quantum computers; however, due to the limited size of existing quantum registers, this can only be achieved by developing flexible algorithms to reduce the dimensionality of quantum problem. These problems have been scrutinized only recently, including local and reduced-dimensionality quantum computing formulations [85–93].

In the light of the above discussion, new high-accuracy CC-based techniques for re-representing the quantum many-body problem in reduced-dimensionality spaces are in high demand. Especially interesting are approaches where the original high-dimensionality problem can be recast in the form of coupled low-dimensionality problems. Also, for quantum computing algorithms, the dimensions of subproblems coupled into a flow should be tunable to the available quantum computing resources to provide, by controlling the number of parameters processed at a given time, optimal utilization of computational tools such as variational quantum eigensolvers (VQEs) [94–103]. Additionally, recent strides made in the development of unitary CC formulations [104–110], such as their disentangled [111] and adaptive VQE variants [112], and qubit representations of unitary

*karol.kowalski@pnnl.gov

CC methods and exact quadratic truncation of the Baker-Campbell-Hausdorff expansion [113,114] provide tools not only for next-generation VQE-type solvers but also for unlocking properties of unitary CC formulations needed in the analysis of reduced-dimensionality methods [85,86].

In this paper we focus on the further extension of recently introduced CC subsystem embedding subalgebra (SES) CC [115] and double-unitary CC (DUCC) downfolding methods [85,86]. In a natural way, these methods allow one to calculate ground-state energies as eigenvalues of effective Hamiltonians in predefined active spaces describing subsystems of the whole quantum system. Since in the construction of effective Hamiltonians all out-of-active-space correlation effects are integrated out, the CC downfolding procedures can be viewed as natural renormalization techniques. The flow equations for the single-reference SES CC case [115] utilize this property for each active space involved in the flow and for this reason can be considered as formulations that have "memory" of each subsystem involved in the flow. Specifically, each subsystem can be characterized by the corresponding effective Hamiltonian that includes interactions with other subsystems. We will illustrate the ability of these approaches to capture the complicated correlation effect and dynamics of the system, through traversing large subspaces of the entire Hilbert space without an unnecessary increase of the size of the numerical problem to be solved at a given time in the flow algorithm. We will also show that it is possible to define flows that decouple the representation of the Schrödinger equation in large subspaces of the Hilbert (often defined by net dimensions beyond classical or quantum computing capabilities) into smaller problems that are numerically tractable.

This paper discusses extensions of the CC flow formalism. Specifically, it includes the following.

(i) The arbitrary CC flow equations are explicitly proven to be equivalent to standard CC equations with a specific form of cluster operator.

(ii) The CC flow algorithms are extended to the time domain. In analogy to the previous point, we also show that time-dependent CC flow equations are equivalent to the time-dependent CC equations with a specific form of the cluster operator.

(iii) The CC flow equations are extended to the localized basis set. In this case, we demonstrate that the CC flow equations provide a rigorous definition (at the level of effective Hamiltonians) of the so-called electron pair. This type of CC flow in a natural way defines density matrices and higher-rank excitations for local CC formulations. The introduction of higher-rank excitations is a well-known problem faced by local formulations of CC methods.

(iv) The CC flows are extended to DUCC formulations. We discuss these flows from the point of view of quantum computing applications, where DUCC flows can be used to probe configurational spaces of the dimensions beyond dimensions treated by existing quantum algorithms. Additionally, DUCC flow for localized orbitals naturally addresses Hamiltonian qubit encoding and controlling antisymmetry of the corresponding wave function.

Since the operator algebra involved in the unitary CC methods is noncommutative, extending canonical SES CC flows to the DUCC case requires the utilization of certain approximations. To this end, we will consider methods based on the use of approximate Trotter formulas.

We will also discuss the difference between two computational strategies involving (a) standard approximations based on the selection of cluster amplitudes and treating them simultaneously (or globally) in numerical implementations and (b) flow equations where only a portion of selected amplitudes are processed at the time. While the former computing approach can take advantage of parallel classical architectures, the latter is ideally suited for noisy intermediate-scale quantum devices, where a small subset of fermionic degrees of freedom can be effectively handled. The flow equation methods also provide a conceptual foundation for introducing certain approximation classes and eliminating possible problems with their postulatory character. We will illustrate these advantages using the example of local CC methods. For simplicity, in this paper we will focus on the CC and DUCC flow equations for closed-shell systems.

II. SUBSYSTEM EMBEDDING SUBALGEBRA CC FORMALISM: STATIONARY AND TIME-DEPENDENT FORMULATIONS

The SES CC formalism is based on the observation that the energy of CC formulations $E_{\rm CC}$, in addition to the well-known formula $\langle\Phi|e^{-T}He^{T}|\Phi\rangle$ (where H represents the many-body Hamiltonian), can be obtained through diagonalization of the whole family of effective Hamiltonians [115]. First, let us discuss the basic tenets of the SES CC formalism. In the exact wave-function limit, the maximum excitation level m included in the cluster operator T is equal to the number of correlated electrons (N) while in the approximate formulations $m \ll N$. Several typical examples are the CC single- and double-excitation (CCSD) ($m = 2$) [5], CC method with single, double, and triple excitations (CCSDT) ($m = 3$) [116–118], and CC with single, double, triple, and quadruple excitations (CCSDTQ) ($m = 4$) [119,120] methods. Using second quantization language, the T_k components of a cluster operator producing k-tuple excitations when acting on the reference function can be expressed as

$$T_k = \frac{1}{(k!)^2} \sum_{i_1,\ldots,i_k;a_1,\ldots,a_k} t^{i_1\ldots i_k}_{a_1\ldots a_k} E^{a_1\ldots a_k}_{i_1\ldots i_k}, \tag{2}$$

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 $E^{a_1\ldots a_k}_{i_1\ldots i_k}$ are defined through strings of standard creation ($a^\dagger_p$) and annihilation (a_p) operators

$$E^{a_1\ldots a_k}_{i_1\ldots i_k} = a^\dagger_{a_1}\ldots a^\dagger_{a_k} a_{i_k}\ldots a_{i_1}, \tag{3}$$

where creation and annihilation operators satisfy the anticommutation rules

$$[a_p, a_q]_+ = [a^\dagger_p, a^\dagger_q]_+ = 0, \tag{4}$$

$$[a_p, a^\dagger_q]_+ = \delta_{pq}. \tag{5}$$

The SES CC approach is based on the particle-hole formalism defined with respect to the reference function $|\Phi\rangle$, where the

quasioperators b_p and $b_p^\dagger$ are defined as

$$b_p = \begin{cases} a_p & \text{if } p \in V \\ a_p^\dagger & \text{if } p \in O \end{cases} \tag{6}$$

and

$$b_p^\dagger = \begin{cases} a_p^\dagger & \text{if } p \in V \\ a_p & \text{if } p \in O, \end{cases} \tag{7}$$

where O and V designate sets of occupied and unoccupied spin orbitals, respectively. Using the particle-hole formalism, we have

$$b_p|\Phi\rangle = 0 \tag{8}$$

and

$$E^{a_1\ldots a_k}_{i_1\ldots i_k} = b^\dagger_{a_1}\ldots b^\dagger_{a_k} b^\dagger_{i_k}\ldots b^\dagger_{i_1} \tag{9}$$

(for applications of various quasiparticle representations and the Bogoliubov transformation in coupled-cluster methods see Refs. [22,121]). Additionally, the b_p ($b_q^\dagger$) operators satisfy the same anticommutation relations as a_p ($a_q^\dagger$) operators, i.e.,

$$[b_p, b_q]_+ = [b_p^\dagger, b_q^\dagger]_+ = 0, \tag{10}$$

$$[b_p, b_q^\dagger]_+ = \delta_{pq}. \tag{11}$$

The particle-hole formalism significantly simplifies the analysis of the CC equations. It is also easy to notice that all excitation operators (3) commute, i.e., for

$$E^{a_1\ldots a_k}_{i_1\ldots i_k} = a^\dagger_{a_1}\ldots a^\dagger_{a_k} a_{i_k}\ldots a_{i_1} = b^\dagger_{a_1}\ldots b^\dagger_{a_k} b^\dagger_{i_k}\ldots b^\dagger_{i_1}, \tag{12}$$

$$\begin{aligned} E^{c_1\ldots c_m}_{j_1\ldots j_m} &= a^\dagger_{c_1}\ldots a^\dagger_{c_m} a_{j_m}\ldots a_{j_1} \\ &= b^\dagger_{c_1}\ldots b^\dagger_{c_m} b^\dagger_{j_m}\ldots b^\dagger_{j_1}, \end{aligned} \tag{13}$$

we have

$$\left[E^{a_1\ldots a_k}_{i_1\ldots i_k}, E^{c_1\ldots c_m}_{j_1\ldots j_m}\right] = 0. \tag{14}$$

After substituting the ansatz (1) into the Schrödinger equation, one gets the energy-dependent form of the CC equations

$$(P+Q)He^T|\Phi\rangle = E(P+Q)e^T|\Phi\rangle, \tag{15}$$

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

$$Q = \sum_{k=1}^{m} \sum_{i_1<i_2<\cdots<i_k;a_1<a_2\cdots<a_k} \left|\Phi^{a_1\ldots a_k}_{i_1\ldots i_k}\right\rangle\left\langle\Phi^{a_1\ldots a_k}_{i_1\ldots i_k}\right|, \tag{16}$$

where

$$\left|\Phi^{a_1\ldots a_k}_{i_1\ldots i_k}\right\rangle = E^{a_1\ldots a_k}_{i_1\ldots i_k}|\Phi\rangle. \tag{17}$$

Diagrammatic analysis [10] leads to an equivalent (*at the solution*) energy-independent form of the CC equations for cluster amplitudes

$$Qe^{-T}He^T|\Phi\rangle = Q(He^T)_C|\Phi\rangle = 0 \tag{18}$$

and an energy expression

$$E = \langle\Phi|e^{-T}He^T|\Phi\rangle = \langle\Phi|(He^T)_C|\Phi\rangle, \tag{19}$$

where C designates a connected part of a given operator expression. In the forthcoming discussion, we refer to $e^{-T}He^T$ as a similarity transformed Hamiltonian $\bar{H}$.

The SES CC formalism hinges upon the notion of excitation subalgebras of algebra $\mathfrak{g}^{(N)}$ generated by $E^{a_l}_{i_l} = b^\dagger_{a_l} b_{i_l}$ operators in the particle-hole representation defined with respect to the reference $|\Phi\rangle$. As a consequence, all generators commute, i.e., $[E^{a_l}_{i_l}, E^{a_k}_{i_k}] = 0$, and algebra $\mathfrak{g}^{(N)}$ (along with all subalgebras considered here) is commutative. The SES CC formalism utilizes an important class of subalgebras of commutative $\mathfrak{g}^{(N)}$ algebra, which contains all possible excitations $E^{a_1\ldots a_m}_{i_1\ldots i_m}$ that excite electrons from a subset of active occupied orbitals (denoted by R) to a subset of active virtual orbitals (denoted by S). These subalgebras will be designated as $\mathfrak{g}^{(N)}(R,S)$. In the following discussion, we will use R and S to denote 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 denotation $\mathfrak{g}^{(N)}(x_R, y_S)$ where the numbers of active orbitals in R and S orbital sets x and y, respectively, are specified). Of special interest in building various approximations are subalgebras that include all n_v virtual orbitals ($y = n_v$); these subalgebras will be denoted by $\mathfrak{g}^{(N)}(x_R)$. As discussed in Ref. [115], configurations generated by elements of $\mathfrak{g}^{(N)}(x_R, y_S)$ along with the reference function span the complete active space (CAS) referred to as $\mathscr{C}(R,S)$ [or equivalently $\mathscr{C}(\mathfrak{g}^{(N)}(x_R, y_S))$].

Each subalgebra $\mathfrak{h} = \mathfrak{g}^{(N)}(x_R, y_S)$ induces partitioning of the cluster operator T into internal part [$T_{\rm int}(\mathfrak{h})$, or $T_{\rm int}$ for short] belonging to $\mathfrak{h}$ and external part [$T_{\rm ext}(\mathfrak{h})$, or $T_{\rm ext}$ for short] not belonging to $\mathfrak{h}$, i.e.,

$$T = T_{\rm int}(\mathfrak{h}) + T_{\rm ext}(\mathfrak{h}). \tag{20}$$

In Ref. [115] it was shown that if the two following criteria are met, then $\mathfrak{h}$ is called a subsystem embedding subalgebra for the cluster operator T: (i) The $|\Psi(\mathfrak{h})\rangle = e^{T_{\rm int}(\mathfrak{h})}|\Phi\rangle$ is characterized by the same symmetry properties as $|\Psi\rangle$ and $|\Phi\rangle$ vectors (for example, spin and spatial symmetries) and (ii) the $e^{T_{\rm int}(\mathfrak{h})}|\Phi\rangle$ ansatz generates full-configuration-interaction. expansion for the subsystem defined by the CAS corresponding to the $\mathfrak{h}$ subalgebra. For any SES $\mathfrak{h}$ we proved the equivalence of two representations of the CC equations at the solution: (i) standard,

$$\langle\Phi|\bar{H}|\Phi\rangle = E, \tag{21}$$

$$Q_{\rm int}\bar{H}\Phi\rangle = 0, \tag{22}$$

$$Q_{\rm ext}\bar{H}|\Phi\rangle = 0, \tag{23}$$

and (ii) hybrid,

$$(P+Q_{\rm int})\bar{H}_{\rm ext}e^{T_{\rm int}}|\Phi\rangle = E(P+Q_{\rm int})e^{T_{\rm int}}|\Phi\rangle, \tag{24}$$

$$Q_{\rm ext}\bar{H}|\Phi\rangle = 0. \tag{25}$$

Here

$$\bar{H}_{\rm ext} = e^{-T_{\rm ext}}He^{T_{\rm ext}} \tag{26}$$

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

$$Q = Q_{\rm int} + Q_{\rm ext}. \tag{27}$$

The above equivalence shows that the CC energy can be calculated by diagonalizing the non-Hermitian effective Hamiltonian $H^{\rm eff}$ defined as

$$H^{\rm eff} = (P + Q_{\rm int})\bar{H}_{\rm ext}(P + Q_{\rm int}) \tag{28}$$

in the complete active space corresponding to *any* SES of the CC formulation defined by the cluster operator T, i.e.,

$$H^{\rm eff}(\mathfrak{h})e^{T_{\rm int}(\mathfrak{h})}|\Phi\rangle = Ee^{T_{\rm int}(\mathfrak{h})}|\Phi\rangle \tag{29}$$

for all SESs $\mathfrak{h}$. Although the idea of effective Hamiltonians has been intensively explored in the past in many areas of physics and chemistry (see Refs. [122–153]), the SES CC formalism enables one to build effective Hamiltonians using single-reference formulations. Moreover, it is an inherent feature of the single-reference CC ansatz, which unlike the multireference formulations does not assume that the wave operator acts on the multidimensional model space and where the corresponding effective Hamiltonian is diagonalized (as an example see the Bloch wave operator formalism). We also believe that Eq. (29) may be an interesting contribution from the point of view of recently explored non-Hermitian extensions of quantum mechanics [154–159].

In contrast to the energy-dependent representation of the CC equation (15), Eq. (29) represents true eigenvalue problems corresponding to the same eigenvalue E and $e^{T_{\rm int}(\mathfrak{h})}|\Phi\rangle$ as eigenvectors. One should also notice that (i) the non-CAS-related CC wave-function components (here referred to as external degrees of freedom) are integrated out and encapsulated in the form of $H^{\rm eff}$ and (ii) the internal part of the wave function $e^{T_{\rm int}}|\Phi\rangle$ is fully determined by diagonalization of $H^{\rm eff}$ in the corresponding CAS. Separation of external degrees of freedom in the effective Hamiltonians is a desired feature, especially for building its reduced-dimensionality representation for quantum computing (QC). However, a factor that impedes the use of SES CC effective Hamiltonians in quantum computing is their non-Hermitian character. It is also worth mentioning that various CC approximations are characterized by various SESs, which is a unique characteristic of each standard CC approximation. For example, for the restricted Hartree-Fock CC formulations $\mathfrak{g}^{(N)}(1_R, y_S)$ and $\mathfrak{g}^{(N)}(2_R, y_S)$ are SESs for CCSD and CCSDTQ approximations [one should also notice that the SES for the lower-rank CC approximation is also a SES of higher-rank CC approximations, i.e., $\mathfrak{g}^{(N)}(1_R, y_S)$ is also a SES for the CCSDTQ approach].

Properties of SES-induced eigenvalue problems (29) can also be utilized to design new CC approximations based on various amplitude selection processes and recasting CC equations in a different form, which offer interesting advantages, especially in the way corresponding equations are solved. This fact can be illustrated using the example of the flow introduced in Ref. [115] (see also Fig. 1). For now (without loss of generality) we will focus on special flow involving computational blocks corresponding to $\mathfrak{g}^{(N)}(2_R)$ subalgebras. While the CCSD equations cannot be represented as a union of equations corresponding to Eq. (29) for various CCSD's SESs $\mathfrak{g}^{(N)}(1_R, y_S)$ (there are no SESs in the CCSD case that would embrace doubly excited amplitudes t^{ij}_{ab} where spin orbitals i and j correspond to distinct orbitals), there exist formalisms which can probe a significant portion of Hilbert space and are defined by the set of equations that correspond to a union of nonsymmetric eigenvalue problems of the type (29) for various SESs. For example, the self-consistent subalgebra flow (SCSAF)–CCSD(2) approach (where 2 refers to the type of SES) of Ref. [115] uses the cluster operator T defined as

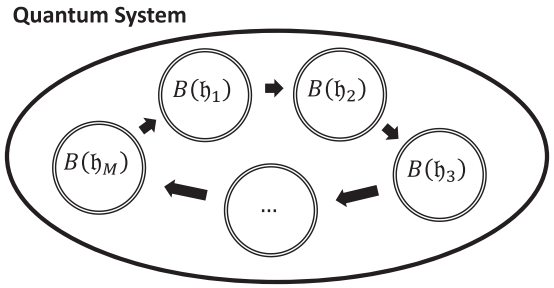

FIG. 1. Schematic representation of the CC flow. The entire quantum system can be probed with various SES eigenvalue problems (29) schematically represented here as $B(\mathfrak{h}_i)$. These computational blocks can be coupled into the flow, where information is passed between various computational blocks $B(\mathfrak{h}_i)$. Subject to the choice of particular classes of SESs defining the flow, the CC flow can probe or traverse a large subspace of the entire Hilbert space.

$$T \simeq T_1 + T_2 + \sum_I T_{{\rm int},3}\left(\mathfrak{g}^{(N)}(2_{R_I})\right) + \sum_I T_{{\rm int},4}\left(\mathfrak{g}^{(N)}(2_{R_I})\right), \tag{30}$$

where T_1 and T_2 are singly and doubly excited cluster operators and $T_{{\rm int},3}(\mathfrak{g}^{(N)}(2_{R_I}))$ and $T_{{\rm int},4}(\mathfrak{g}^{(N)}(2_{R_I}))$ contain triple and quadruple excitations corresponding to SES $\mathfrak{g}^{(N)}(2_{R_I})$. Summation over I in (30) runs over all possible SESs $\mathfrak{g}^{(N)}(2_R)$. It can be shown (see Appendix A) that in this case, the *global* set of CC equations

$$Q(e^{-T}He^{T})|\Phi\rangle = 0, \tag{31}$$

where all equations are processed simultaneously in the iterative process of finding the solution, can be recast (at the CC solution) in the form of coupled equations (29) of the form

$$H^{\rm eff}(\mathfrak{h})e^{T_{\rm int}(\mathfrak{h})}|\Phi\rangle = Ee^{T_{\rm int}(\mathfrak{h})}|\Phi\rangle \,\forall\, \mathfrak{h} = \mathfrak{g}^{(N)}\left(2_{R_I}\right). \tag{32}$$

As shown in Fig. 2, the solution process of Eq. (31) can be organized in the form of flow where the algebraic form of each computational blocks $B(\mathfrak{g}^{(N)}(2_{R_I}))$ represents an eigenvalue problem (29) for subalgebra $\mathfrak{g}^{(N)}(2_{R_I})$. In Fig. 2(a) we represent flow where particular computational blocks $B(\mathfrak{g}^{(N)}(2_{R_I}))$ are communicating in series. For this purpose, we first establish an ordering of active spaces defined by $\mathfrak{g}^{(N)}(2_{R_I})$, in a way that reflects their importance (for example, the first active space contains the most important effects related to the sought electronic state). Then we define a protocol for passing information between $B(\mathfrak{g}^{(N)}(2_{R_I}))$

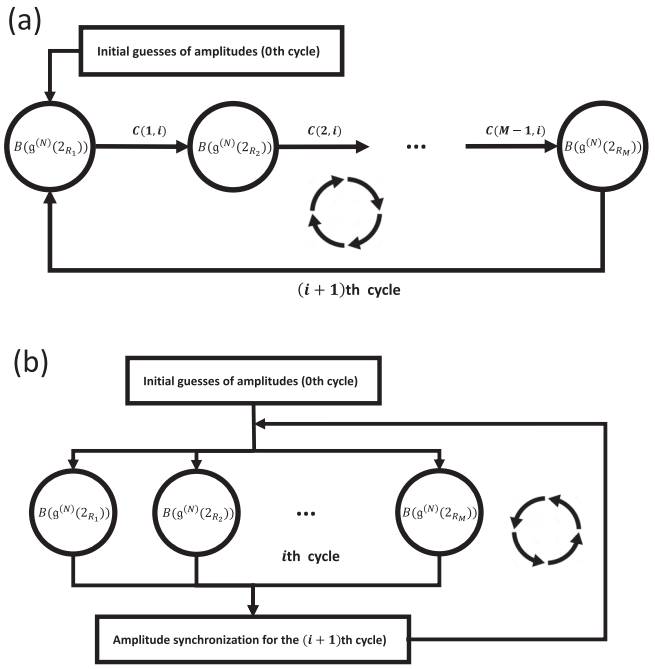

FIG. 2. Two types of CC flow formulations for $\mathfrak{g}^{(N)}(2_{R_I})$ subalgebras: (a) serial executions and (b) parallel processing of computational blocks (see the text for details).

including "shared" cluster amplitudes between various blocks. This problem is caused by the fact that two distinct SESs $\mathfrak{g}^{(N)}(2_{R_I})$ and $\mathfrak{g}^{(N)}(2_{R_J})$ can share a single orbital and effectively share all single excitations from this orbital and double excitations exciting α and β electrons from the shared orbital. This redundancy is very small compared to the total number of excitations defining distinct subalgebras $\mathfrak{g}^{(N)}(2_{R_I})$ and $\mathfrak{g}^{(N)}(2_{R_J})$. For example, there is no overlap with the largest classes of excitations corresponding to triple and quadruple excitations. At the solution, these redundancies are irrelevant because the equations for shared amplitudes are the same irrespective of the SESs eigenvalue problem (32) they are part of. To control this effect, the common pool of amplitudes obtained in the previous K steps of the ith iteration [denoted by $C(i,K)$] is passed to the $K+1$ computational block and external amplitudes [needed to construct the $\mathfrak{g}^{(N)}(2_{R_{K+1}})$ effective Hamiltonian] as well as shared amplitudes that correspond to excitations in $\mathfrak{g}^{(N)}(2_{R_{K+1}})$ enter the computational block $B(\mathfrak{g}^{(N)}(2_{R_{K+1}}))$ as known parameters. In this case, the algebraic form of $B(\mathfrak{g}^{(N)}(2_{R_{K+1}}))$ still takes the form of an eigenvalue problem of smaller size

$$\begin{aligned}
&\left(P+Q^{\mathrm{X}}_{\mathrm{int}}\right)\left[e^{-T^{\mathrm{CP}}_{\mathrm{int}}(\mathfrak{h})}H^{\mathrm{eff}}(\mathfrak{h})e^{T^{\mathrm{CP}}_{\mathrm{int}}(\mathfrak{h})}\right]e^{T^{\mathrm{X}}_{\mathrm{int}}(\mathfrak{h})}|\Phi\rangle \\
&\quad = Ee^{T^{\mathrm{X}}_{\mathrm{int}}(\mathfrak{h})}|\Phi\rangle, \\
&\mathfrak{h} = \mathfrak{g}^{(N)}\left(2_{R_{K+1}}\right), \\
&T_{\mathrm{int}}(\mathfrak{h}) = T^{\mathrm{CP}}_{\mathrm{int}}(\mathfrak{h}) + T^{\mathrm{X}}_{\mathrm{int}}(\mathfrak{h}), \quad \mathfrak{h} = \mathfrak{g}^{(N)}\left(2_{R_{K+1}}\right), \qquad (33)
\end{aligned}$$

where $T^{\mathrm{CP}}_{\mathrm{int}}(\mathfrak{h})$ is a part of $T_{\mathrm{int}}(\mathfrak{h})$ determined by shared amplitudes from the common pool of amplitudes and $T^{\mathrm{X}}_{\mathrm{int}}(\mathfrak{h})$ is a part of $T_{\mathrm{int}}(\mathfrak{h})$ that is determined in the $K+1$ computational blocks. After Eq. (33) is solved, the $C(i,K)$ is updated for the $T^{\mathrm{X}}_{\mathrm{int}}(\mathfrak{h})$ amplitudes, defining in this way $C(i,K+1)$, and the process is continued with the $K+2$ block. After M steps, $C(i,M)$ is used as a starting common pool of amplitudes for the $i+1$ iteration. In Eq. (33), the $Q^{\mathrm{X}}_{\mathrm{int}}$ operator is the projection operator on excited configurations generated by $T^{\mathrm{X}}_{\mathrm{int}}(\mathfrak{h})$ when acting on the reference function $|\Phi\rangle$. In Fig. 2(b) we see an alternative "parallel" flow where computational blocks are independent and which corresponds to the original eigenproblem (29) for SESs $\mathfrak{g}^{(N)}(2_{R_I})$. This step is followed by a synchronization of all shared amplitudes by various SESs. More details on the CC flows can be found in Appendixes A, B, C, and D, where we discuss the equivalence of the global representation and coupled computational blocks involved in the flow, the time domain extension, approximate solvers for computational blocks, and the general algorithmic structure of the practical CC flow realization, respectively.

The CC flow equation (29) or (32) can also be viewed as a configurational (or more aptly subspace) version of the aufbau principle, which is a consequence of the fact that each problem corresponding to some SES $\mathfrak{h}$ provides a rigorous mechanism for extending the subspace probed in a flow. In other words, the spaces probed in each SES problem (29) are additive. This fact is a unique feature, which should be referred to as the subsystem memory of the CC wave function. Additionally, CC flow ensures size consistency of the calculated ground-state energies. Similar flows cannot be easily constructed using configuration-interaction-type methods or standard many-body perturbation techniques. We believe that this is yet another argument in favor of nonperturbative analysis of CC equations.

In general, flow-based CC formulations are very flexible and allow one to use subalgebras $\mathfrak{g}^{(N)}(x_R, y_S)$ defined by various x and y parameters. This property may be used to introduce selective groups of higher excitations and tune the cost of flow equations to available computing resources. Although the numerical implementation of a flow-based formalism may be numerically less efficient than the implementation based on the global representation, its advantage lies in the fact that computational blocks contributing to flow are physically interpretable in terms of Schrödinger-type equations for subsystems described by relevant SESs. This fact has profound consequences and allows one to construct more justified (or, equivalently, less postulated) and better-controlled approximations based on the flow equations. An interesting illustration of this fact will be CC flow equations for localized orbitals (see Sec. II B).

Summarizing, the flow equations as shown in Fig. 3 can be represented in the form of the globally connected CC equations with the cluster operator T defined as a union of unique internal excitations of all subsystems included in the flow. The inverse statement is also true: For specific choices of the excitation domain included in the cluster operator, the CC equations can be represented in the form of coupled eigenvalue problems corresponding to various subsystem embedding algebras. This statement is the foundation for the reduced-scaling formulations discussed in this paper.

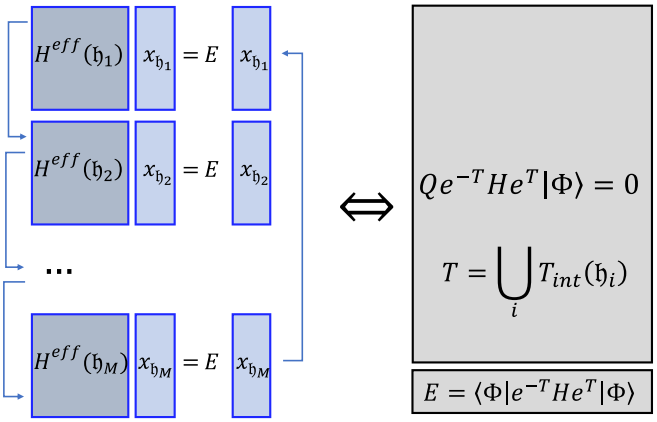

FIG. 3. Schematic representation of the equivalence between the global representation of the CC equations and coupled SES eigenvalue problems for properly defined cluster operators (see the text for details).

A. Time-dependent CC flows

The extension of the CC methods to the time domain keeps attracting much attention in various fields of chemistry and physics. Several developments in this area, including Arponen's seminal papers on this subject [6] (see also Refs. [13–16,160–164]), paved the way for mature applications of these formulations to describe time-dependent physical and chemical processes.

In Ref. [86] we demonstrated that the SES-based downfolding techniques could be extended to the time-dependent Schrödinger equation when all orbitals and the reference functions $|\Phi\rangle$ are assumed to be time independent. As in the stationary case, we will assume a general partitioning of the time-dependent cluster operator $T(t)$ into its internal $[T_{\rm int}(\mathfrak{h},t)]$ and external $[T_{\rm ext}(\mathfrak{h},t)]$ parts, i.e.,

$$|\Psi(t)\rangle = e^{T_{\rm ext}(\mathfrak{h},t)}e^{T_{\rm int}(\mathfrak{h},t)}|\Phi\rangle \tag{34}$$

for all $\mathfrak{h}$ in the SES. For generality, we also include a phase factor $T_0(\mathfrak{h},t)$ in the definition of the $T_{\rm int}(\mathfrak{h},t)$ operator. After substituting (34) into time-dependent Schrödinger equation and utilizing properties of SESs, we demonstrated that the ket dynamics of the subsystem wave function $e^{T_{\rm int}(\mathfrak{h},t)}|\Phi\rangle$, corresponding to the arbitrary SES $\mathfrak{h}$, is given by the equation

$$i\hbar\frac{\partial}{\partial t}e^{T_{\rm int}(\mathfrak{h},t)}|\Phi\rangle = H^{\rm eff}(\mathfrak{h},t)e^{T_{\rm int}(\mathfrak{h},t)}|\Phi\rangle, \tag{35}$$

where

$$H^{\rm eff}(\mathfrak{h},t) = [P + Q_{\rm int}(\mathfrak{h})]\bar{H}_{\rm ext}(\mathfrak{h},t)[P + Q_{\rm int}(\mathfrak{h})], \tag{36}$$

with

$$\bar{H}_{\rm ext}(\mathfrak{h},t) = e^{-T_{\rm ext}(\mathfrak{h},t)}He^{T_{\rm ext}(\mathfrak{h},t)}. \tag{37}$$

In analogy to the stationary cases, various subsystem computational blocks can be integrated into a flow enabling sampling of large subspaces of Hilbert space through a number of coupled reduced-dimensionality problems. For example, the time-dependent variant of the SCSAF-CCSD(2) approach uses the time-dependent cluster operator $T(t)$ in the form

$$T(t) \simeq T_1(t) + T_2(t) + \sum_I T_{{\rm int},3}\big(\mathfrak{g}^{(N)}(2_{R_I}),t\big) + \sum_I T_{{\rm int},4}\big(\mathfrak{g}^{(N)}(2_{R_I}),t\big)\big), \tag{38}$$

which can be equivalently represented as coupled time-evolution problems for subsystems

$$i\hbar\frac{\partial}{\partial t}e^{T_{\rm int}(\mathfrak{h},t)}|\Phi\rangle = H^{\rm eff}(\mathfrak{h},t)e^{T_{\rm int}(\mathfrak{h},t)}|\Phi\rangle\ \forall\,\mathfrak{h} = \mathfrak{g}^{(N)}(2_{R_I}) \tag{39}$$

(for details see Appendix B). These equations can be solved using flows similar to those shown in Fig. 2, with the difference that now the iterative cycles for converging amplitudes or energy correspond to elementary time steps with increment corresponding to Δt. As in the stationary case, the time-dependent CC flow equations represent an extension of the subspace aufbau principle mentioned earlier, where each SES problem (39) extends the space probed in time-dependent CC formalism. In view of the deep analogies between stationary CC flow equations based on the localized orbitals and local CC formulations developed in the past few decades in quantum chemistry (see the following section), the flow described by Eq. (39) can be considered as a reduced-scaling variant of the time-dependent CC formulations.

B. CC flows for localized orbital basis and localized subsystems

The SES CC flow formalism also systematizes and further extends the notion of a subsystem composed of orbital pairs. This problem has been studied intensively in early nonorthogonal pseudonatural-orbital-based formulations of configuration-interaction (CI) methods [165], the coupled-electron-pair approximation (CEPA) [166], and their extensions to local CEPA CC methods based on the local pair natural orbitals (LPNOs) and their domain-based LPNO (DLPNO) variant [77,167]. To analyze SES CC approximations, let us, in analogy to the DLPNO CC formulations, assume that the set of selected orbital pairs (for simplicity, we focus on the closed-shell formulations) $\mathscr{P} = \{(i,j)\}$ that significantly contribute to the correlation energy is known. These pairs are also employed to define pair natural orbital (PNO) spaces and corresponding CCSD cluster amplitudes. In the standard pair-driven DLPNO CCSD approximation orbital pairs (i,j) [including pairs where $i = j$, i.e., (i,i)] along with (i,j)-specific natural virtual orbitals are used to select PNO spaces and relevant single and double excitations. The (i,j)-specific density matrix defined as a second-order Møller-Plesset-type density matrix $\mathbf{D}^{ij}$ (see Ref. [40]) is used to determine virtual PNOs in a way that only natural orbitals characterized by occupation numbers greater than the user-defined threshold are retained. This leads to a significant reduction in the size of pair-specific PNO spaces and consequently to a significant reduction in the number of pair-specific singly ($t^i_{a_{ii}}$) and doubly ($t^{ij}_{a_{ij}b_{ij}}$) excited amplitudes, where virtual indices a_{ii}, a_{ij}, and b_{ij} are defined by reduced-size PNOs. It should be noted that each pair (i,j) introduces

its own set of PNO virtual orbitals, which may not be orthogonal to PNOs corresponding to distinct pairs.

The CC $\mathfrak{g}^{(N)}(2_R)$ flow employing localized occupied orbitals in a natural way introduces several elements underlying standard DLPNO CCSD design. Our analysis is based on the observation that there is a natural correspondence between orbital pairs from $\mathscr{P}$ (along with all virtual orbitals) with $\mathfrak{g}^{(N)}(2_R)$ subalgebras, where

$$R \equiv (i, j), \quad (i, j) \in \mathscr{P}. \tag{40}$$

For brevity we will refer to these SESs as $\mathfrak{g}^{(N)}(2_{ij})$ [$(i, j) \in \mathscr{P}$]. Additionally, each Schrödinger-type equation in (29) or (32),

$$H^{\text{eff}}(\mathfrak{h})e^{T_{\text{int}}(\mathfrak{h})}|\Phi\rangle = Ee^{T_{\text{int}}(\mathfrak{h})}|\Phi\rangle, \quad \mathfrak{h} = \mathfrak{g}^{(N)}(2_{ij}), \quad (i, j) \in \mathscr{P}. \tag{41}$$

naturally defines the corresponding one-body density matrix $\rho(\mathfrak{g}^{(N)}(2_{ij}))$ and its PNOs (or DLPNOs) without any additional assumptions regarding the form and the origin of the pair density matrix. One can readily notice that the $\mathbf{D}^{ij}$ density matrices used in original DLPNO CC papers are its low-order approximation. This feature of SES equations (41) can be viewed as a CC-derived systematization of the subsystem (or pair) concepts discussed in original works of Sinanoğlu [168,169] and Meyer and Rosmus [165,166,170].

It is worth mentioning that in contrast to the DLPNO CCSD formalism, the $\mathfrak{g}^{(N)}(2_{ij})$ include specific classes of triple and quadruple excitations. This feature may be a possible way to define the balanced inclusion of higher-rank excitations in the local CC formulations. For this purpose one can also envision CC flows based on $\mathfrak{g}^{(N)}(x_R)$ subalgebras with $x > 2$ that employ localized orbitals.

Since each SES $[\mathfrak{g}^{(N)}(2_{ij})]$ computational block contributing to flow (41) defines its own set of PNOs, in analogy to DLPNO CC approaches, it can be reexpressed through its own set of PNOs and set of preselected internal amplitudes (utilizing predefined thresholds). However, introducing a threshold in the CC flow equations can be performed less abruptly than in the existing DLPNO CC methods. In fact, the amplitude selection process is equivalent to selecting a subalgebra $\mathfrak{g}^{(N)}(2_{ij}, y_S)$ of $\mathfrak{g}^{(N)}(2_{ij})$ in a way that S is the set of PNOs corresponding to occupation numbers greater than the predefined threshold and y is the total number of virtual PNOs selected this way. This selection induces a natural partitioning of the $T_{\text{int}}(\mathfrak{g}^{(N)}(2_{ij}))$ into a part belonging to $\mathfrak{g}^{(N)}(2_{ij}, y_S)$ $[T_{\text{int}}(\mathfrak{g}^{(N)}(2_{ij}, y_S))]$ and a remaining "negligible" part of excitations $[\Delta T_{\text{int}}(\mathfrak{g}^{(N)}(2_{ij}))]$,

$$T_{\text{int}}(\mathfrak{g}^{(N)}(2_{ij})) = T_{\text{int}}(\mathfrak{g}^{(N)}(2_{ij}, y_S)) + \Delta T_{\text{int}}(\mathfrak{g}^{(N)}(2_{ij})). \tag{42}$$

The controlled version of the selection step is achieved by noticing that the effect of the negligible amplitudes $\Delta T_{\text{int}}(\mathfrak{g}^{(N)}(2_{ij}))$ can still be absorbed [using another downfolding step within the $\mathfrak{g}^{(N)}(2_{ij})$ CAS] in the form of additional similarity transformation

$$[P + Q_{\text{int}}(\mathfrak{f}_{ij})][e^{-\Delta T_{\text{int}}(\mathfrak{h}_{ij})}H^{\text{eff}}(\mathfrak{h}_{ij})e^{\Delta T_{\text{int}}(\mathfrak{h}_{ij})}]e^{T_{\text{int}}(\mathfrak{f}_{ij})}|\Phi\rangle = Ee^{T_{\text{int}}(\mathfrak{f}_{ij})}|\Phi\rangle, \quad \mathfrak{f}_{ij} = \mathfrak{g}^{(N)}(2_{ij}, y_S), \ \mathfrak{h}_{ij} = \mathfrak{g}^{(N)}(2_{ij}), \tag{43}$$

where $Q_{\text{int}}(\mathfrak{g}^{(N)}(2_{ij}, y_S))$ is a projection operator on excited configurations generated by the $T_{\text{int}}(\mathfrak{g}^{(N)}(2_{ij}, y_S))$ when acting on the reference function $|\Phi\rangle$.

The CC flow equations can also be naturally linked to approximate CC schemes used in studies of spin systems. In Refs. [171,172] Bishop *et al.* considered a hierarchy of approximations where excitation manifolds are defined using the so-called subsystems defined by contiguous lattice sites, each of which is a nearest neighbor to at least one other in the subsystem. These subsystems can be naturally identified with the active spaces, making CC flow equations similar to the SUB*n*-*m* and LSUB*m* schemes discussed in Refs. [171,172] As shown in the previous paragraphs, the application of CC flows to the spin systems offers an interesting way of defining reduced-scaling methods for quantum lattice models. This can be achieved by selecting the essential class of excitations (for a given subsystem) using density matrices corresponding to subsystem's downfolded Hamiltonians. This approach can address problems associated with the high numerical overhead of the highly accurate SUB*n*-*m* and LSUB*m* approaches. In analogy to the seminal paper on the non-Hermitian many-body CC formulations discussed in Ref. [173], the proposed CC flow equation formulations indicate the advantages of utilizing non-Hermitian formulations. Especially interesting are CC flow formalism extensions based on the normal and extended CC formalisms for bosonic and/or fermionic systems (see, for example, Refs. [6,13–16,173]).

Summarizing, several basic threads of DLPNO CCSD equations are consequences of CC flow equations defined by $\mathfrak{g}^{(N)}(2_{ij})$ subalgebras. The local character of correlation effects is a net effect of the local character of the basis set used, asymptotic properties of one- and two-electron interactions, and fundamental properties of the CC formalism associated with the CC subsystem memory. This feature allows one to construct, in a rigorous way, Schrödinger-type equations for subsystems (in this case, a pair of orbitals) defining the flow. Additionally, rigorous definitions of the subsystem and the associated wave function lead to natural definitions of the subsystem density matrix and natural orbitals. We believe that the CC flow equations based on the SES formalism are an interesting tool for constructing various approximations for correlated systems. This formulation can be universally used in stationary formulations of canonical and local CC formulations and extended to the time-dependent CC equations. The general CC flow formalism is not limited to types of interactions that are considered molecular systems and can also be extended to other types of many-body interactions encountered in chemical and physical applications.

III. SUBSYSTEM FLOWS BASED ON THE DOUBLE-UNITARY CC REPRESENTATION OF THE WAVE FUNCTION

We find properties of SR CC flows very appealing from the point of view of quantum computing. Instead of considering expensive global space approaches (as done in the majority of existing QC formalisms) that require too many parameters to be optimized at the same time, one could partition the problem into smaller computational subproblems that can be tuned to available systems of qubits. For this reason, we would

like to adapt the SR CC ideas from previous sections to the double-unitary CC ansatz (see Ref. [85]). While the DUCC formalism mirrors some properties of the SES CC formalism and additionally ensures the Hermitian character of the effective Hamiltonians in $\mathscr{C}(\mathfrak{h})$, due to the noncommutative nature of the anti-Hermitian cluster operators employed by this formalism, coupling various DUCC problems into a flow requires several approximations, described in the following section.

The DUCC formalism discussed in Refs. [85,86] uses a composite unitary CC ansatz to represent the exact wave function $|\Psi\rangle$, i.e.,

$$|\Psi\rangle = e^{\sigma_{\rm ext}(\mathfrak{h})} e^{\sigma_{\rm int}(\mathfrak{h})} |\Phi\rangle, \tag{44}$$

where $\sigma_{\rm ext}(\mathfrak{h})$ and $\sigma_{\rm int}(\mathfrak{h})$ are general-type anti-Hermitian operators

$$\sigma^{\dagger}_{\rm int}(\mathfrak{h}) = -\sigma_{\rm int}(\mathfrak{h}), \tag{45}$$

$$\sigma^{\dagger}_{\rm ext}(\mathfrak{h}) = -\sigma_{\rm ext}(\mathfrak{h}). \tag{46}$$

All cluster amplitudes defining the $\sigma_{\rm int}(\mathfrak{h})$ cluster operator carry active indices only (or indices of active orbitals defining a given $\mathfrak{h}$). The external part $\sigma_{\rm ext}(\mathfrak{h})$ is defined by amplitudes carrying at least one inactive orbital index. In contrast to the SR CC approach, internal (external) parts of anti-Hermitian cluster operators are not defined in terms of excitations belonging explicitly to a given subalgebra but rather by indices defining active (inactive) orbitals specific to a given $\mathfrak{h}$. Therefore, $\mathfrak{h}$ will be used here in the context of the CAS's generator.

When the external cluster amplitudes are known (or can be effectively approximated), in analogy to single-reference SES CC formalism, the energy (or its approximation) can be calculated by diagonalizing the Hermitian effective or downfolded Hamiltonian in the active space using various quantum or classical diagonalizers. An important step towards developing practical computational schemes is to simplify the infinite expansions defining both cluster amplitudes and nonterminating commutator expansions defining downfolded Hamiltonians. A legitimate approximation of $\sigma_{\rm ext}(\mathfrak{h})$ and $\sigma_{\rm int}(\mathfrak{h})$ in Eq. (44) for well-defined active spaces is to retain lowest-order terms only, i.e.,

$$\sigma_{\rm int}(\mathfrak{h}) \simeq T_{\rm int}(\mathfrak{h}) - T_{\rm int}(\mathfrak{h})^{\dagger}, \tag{47}$$

$$\sigma_{\rm ext}(\mathfrak{h}) \simeq T_{\rm ext}(\mathfrak{h}) - T_{\rm ext}(\mathfrak{h})^{\dagger}, \tag{48}$$

which has been discussed in Ref. [85]. In particular, $T_{\rm ext}(\mathfrak{h})$ can be approximated by SR CCSD amplitudes that carry at least one external spin-orbital index. Other possible sources for obtaining external cluster amplitudes are higher-rank SR CC methods and approximate unitary CC formulations such as UCC(n) methods [105,106].

Using the DUCC representation (44), it can be shown that in analogy to the SR CC case, the energy of the entire system [once the exact form of the $\sigma_{\rm ext}(\mathfrak{h})$ operator is known] can be calculated through the diagonalization of the effective or downfolded Hamiltonian in SES-generated active space, i.e.,

$$H^{\rm eff}(\mathfrak{h}) e^{\sigma_{\rm int}(\mathfrak{h})} |\Phi\rangle = E e^{\sigma_{\rm int}(\mathfrak{h})} |\Phi\rangle, \tag{49}$$

where

$$H^{\rm eff}(\mathfrak{h}) = [P + Q_{\rm int}(\mathfrak{h})] \bar{H}_{\rm ext}(\mathfrak{h}) [P + Q_{\rm int}(\mathfrak{h})], \tag{50}$$

with

$$\bar{H}_{\rm ext}(\mathfrak{h}) = e^{-\sigma_{\rm ext}(\mathfrak{h})} H e^{\sigma_{\rm ext}(\mathfrak{h})}. \tag{51}$$

Typical approximations for the downfolded Hamiltonian utilize (i) various sources for evaluation of the $T_{\rm ext}(\mathfrak{h})$ operator in (48), (ii) various lengths of commutator expansion defining the $\bar{H}_{\rm ext}(\mathfrak{h})$ operator, (iii) various excitation ranks in the many-body expansion of the $\bar{H}_{\rm ext}(\mathfrak{h})$ operator, and (iv) various molecular basis choices.

Recently, applications of QPE and VQE quantum algorithms to evaluate eigenvalues of downfolded Hamiltonians $H^{\rm eff}(\mathfrak{h})$ became a subject of intensive studies. In the case of the VQE method, the energy functional

$$\min_{\boldsymbol{\theta}(\mathfrak{h})} \langle \Psi(\boldsymbol{\theta}(\mathfrak{h})) | H^{\rm eff}(\mathfrak{h}) | \Psi(\boldsymbol{\theta}(\mathfrak{h})) \rangle \tag{52}$$

is optimized with respect to variational parameters $\boldsymbol{\theta}(\mathfrak{h})$, where $|\Psi(\boldsymbol{\theta}(\mathfrak{h}))\rangle$ approximates $e^{\sigma_{\rm int}(\mathfrak{h})}|\Phi\rangle$,

$$|\Psi(\boldsymbol{\theta}(\mathfrak{h}))\rangle \simeq e^{\sigma_{\rm int}(\mathfrak{h})} |\Phi\rangle, \tag{53}$$

at the level of the quantum circuit. This approach turned out to be very efficient, especially when "correlated" natural orbitals are employed. The advantage of using the VQE approach is the possibility of extracting the information about cluster amplitudes defining $\sigma_{\rm int}(\mathfrak{h})$ from the optimized parameters $\boldsymbol{\theta}(\mathfrak{h})$. This feature plays a vital role in designing DUCC subsystem flows and ensures the mechanism of quantum information passing between various computational blocks. In the following analysis we will assume that the variational parameters $\boldsymbol{\theta}(\mathfrak{h})$ correspond to cluster amplitudes in the $\sigma_{\rm int}(\mathfrak{h})$ expansion.

DUCC flow equations: Applications in quantum computing

The DUCC flow idea is very interesting from the point of view of its applications in quantum computing, where a quantum computer can process computational blocks (corresponding to either energy functional minimization or diagonalization of the downfolded Hamiltonians). In this section we extend the idea of the SR CC subsystem flow to the DUCC formalism and we highlight the similarities and differences between these two approaches. The main differences between the SR CC and DUCC methods should be attributed to the noncommutative nature of many-body components defining anti-Hermitian DUCC cluster operators. This fact, in the case of the DUCC approach, significantly impedes the analysis of the equations and partitioning them into separate computational blocks that can be integrated into subsystem flow equations. However, this can be achieved with a sequence of approximations that we describe below.

We start our analysis by assuming that we would like to perform DUCC effective simulations for a SES $\mathfrak{h}$ problem (49) which is, for whatever reason, too complex or too big for quantum processing. We will assume that external amplitudes $\sigma_{\rm ext}(\mathfrak{h})$ can be effectively evaluated using perturbative formulations. For simplicity, we will introduce a DUCC Hermitian Hamiltonian $A(\mathfrak{h})$, which is defined as $H^{\rm eff}(\mathfrak{h})$, or its approximation in the $[P + Q(\mathfrak{h})]$ space (in the simplest case it can

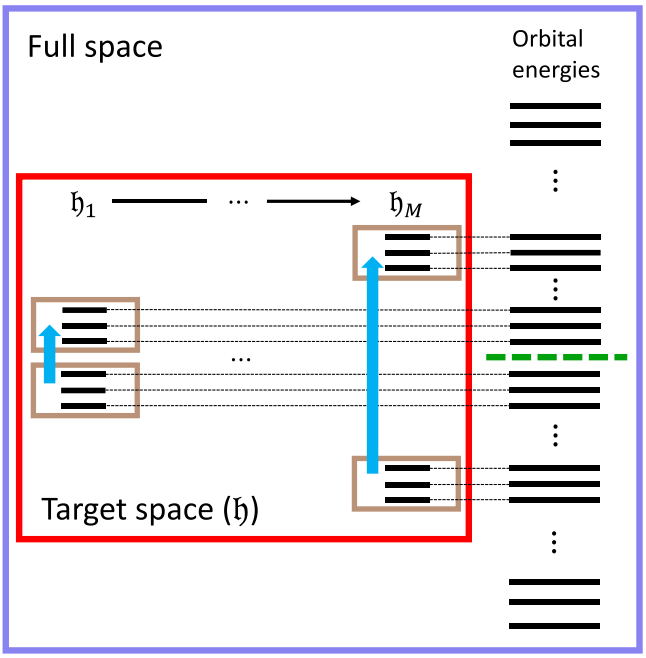

FIG. 4. Schematic representation of the DUCC flow. It is assumed that the most important classes of excitations required to describe a state of interest are captured by the target active space (or virtual space) too large for direct QC simulations and that the target active space (corresponding to subalgebra $\mathfrak{h}$) can be approximated by excitations included in smaller yet computationally feasible active spaces corresponding to subalgebras $\mathfrak{h}_1, \ldots, \mathfrak{h}_M$ (see the text). The DUCC flow combines computational blocks that correspond to variational problems associated with each subalgebra $\mathfrak{h}_i$ $(i = 1, \ldots, M)$. The green dashed line represents the Fermi level.

be just the $[P + Q(\mathfrak{h})]H[P + Q(\mathfrak{h})]$ operator). We will denote $A(\mathfrak{h})$ simply by A. We will also assume that the situation where excitations from $\mathfrak{h}$ that are relevant to state of interest can be captured by excitation subalgebras $\mathfrak{h}_1, \mathfrak{h}_2, \ldots, \mathfrak{h}_M$ (see Fig. 4), where, in analogy to the SR CC case, we admit the possibility of sharing excitations or deexcitations between these subalgebras. We also assume that the number of excitations belonging to each $\mathfrak{h}_i$ $(i = 1, \ldots, M)$ is significantly smaller than the number of excitations in $\mathfrak{h}$ and therefore numerically tractable in quantum simulations. Below we will discuss the challenges and approximations that are needed to obtain well-defined DUCC flow equations.

The $A(\mathfrak{h})$ Hamiltonian and the $[P + Q(\mathfrak{h})]$ space can be treated as a starting point for the secondary DUCC decompositions generated by subsystem algebras $\mathfrak{h}_i$ $(i = 1, \ldots, M)$ defined above, i.e.,

$$A^{\mathrm{eff}}(\mathfrak{h}_i)e^{\sigma_{\mathrm{int}}(\mathfrak{h}_i)}|\Phi\rangle = Ee^{\sigma_{\mathrm{int}}(\mathfrak{h}_i)}|\Phi\rangle \quad (i = 1, \ldots, M), \tag{54}$$

or in the VQE-type variational representation as

$$\min_{\boldsymbol{\theta}(\mathfrak{h}_i)} \langle \Psi(\boldsymbol{\theta}(\mathfrak{h}_i))|A^{\mathrm{eff}}(\mathfrak{h}_i)|\Psi(\boldsymbol{\theta}(\mathfrak{h}_i))\rangle \quad (i = 1, \ldots, M). \tag{55}$$

Each $A^{\mathrm{eff}}(\mathfrak{h}_i)$ is defined as

$$A^{\mathrm{eff}}(\mathfrak{h}_i) = [P + Q_{\mathrm{int}}(\mathfrak{h}_i)]\bar{A}_{\mathrm{ext}}(\mathfrak{h}_i)[P + Q_{\mathrm{int}}(\mathfrak{h}_i)] \tag{56}$$

and

$$\bar{A}_{\mathrm{ext}}(\mathfrak{h}_i) = e^{-\sigma_{\mathrm{ext}}(\mathfrak{h}_i)}Ae^{\sigma_{\mathrm{ext}}(\mathfrak{h}_i)}, \tag{57}$$

where we have defined the external $\sigma_{\mathrm{ext}}(\mathfrak{h}_i)$ operator with respect to $\mathfrak{h}$ or $[P + Q_{\mathrm{int}}(\mathfrak{h})]$ space [i.e., cluster amplitudes defining $\sigma_{\mathrm{ext}}(\mathfrak{h}_i)$ must carry at least one index belonging to active spin orbitals defining $\mathfrak{h}$ and not belonging to the set of active spin orbitals defining $\mathfrak{h}_i$]. In other words, subalgebras $\mathfrak{h}_i$ generate active subspaces in larger active space $\mathfrak{h}$, i.e., $[P + Q_{\mathrm{int}}(\mathfrak{h}_i)] \subset [P + Q(\mathfrak{h})]$. However, connecting DUCC computational blocks (54) or (55) directly into a flow is a rather challenging task. In contrast to the SR CC subsystem flows where cluster amplitudes are universal for all subalgebra-induced problems (i.e., the given amplitude carries the same value across all computational blocks), the same is no longer valid for DUCC flows. Again, this is a consequence of the noncommutativity of the anti-Hermitian operators defining the DUCC representation of the wave function. For example, the internal amplitude for some $\mathfrak{h}_i$ problem may assume a value different from the same amplitude being an internal amplitude for a different problem corresponding to subalgebra $\mathfrak{h}_j$ $(i \neq j)$, which means that DUCC amplitudes explicitly depend on the subalgebra index $\mathfrak{h}_i$ (as opposed to the SR CC flow formalism, where values of particular amplitudes are independent of the subalgebra index). Similar effects could be observed in adaptive derivative-assembled pseudo-Trotter VQE formulations [112], where amplitudes from the excitation poll may appear multiple times carrying various values in the wave-function expansion. An additional problem is related to the fact that while for the SR CC flows the effective Hamiltonians corresponding to various SESs can be constructed exactly, for the DUCC case $A^{\mathrm{eff}}(\mathfrak{h}_i)$ can be constructed only in an approximate way, and therefore their ground-state eigenvalues may not be exactly equal.

To address these issues and define practical DUCC flow we will discuss the algorithm that combines secondary downfolding steps with Trotterization of the unitary CC operators. Let us assume that the $\sigma_{\mathrm{int}}(\mathfrak{h})$ operator can be approximated by $\sigma_{\mathrm{int}}(\mathfrak{h}_i)$ $(i = 1, \ldots, M)$, i.e.,

$$\sigma_{\mathrm{int}}(\mathfrak{h}) \simeq \sum_{i=1}^{M} \sigma_{\mathrm{int}}(\mathfrak{h}_i) + X(\mathfrak{h}, \mathfrak{h}_1, \ldots, \mathfrak{h}_M), \tag{58}$$

where the $X(\mathfrak{h}, \mathfrak{h}_1, \ldots, \mathfrak{h}_M)$ operator (or X for short) eliminates possible overcounting of the shared amplitudes. This enables us to reexpress $\sigma_{\mathrm{int}}(\mathfrak{h})$ as

$$\sigma_{\mathrm{int}}(\mathfrak{h}) = \sigma_{\mathrm{int}}(\mathfrak{h}_i) + R(\mathfrak{h}_i) \quad (i = 1, \ldots, M), \tag{59}$$

where

$$R(\mathfrak{h}_i) = {}^{(i)}\sum_{j=1}^{M} \sigma_{\mathrm{int}}(\mathfrak{h}_j) + X \tag{60}$$

with ${}^{(i)}\sum_{j=1}^{M}$ designating the sum where the ith element is neglected. Consequently, we get

$$e^{\sigma_{\mathrm{int}}(\mathfrak{h})}|\Phi\rangle = e^{\sigma_{\mathrm{int}}(\mathfrak{h}_i)+R(\mathfrak{h}_i)}|\Phi\rangle \quad (i = 1, \ldots, M). \tag{61}$$

Using the Trotter formula, we can approximate the right-hand side of (61) for a given j as

$$e^{\sigma_{\mathrm{int}}(\mathfrak{h})}|\Phi\rangle \simeq (e^{R(\mathfrak{h}_i)/N}e^{\sigma_{\mathrm{int}}(\mathfrak{h}_i)/N})^N|\Phi\rangle. \tag{62}$$

Introducing the auxiliary operator $G_i^{(N)}$,

$$G_i^{(N)} = (e^{R(\mathfrak{h}_i)/N} e^{\sigma_{\rm int}(\mathfrak{h}_i)/N})^{N-1} e^{R(\mathfrak{h}_i)/N} \quad (i = 1, \ldots, M), \tag{63}$$

the internal wave function (61) can be expressed as

$$e^{\sigma_{\rm int}(\mathfrak{h})}|\Phi\rangle \simeq G_i^{(N)} e^{\sigma_{\rm int}(\mathfrak{h}_i)/N}|\Phi\rangle \quad (i = 1, \ldots, M). \tag{64}$$

One should recall that $G_i^{(N)}$ is a complicated function of all $\sigma_{\rm int}(\mathfrak{h}_j)$ $(j = 1, \ldots, M)$ and the above expression does not decouple $\sigma_{\rm int}(\mathfrak{h}_i)$ from the $G_i^{(N)}$ term. However, this expression may help define a practical way of determining computational blocks for flow equations. To see this, let us introduce the expansion (64) to Eq. (49) [with $H^{\rm eff}(\mathfrak{h})$ replaced by the A operator], premultiply both sides by $[G_i^{(N)}]^{-1}$, and project onto $[P + Q_{\rm int}(\mathfrak{h}_i)]$ subspace, which leads to the nonlinear eigenvalue problem

$$[P + Q_{\rm int}(\mathfrak{h}_i)]\left[G_i^{(N)}\right]^{-1} A G_i^{(N)} e^{\sigma_{\rm int}(\mathfrak{h}_i)/N}|\Phi\rangle \simeq E e^{\sigma_{\rm int}(\mathfrak{h}_i)/N}|\Phi\rangle \quad (i = 1, \ldots, M). \tag{65}$$

We will utilize this equation as a computational block for the DUCC flow. To make practical use of Eq. (65) let us linearize it by defining the downfolded Hamiltonian $\Gamma_i^{(N)}$, $\Gamma_i^{(N)} = [P + Q_{\rm int}(\mathfrak{h}_i)][G_i^{(N)}]^{-1} A G_i^{(N)} [P + Q_{\rm int}(\mathfrak{h}_i)]$, as a function of all $\sigma_{\rm int}(\mathfrak{h}_j)$ $(j = 1, \ldots, M)$ from the previous flow cycle(s) $\mathfrak{p}$. We will symbolically represent this by using a special symbol for the $\Gamma_i^{(N)}$ effective Hamiltonian, i.e., the $\Gamma_i^{(N)}(\mathfrak{p})$ Hamiltonian. Now we replace eigenvalue problems (65) by optimization procedures described by Eq. (55), which also offer an easy way to deal with shared amplitudes. Namely, if in analogy to SR CC subsystem flow we establish an ordering of $\mathfrak{h}_i$ subalgebras, with $\mathfrak{h}_1$ corresponding to the CAS closest to the wave function of interest, then in the $\mathfrak{h}_i$ problem we partition [in analogy to Eq. (33)] a set of parameters $\boldsymbol{\theta}_N(\mathfrak{h}_i)$ into a subset $\boldsymbol{\theta}_N^{\rm CP}(\mathfrak{h}_i)$ that refers to a common pool of amplitudes determined in the preceding steps [say, for $\mathfrak{h}_j$ $(j = 1, \ldots, i-1)$] and a subset $\boldsymbol{\theta}_N^{\rm X}(\mathfrak{h}_i)$ that is uniquely determined in the $\mathfrak{h}_i$ minimization step, i.e.,

$$\min_{\boldsymbol{\theta}_N^{\rm X}(\mathfrak{h}_i)} \left\langle \Psi\left(\boldsymbol{\theta}_N^{\rm X}(\mathfrak{h}_i), \boldsymbol{\theta}_N^{\rm CP}(\mathfrak{h}_i)\right)\middle|\Gamma_i^{(N)}(\mathfrak{p})\middle|\Psi\left(\boldsymbol{\theta}_N^{\rm X}(\mathfrak{h}_i), \boldsymbol{\theta}_N^{\rm CP}(\mathfrak{h}_i)\right)\right\rangle \quad (i = 1, \ldots, M), \tag{66}$$

where $|\Psi(\boldsymbol{\theta}_N^{\rm X}(\mathfrak{h}_i), \boldsymbol{\theta}_N^{\rm CP}(\mathfrak{h}_i))\rangle$ approximates $e^{\sigma_{\rm int}(\mathfrak{h}_i)/N}|\Phi\rangle$. In this way, each computational block coupled into a flow corresponds to a minimization procedure that optimizes the parameters $\boldsymbol{\theta}_N^{\rm X}(\mathfrak{h}_i)$ using quantum algorithms such as the VQE approach. At the end of the iterative cycle, once all amplitudes are converged, in contrast to the SR CC flows, the energy is calculated using the $\mathfrak{h}_1$ problem as an expectation value of the converged $\Gamma_1^{(N)}$ operator. The DUCC flow is composed of classical computing steps, where the approximate second-quantized form of the $\Gamma_i^{(N)}(\mathfrak{p})$ operators (at the cost of additional similarity transformations or their approximate variants in small-size active space) is calculated, and quantum computing steps, where cluster amplitudes are determined using the VQE algorithm. The discussed formalism introduces a broad class of control parameters, which define each computational step's dimensionality. These are the numbers of occupied (unoccupied) active orbitals defining $\mathfrak{h}_i$ subalgebras x_{R_i} (y_{S_i}). Similar results can be obtained by using the Zassenhaus formula. Moreover, the present formalisms, in analogy to the SR CC flows, can be extended to the time domain.

An essential feature of the DUCC flow equation is associated with the fact that each computational block (66) can be encoded using a much smaller number of qubits compared to the full size of the global problem. In fact, the maximum size of the qubit register $\mathcal{Q}(\mathfrak{m}_{\rm max})$ required in DUCC quantum flow is associated with the maximum size of the subsystem and not with the size of the entire quantum system of interest

$$\mathcal{Q}(\mathfrak{m}_{\rm max}) \ll \mathcal{Q}(\mathfrak{g}^{(N)}), \tag{67}$$

where $\mathcal{Q}(\mathfrak{g}^{(N)})$ is the total number of qubits required to describe the whole system. This observation significantly simplifies the qubit encoding of the effective Hamiltonians included in quantum DUCC flows, especially in formulations based on the utilization of the localized molecular basis set as discussed in Sec. II C (for early quantum algorithms exploiting locality of interactions see Ref. [174]).

IV. CONCLUSION

This paper discussed the properties of SR CC subsystem flow equations stemming from the SES CC formalism for restricted Hartree-Fock reference functions. It was shown that flow equations define an alternative (to the canonical formulations) way of introducing selected classes of higher-rank excitations based on system partitioning or choice of subsystem excitation subalgebras corresponding to various active spaces. An essential feature of the SR CC flow lies in the fact that flow equations can be built upon $\mathfrak{g}^{(N)}(x_R, y_S)$ subalgebras with x_R and y_S chosen in a way that makes the flow tunable to available computational resources. We also demonstrated that the idea of CC flow naturally extends to the time domain, offering a possibility of performing calculations for the quantum system's time evolution affordably. Interestingly, the ideas behind SES CC and SR CC subsystem flows can also provide a deeper understanding of local CC formulations and the concept of locality of correlation effects. As explained in Sec. II B, the SR CC flows based on the utilization of local molecular orbitals provide a rigorous way of defining the subsystem through the effective Hamiltonian corresponding to the (i, j)-determined SES $\mathfrak{g}^{(N)}(2_{ij})$. The (i, j)-pair density matrix can be further used to calculate pair natural orbitals and select leading excitation as postulated in the DLPNO CCSD formulations. We believe that the SR CC flows defined by larger active spaces also provide a natural way of introducing higher-rank excitations, although maintaining linear scaling of the resulting local CC formulation may not be possible. On the other hand, following the SR CC flow philosophy for localized orbitals, although numerically more expensive, may help in reestablishing the desired level of accuracy in perturbative (noniterative) energy corrections due to the higher-rank cluster excitations.

Due to the noncommutative nature of the general type of unitary CC formulations, the direct extension of SR CC subsystem flows to DUCC-type flow is a rather challenging endeavor. However, utilizing the Trotter formula in downfolding procedures leads to computationally feasible algorithms. In the quantum computing variant, the flow represents a

sequence of coupled Hermitian eigenproblems, where diagonalization is replaced by the VQE-type optimization to obtain a corresponding subset of amplitudes. In this formulation, the flow of quantum information corresponding to shared or external amplitudes (defined for a given subsystem) can be easily implemented at the level of the quantum circuit. In analogy to the SR CC flows, the DUCC flows can be tuned to the available quantum resources. As such, the DUCC flows offer an interesting possibility of decomposing large-dimensionality problems into a collection of reduced dimensionality computational blocks. We believe that the DUCC flow methods can significantly extend the limits of system-size tractability in quantum simulations. It should also be stressed that the SR CC or DUCC flow methods allow one to enlarge the size of the probed space systematically while retaining the size extensivity of the energies calculated in this way. This feature is especially important in applications of DUCC flows to chemical reactions and extended systems.

An exciting feature of the SES CC formalism and CC flows is their universal character irrespective of the particular form of interactions defining correlated many-body systems.

ACKNOWLEDGMENTS

This work was supported by the Quantum Science Center, a National Quantum Information Science Research Center of the U.S. Department of Energy. Part of this work was supported by the "Embedding QC into Many-Body Frameworks for Strongly Correlated Molecular and Materials Systems" project, which is funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, the Division of Chemical Sciences, Geosciences, and Biosciences.

APPENDIX A

In this Appendix we will analyze properties of the CC flow equations. Let us assume that flow equations involve M eigenvalue problems defined by subalgebras $\{\mathfrak{h}_i\}_{i=1}^{M}$. For generality, let us also assume that each eigenvalue problem yields its own value of ground-state energy $E(\mathfrak{h}_i)$ [see Eq. (32)],

$$H^{\rm eff}(\mathfrak{h}_i)e^{T_{\rm int}(\mathfrak{h}_i)}|\Phi\rangle = E(\mathfrak{h}_i)e^{T_{\rm int}(\mathfrak{h}_i)}|\Phi\rangle \quad (i=1,\ldots,M). \tag{A1}$$

The ith computational block can be written in the form

$$[P+Q_{\rm int}(\mathfrak{h}_i)][e^{-T_{\rm ext}(\mathfrak{h}_i)}He^{T_{\rm ext}(\mathfrak{h}_i)}-E(\mathfrak{h}_i)]e^{T_{\rm int}(\mathfrak{h}_i)}|\Phi\rangle = 0, \tag{A2}$$

where the $T_{\rm ext}(\mathfrak{h}_i)$ operator contains excitations from all remaining cluster operators $T_{\rm int}(\mathfrak{h}_j)$ $(j=1,\ldots,M;\ j\neq i)$ not belonging to the set of excitations defining the $T_{\rm int}(\mathfrak{h}_i)$ operator. After introducing the resolution of identity

$$e^{-T_{\rm int}(\mathfrak{h}_i)}e^{T_{\rm int}(\mathfrak{h}_i)} = 1 \tag{A3}$$

right to the projection operator $[P+Q_{\rm int}(\mathfrak{h}_i)]$ in Eq. (A2) one obtains

$$[P+Q_{\rm int}(\mathfrak{h}_i)]e^{T_{\rm int}(\mathfrak{h}_i)}[e^{-T}He^{T}-E(\mathfrak{h}_i)]|\Phi\rangle = 0, \tag{A4}$$

where

$$T = T_{\rm int}(\mathfrak{h}_i)+T_{\rm ext}(\mathfrak{h}_i). \tag{A5}$$

It should be stressed that the T operator is not carrying an index of any subalgebra and T is defined as a sum of unique excitations defining $\{T_{\rm int}(\mathfrak{h}_i)\}_{i=1}^{M}$ operators. We will symbolically represent T as a union of unique excitations originating in various $T_{\rm int}(\mathfrak{h}_i)$,

$$T = \bigcup_{i=1}^{M} T_{\rm int}(\mathfrak{h}_i). \tag{A6}$$

This is a consequence of the CC flow definition. Given the fact that the operator $e^{T_{\rm int}(\mathfrak{h}_i)}$ is nonsingular and that

$$[P+Q_{\rm int}(\mathfrak{h}_i)]e^{T_{\rm int}} = [P+Q_{\rm int}(\mathfrak{h}_i)]e^{T_{\rm int}}[P+Q_{\rm int}(\mathfrak{h}_i)], \tag{A7}$$

the eigenvalue problem is equivalent at the solution to

$$[P+Q_{\rm int}(\mathfrak{h}_i)][e^{-T}He^{T}-E(\mathfrak{h}_i)]|\Phi\rangle = 0 \tag{A8}$$

or in the "standard" form of CC equations

$$[P+Q_{\rm int}(\mathfrak{h}_i)][e^{-T}He^{T}]|\Phi\rangle = 0, \tag{A9}$$

$$E(\mathfrak{h}_i) = \langle\Phi|e^{-T}He^{T}|\Phi\rangle = E. \tag{A10}$$

Using Eqs. (A9) and (A10), one can draw the following conclusions.

Conclusion 1. The CC flow equations (A1) at the solution are equivalent to the standard connected CC equations for the T cluster operator.

Conclusion 2. All converged ground-state eigenvalues $E(\mathfrak{h}_i)$ of computational blocks given by Eq. (A2) are equal and at the solution assume the value of CC energy E calculated using the standard formulation for the T cluster operator.

Conclusion 2 indicates that all energies $E(\mathfrak{h}_i)$ from the onset of the iterative solution of the flow equations can be assumed to be equal, which allows rewriting Eq. (A1) as

$$H^{\rm eff}(\mathfrak{h}_i)e^{T_{\rm int}(\mathfrak{h}_i)}|\Phi\rangle = Ee^{T_{\rm int}(\mathfrak{h}_i)}|\Phi\rangle \quad (i=1,\ldots,M). \tag{A11}$$

The final remark concerns the size of the subspace sampled by our flow equations, which is defined by excitations included in the T cluster operator. For the CC flow defined by all possible $\mathfrak{g}^{(N)}(2_{R_i})$ subalgebras, the T operator contains all singles, doubles, and subsets of triple and quadruple excitations as shown in Eq. (30). For the CC flow defined by all $\mathfrak{g}^{(N)}(3_{R_i})$ subalgebras, the T operator contains all singles, doubles, triples, and subsets of quadruples, pentuples, and hextuples. The CC flows equations also offer flexibility in choosing subalgebras involved in the flow, for example, the flow can involve various $\mathfrak{g}^{(N)}(x_{R_i},y_{S_i})$ subalgebras. As long as T is defined by unique excitations of the internal cluster operators corresponding to the subalgebras involved in the flow, conclusions 1 and 2 are still valid.

APPENDIX B

The analysis in Appendix A can be extended to the CC flows in the time domain, where the flow is composed of coupled time-dependent CC equations

$$i\hbar\frac{\partial}{\partial t}e^{T_{\rm int}(\mathfrak{h}_i,t)}|\Phi\rangle = H^{\rm eff}(\mathfrak{h}_i,t)e^{T_{\rm int}(\mathfrak{h}_i,t)}|\Phi\rangle \quad (i=1,\ldots,M). \tag{B1}$$

For a given subalgebra $\mathfrak{h}_i$ time-dependent equations can be cast in the form (we assume that spin orbitals are time independent)

$$i\hbar[P+Q_{\rm int}(\mathfrak{h}_i)]\frac{\partial}{\partial t}e^{T_{\rm int}(\mathfrak{h}_i,t)}|\Phi\rangle = H^{\rm eff}(\mathfrak{h}_i,t)e^{T_{\rm int}(\mathfrak{h}_i,t)}|\Phi\rangle. \tag{B2}$$

By expanding $H^{\rm eff}(\mathfrak{h}_i,t)$, Eq. (B2) can be rewritten as

$$[P+Q_{\rm int}(\mathfrak{h}_i)]e^{T_{\rm int}(\mathfrak{h}_i,t)}[P+Q_{\rm int}(\mathfrak{h}_i)] \left\{i\hbar\frac{\partial}{\partial t}T(t)-e^{-T(t)}He^{T(t)}\right\}|\Phi\rangle = 0, \tag{B3}$$

where $T(t)$ is defined as

$$T(t)=\bigcup_{i=1}^{M}T_{\rm int}(\mathfrak{h}_i,t). \tag{B4}$$

Using a matrix representation of the $T_{\rm int}(\mathfrak{h}_i,t)$ operator in the $\mathfrak{h}_i$-generated CAS denoted by $\boldsymbol{T}_{\rm int}(\mathfrak{h}_i,t)$, we get

$$\det(e^{\boldsymbol{T}_{\rm int}(\mathfrak{h}_i,t)}) = e^{{\rm Tr}[\boldsymbol{T}_{\rm int}(\mathfrak{h}_i,t)]} = 1 \tag{B5}$$

for arbitrary time t. This is a consequence of the fact that $\boldsymbol{T}_{\rm int}(\mathfrak{h}_i,t)$ is a lower diagonal matrix with zeros on the diagonal. Therefore, Eq. (B1) is equivalent to standard time-dependent equations

$$[P+Q_{\rm int}(\mathfrak{h}_i)]\left\{i\hbar\frac{\partial}{\partial t}T(t)-e^{-T(t)}He^{T(t)}\right\}|\Phi\rangle = 0. \tag{B6}$$

Following the same reasoning as in Appendix A, we can state the following.

Conclusion 3. The time-dependent CC flow approach (B1) is equivalent to the standard representation of the time-dependent CC equations defined by the $T(t)$.

APPENDIX C

In this Appendix we discuss properties of the CC flows defined by approximate methods for solving computational blocks (A1). First, let us assume that the $T_{\rm int}(\mathfrak{h}_i)$ (defined by excitation level m_i) is approximated by the operator $T^{(A)}_{\rm int}(\mathfrak{h}_i)$, which is by defined by excitations of maximum rank $m(A)_i$ $[m(A)_i < m_i]$. In this case, to obtain working equations for $T^{(A)}_{\rm int}(\mathfrak{h}_i)$ amplitudes, we will project Eq. (A2) for a given $\mathfrak{h}_i$ onto $P+Q^{(A)}_{\rm int}(\mathfrak{h}_i)$, where $Q^{(A)}_{\rm int}(\mathfrak{h}_i)$ is a projection operator on excitations generated by $T^{(A)}_{\rm int}(\mathfrak{h}_i)$ when acting on $|\Phi\rangle$, i.e.,

$$\left[P+Q^{(A)}_{\rm int}(\mathfrak{h}_i)\right][H^{\rm eff}(\mathfrak{h}_i)-E]e^{T^{(A)}_{\rm int}(\mathfrak{h}_i)}|\Phi\rangle = 0, \tag{C1}$$

where the full projection operator $Q_{\rm int}(\mathfrak{h}_i)$ can be partitioned as

$$Q_{\rm int}(\mathfrak{h}_i) = Q^{(A)}_{\rm int}(\mathfrak{h}_i)+R^{(A)}_{\rm int}(\mathfrak{h}_i). \tag{C2}$$

Equation (C1) can be now rewritten in the form

$$\left[P+Q^{(A)}_{\rm int}(\mathfrak{h}_i)\right][H^{\rm eff}(\mathfrak{h}_i)-E]\left[Q^{(A)}_{\rm int}(\mathfrak{h}_i)+R^{(A)}_{\rm int}(\mathfrak{h}_i)\right] \times e^{T^{(A)}_{\rm int}(\mathfrak{h}_i)}|\Phi\rangle = 0, \tag{C3}$$

which clearly shows that truncating the full form of $T_{\rm int}(\mathfrak{h}_i)$ results in equations that, due to the presence of the $R^{(A)}_{\rm int}(\mathfrak{h}_i)$-dependent term, no longer represent the eigenvalue problem. A similar form of nonlinear eigenvalue representation of CC flow has been analyzed by Živković and Monkhorst in Ref. [175]. Nevertheless, using reasoning similar to that in Appendix A, it can be shown that even in the case of standard approximations, Eq. (C1) can be recast in the standard connected form

$$\left[P+Q^{(\rm A)}_{\rm int}(\mathfrak{h}_i)\right]e^{-T^{(\rm A)}}He^{T^{(\rm A)}}|\Phi\rangle = 0, \tag{C4}$$

$$E = \langle\Phi|e^{-T^{(\rm A)}}He^{T^{(\rm A)}}|\Phi\rangle, \tag{C5}$$

where

$$T^{(A)}=\bigcup_{i=1}^{M}T^{(\rm A)}_{\rm int}(\mathfrak{h}_i). \tag{C6}$$

APPENDIX D

In this Appendix we focus on details of the numerical realization of the CC flow shown in Fig. 2. Without loss of generality, we focus on the serial flow shown in Fig. 2(a). The following steps are involved in the iterative process.

Step 1. Defining subalgebras or active spaces forming the flow. In this step we define a set of active spaces corresponding to subalgebras $\mathfrak{h}_i$ $(i=1,\ldots,M)$. In the flow we solve for the cluster operator T, $T=\bigcup_{i=1}^{M}T_{\rm int}(\mathfrak{h}_i)$.

Step 2. Ordering of active spaces. In serial flows, an important step is associated with establishing the importance of active spaces. For example, this can be achieved using values of the second order of many-body perturbation theory correlation energy contributions in active spaces included in the flow.

Step 3. Initialization of the T operator. For this purpose we can use simple perturbative or low-rank CC approximations (CCSD).

Step 4. Solving eigenvalue problems for active spaces. In this step we solve for the $T_{\rm int}(\mathfrak{h}_i)$ update by diagonalizing $e^{-T_{\rm ext}(\mathfrak{h}_i)}He^{T_{\rm ext}(\mathfrak{h}_i)}$ in the corresponding active space $[T_{\rm ext}(\mathfrak{h}_i) = T-T_{\rm int}(\mathfrak{h}_i)]$. In this step, the resulting CI-type coefficients have to be transformed, using cluster analysis, to the $T_{\rm int}(\mathfrak{h}_i)$ amplitudes.

Step 5. Update of the global T operator. All $T_{\rm int}(\mathfrak{h}_i)$ $(i=1,\ldots,M)$ define a new T operator.

Step 6. Convergence check. If the T operator satisfies convergence criteria, the final value of the correlation energy is calculated using either the standard CC energy expression or diagonalizing any of the effective Hamiltonians involved in the flow. If it does not, we repeat the procedure from step 4.

The peak computational cost of the CC flow is defined by the maximum-size active-space problem ($C_{\rm max}$). Therefore, the cost per iteration is proportional to $M\times C_{\rm max}$. The CC flow equation approach offers flexibility in the choice of the number of active spaces (M) and their size ($C_{\rm max}$), thus providing a framework where the resulting computational model is tuned to available computational resources.

It is also instructive to analyze the numerical cost of solving each computational block with approximate methods such as CCSDT or CCSDTQ (see Appendix C). Without loss of generality, let us assume a CC flow defined by $\mathfrak{g}^{(N)}(3_{R_i},y_{S_i})$ $(i=1,\ldots,M)$ problems. We assume that for each $i=1,\ldots,M$ the number of active virtual orbitals is the same and equals y. For the CCSDT solver the upper bound for

the numerical cost of the flow $\mathscr{F}_{\mathrm{CCSDT}}$ is given by the following formula, which is obtained by analyzing the contributions from the the most expensive terms:

$$\mathscr{F}_{\mathrm{CCSDT}} \leqslant \alpha \times M \times \binom{y}{3} \times n_v^2. \tag{D1}$$

Using the CCSDTQ solver for the same type of flow, the numerical cost of the upper bound $\mathscr{F}_{\mathrm{CCSDTQ}}$ is given by the formula

$$\mathscr{F}_{\mathrm{CCSDTQ}} \leqslant \beta \times M \times \binom{y}{4} \times n_v^2. \tag{D2}$$

In (D1) and (D2), α and β are constant prefactors. Both upper bounds depend on M and y, whose values can be chosen to match available computational resources and/or provide the desired level of accuracy.

[1] F. Coester, Nucl. Phys. **7**, 421 (1958).
[2] F. Coester and H. Kümmel, Nucl. Phys. **17**, 477 (1960).
[3] J. Čížek, J. Chem. Phys. **45**, 4256 (1966).
[4] J. Paldus, J. Čížek, and I. Shavitt, Phys. Rev. A **5**, 50 (1972).
[5] G. Purvis and R. Bartlett, J. Chem. Phys. **76**, 1910 (1982).
[6] J. Arponen, Ann. Phys. (NY) **151**, 311 (1983).
[7] R. F. Bishop and H. Kümmel, Phys. Today **40**(3), 52 (1987).
[8] R. F. Bishop, in *Microscopic Quantum Many-Body Theories and Their Applications*, edited by J. Navarro and A. Polls, Lecture Notes in Physics Vol. 510 (Springer, Berlin, 1998), pp. 1–70.
[9] H. Koch and P. Jørgensen, J. Chem. Phys. **93**, 3333 (1990).
[10] J. Paldus and X. Li, Adv. Chem. Phys. **110**, 1 (1999).
[11] T. D. Crawford and H. F. Schaefer, Rev. Comput. Chem. **14**, 33 (2000).
[12] R. J. Bartlett and M. Musiał, Rev. Mod. Phys. **79**, 291 (2007).
[13] J. S. Arponen, R. F. Bishop, and E. Pajanne, Phys. Rev. A **36**, 2519 (1987).
[14] J. S. Arponen, R. F. Bishop, and E. Pajanne, Phys. Rev. A **36**, 2539 (1987).
[15] J. Arponen and R. F. Bishop, Ann. Phys. (NY) **207**, 171 (1991).
[16] J. Arponen and R. F. Bishop, Ann. Phys. (NY) **227**, 275 (1993).
[17] N. I. Robinson, R. F. Bishop, and J. Arponen, Phys. Rev. A **40**, 4256 (1989).
[18] J. S. Arponen and R. F. Bishop, Theor. Chim. Acta **80**, 289 (1991).
[19] R. F. Bishop and K. H. Lührmann, Phys. Rev. B **17**, 3757 (1978).
[20] R. F. Bishop and K. H. Lührmann, Phys. Rev. B **26**, 5523 (1982).
[21] J. Arponen, R. F. Bishop, E. Pajanne, and N. I. Robinson, Phys. Rev. A **37**, 1065 (1988).
[22] K. Emrich and J. G. Zabolitzky, Phys. Rev. B **30**, 2049 (1984).
[23] R. F. Bishop, Theor. Chim. Acta **80**, 95 (1991).
[24] M. Funke, U. Kaulfuss, and H. Kümmel, Phys. Rev. D **35**, 621 (1987).
[25] H. G. Kümmel, Phys. Rev. B **64**, 014301 (2001).
[26] G. Hasberg and H. Kümmel, Phys. Rev. C **33**, 1367 (1986).
[27] R. F. Bishop, N. Ligterink, and N. R. Walet, Int. J. Mod. Phys. B **20**, 4992 (2006).
[28] N. Ligterink, N. Walet, and R. F. Bishop, Ann. Phys. (NY) **267**, 97 (1998).
[29] J. Arponen, R. F. Bishop, E. Pajanne, and N. I. Robinson, in *Condensed Matter Theories*, edited by J. S. Arponen, R. F. Bishop, and M. Manninen (Springer, Berlin, 1988), Vol. 3, pp. 51–66.
[30] R. F. Bishop, N. Robinson, J. Arponen, and E. Pajanne, in *Aspects of Many-Body Effects in Molecules and Extended Systems*, edited by D. Mukherjee, Lecture Notes in Chemistry Vol. 50 (Springer, Berlin, 1989), pp. 241–260.
[31] D. J. Dean and M. Hjorth-Jensen, Phys. Rev. C **69**, 054320 (2004).
[32] K. Kowalski, D. J. Dean, M. Hjorth-Jensen, T. Papenbrock, and P. Piecuch, Phys. Rev. Lett. **92**, 132501 (2004).
[33] G. Hagen, T. Papenbrock, D. J. Dean, and M. Hjorth-Jensen, Phys. Rev. Lett. **101**, 092502 (2008).
[34] A. C. Scheiner, G. E. Scuseria, J. E. Rice, T. J. Lee, and H. F. Schaefer III, J. Chem. Phys. **87**, 5361 (1987).
[35] M. O. Sinnokrot, E. F. Valeev, and C. D. Sherrill, J. Am. Chem. Soc. **124**, 10887 (2002).
[36] L. V. Slipchenko and A. I. Krylov, J. Chem. Phys. **117**, 4694 (2002).
[37] A. Tajti, P. G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vázquez, and J. F. Stanton, J. Chem. Phys. **121**, 11599 (2004).
[38] T. D. Crawford, Theor. Chem. Acc. **115**, 227 (2006).
[39] J. A. Parkhill, K. Lawler, and M. Head-Gordon, J. Chem. Phys. **130**, 084101 (2009).
[40] C. Riplinger and F. Neese, J. Chem. Phys. **138**, 034106 (2013).
[41] S. H. Yuwono, I. Magoulas, and P. Piecuch, Sci. Adv. **6**, eaay4058 (2020).
[42] H. Stoll, Phys. Rev. B **46**, 6700 (1992).
[43] S. Hirata, R. Podeszwa, M. Tobita, and R. J. Bartlett, J. Chem. Phys. **120**, 2581 (2004).
[44] H. Katagiri, J. Chem. Phys. **122**, 224901 (2005).
[45] G. H. Booth, A. Grüneis, G. Kresse, and A. Alavi, Nature (London) **493**, 365 (2013).
[46] M. Degroote, T. M. Henderson, J. Zhao, J. Dukelsky, and G. E. Scuseria, Phys. Rev. B **93**, 125124 (2016).
[47] J. McClain, Q. Sun, G. K.-L. Chan, and T. C. Berkelbach, J. Chem. Theory Comput. **13**, 1209 (2017).
[48] X. Wang and T. C. Berkelbach, J. Chem. Theory Comput. **16**, 3095 (2020).
[49] T. S. Haugland, E. Ronca, E. F. Kjønstad, A. Rubio, and H. Koch, Phys. Rev. X **10**, 041043 (2020).
[50] D. J. J. Farnell and R. F. Bishop, in *Quantum Magnetism*, edited by U. Schollwöck, J. Richter, D. J. J. Farnell, and R. F. Bishop, Lecture Notes in Physics Vol. 645 (Springer, Berlin, 2004), pp. 307–348.
[51] D. J. J. Farnell, O. Götze, J. Schulenburg, R. F. Zinke, R. F. Bishop, and P. H. Y. Li, Phys. Rev. B **98**, 224402 (2018).
[52] R. F. Bishop, P. H. Y. Li, O. Götze, and J. Richter, Phys. Rev. B **100**, 024401 (2019).
[53] B. H. Brandow, Rev. Mod. Phys. **39**, 771 (1967).

[54] I. Lindgren and J. Morrison, *Atomic Many-Body Theory*, Springer Series on Atomic, Optical, and Plasma Physics Vol. 3 (Springer, Berlin, 2012).

[55] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).

[56] S. A. Kucharski and R. J. Bartlett, J. Chem. Phys. **108**, 5243 (1998).

[57] S. A. Kucharski and R. J. Bartlett, J. Chem. Phys. **108**, 5255 (1998).

[58] T. D. Crawford and J. F. Stanton, Int. J. Quantum Chem. **70**, 601 (1998).

[59] S. R. Gwaltney and M. Head-Gordon, Chem. Phys. Lett. **323**, 21 (2000).

[60] S. R. Gwaltney, C. D. Sherrill, M. Head-Gordon, and A. I. Krylov, J. Chem. Phys. **113**, 3548 (2000).

[61] S. R. Gwaltney and M. Head-Gordon, J. Chem. Phys. **115**, 2014 (2001).

[62] S. Hirata, M. Nooijen, I. Grabowski, and R. J. Bartlett, J. Chem. Phys. **114**, 3919 (2001).

[63] Y. J. Bomble, J. F. Stanton, M. Kallay, and J. Gauss, J. Chem. Phys. **123**, 054101 (2005).

[64] J. B. Robinson and P. J. Knowles, J. Chem. Phys. **138**, 074104 (2013).

[65] U. Bozkaya and H. F. Schaefer III, J. Chem. Phys. **136**, 204114 (2012).

[66] M. Kallay and J. Gauss, J. Chem. Phys. **129**, 144101 (2008).

[67] L. Meissner and R. J. Bartlett, J. Chem. Phys. **115**, 50 (2001).

[68] K. Kowalski and P. Piecuch, J. Chem. Phys. **113**, 18 (2000).

[69] P. Piecuch, J. R. Gour, and M. Włoch, Int. J. Quantum Chem. **109**, 3268 (2009).

[70] N. P. Bauman, J. Shen, and P. Piecuch, Mol. Phys. **115**, 2860 (2017).

[71] A. J. W. Thom, Phys. Rev. Lett. **105**, 263004 (2010).

[72] J. E. Deustua, J. Shen, and P. Piecuch, Phys. Rev. Lett. **119**, 223003 (2017).

[73] C. Hampel and H.-J. Werner, J. Chem. Phys. **104**, 6286 (1996).

[74] M. Schütz, J. Chem. Phys. **113**, 9986 (2000).

[75] M. Schütz and H.-J. Werner, Chem. Phys. Lett. **318**, 370 (2000).

[76] M. Schütz and H.-J. Werner, J. Chem. Phys. **114**, 661 (2001).

[77] F. Neese, F. Wennmohs, and A. Hansen, J. Chem. Phys. **130**, 114108 (2009).

[78] F. Neese, A. Hansen, and D. G. Liakos, J. Chem. Phys. **131**, 064103 (2009).

[79] C. Riplinger, B. Sandhoefer, A. Hansen, and F. Neese, J. Chem. Phys. **139**, 134101 (2013).

[80] C. Riplinger, P. Pinski, U. Becker, E. F. Valeev, and F. Neese, J. Chem. Phys. **144**, 024109 (2016).

[81] F. Pavošević, P. Pinski, C. Riplinger, F. Neese, and E. F. Valeev, J. Chem. Phys. **144**, 144109 (2016).

[82] F. Pavošević, C. Peng, P. Pinski, C. Riplinger, F. Neese, and E. F. Valeev, J. Chem. Phys. **146**, 174108 (2017).

[83] M. Saitow, U. Becker, C. Riplinger, E. F. Valeev, and F. Neese, J. Chem. Phys. **146**, 164105 (2017).

[84] Y. Guo, C. Riplinger, U. Becker, D. G. Liakos, Y. Minenkov, L. Cavallo, and F. Neese, J. Chem. Phys. **148**, 011101 (2018).

[85] N. P. Bauman, E. J. Bylaska, S. Krishnamoorthy, G. H. Low, N. Wiebe, C. E. Granade, M. Roetteler, M. Troyer, and K. Kowalski, J. Chem. Phys. **151**, 014107 (2019).

[86] K. Kowalski and N. P. Bauman, J. Chem. Phys. **152**, 244127 (2020).

[87] N. P. Bauman, G. H. Low, and K. Kowalski, J. Chem. Phys. **151**, 234114 (2019).

[88] M. Metcalf, N. P. Bauman, K. Kowalski, and W. A. de Jong, J. Chem. Theory Comput. **16**, 6165 (2020).

[89] N. P. Bauman, J. Chládek, L. Veis, J. Pittner, and K. Kowalski, Quantum Sci. Technol. **6**, 034008 (2021).

[90] T. Takeshita, N. C. Rubin, Z. Jiang, E. Lee, R. Babbush, and J. R. McClean, Phys. Rev. X **10**, 011004 (2020).

[91] M. Motta, T. P. Gujarati, J. E. Rice, A. Kumar, C. Masteran, J. A. Latone, E. Lee, E. F. Valeev, and T. Y. Takeshita, Phys. Chem. Chem. Phys. **22**, 24270 (2020).

[92] S. McArdle and D. P. Tew, arXiv:2006.11181.

[93] B. Şahinoğlu and R. D. Somma, arXiv:2006.02660.

[94] A. Peruzzo, J. McClean, P. Shadbolt, M.-H. Yung, X.-Q. Zhou, P. J. Love, A. Aspuru-Guzik, and J. L. O'Brien, Nat. Commun. **5**, 4213 (2014).

[95] J. R. McClean, J. Romero, R. Babbush, and A. Aspuru-Guzik, New J. Phys **18**, 023023 (2016).

[96] J. Romero, R. Babbush, J. R. McClean, C. Hempel, P. J. Love, and A. Aspuru-Guzik, Quantum Sci. Technol. **4**, 014008 (2018).

[97] Y. Shen, X. Zhang, S. Zhang, J.-N. Zhang, M.-H. Yung, and K. Kim, Phys. Rev. A **95**, 020501(R) (2017).

[98] A. Kandala, A. Mezzacapo, K. Temme, M. Takita, M. Brink, J. M. Chow, and J. M. Gambetta, Nature (London) **549**, 242 (2017).

[99] A. Kandala, K. Temme, A. D. Corcoles, A. Mezzacapo, J. M. Chow, and J. M. Gambetta, Nature (London) **567**, 491 (2019).

[100] J. I. Colless, V. V. Ramasesh, D. Dahlen, M. S. Blok, M. E. Kimchi-Schwartz, J. R. McClean, J. Carter, W. A. de Jong, and I. Siddiqi, Phys. Rev. X **8**, 011021 (2018).

[101] W. J. Huggins, J. Lee, U. Baek, B. O'Gorman, and K. B. Whaley, New J. Phys. **22**, 073009 (2020).

[102] Y. Cao, J. Romero, J. P. Olson, M. Degroote, P. D. Johnson, M. Kieferová, I. D. Kivlichan, T. Menke, B. Peropadre, N. P. Sawaya *et al.*, Chem. Rev. **119**, 10856 (2019).

[103] I. G. Ryabinkin, R. A. Lang, S. N. Genin, and A. F. Izmaylov, J. Chem. Theory Comput. **16**, 1055 (2020).

[104] M. R. Hoffmann and J. Simons, J. Chem. Phys. **88**, 993 (1988).

[105] R. J. Bartlett, S. A. Kucharski, and J. Noga, Chem. Phys. Lett. **155**, 133 (1989).

[106] A. G. Taube and R. J. Bartlett, Int. J. Quantum Chem. **106**, 3393 (2006).

[107] G. Harsha, T. Shiozaki, and G. E. Scuseria, J. Chem. Phys. **148**, 044107 (2018).

[108] J. Lee, W. J. Huggins, M. Head-Gordon, and K. B. Whaley, J. Chem. Theory Comput. **15**, 311 (2018).

[109] A. F. Izmaylov, M. Díaz-Tinoco, and R. A. Lang, Phys. Chem. Chem. Phys. **22**, 12980 (2020).

[110] H. R. Grimsley, D. Claudino, S. E. Economou, E. Barnes, and N. J. Mayhall, J. Chem. Theory Comput. **16**, 1 (2019).

[111] F. A. Evangelista, G. K.-L. Chan, and G. E. Scuseria, J. Chem. Phys. **151**, 244112 (2019).

[112] H. R. Grimsley, S. E. Economou, E. Barnes, and N. J. Mayhall, Nat. Commun. **10**, 3007 (2019).

[113] I. G. Ryabinkin, T.-C. Yen, S. N. Genin, and A. F. Izmaylov, J. Chem. Theory Comput. **14**, 6317 (2018).

[114] R. A. Lang, I. G. Ryabinkin, and A. F. Izmaylov, J. Chem. Theory Comput. **17**, 66 (2020).
[115] K. Kowalski, J. Chem. Phys. **148**, 094104 (2018).
[116] J. Noga and R. J. Bartlett, J. Chem. Phys. **86**, 7041 (1987).
[117] J. Noga and R. J. Bartlett, J. Chem. Phys. **89**, 3401 (1988).
[118] G. E. Scuseria and H. F. Schaefer, Chem. Phys. Lett. **152**, 382 (1988).
[119] S. A. Kucharski and R. J. Bartlett, Theor. Chem. Acc. **80**, 387 (1991).
[120] N. Oliphant and L. Adamowicz, J. Chem. Phys. **95**, 6645 (1991).
[121] W. Lahoz and R. F. Bishop, Z. Phys. B **73**, 363 (1988).
[122] C. Bloch, Nucl. Phys. **6**, 329 (1958).
[123] J. Des Cloizeaux, Nucl. Phys. **20**, 321 (1960).
[124] P.-O. Löwdin, J. Mol. Spectrosc. **10**, 12 (1963).
[125] J. R. Schrieffer and P. A. Wolff, Phys. Rev. **149**, 491 (1966).
[126] B. H. Brandow, Adv. Quantum Chem. **10**, 187 (1977).
[127] C. Soliverez, J. Phys. C **2**, 2161 (1969).
[128] T. Schucan and H. Weidenmüller, Ann. Phys. (NY) **73**, 108 (1972).
[129] F. Jørgensen, Mol. Phys. **29**, 1137 (1975).
[130] D. Mukherjee, R. K. Moitra, and A. Mukhopadhyay, Mol. Phys. **30**, 1861 (1975).
[131] B. Jeziorski and H. J. Monkhorst, Phys. Rev. A **24**, 1668 (1981).
[132] W. Kutzelnigg, J. Chem. Phys. **77**, 3081 (1982).
[133] L. Z. Stolarczyk and H. J. Monkhorst, Phys. Rev. A **32**, 725 (1985).
[134] D. Mukherjee, Chem. Phys. Lett. **125**, 207 (1986).
[135] P. Durand, Phys. Rev. A **28**, 3184 (1983).
[136] P. Durand and J.-P. Malrieu, in *Ab Initio Methods in Quantum Chemistry*, edited by K. P. Lawley (Wiley, New York, 1987), Pt. I, p. 321.
[137] B. Jeziorski and J. Paldus, J. Chem. Phys. **90**, 2714 (1989).
[138] U. Kaldor, Theor. Chim. Acta **80**, 427 (1991).
[139] C. Rittby and R. Bartlett, Theor. Chim. Acta **80**, 469 (1991).
[140] K. Andersson, P.-Å. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski, J. Phys. Chem. **94**, 5483 (1990).
[141] K. Andersson, P.-Å. Malmqvist, and B. O. Roos, J. Chem. Phys. **96**, 1218 (1992).
[142] K. Hirao, Chem. Phys. Lett. **196**, 397 (1992).
[143] J. P. Finley, R. K. Chaudhuri, and K. F. Freed, J. Chem. Phys. **103**, 4990 (1995).
[144] S. D. Głazek and K. G. Wilson, Phys. Rev. D **48**, 5863 (1993).
[145] L. Meissner and M. Nooijen, J. Chem. Phys. **102**, 9604 (1995).
[146] L. Meissner, J. Chem. Phys. **108**, 9227 (1998).
[147] H. Nakano, K. Hirao, and M. S. Gordon, J. Chem. Phys. **108**, 5660 (1998).
[148] C. Angeli, R. Cimiraglia, and J.-P. Malrieu, Chem. Phys. Lett. **350**, 297 (2001).
[149] C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, and J.-P. Malrieu, J. Chem. Phys. **114**, 10252 (2001).
[150] T. Yanai and G. K.-L. Chan, J. Chem. Phys. **124**, 194106 (2006).
[151] D. I. Lyakh, M. Musiał, V. F. Lotrich, and R. J. Bartlett, Chem. Rev. **112**, 182 (2012).
[152] S. Bravyi, D. P. DiVincenzo, and D. Loss, Ann. Phys. (NY) **326**, 2793 (2011).
[153] B. Şahinoğlu and R. D. Somma, arXiv:2006.02660.
[154] C. M. Bender and S. Boettcher, Phys. Rev. Lett. **80**, 5243 (1998).
[155] C. M. Bender, D. C. Brody, and H. F. Jones, Phys. Rev. Lett. **89**, 270401 (2002).
[156] A. Mostafazadeh, J. Math. Phys. **43**, 205 (2002).
[157] M. Znojil *et al.*, SIGMA **5**, 001 (2009).
[158] R. F. Bishop and M. Znojil, Acta Polytech. **54**, 85 (2014).
[159] R. F. Bishop and M. Znojil, Eur. Phys. J. Plus **135**, 374 (2020).
[160] J. Arponen and R. F. Bishop, Ann. Phys. (NY) **227**, 334 (1993).
[161] S. Kvaal, J. Chem. Phys. **136**, 194109 (2012).
[162] T. B. Pedersen and S. Kvaal, J. Chem. Phys. **150**, 144106 (2019).
[163] S. Kvaal, A. Laestadius, and T. Bodenstein, Mol. Phys. **118**, e1810349 (2020).
[164] T. Sato, H. Pathak, Y. Orimo, and K. L. Ishikawa, J. Chem. Phys. **148**, 051101 (2018).
[165] W. Meyer, J. Chem. Phys. **58**, 1017 (1973).
[166] W. Meyer and P. Rosmus, J. Chem. Phys. **63**, 2356 (1975).
[167] F. Neese, A. Hansen, F. Wennmohs, and S. Grimme, Acc. Chem. Res. **42**, 641 (2009).
[168] O. Sinanoğlu, J. Chem. Phys. **36**, 3198 (1962).
[169] O. Sinanoğlu, Adv. Chem. Phys. **6**, 315 (1964).
[170] W. Meyer, Int. J. Quantum Chem. **5**, 341 (1971).
[171] R. F. Bishop, J. B. Parkinson, and Y. Xian, Phys. Rev. B **44**, 9425 (1991).
[172] R. F. Bishop and P. H. Y. Li, Phys. Rev. A **83**, 042111 (2011).
[173] J. Arponen, Phys. Rev. A **55**, 2686 (1997).
[174] J. R. McClean, R. Babbush, P. J. Love, and A. Aspuru-Guzik, J. Phys. Chem. Lett. **5**, 4368 (2014).
[175] T. P. Živković and H. J. Monkhorst, J. Math. Phys. **19**, 1007 (1978).