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Algebraic propagator approaches and intermediate-state representations. I. The biorthogonal and unitary coupled-cluster methods

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As a general common concept, underlying diverse methods used to compute generalized electronic excitations in atoms and molecules, intermediate-state representations (ISR's), are considered and analyzed. Essentially, an ISR results by representing the excitation energy operator in terms of so-called correlated excited states (CES's) or states derived thereof. Three different ISR schemes are compared, namely the biorthogonal coupled-cluster (BCC) representation used in both the coupled-cluster linear response and equation-of-motion coupled-cluster methods, a unitary coupled-cluster (UCC) representation, and the excitation class orthogonalized (ECO) representation resulting from a Gram-Schmidt orthogonalization procedure for the CES. Moreover, the relationship between the BCC scheme and the symmetry-adapted-cluster–configuration-interaction method is discussed. The relevance of the ISR schemes, as opposed to the much simpler configuration-interaction (CI) expansions, arises from two basic properties referred to as separability and compactness. The former property is a sufficient condition for size-consistent results, while the latter allows one to use smaller explicit configuration spaces than in comparable CI treatments. We show that the ECO and UCC representations are both separable and compact, whereas a somewhat restricted compactness property applies in the BCC case.

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I. INTRODUCTION

Propagator methods and related approaches are a natural starting point for studying electronic transitions in atoms and molecules. Here transitions are meant in a more generalized sense, comprising, in addition to neutral excitations, ionization, electron attachment, double ionization processes, etc., as well, that is, processes in which the number of electrons may change. For an introduction, overview, and references to the original literature the reader is referred to textbooks [1–3] and various review articles [4–11]. In comparison with the more conventional wave function approach, e.g., the configuration-interaction (CI) treatment, the propagator methods have two basic advantages. First, the excitation energies and transition moments (spectral intensities) are determined directly, that is, without the necessity of performing separate calculations for the initial and final states. Second, these methods are potentially size-consistent (more precisely size-intensive), which means that for a system consisting of separate (noninteracting) fragments the results do not depend on whether the method is applied to the total system or to the individual fragments. As is well known, this property is a precondition for obtaining meaningful results in applications to large molecules (for example, see [3]).

Various computational schemes have been developed deriving from or being related to propagator theory. Roughly, one may distinguish between so-called algebraic methods and methods based on diagrammatic perturbation theory. Well known algebraic approaches are the equation-of-motion (EOM) method [4,9,12] and the essentially equivalent superoperator formulation of propagators [6–8,10,13,14]. As an example of diagrammatic approaches we mention the outer valence Green's function (OVGF) method [11,15] for the electron propagator. A general procedure referred to as algebraic-diagrammatic construction (ADC) has been used to derive higher-order approximations within the diagrammatic approach [16–19].

In practice, most of the proposed approximation schemes take on the form of an eigenvalue problem of a (not necessarily Hermitian) secular matrix. Here, the physically interesting quantities, such as the (generalized) excitation energies, are given essentially by the eigenvalues while the associated transition moments are derived from the respective eigenvectors. What is the relationship of the various—at first glance quite different—computational schemes? As an explanatory, unifying concept one may regard the so-called intermediate-state representations (ISR's). Basically, intermediate-state representations result from representing the excitation energy operator (shifted Hamiltonian) $\hat{\boldsymbol{H}}-E_0^N$ (or a more general operator) in terms of a (complete) basis of states $|\tilde{\Psi}_J\rangle$, which in a certain sense "mediate" between the exact excited states $|\Psi_n\rangle$ (of the considered $N, N\pm1, N\pm2, \ldots,$ particle system) and the familiar Hartree-Fock (HF) configurations $|\Phi_J\rangle = \hat{\boldsymbol{C}}_J|\Phi_0^N\rangle$ used, e.g., in the CI treatment. Here $|\Phi_0^N\rangle$ is the N-electron Hartree-Fock ground state, and $\hat{\boldsymbol{C}}_J$ denote physical excitation operators (of $\nu=0,\pm1,\pm2,\ldots,$ electrons). The intermediate states $|\tilde{\Psi}_J\rangle$ may be generated in specific ways from the so-called correlated excited states (CES's) $\hat{\boldsymbol{C}}_J|\Psi_0^N\rangle$ obtained by applying the physical (or more general) excitation operators $\hat{\boldsymbol{C}}_J$ to the exact N-electron ground state $|\Psi_0^N\rangle$ (with energy E_0^N). The use of correlated excited states as expansion manifolds has been considered for a long time in the context of propagator theory [20–22]. Explicit use of intermediate-state representations has been made, for example, by Prasad *et al.* [23], by Mukherjee and Kutzelnigg [24], and by the present authors [25,26]. Moreover, several methods extending the coupled-cluster (CC) approach to the treatment of (generalized) electronic excitations may be viewed as examples of intermediate-state representations. The latter methods comprise the SAC-CI (symmetry-adapted-cluster–configuration-interaction) approach of Nakatsuji and Hirao [27–29], the coupled-cluster linear response (CCLR) theory [30–36], and the related equation-of-motion coupled-cluster (EOM-CC) approach [37–39].

Clearly, a representation of the Hamiltonian or more general operators based on correlated excited states is distinctly more complicated than, e.g., the familiar CI representation in terms of HF configurations. Thus it is legitimate to ask what are the advantages of using the intermediate-state representations. If one tries to analyze this issue beyond the naive expectation that it should be good to include (ground state) correlation effects already in the expansion manifold used in the excitation problem, one is led to two basic properties referred to as compactness and separability [25,26]. As will be explained in more detail below, compactness means that the explicit configuration spaces required in the ISR methods are smaller than those of comparable CI treatments. The separability property is a sufficient condition for the size-consistency (more specifically, size-intensivity) of the ISR methods. Essentially it means that in the secular problem for a system consisting of noninteracting (separable) fragments, so-called local excitations (associated with one of the subsystems) are strictly decoupled from nonlocal excitations. The interesting point elaborated further in this paper is that these two properties are not obtained by simply adopting the CES representation. As will be seen, the orthonormalization procedure imposed on the CE states plays a decisive role.

In this paper we compare three different intermediate-state representations, namely the biorthogonal coupled cluster (BCC) representation used both in the CCLR [30–36] and the EOM-CC methods [37–39], the unitary coupled-cluster (UCC) representation [23,24], and the excitation class orthogonalized (ECO) representation resulting from a special orthonormalization procedure for the correlated excited states [25,26]. In particular, the compactness and separability properties are analyzed. As will be seen, both the ECO and UCC representations comply fully with these important requirements, while a more restrictive compactness property applies to the BCC representation. In a subsequent paper [40] a similar analysis will be given of the EOM method for N, $N\pm1$, and $N\pm2$ particles.

An outline of this paper is as follows. Section II is used to introduce some basic definitions and, moreover, gives a brief review of the familiar CI representation with regard to the properties of interest here. The ensuing Secs. III, IV, and V treat separately the cases of the ECO, BCC, and UCC representations, respectively. A brief summary and some conclusions are given in the final Sec. VI.

II. GENERAL ASPECTS OF INTERMEDIATE-STATE REPRESENTATIONS

While the intermediate representations to be considered in the following were originally brought forth in the context of propagator theory, they may as well be introduced directly without reference to propagators. Let us consider a system of N electrons having a nondegenerate ground state $|\Psi_0^N\rangle$ of energy E_0^N. It is convenient to use the language of second quantization, where $c_p^\dagger$ (c_p) denote creation (destruction) operators associated with a suitably chosen basis of single-particle states (orbitals) $|\phi_p\rangle$. Usually, the set of orbitals $|\phi_p\rangle$ will be generated by a Hartree-Fock calculation for the N-electron ground state. According to the occupation numbers in the HF ground state $|\Phi_0^N\rangle$, $n_p=1-\bar{n}_p=1,0$, the orbitals $|\phi_p\rangle$ are denoted as occupied orbitals (or hole states) and unoccupied orbitals (or particle states), respectively. The Hamiltonian $\hat{\boldsymbol{H}}$ of the system reads in second-quantized notation

$$\hat{\boldsymbol{H}}=\hat{\boldsymbol{T}}+\hat{\boldsymbol{V}}=\sum_{pq} t_{pq}c_p^\dagger c_q+\frac{1}{2}\sum_{pqrs} V_{pqrs}c_p^\dagger c_q^\dagger c_s c_r\,, \tag{1}$$

where t_{pq} denote matrix elements of the single-particle part of the energy and $V_{pqrs}=\langle\phi_p\phi_q|v|\phi_r\phi_s\rangle$ denote the Coulomb integrals arising from the electronic repulsion. In the form of Eq. (1) $\hat{\boldsymbol{H}}$ does not depend explicitly on the number of electrons, and thus may be used as well to describe the corresponding systems of $N\pm1,N\pm2,\ldots$, electrons. For the purpose of using perturbation theory, the Hamiltonian may be decomposed according to

$$\hat{\boldsymbol{H}}=\hat{\boldsymbol{H}}_0+\hat{\boldsymbol{H}}_I \tag{2}$$

into an unperturbed (diagonal) one-particle part

$$\hat{\boldsymbol{H}}_0=\sum_p \epsilon_p c_p^\dagger c_p\,, \tag{3}$$

where ϵ_i denote the orbital energies, and an interaction part

$$\hat{\boldsymbol{H}}_I=\hat{\boldsymbol{W}}+\hat{\boldsymbol{V}}, \tag{4}$$

where $\hat{\boldsymbol{V}}$ is the electronic repulsion and $\hat{\boldsymbol{W}}=\hat{\boldsymbol{T}}-\hat{\boldsymbol{H}}_0$ is a residual nondiagonal single-particle part.

Generalized excitation energies of N' electrons ($N'=N,N\pm1,\ldots$)

$$\omega_n=E_n^{N'}-E_0^N \tag{5}$$

and the associated excited states $|\Psi_n^{N'}\rangle$ may be obtained as the eigenvalues and eigenfunctions, respectively, of the "shifted" Hamiltonian $\hat{\boldsymbol{H}}-E_0^N$:

$$(\hat{\boldsymbol{H}}-E_0^N)|\Psi_n^{N'}\rangle=\omega_n|\Psi_n^{N'}\rangle. \tag{6}$$

Besides the energies, one is interested in spectral intensities derived from (generalized) transition moments

$$T_n=\langle\Psi_n^{N'}|\hat{\boldsymbol{D}}^{(r)}|\Psi_0^N\rangle, \tag{7}$$

where $\hat{\boldsymbol{D}}^{(r)}$, $r=N'-N$, is a suitably chosen transition operator, e.g., the N-electron dipole operator in the case of neutral excitations ($r=0$).

In general, the solution of the eigenvalue problem (6) requires one to introduce a basis set representation of $\hat{\boldsymbol{H}}-E_0^N$ and a subsequent treatment of the corresponding secular equation. Let $|\tilde{\Psi}_J\rangle$, $J=1,2,\ldots$, denote a complete orthonormal basis in the Hilbert space of N' electrons, giving rise to a Hermitian matrix representation $\underline{\underline{\tilde{H}}}$ of the Hamiltonian,

$$\tilde{H}_{IJ}=\langle\tilde{\Psi}_I|\hat{\boldsymbol{H}}|\tilde{\Psi}_J\rangle. \tag{8}$$

Using this basis set representation, Eq. (6) is transformed into the algebraic eigenvalue problem

$$(\underline{\underline{\tilde{H}}}-E_0^N\underline{\underline{1}})\underline{\underline{Y}}=\underline{\underline{Y}}\ \underline{\underline{\Omega}},\qquad \underline{\underline{Y}}^\dagger\underline{\underline{Y}}=\underline{\underline{1}} \tag{9}$$

for the matrix $\underline{\underline{\tilde{H}}}-E_0^N\underline{\underline{1}}$. Here $\underline{\underline{\Omega}}$ denotes the diagonal matrix of excitation energies ω_n, and $\underline{\underline{Y}}$ denotes the matrix of eigenvectors. The transition moments can be obtained according to

$$T_n=\sum_J Y_{nJ}^*\tilde{F}_J \tag{10}$$

as the scalar product of the nth eigenvector $\underline{Y}_n$ and the vector $\underline{\tilde{F}}$ of the transition moments

$$\tilde{F}_I=\langle\tilde{\Psi}_I|\hat{\boldsymbol{D}}^{(r)}|\tilde{\Psi}_0^N\rangle \tag{11}$$

defined with respect to the states $|\tilde{\Psi}_I\rangle$.

Before turning to the intermediate representations it may be helpful to take a brief view of the familiar configuration-interaction representation. To be more specific we will confine ourselves in the following to the case of excitations in the $(N-1)$-electron system (single-electron ionization), but the ensuing discussion can easily be generalized to any N'-electron states (see Sec. III D). A complete and orthonormal set of CI configurations (or HF configurations) for the $(N-1)$-particle Hilbert space is given by the states

$$|\Phi_J\rangle=\hat{\boldsymbol{C}}_J|\Phi_0^N\rangle \tag{12}$$

where $\hat{\boldsymbol{C}}_J$ denote "physical" excitation operators from the operator manifold

$$\{\hat{\boldsymbol{C}}_J\}\equiv\{c_i, c_a^\dagger c_i c_j, i<j; c_a^\dagger c_b^\dagger c_i c_j c_k, a<b, i<j<k; \ldots\}. \tag{13}$$

Here the subscripts $a,b,c,\ldots,$ and $i,j,k,l,\ldots,$ refer to unoccupied and occupied orbitals, respectively; capital latin subscripts are used as a shorthand notation for the respective strings of single-particle indices: $J\equiv(a,b,c,\ldots;i,j,k,l,\ldots)$. The operators $\hat{\boldsymbol{C}}_J$ are called "physical" since their action on the HF ground state consists in removing electrons from occupied orbitals and adding electrons into unoccupied orbitals. The excitation operators $\hat{\boldsymbol{C}}_J$ decompose into obvious classes, referred to as μ-hole–$(\mu-1)$-particle excitations $[\mu h$–$(\mu-1)p]$, $\mu=1,2,3,\ldots,N$ according to the number μ of destruction operators. The class of an arbitrary excitation J will be denoted by $[J]$.

The CI representation of $\hat{\boldsymbol{H}}$ is a matrix $\underline{\underline{H}}$ with the elements $H_{IJ}=\langle\Phi_I|\hat{\boldsymbol{H}}|\Phi_J\rangle$. The partitioning of the CI configurations into excitation classes generates a block structure of $\underline{\underline{H}}=(\underline{\underline{H}}(\mu,\nu))$, $\mu,\nu=1,\ldots,N$. Because $\hat{\boldsymbol{H}}$ contains (at most) a two-body operator, the blocks $\underline{\underline{H}}(\mu,\nu)$ vanish when $|\mu-\nu|>2$. The nonvanishing matrix elements for $|\mu-\nu|=1,2$ are linear expressions of the Coulomb integrals, or of "first order" in the language of perturbation theory. Only the diagonal elements of $\underline{\underline{H}}$ (and of $\underline{\underline{H}}-E_0^N\underline{\underline{1}}$) contain the (HF) orbital energies, that is, zeroth-order contributions. This "order structure" of $\hat{\boldsymbol{H}}$ is depicted in Fig. 1. Complete CI expansions (full CI) [41,42] are practical only for limited one-particle basis sets and small systems. Usually the number of CI configurations must be restricted. A systematical truncation scheme, leading to perturbation-theoretical consistency, is to include all configurations up to a certain excitation class. For example, a configuration space comprising the classes $\mu=1$, 2, and 3 allows for a consistent second-order description of the primary states [i.e., states essentially characterized as $1h$ states (or Koopmans states)]. For a Hamiltonian containing one- and two-particle interaction, the general rule is that the consistent description of the primary states through order $2m$ and $2m+1$ requires one to include the first $2m+1$ classes in the CI configuration space. Stated differently, the CI configuration space (beginning at $\mu=1$ for $n=1$) grows in each even order n of perturbation theoretical consistency by two excitation classes. As will be discussed below, the intermediate-state representations require distinctly smaller (*compact*) configuration spaces for a comparable description.

	1h	2h1p	3h2p	4h3p	5h4p ···
1h	0	1	1		
2h1p	1	0	1	1	
3h2p	1	1	0	1	1
4h3p		1	1	0	1
5h4p			1	1	0
⋮					

FIG. 1. Order relations of the CI matrix $\underline{\underline{H}}$ in the case of $(N-1)$-electron states. The numbers in the blocks of $\underline{\underline{H}}$ indicate the (lowest) perturbation theoretical order; empty blocks vanish.

As is well known, limited CI expansions for (generalized) electronic excitations are not size-consistent (here, more specifically, size-intensive). This means that for a system S consisting of two noninteracting (separate) parts A and B the method gives different results for, say, a "local" excitation on A when applied to S or to A alone [43]. The reason for this behavior is that the CI matrix is not "separable," that is, "local" excitations, say, on A do not decouple from nonlocal excitations involving both A and B. The mixing of local and nonlocal configurations is introduced, for example, via the block $\underline{\underline{H}}(1,3)$ containing matrix elements of the kind

$$H_{p,abijk}=-\delta_{pk}V_{ab[ij]}-\delta_{pi}V_{ab[jk]}-\delta_{pj}V_{ab[ik]}. \tag{14}$$

Here $V_{ab[ij]}$ denotes the antisymmetrized Coulomb integral. Obviously these matrix elements allow for a coupling of a $1h$ configuration (p) local on A and a $3h$-$2p$ configuration $(abijk)$ in which a hole on A is accompanied by a $2p$-$2h$ (double) excitation on B. By contrast to the CI treatment, the intermediate-state representations are separable and, thus, size-intensive, as will be discussed in the ensuing Sec. III.

III. EXCITATION CLASS ORTHONORMALIZED INTERMEDIATE-STATE REPRESENTATION

A. Gram-Schmidt orthogonalization of correlated excited states

The common starting point for the intermediate-state representations is the set of "correlated" excited (CE) states

$$|\Psi_J^0\rangle = \hat{\boldsymbol{C}}_J|\Psi_0^N\rangle \tag{15}$$

obtained by applying the excitation operators (13) to the correlated ground state $|\Psi_0^N\rangle$. As above we shall confine ourselves for the moment to the case of excitations in the $(N-1)$-electron system. The following treatment can be easily transferred to the other cases, as is briefly discussed in Sec. III D. As was shown by Manne [20] and Dalgaard [21], the CE states (15) form a complete set of $(N-1)$-electron states, provided that $\langle\Psi_0^N|\Phi_0^N\rangle \neq 0$ (see also Sec. IV). Obviously the CE states are not orthonormal. The overlap integrals

$$\rho_{IJ} = \langle\Psi_0^N|\hat{\boldsymbol{C}}_I^\dagger\hat{\boldsymbol{C}}_J|\Psi_0^N\rangle \tag{16}$$

may be considered as the matrix elements of a generalized density matrix $\underline{\underline{\rho}}$. Orthonormal states $|\overline{\Psi}_J\rangle$ may be obtained by the symmetrical orthonormalization (SO) procedure according to

$$|\overline{\Psi}_J\rangle = \sum_I |\Psi_I^0\rangle(\underline{\underline{\rho}}^{-1/2})_{IJ}. \tag{17}$$

However, the representation of $\hat{\boldsymbol{H}} - E_0^N$ defined with respect to these SO states is neither separable nor compact. This can be seen by inspecting, for example, the $1h/3h$-$2p$ coupling matrix elements $\overline{H}_{p,abijk}$. These matrix elements have contributions allowing for the coupling of local and nonlocal configurations [26], similar to the CI matrix elements (14). A different possibility of generating orthonormal states is the Gram-Schmidt (GS) orthogonalization of successive excitation classes in which the CE states can be divided. Since this procedure has been considered in some detail elsewhere [25,26], we may confine ourselves here to a brief review of its essential features. The excitation class orthogonalized intermediate states $|\tilde{\Psi}_J\rangle$ can be constructed recursively as follows:

(i) Assume that the intermediate states $|\tilde{\Psi}_K\rangle$ of the classes $1,\ldots,\nu-1$ have been constructed. Then the states $|\Psi_J^0\rangle$ of class $[J]=\nu$ are orthogonalized to all intermediate states $|\tilde{\Psi}_K\rangle$ of the lower classes, $[K]<\nu$ according to

$$|\Psi_J^\#\rangle = |\Psi_J^0\rangle - \sum_{\substack{K\\ [K]<[J]}} |\tilde{\Psi}_K\rangle\langle\tilde{\Psi}_K|\Psi_J^0\rangle. \tag{18}$$

(ii) The "precursor" states $|\Psi_J^\#\rangle$ of class ν may then be orthonormalized symmetrically among each other, yielding

$$|\tilde{\Psi}_J\rangle = \sum_{\substack{J'\\ [J']=[J]}} |\Psi_{J'}^\#\rangle(\underline{\underline{\rho}}^{\#-1/2})_{J'J}. \tag{19}$$

Here $\underline{\underline{\rho}}^\#$ denotes the matrix of overlap integrals $\rho_{J'J}^\# = \langle\Psi_{J'}^\#|\Psi_J^\#\rangle$ of the precursor states of class ν.

For later use it is convenient to transfer the GS procedure (18,19) to the excitation operators $\hat{\boldsymbol{C}}_J$ themselves. This leads to ECO operators $\tilde{\boldsymbol{C}}_J$, with the property that

$$|\tilde{\Psi}_J\rangle = \tilde{\boldsymbol{C}}_J|\Psi_0^N\rangle. \tag{20}$$

Note that any ECO operator is given by a linear combination

$$\tilde{\boldsymbol{C}}_J = \sum_{\substack{K\\ [K]\leq[J]}} a_{JK}\hat{\boldsymbol{C}}_K \tag{21}$$

of excitation operators of the same and lower classes, where the coefficients a_{JK} are uniquely determined by $|\Psi_0^N\rangle$.

The ECO intermediate states $|\tilde{\Psi}_J\rangle$ obtained by the GS procedure (18,19) define a matrix representation $\underline{\underline{\tilde{H}}} - E_0^N\underline{\underline{1}}$ of $\hat{\boldsymbol{H}} - E_0^N$, where

$$\tilde{H}_{IJ} - E_0^N\delta_{IJ} = \langle\tilde{\Psi}_I|\hat{\boldsymbol{H}} - E_0^N|\tilde{\Psi}_J\rangle = \langle\Psi_0^N|\tilde{\boldsymbol{C}}_I^\dagger[\hat{\boldsymbol{H}},\tilde{\boldsymbol{C}}_J]|\Psi_0^N\rangle. \tag{22}$$

Note that in the last expression E_0^N is no longer explicit, while the knowledge of $|\Psi_0^N\rangle$ is required both to determine the ECO operators and to evaluate the secular matrix. For explicit expressions see [25]. The resulting eigenvalue problem to be solved is as formulated by Eqs. (9). The question as to what is gained by using the more complicated ECO representation instead of the CI representation will be addressed in the ensuing Secs. III B and III C.

B. Compactness property

Practical computational schemes can be deduced from the general ECO representation (22) by introducing approximations for the reference state $|\Psi_0^N\rangle$ and by truncating the ECO configuration space. As in the CI approximations, one may investigate the resulting truncation error. For this purpose we consider the block structure of $\underline{\underline{\tilde{H}}} - E_0^N\underline{\underline{1}}$ according to the excitation classes $(\mu=1,\ldots,N)$ of the ECO states. Unlike in the CI matrix, there will be, in general, no vanishing blocks of $\underline{\underline{\tilde{H}}} - E_0^N\underline{\underline{1}}$. However, the matrix elements of $\underline{\underline{\tilde{H}}} - E_0^N\underline{\underline{1}}$ are subject to well-behaved ("regular") perturbation expansions (see the discussion below), for which the following ("canonical") order relations apply:

$$(\underline{\underline{\tilde{H}}} - E_0^N\underline{\underline{1}})(\mu,\nu) = 0(|\mu-\nu|). \tag{23}$$

This means that, for example, the coupling matrix element $\tilde{H}_{p,abijk}$ between a $1h$ $(\mu=1)$ state and a $3h$-$2p$ state $(\nu=3)$ is of second order (at least). This order structure of $\underline{\underline{\tilde{H}}} - E_0^N\underline{\underline{1}}$ is schematically shown in Fig. 2.

As a direct consequence of the order relations (23), in the following referred to as canonical order relations, the error introduced (for the primary states) by truncating the ECO configuration space beyond class m is of order $2m$. Or stated differently, a consistent treatment of the primary states through order $2m$ and $2m+1$ only requires one to take the configuration classes $\mu=1,\ldots,m+1$ into account. This is called the compactness property of the ECO intermediate-

	1h	2h1p	3h2p	4h3p	5h4p ⋯
1h	0	1	2	3	4
2h1p	1	0	1	2	3
3h2p	2	1	0	1	2
4h3p	3	2	1	0	1
5h4p	4	3	2	1	0
⋮					

FIG. 2. Order relations of the secular matrix $\tilde{\underline{\underline{H}}}$, Eq. (23), of the ECO intermediate-state representation in the case of $(N-1)$-electron states. The numbers in the blocks of $\tilde{\underline{\underline{H}}}$ indicate the (lowest) nonvanishing perturbation theoretical order.

state representation. One should recall that a comparable CI expansion comprises the first $2m+1$ excitation classes. A similar order relation holds for the intermediate transition moments

$$\tilde{F}_J = \langle \tilde{\Psi}_J | \hat{\boldsymbol{D}} | \Psi_0^N \rangle. \tag{24}$$

Let $\hat{\boldsymbol{D}}$ denote an arbitrary (not necessarily physical) rh-$(r-1)p$ operator. Then the order relation

$$\tilde{F}_J = O([J]-r); \;\; [J] \geqslant r \tag{25}$$

holds for the states J of class $[J] \geqslant r$.

A proof of the compactness property of the ECO intermediate representation has been given in [25]. The essential step here was to show that the unitary matrix $\underline{\underline{Q}}$ transforming the intermediate states into the exact energy eigenstates,

$$Q_{nJ} = \langle \Psi_n | \tilde{\Psi}_J \rangle, \tag{26}$$

fulfills the canonical order relation (23), that is,

$$\underline{\underline{Q}}(\mu,\nu) = O(|\mu-\nu|). \tag{27}$$

Here it is assumed $\underline{\underline{Q}}$ can be organized in blocks $\underline{\underline{Q}}(\mu,\nu)$ according to the excitation classes. Since

$$\tilde{\underline{\underline{H}}} - E_0^N \underline{\underline{1}} = \underline{\underline{Q}}^\dagger \underline{\underline{\Omega}} \;\; \underline{\underline{Q}}, \tag{28}$$

where $\underline{\underline{\Omega}}$ is the diagonal matrix of exact excitation energies [for which $\omega_n \cong O(0)$], one may easily convince oneself that the canonical order relation (23) holds for the ECO secular matrix $\tilde{\underline{\underline{H}}} - E_0^N \underline{\underline{1}}$. A more direct proof of the compactness of $\tilde{\underline{\underline{H}}} - E_0^N \underline{\underline{1}}$ is given in Appendix A.

The construction of the ECO states $|\tilde{\Psi}_J\rangle$ depends solely on the correlated ground state $|\Psi_0^N\rangle$. This suggests that perturbation theory for $|\Psi_0^N\rangle$ can be used to generate well-defined perturbation expansions for the secular matrix elements $\tilde{H}_{IJ} - E_0^N \delta_{IJ}$ and the intermediate transition moments $\tilde{F}_J$:

$$\tilde{\underline{\underline{H}}} - E_0^N \underline{\underline{1}} = \underline{\underline{K}} + \underline{\underline{C}}^{(1)} + \underline{\underline{C}}^{(2)} + \cdots, \tag{29}$$

$$\tilde{F}_J = \tilde{F}_J^{(0)} + \tilde{F}_J^{(1)} + \cdots. \tag{30}$$

Here, in accordance with the notation of [25], we write $\tilde{\underline{\underline{H}}} - E_0^N \underline{\underline{1}} = \underline{\underline{K}} + \underline{\underline{C}}$ where $\underline{\underline{K}}$ is the diagonal matrix of (zeroth-order) HF ionization energies, while $\underline{\underline{C}}$ comprises the first- and higher-order contributions. The perturbation expansions are "regular," that is, they behave essentially like the usual Rayleigh-Schrödinger perturbation expansions for $|\Psi_0^N\rangle$ and E_0^N, respectively [25]. This means, in particular, that the absolute values of the occurring energy denominators are not smaller than the energy gap between occupied and unoccupied orbitals in the N-electron HF ground state. Provided that these perturbation expansions converge sufficiently well, one may generate practical systematic approximation schemes by truncating the perturbation series in Eqs. (29,30) at some low order. Such schemes have been derived previously by a procedure referred to as algebraic diagrammatic construction (ADC) from a reformulation of the familiar diagrammatic perturbation expansions for the various propagators [16–19]. In the ADC schemes, the maximal order of perturbation theory required for a consistent nth-order description of the primary states depends on the respective block of $\underline{\underline{K}} + \underline{\underline{C}}$ and $\tilde{\underline{F}}$. For $n=3$, for example, $\underline{\underline{C}}(1,1)$, $\underline{\underline{C}}(1,2)$, and $\underline{\underline{C}}(2,2)$ are required through third, second, and first order, respectively; no other blocks are needed.

C. Separability

To discuss the size-consistency of the ECO intermediate representation we reconsider the separate fragments model S consisting of two noninteracting parts A and B. We may assume that the single-particle states are localized on A or on B, respectively. This allows us to specify the general excitations J of S according to $J \equiv (J_A J_B)$ where the "subexcitations" J_A and J_B refer to the fragments A and B, respectively. As shown in [26], the obvious factorization

$$|\Psi^0_{J_A J_B}\rangle = |\Psi^A_{J_A}\rangle |\Psi^B_{J_B}\rangle \tag{31}$$

of the correlated excited states holds also for the ECO intermediate states, that is,

$$|\tilde{\Psi}_{J_A J_B}\rangle = |\tilde{\Psi}^A_{J_A}\rangle |\tilde{\Psi}^B_{J_B}\rangle. \tag{32}$$

As an immediate consequence, the ECO intermediate representation of $\hat{\boldsymbol{H}} = \hat{\boldsymbol{H}}_A + \hat{\boldsymbol{H}}_B$ is separable, which means that a purely local excitation $I \equiv I_A$ does not couple to nonlocal excitations of the type $J \equiv (J_A J_B)$. This leads to the following block structure of $\tilde{\underline{\underline{H}}}$:

$$\tilde{\underline{\underline{H}}} = \begin{pmatrix} \tilde{\underline{\underline{H}}}_{AA} & 0 & 0 \\ 0 & \tilde{\underline{\underline{H}}}_{BB} & 0 \\ 0 & 0 & \tilde{\underline{\underline{H}}}_{AB\,AB} \end{pmatrix}. \tag{33}$$

Obviously, the separability property also holds for the secular matrix $\tilde{\underline{\underline{H}}} - E_0^N \underline{\underline{1}}$. Moreover, here the local blocks of $\tilde{\underline{\underline{H}}} - E_0^N \underline{\underline{1}}$ are identical to the corresponding secular matrices $(\tilde{\underline{\underline{H}}}^{(A)} - E_0^N \underline{\underline{1}}^{(A)})$ and $(\tilde{\underline{\underline{H}}}^{(B)} - E_0^N \underline{\underline{1}}^{(B)})$ obtained for the individual systems A and B, respectively. A similar property applies to the intermediate transition moments (see [26]).

The intermediate transition moment $\tilde{F}_{J_A}$ for a local excitation $J \equiv J_A$ is identical to the corresponding transition moment $\tilde{F}^{(A)}_{J_A}$ of subsystem A,

$$\tilde{F}_{J_A} = \tilde{F}^{(A)}_{J_A}. \tag{34}$$

Equations (33) and (34) establish the size-consistency (intensity) of the ECO-ISR approach: the results obtained for, say, A alone are identical to those obtained for $A+B$ at any common level of approximation.

D. The ECO representations in other cases and the relationship to propagators

The construction of intermediate $(N+1)$-, $(N\pm 2)$-, $(N\pm 3)$-, . . . , particle states is completely analogous to the procedure described in Sec. III A. The corresponding correlated excitations are defined as in Eq. (15) using the respective sets of physical excitation operators specified below.

(a) $N+1$ particle states:

$$\{\hat{\boldsymbol{C}}_J\} = \{c_a^\dagger, c_a^\dagger c_b^\dagger c_i, c_a^\dagger c_b^\dagger c_c^\dagger c_i c_j, \ldots\}. \tag{35}$$

(b) $N-2$ particle states:

$$\{\hat{\boldsymbol{C}}_J\} = \{c_i c_j, c_a^\dagger c_i c_j c_k, c_a^\dagger c_b^\dagger c_i c_j c_k c_l, \ldots\}. \tag{36}$$

(c) $N+2$ particle states:

$$\{\hat{\boldsymbol{C}}_J\} = \{c_a^\dagger c_b^\dagger, c_a^\dagger c_b^\dagger c_c^\dagger c_i, c_a^\dagger c_b^\dagger c_c^\dagger c_d^\dagger c_i c_j, \ldots\}. \tag{37}$$

Here the creation and destruction operators are associated with unoccupied (particle) and occupied (hole) one-particle states, respectively. Obvious index restrictions, e.g., $a < b$ for the set $c_a^\dagger c_b^\dagger c_i$ are assumed.

For the case of N-particle states the definition of the correlated excitations has to be modified slightly according to

$$|\Psi_J^0\rangle = \hat{\boldsymbol{C}}_J |\Psi_0^N\rangle - |\Psi_0^N\rangle\langle\Psi_0^N|\hat{\boldsymbol{C}}_J|\Psi_0^N\rangle \tag{38}$$

in order to ensure their orthogonality to the exact ground state $|\Psi_0^N\rangle$. The set of physical excitation operators here is

$$\{\hat{\boldsymbol{C}}_J\} = \{c_a^\dagger c_i, c_a^\dagger c_b^\dagger c_i c_j, c_a^\dagger c_b^\dagger c_c^\dagger c_i c_j c_k, \ldots\}. \tag{39}$$

Formally the orthogonalization of the states $|\Psi_J^0\rangle$ to the N-electron ground state according to Eq. (38) may be included in the general GS orthogonalization procedure (18,19) by regarding $|\Psi_0^N\rangle$ as a zeroth excitation class $(\nu = 0)$. For all cases, the partitioning of the correlated excitations into excitation classes $\nu = 1,2,3, \ldots$, is obvious.

Finally we discuss the use of the intermediate states in representing the various propagators. As an example let us consider the one-particle Green's function (electron propagator) $\boldsymbol{G}(\omega)$. In energy representation $\boldsymbol{G}(\omega)$ is a matrix of elements [1]

$$G_{pq}(\omega) = G_{pq}^-(\omega) + G_{pq}^+(\omega), \tag{40}$$

where

$$G_{pq}^-(\omega) = \langle\Psi_0^N|c_q^\dagger(\omega + \hat{\boldsymbol{H}} - E_0^N - i\eta)^{-1} c_p|\Psi_0^N\rangle, \tag{41}$$

$$G_{pq}^+(\omega) = \langle\Psi_0^N|c_p(\omega - \hat{\boldsymbol{H}} + E_0^N + i\eta)^{-1} c_q^\dagger|\Psi_0^N\rangle. \tag{42}$$

Here η is a positive infinitesimal required to define the Fourier transformation between time and energy representations. $\boldsymbol{G}(\omega)$ is seen as consisting of two parts $\boldsymbol{G}^-(\omega)$ and $\boldsymbol{G}^+(\omega)$ containing physical information on the $(N-1)$- and the $(N+1)$-particle systems, respectively. By inserting the (complete) set of intermediate $(N-1)$-particle states $|\tilde{\Psi}_J\rangle$ on the right hand side of Eq. (41) one arrives at the ECO intermediate-state representation of $\boldsymbol{G}^-(\omega)$,

$$\underline{\underline{\boldsymbol{G}}}^-(\omega) = \underline{\underline{f}}^\dagger(\omega\underline{\underline{1}} - \underline{\underline{K}} - \underline{\underline{C}} - i\eta)^{-1}\underline{\underline{f}}, \tag{43}$$

where $-(\underline{\underline{K}} + \underline{\underline{C}})$ is the ECO secular matrix given by Eq. (22) and $\underline{\underline{f}}$ is the matrix of intermediate transition moments $\langle\tilde{\Psi}_J|c_p|\Psi_0^N\rangle$. An analogous expression is obtained for $\boldsymbol{G}^+(\omega)$ by using the set of intermediate $(N+1)$-states. It is readily seen that the solution of the ECO intermediate-state eigenvalue problem [Eqs. (9–11)] leads to the (diagonal) spectral representation

$$\underline{\underline{\boldsymbol{G}}}^-(\omega) = \underline{\underline{x}}^\dagger(\omega\underline{\underline{1}} - \underline{\underline{\Omega}} - i\eta)^{-1}\underline{\underline{x}}, \tag{44}$$

in which the physical content of $\boldsymbol{G}^-(\omega)$ is explicit. Here $\underline{\underline{\Omega}}$ is the diagonal matrix of (negative) ionization energies and $\underline{\underline{x}}$ denotes the matrix of the spectroscopic amplitudes $x_{np} = \langle\Psi_n|c_p|\Psi_0^N\rangle$. In a similar way, the ECO intermediate states for N and $N\pm 2$ electrons may be used to obtain representations of the polarization propagator and the $2p(2h)$ propagator, respectively. The reformulation of propagators in the form of Eq. (43) has been considered previously in the context of the ADC method [16–19]. In this method the matrix elements of the effective quantities $\underline{\underline{C}}$ and $\underline{\underline{f}}$ are determined indirectly by comparing the perturbation expansion of the algebraic form [here Eq. (43)] with the diagrammatic perturbation series for the respective propagator [here $\boldsymbol{G}^-(\omega)$]. By performing this comparison successively through higher order n of perturbation theory, systematic approximation schemes [ADC(n) schemes] can be derived, which represent complete summations of the diagrammatic series through order n and, moreover, infinite partial summations of higher-order terms. While this procedure can easily be performed for small n and has led to useful computational schemes, it becomes impractical at higher order due to the rapidly increasing number of diagrams. The ECO-ISR introduced as a closed-form version of the ADC allows for a *direct* access to the matrix elements of $\underline{\underline{C}}$ and $\underline{\underline{f}}$, but will be useful also for deriving nonperturbative approximation schemes.

IV. BIORTHOGONAL COUPLED-CLUSTER REPRESENTATION

A. General concept

Various methods have been developed extending the successful coupled-cluster approach to the treatment of (generalized) excitation energies and transition moments. Besides the CCLR theory [30–36] and the related EOM-CC method [37–39] the reader should be referred to the open-shell or multireference (MR) coupled-cluster methods (see Mukherjee and Pal [44] and references therein) and to methods combining propagator and coupled-cluster theory [45–47]. In the following we will consider the CCLR theory in the form obtained by Koch and Jørgensen [33] and the related EOM-CC method as formulated by Stanton and Bartlett [39]. Both versions lead to the same secular equations for the excitation energies while differences remain in the treatment of transition moments. The CCLR and EOM-CC methods are quite general and can be adopted to excitations in $N, N\pm1, N\pm2, \ldots,$ electron systems. For notational ease we will consider the $(N-1)$-electron case (ionization) in the following. Some remarks concerning the slightly more complicated case of the neutral excitations (in the N-electron system) will be given in Sec. VI D. The relationship between the BCC representation and the SAC-CI method of Nakatsuji and Hirao [27–29] will be briefly addressed in the end of this section.

In the coupled-cluster method the N-electron ground state is written in the form

$$|\Psi_0^N\rangle = \exp(\hat{\boldsymbol{T}})|\Phi_0^N\rangle, \tag{45}$$

where the so-called cluster operator $\hat{\boldsymbol{T}}$ is given by a linear combination of physical excitation operators (39):

$$\hat{\boldsymbol{T}} = \sum_{i=1}^{N} \hat{\boldsymbol{T}}_I = \sum_{a,i} T_{ai} c_a^\dagger c_i + \sum_{a,b,i,j} T_{abij} c_a^\dagger c_b^\dagger c_i c_j + \cdots . \tag{46}$$

Using the coupled-cluster ansatz (45), the correlated excited $[(N-1)$-electron$]$ states take on the form

$$|\Psi_J^0\rangle = \hat{\boldsymbol{C}}_J \exp(\hat{\boldsymbol{T}})|\Phi_0^N\rangle = \exp(\hat{\boldsymbol{T}})\hat{\boldsymbol{C}}_J|\Phi_0^N\rangle. \tag{47}$$

Note that $\hat{\boldsymbol{T}}$ and thus $\exp(\hat{\boldsymbol{T}})$ commute with any physical excitation operator $\hat{\boldsymbol{C}}_J$. Equation (47) also shows that the correlated excited states result via a similarity transformation from the complete set of HF configurations. This proves that the set $\{|\Psi_J^0\rangle\}$ is complete, since a similarity transformation does not lead to linear dependencies.

Instead of orthogonalizing the states $|\Psi_J^0\rangle$ as advocated in Sec. III B, here it is more natural to introduce the set of biorthogonal states $\langle\Psi_J^\perp|$ obeying the relations

$$\langle\Psi_I^\perp|\Psi_J^0\rangle = \delta_{IJ}. \tag{48}$$

The CC form of $|\Psi_J^0\rangle$ allows one to write the bra states $\langle\Psi_I^\perp|$ explicitly as

$$\langle\Psi_I^\perp| = \langle\Phi_0^N|\hat{\boldsymbol{C}}_I^\dagger \exp(-\hat{\boldsymbol{T}}). \tag{49}$$

The "mixed" representation of $\hat{\boldsymbol{H}}-E_0^N$ defined with respect to the biorthogonal sets of states, leads to the non-Hermitian secular matrix $\underline{\underline{M}}$, where

$$\begin{aligned} M_{IJ} &= \langle\Psi_I^\perp|\hat{\boldsymbol{H}}-E_0^N|\Psi_J^0\rangle \\ &= \langle\Phi_0^N|\hat{\boldsymbol{C}}_I^\dagger \exp(-\hat{\boldsymbol{T}})[\hat{\boldsymbol{H}},\hat{\boldsymbol{C}}_J]\exp(\hat{\boldsymbol{T}})|\Phi_0^N\rangle. \end{aligned} \tag{50}$$

The resulting secular equation

$$\underline{\underline{M}}\ \underline{\underline{X}} = \underline{\underline{X}}\ \underline{\underline{\Omega}} \tag{51}$$

is used both in the CCLR and EOM-CC methods. Here $\underline{\underline{\Omega}}$ is the diagonal matrix of ionization (excitation) energies and $\underline{\underline{X}}$ is the matrix of right-hand eigenvectors. An analogous equation arises for the matrix $\underline{\underline{Y}}$ of the left-hand eigenvectors of $\underline{\underline{M}}$ reading

$$\underline{\underline{Y}}^\dagger \underline{\underline{M}} = \underline{\underline{\Omega}}\ \underline{\underline{Y}}^\dagger, \tag{52}$$

and both equations can be combined

$$\underline{\underline{Y}}^\dagger \underline{\underline{M}}\ \underline{\underline{X}} = \underline{\underline{\Omega}}, \quad \underline{\underline{Y}}^\dagger \underline{\underline{X}} = \underline{\underline{1}}. \tag{53}$$

Note that the left-hand and right-hand eigenvectors are biorthogonal but in general not normalized.

	1h	2h1p	3h2p	4h3p	5h4p ⋯
1h	0	1	1	2	3
2h1p	1	0	1	1	2
3h2p	2	1	0	1	1
4h3p	3	2	1	0	1
5h4p	4	3	2	1	0
⋮					

FIG. 3. Order relations of the secular matrix $\underline{\underline{M}}$ of the biorthogonal coupled-cluster (BCC) representation in the case of $(N-1)$-electron states. The numbers in the blocks of $\underline{\underline{M}}$ indicate the (lowest) nonvanishing perturbation theoretical order.

B. Compactness of the BCC representation

As described by Stanton and Bartlett [39] the matrix elements of $\underline{\underline{M}}$ can be obtained quite efficiently once the cluster operator $\hat{\boldsymbol{T}}$ has been determined by a CC calculation for the N-electron ground state. The biorthogonal coupled-cluster representation gives rise to practical approximation schemes according to the various ways of treating the N-electron ground state and by truncating the excitation manifold. Although the resulting methods are nonperturbative, it should be of interest to analyze the error introduced by restricting the configuration space.

The order relations holding for the biorthogonal representation $\underline{\underline{M}}$ of $\hat{\boldsymbol{H}}-E_0^N$ are shown in Fig. 3; their proof is given in Appendix A. It is seen that these order relations are less stringent than the canonical order relations (23) of the ECO representation. The lower left triangular of $\underline{\underline{M}}$ is of the canonical form, but in the upper right triangle there are two first-order blocks adjacent to the diagonal, as is the case in the CI representation. The consequence for the perturbation-theoretical consistency of the results (for the primary states) is as follows: the consistency through order $2m-1$ and $2m$ requires one to include the excitation classes $\mu=1,\ldots,m+1$ in the configuration space. For example, if the configuration space comprises classes 1 and 2, the description of the primary states is consistent only through second order and not to third order as in the ECO representation. This shows that a modified compactness property applies the biorthogonal representation, which is somewhat weaker than that of the ECO-ISR.

Similarly one may analyze the results for the transition moments. In the EOM-CC approach the squared transition moments are obtained from the left-hand and right-hand eigenvectors as

$$|\langle\Psi_n|\hat{\boldsymbol{D}}|\Psi_0^N\rangle|^2=\left(\sum_I X_{In}F_I^*\right)\left(\sum_J Y_{Jn}^*F_J^{\perp}\right), \tag{54}$$

where

$$F_I=\langle\Psi_0^N|\hat{\boldsymbol{D}}^{\dagger}\hat{\boldsymbol{C}}_I\exp(\hat{\boldsymbol{T}})|\Phi_0^N\rangle^*, \tag{55}$$

$$F_J^{\perp}=\langle\Phi_0^N|\hat{\mathbf{C}}_J^{\dagger}\exp(-\hat{\mathbf{T}})\hat{\mathbf{D}}|\Psi_0^N\rangle \tag{56}$$

are intermediate transition moments associated with the BCC representation. While the components of $\underline{F}^{\perp}$ fulfill the canonical order relations (25) for the transition moments (see Appendix A), this is not the case for the components of $\underline{F}$ [corresponding to the correlated excited states (15)]. For a usual transition operator (of lowest rank) the order relations of $\underline{F}$ are $F_J=O(\mu)$ for $[J]=2\mu,2\mu+1$. This means that the right-hand transition moment $T_n^{(r)}=\Sigma_I X_{In}^* F_I$ is not compact. For example, $T_n^{(r)}$ is not consistent through second order (for primary states) if the BCC space is truncated after the first two excitation classes (here $1h$ and $2h$-$1p$). The lack of compactness is accompanied by another deficiency, namely the violation of size-consistency, as will be seen below. In the CCLR method [33] the transition moments are calculated in a size-consistent though more complicated way, which shall not be analyzed here.

C. Separability

Koch *et al.* [34,48] have shown that the excitation energies deriving from biorthogonal representation (50) are size-consistent. Their proof may be briefly stated as follows. The cluster operator of the separate fragment model can be written as the sum

$$\hat{\boldsymbol{T}}=\hat{\boldsymbol{T}}_A+\hat{\boldsymbol{T}}_B \tag{57}$$

of the cluster operators of the two fragments, and, thus, $\exp(\hat{\boldsymbol{T}})=\exp(\hat{\boldsymbol{T}}_A)\exp(\hat{\boldsymbol{T}}_B)$. A general correlated excitation $|\Psi_J^0\rangle$ with $J\equiv(J_AJ_B)$ factorizes according to

$$|\Psi_J^0\rangle=\exp(\hat{\boldsymbol{T}}_A)\hat{\boldsymbol{C}}_{J_A}|\Phi_0^A\rangle\exp(\hat{\boldsymbol{T}}_B)\hat{\boldsymbol{C}}_{J_B}|\Phi_0^B\rangle, \tag{58}$$

and an analogous relation holds for the biorthogonal states $|\Psi_J^{\perp}\rangle$. It is readily seen that the matrix element of $\hat{\boldsymbol{H}}=\hat{\boldsymbol{H}}_A+\hat{\boldsymbol{H}}_B$ taken with respect to a nonlocal configuration $I\equiv(I_AI_B)$ and a local configuration, say, $J\equiv J_A$ vanishes:

$$\langle\Psi_{I_AI_B}^{\perp}|\hat{\boldsymbol{H}}|\Psi_{J_A}^0\rangle=E_0^B\langle\Phi_0^B|\hat{\boldsymbol{C}}_{I_B}^{\dagger}|\Phi_0^B\rangle\delta_{I_AJ_A}=0. \tag{59}$$

The transposed matrix elements

$$\langle\Psi_{J_A}^{\perp}|\hat{\boldsymbol{H}}|\Psi_{I_AI_B}^0\rangle=\langle\Phi_0^B|\exp(-\hat{\boldsymbol{T}}_B)\hat{\boldsymbol{H}}_B\exp(\hat{\boldsymbol{T}}_B)\hat{\boldsymbol{C}}_{I_B}|\Psi_0^B\rangle\delta_{I_AJ_A}, \tag{60}$$

however, need not vanish. Thus, one arrives at the following block structure of $\underline{\underline{M}}$:

$$\underline{\underline{M}}=\begin{pmatrix}\underline{\underline{M}}_{AA} & 0 & \underline{\underline{M}}_{A\,AB}\\ 0 & \underline{\underline{M}}_{BB} & \underline{\underline{M}}_{B\,AB}\\ 0 & 0 & \underline{\underline{M}}_{AB\,AB}\end{pmatrix}. \tag{61}$$

Although here the local and nonlocal blocks are not strictly decoupled, the particular structure of $\underline{\underline{M}}$ shows that the eigenvalues of $\underline{\underline{M}}_{AA}$ and $\underline{\underline{M}}_{BB}$ are those of the entire matrix $\underline{\underline{M}}$. This shows that the results for the excitation energies are size intensive. It should be noted that the right-hand eigenvectors $\underline{X}_n$ are locally correct, that is, all components referring to nonlocal configurations vanish for a local solution n. In contrast, this does not hold for the left eigenvectors $\underline{Y}_n$.

With regard to the spectral intensities it should be noted that the intermediate quantities F_I [Eq. (55)] used in the right-hand transition moments can lack the separability property. Indeed, for a local configuration I_A one finds

$$F_{I_A}=F_{I_A}^{(A)}+\langle\Psi_0^A|\hat{\boldsymbol{C}}_{I_A}|\Psi_0^A\rangle^*\langle\Psi_0^B|\hat{\boldsymbol{D}}_B^{\dagger}|\Psi_0^B\rangle^*. \tag{62}$$

In the N-electron case (discussed below) where $\hat{\boldsymbol{C}}_{I_A}$ does not change the number of electrons, the second contribution on the right-hand side need not vanish if $\langle\Psi_0^B|\hat{\boldsymbol{D}}_B^{\dagger}|\Psi_0^B\rangle$ does not vanish for symmetry reasons. Then $F_{I_A}\neq F_{I_A}^{(A)}$, and, as a consequence, the squared transition moment calculated according to Eq. (54) is not size-consistent. This was observed already by Koch *et al.* [48]. The left intermediate transition moments $F_J^{\perp}$ are separable, that is, $F_{I_A}^{\perp}=F_{I_A}^{\perp(A)}$. Moreover, the left form of the transition moment is size-consistent, although the left eigenvectors can have nonlocal components. As can be readily verified, the corresponding intermediate transition moments $F_J^{\perp}$ vanish for these nonlocal configurations.

D. The *N*-electron case

Finally we consider briefly the case of N electrons. To achieve completeness here, generally the biorthogonal expansion manifolds must be extended by the (exact) ground state $|\Psi_0^N\rangle=\exp(\hat{\boldsymbol{T}})|\Phi_0^N\rangle$ and $\langle\Phi_0^N|\exp(-\hat{\boldsymbol{T}})=\langle\Phi_0^N|$, respectively. The resulting representation of $\hat{\boldsymbol{H}}-E_0^N$ takes on the form

$$\underline{\underline{M}}'=\begin{pmatrix}0 & \underline{v}\\ \underline{0} & \underline{\underline{M}}\end{pmatrix}, \tag{63}$$

where $\underline{\underline{M}}$ is as specified by Eq. (50) and $\underline{v}$ is a (row) vector of matrix elements

$$v_I=\langle\Phi_0^N|\exp(-\hat{\boldsymbol{T}})[\hat{\boldsymbol{H}},\hat{\boldsymbol{C}}_I]\exp(\hat{\boldsymbol{T}})|\Phi_0^N\rangle. \tag{64}$$

The secular matrix $\underline{\underline{M}}'$ is used in the method of Stanton and Bartlett [39] (apart from the subtraction of the ground state energy E_0^N in the diagonal). Obviously, for the excitation energies the roots of $\underline{\underline{M}}'$ and $\underline{\underline{M}}$ are identical and the left- and right-hand eigenvectors are trivially modified by adding a vanishing zeroth component. $\underline{\underline{M}}'$ has an additional eigenvalue zero corresponding to the exact ground state. The right-hand eigenvector $\underline{X}'_0$ is trivial: $X'_{I0}=\delta_{0I}$; while the corresponding left-hand eigenvector $\underline{Y}'_0$ is given by

$$\underline{Y}'_0=\begin{pmatrix}1\\ \underline{Y}_0\end{pmatrix}, \tag{65}$$

where $\underline{Y}_0$ is obtained from the linear equation

$$\underline{Y}_0^{\dagger}=-\underline{v}\ \underline{\underline{M}}^{-1}. \tag{66}$$

This may be used to write the exact ground state (using intermediate normalization) in the form

$$\langle\Psi_0^N|=\langle\Phi_0^N|+\sum_I\ \langle\Phi_0^N|\hat{\boldsymbol{C}}_I^{\dagger}\exp(-\hat{\boldsymbol{T}})Y_{I0}. \tag{67}$$

Note that this representation has been termed $\langle\Lambda|$ in the work of Koch *et al.* [33,34,48] [see Eq. (9) in [48]].

E. Relationship to the SAC-CI method

The (nonvariational) SAC-CI method of Nakatsuji and Hirao [27–29] is based on the mixed representation

$$M_{IJ}^{SAC}=\langle\Phi_I|\hat{\boldsymbol{H}}-E_0^N|\Psi_J^0\rangle, \tag{68}$$

where the CI configurations (12) and the correlated excited states in the CC parametrization (47) are used on the left- and right-hand sides, respectively. To be specific we confine ourselves, as above, to the case of $(N-1)$-electron states. The overlap matrix

$$S_{IJ}=\langle\Phi_I|\Psi_J^0\rangle \tag{69}$$

of the left- and right-hand basis functions is of lower triangular form. The SAC-CI secular equations (right-hand form) read

$$\underline{\underline{M}}^{SAC}\underline{\underline{X}}=\underline{\underline{S}}\ \underline{\underline{X}}\ \underline{\underline{\Omega}}, \tag{70}$$

where $\underline{\underline{\Omega}}$ is the diagonal matrix of excitation (ionization) energies and $\underline{\underline{X}}$ denotes the matrix of right-hand eigenvectors. An analogous equation applies to the matrix $\underline{\underline{Y}}$ of left-hand eigenvectors. A mutual orthonormalization is obtained according to

$$\underline{\underline{Y}}^{\dagger}\underline{\underline{S}}\ \underline{\underline{X}}=\underline{\underline{1}}. \tag{71}$$

Although the SAC-CI equations differ from the BCC representation in the use of the left-hand basis states, they give identical results for the energies, provided that the configuration spaces extend to the same excitation class and the same treatment for $\exp(\hat{\boldsymbol{T}})$ is used. To see this, consider a biorthogonal state of the μth excitation class:

$$\langle\Psi_I^{\perp}|=\langle\Phi_I|\exp(-\hat{\boldsymbol{T}}),\quad [I]=\mu. \tag{72}$$

The expansion

$$\langle\Psi_I^{\perp}|=\sum_J\ \langle\Phi_I|\exp(-\hat{\boldsymbol{T}})|\Phi_J\rangle\langle\Phi_J| \tag{73}$$

with respect to the CI configurations $|\Phi_J\rangle$ does not contain configurations of higher classes than μ, because $\langle\Phi_I|\exp(-\hat{\boldsymbol{T}})|\Phi_J\rangle=0$ for $[J]>[I]$. This shows that the sets $\{\langle\Phi_I|,[I]\leqslant\mu\}$ and $\{\langle\Psi_I^{\perp}|,[I]\leqslant\mu\}$ differ only by a similarity transformation. As a consequence, the BCC and SAC-CI secular equations (truncated after a given class μ) are equivalent. In particular, the compactness properties of the BCC representation apply as well to the SAC-CI method. The SAC-CI equations are not separable, but, of course, the equivalence to the BCC guarantees analogous size-consistency properties.

V. UNITARY COUPLED-CLUSTER REPRESENTATION

An intermediate representation based on the unitary coupled-cluster (UCC) approach has been considered by Prasad *et al.* [23] and by Mukherjee and Kutzelnigg [24]. Here the N-electron ground state is expressed in the CC form

$$|\Psi_0^N\rangle=\exp(\hat{\boldsymbol{\sigma}})|\Phi_0^N\rangle, \tag{74}$$

however, using an anti-Hermitian cluster operator $\hat{\boldsymbol{\sigma}}=-\hat{\boldsymbol{\sigma}}^{\dagger}$. Usually $\hat{\boldsymbol{\sigma}}$ is written as

$$\hat{\boldsymbol{\sigma}}=\hat{\boldsymbol{S}}-\hat{\boldsymbol{S}}^{\dagger}, \tag{75}$$

where the operator $\hat{\boldsymbol{S}}$ (like $\hat{\boldsymbol{T}}$) is given by a linear combination of physical (N-electron) excitation operators,

$$\hat{\boldsymbol{S}}=\sum_{i=1}^{N}\ \hat{\boldsymbol{S}}_i=\sum_{a,i}\ S_{ai}c_a^{\dagger}c_i+\sum_{a,b,i,j}\ S_{abij}c_a^{\dagger}c_b^{\dagger}c_ic_j+\cdots. \tag{76}$$

Then, since $\hat{\boldsymbol{S}}^{\dagger}$ contains unphysical operators only, $\hat{\boldsymbol{S}}^{\dagger}|\Phi_0^N\rangle=0$. In contrast to the normal cluster operator $\hat{\boldsymbol{T}}$, $\hat{\boldsymbol{\sigma}}$ does not commute with physical excitation operators. The intermediate states $|\tilde{\tilde{\Psi}}_J\rangle$ considered by Mukherjee and Kutzelnigg (referred to in the following as unitary coupled cluster states) are obtained by applying the so-called consistent operators $\exp(\hat{\boldsymbol{\sigma}})\hat{\mathbf{C}}_J\exp(-\hat{\boldsymbol{\sigma}})$ to the exact ground state:

$$|\tilde{\tilde{\Psi}}_J\rangle=\exp(\hat{\boldsymbol{\sigma}})\hat{\mathbf{C}}_J\exp(-\hat{\boldsymbol{\sigma}})|\Psi_0^N\rangle=\exp(\hat{\boldsymbol{\sigma}})\hat{\mathbf{C}}_J|\Phi_0^N\rangle. \tag{77}$$

Again we confine ourselves for the moment to the operators $\hat{\boldsymbol{C}}_J$ of the $(N-1)$-particle case specified in Eq. (13). By definition, the UCC states result via a unitary transformation from the HF configurations $\hat{\boldsymbol{C}}_J|\Phi_0^N\rangle$, which shows that they form a complete and orthonormal set. The UCC representation of $\hat{\boldsymbol{H}}-E_0^N$ is given by the matrix elements

$$\begin{aligned}\tilde{\tilde{H}}_{IJ}-E_0^N\delta_{IJ}&=\langle\tilde{\tilde{\Psi}}_I|\hat{\boldsymbol{H}}-\boldsymbol{E}_0^N|\tilde{\tilde{\Psi}}_J\rangle\\ &=\langle\Phi_0^N|\hat{\boldsymbol{C}}_I^{\dagger}[\exp(-\hat{\boldsymbol{\sigma}})\hat{\boldsymbol{H}}\exp(\hat{\boldsymbol{\sigma}}),\hat{\boldsymbol{C}}_J]|\Phi_0^N\rangle.\end{aligned} \tag{78}$$

Note that the ground state energy E_0^N is no longer explicit in the last line of Eq. (78). Analogous to Eq. (11), the intermediate transition moments for the UCC representation are defined as

$$\tilde{\tilde{F}}_{IJ}=\langle\tilde{\tilde{\Psi}}_J|\hat{\boldsymbol{D}}|\Psi_0^N\rangle=\langle\Phi_0^N|\hat{\boldsymbol{C}}_J^{\dagger}\exp(-\hat{\boldsymbol{\sigma}})\hat{\boldsymbol{D}}\exp(\hat{\boldsymbol{\sigma}})|\Phi_0^N\rangle. \tag{79}$$

The UCC states $|\tilde{\tilde{\Psi}}_I\rangle$ and ECO intermediate states $|\tilde{\Psi}_J\rangle$ considered in Sec. III are related by a unitary transformation $\underline{\underline{U}}$,

$$U_{IJ}=\langle\tilde{\tilde{\Psi}}_I|\tilde{\Psi}_J\rangle. \tag{80}$$

As shown in Appendix B, the blocks of $\underline{\underline{U}}$ fulfill the canonical order relations:

$$U_{IJ}=O(|[I]-[J]|). \tag{81}$$

As one may easily convince oneself (see Appendix C), the canonical order relations hold for the product $\underline{\underline{A}}\ \underline{\underline{B}}$ of two matrices if they hold for $\underline{\underline{A}}$ and $\underline{\underline{B}}$. Using the relation

$$\underline{\underline{\tilde{\tilde{H}}}}=\underline{\underline{U}}\ \underline{\underline{\tilde{H}}}\ \underline{\underline{U}}^{\dagger} \tag{82}$$

between $\underline{\underline{\tilde{\tilde{H}}}}$ and the (compact) ECO-ISR matrix $\underline{\underline{\tilde{H}}}$, one may establish the canonical order relations of $\underline{\underline{\tilde{\tilde{H}}}}$ and thus the compactness property of the UCC representation. Similarly, we arrive at the order relations (25) for the intermediate UCC transition moments $\underline{\tilde{\tilde{F}}}$ related to the ECO-ISR moments according to

$$\underline{\tilde{\tilde{F}}}=\underline{\tilde{F}}\ \ \underline{\underline{U}}^{\dagger}. \tag{83}$$

Here the moments $\tilde{\tilde{F}}_J$ ($\tilde{F}_J$) are collected in the row vector $\underline{\tilde{\tilde{F}}}$ ($\underline{\tilde{F}}$).

As an obvious generalization of the proof given here, we may state that the compactness property holds for any (intermediate) representation differing from the ECO-ISR (or the UCC-ISR) by a unitary transformation $\underline{\underline{U}}$ if $\underline{\underline{U}}$ fulfills the canonical order relations (81). Here the "identity" of the configurations J in the two sets of states is reflected by the fact that the diagonal elements U_{IJ} are of zeroth order.

The separability property of the UCC representation is almost trivial. Again, the cluster operator $\hat{\boldsymbol{\sigma}}$ of the separate fragment model decomposes into the sum

$$\hat{\boldsymbol{\sigma}}=\hat{\boldsymbol{\sigma}}_A+\hat{\boldsymbol{\sigma}}_B \tag{84}$$

of the cluster operators of the fragments, and the UCC states factorize according to

$$|\tilde{\tilde{\Psi}}_{I_AI_B}\rangle=|\tilde{\tilde{\Psi}}_{I_A}\rangle|\tilde{\tilde{\Psi}}_{I_B}\rangle. \tag{85}$$

One may readily convince oneself that the resulting block structure for $\underline{\underline{\tilde{\tilde{H}}}}$ is the same as the one of $\underline{\underline{\tilde{H}}}$ given in Eq. (33).

VI. CONCLUDING REMARKS

As a general common concept underlying diverse propagator and related methods, intermediate-state representations have been considered and analyzed. Here the expansion manifolds (intermediate states) are constructed from correlated excited states obtained by applying (e.g., physical) excitation operators $\hat{\boldsymbol{C}}_J$ to the exact N-electron ground state $|\Psi_0^N\rangle$. Generalized excitation energies are given as the eigenvalues of the ISR secular matrix $\underline{\underline{\tilde{M}}}$, that is, the matrix representation of the excitation energy operator (shifted Hamiltonian) $\hat{\boldsymbol{H}}-E_0^N$ with respect to the intermediate states $|\tilde{\Psi}_J\rangle$. The associated transition moments can be derived from the eigenvectors of $\underline{\underline{\tilde{M}}}$ and the intermediate transition moments $\langle\tilde{\Psi}_J|\hat{\boldsymbol{D}}|\Psi_0^N\rangle$. While the excitation operators $\hat{\boldsymbol{C}}_J$ can be defined with respect to an appropriate basis of single-particle states (usually ground state HF orbitals), the ISR secular matrix elements and moments depend on the exact (correlated) ground state. Thus the calculation of the latter quantities in practical computational schemes presupposes—besides truncating the configuration space—a suitable approximation for $|\Psi_0^N\rangle$.

An obvious approach to deriving approximation schemes from the general ISR formulation is to use perturbation theory for $|\Psi_0^N\rangle$. This leads to perturbation expansions of the ISR secular matrix elements and transition moments which may be truncated in a systematical way at finite order. The ADC(n) schemes for the various propagators arise in such a way from the ECO representation considered in Sec. III. Another possibility is to exploit the powerful coupled-cluster parametrization, $|\Psi_0^N\rangle=\exp(\hat{\boldsymbol{T}})|\Phi_0^N\rangle$, of the N-electron ground state. This is the starting point for the BCC representation used in the CCLR and EOM-CC methods. The unitary CC formulations $|\Psi_0^N\rangle=\exp(\hat{\boldsymbol{\sigma}})|\Phi_0^N\rangle$ of the ground state and excitation operators of the form $\exp(\hat{\boldsymbol{\sigma}})\hat{\boldsymbol{C}}_J\exp(-\hat{\boldsymbol{\sigma}})$ are used in the UCC representation.

The relevance of the ISR as a means of deriving approximation schemes is due to the two basic properties referred to as compactness and separability:

(i) Compactness means that the explicit configuration spaces are systematically smaller than those of comparable CI expansions. For a consistent treatment, say, of the main excitation energies through order $2m+1$, the configuration space of a compact representation can be truncated after the class $\nu=m+1$, whereas a comparable CI expansion must extend through class $\nu=2m+1$. This rule applies to the usual electronic Hamiltonian consisting of a one-body and a two-body part. It can readily be generalized to an r-body Hamiltonian [26].

(ii) Separability is a sufficient condition for size-consistent (more specifically, size-intensive) results. An ISR method is separable if, for a system of separate fragments, the secular matrix of the total system decomposes into a block-diagonal form consisting of "local" blocks associated with each fragment plus an additional block corresponding to nonlocal excitations. Moreover, a local block must be identical to the secular matrix associated with the separated fragment. In a similar way, this property can be introduced in the intermediate transition moments.

It should be emphasized once more that these two key properties are only potentially inherent in the ISR methods. Their validity depends critically on the procedure adopted to orthonormalize the correlated excited states. The representations obtained from symmetrical orthonormalization are neither separable nor compact. The biorthogonal representation used in the CCLR and EOM-CC methods exhibits a somewhat restricted compactness property, as explained in Sec. IV. The ECO representations, arising from Gram-Schmidt orthogonalization with respect to the excitation classes, fully comply with these properties as do the unitary CC representations considered in Sec. V.

Another property of interest is the invariance of the ISR with respect to independent unitary transformations of occupied and virtual orbitals. Orbital transformations of this kind induce classwise unitary transformations of the physical excitation operators $\hat{\boldsymbol{C}}_J$. As an immediate conclusion, the invariance property holds for the ECO-ISR, BCC, and UCC schemes, provided that the configuration space comprises all configurations through a given excitation class (systematical truncation).

The proofs of compactness and separability given here and elsewhere presuppose the use of an exact ground state $|\Psi_0^N\rangle$. Therefore the results cannot be transferred simply to representations based on an approximate ground state wave function. For example, in the case where the operator manifold used in the ground state CC treatment is smaller than that used in the excited state calculation, the factorization according to Eq. (58) is valid, whereas Eq. (59) is no longer strictly fulfilled. As should be recalled, the perturbation theoretical approach to the ECO representation giving rise to the ADC(n) approximation schemes (see Sec. III B) is separable and compact at all orders n, as one may easily verify. This finding applies to any separable ground state perturbation theory.

The compactness and separability conditions do not single out a unique representation, as the example of the ECO and UCC representations shows. As shown in Sec. V these representations differ by a nontrivial unitary transformation $\underline{\underline{U}}$ fulfilling the so-called canonical order relations (81). Moreover, $\underline{\underline{U}}$ adopts the separable (block-diagonal) form in the case of the separate fragment model. Obviously any representation differing from the ECO (or UCC) representations by such a compact and separable unitary transformation $\underline{\underline{U}}$ is itself compact and separable. In this sense the two properties define a class of equivalent representations. Despite this equivalence there may be interesting differences with respect to their use in practical computational schemes.

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APPENDIX A: PROOF OF THE ORDER RELATIONS FOR THE BCC AND THE ECO REPRESENTATIONS

The diagrammatic perturbation theory for the cluster operator $\hat{\boldsymbol{T}}=\Sigma_{\nu=1}^{N}\hat{\boldsymbol{T}}_\nu$ makes it evident that the νp-νh parts $\hat{\boldsymbol{T}}_\nu$ are (at least) of the order $\nu-1$,

$$\hat{\boldsymbol{T}}_\nu \equiv O(\nu-1). \tag{A1}$$

For example, the double excitation part $\hat{\boldsymbol{T}}_2$ contains only first- and higher-order terms. Note that the relation (A1) becomes trivial for $\hat{\boldsymbol{T}}_1$ (appearing actually in second-order Møller-Plesset perturbation theory). Let us now consider the matrix element

$$\langle\Psi_I^{\perp}|\hat{\boldsymbol{A}}_{(\mu)}|\Psi_J^0\rangle=\langle\Phi_0^N|\hat{\boldsymbol{C}}_I^{\dagger}\exp(-\hat{\boldsymbol{T}})\hat{\boldsymbol{A}}_{(\mu)}\exp(\hat{\boldsymbol{T}})\hat{\boldsymbol{C}}_J|\Phi_0^N\rangle, \tag{A2}$$

where

$$\hat{\boldsymbol{A}}_{(\mu)}=c_{j_1}^{\dagger}\ldots c_{j_\mu}^{\dagger}c_{l_1}\ldots c_{l_\mu} \tag{A3}$$

denotes an arbitrary operator of rank μ, that is, $\hat{\boldsymbol{A}}_{(\mu)}$ is a product of μ creation and μ destruction operators. According to the Baker-Hausdorff formula we may write

$$\exp(-\hat{\boldsymbol{T}})\hat{\boldsymbol{A}}_{(\mu)}\exp(\hat{\boldsymbol{T}})=\hat{\boldsymbol{A}}_{(\mu)}+[\hat{\boldsymbol{A}}_{(\mu)},\hat{\boldsymbol{T}}]+\frac{1}{2}[[\hat{\boldsymbol{A}}_{(\mu)},\hat{\boldsymbol{T}}],\hat{\boldsymbol{T}}]+\cdots. \tag{A4}$$

Obviously the commutator $[\hat{\boldsymbol{A}}_{(\mu)},\hat{\boldsymbol{T}}_\nu]$ is an operator of rank $\mu+\nu-1$. Similarly, $[[\hat{\boldsymbol{A}}_{(\mu)},\hat{\boldsymbol{T}}_\nu],\hat{\boldsymbol{T}}_\rho]$ is an operator of rank $\mu+\nu+\rho-2$, etc. This means that commutation with $\hat{\boldsymbol{T}}_1$ does not increase the rank; commutation with $\hat{\boldsymbol{T}}_2$ increases the rank by 1, but also increases due to (A1) the perturbation theoretical order of the resulting operator by 1; generally, the commutation with $\hat{\boldsymbol{T}}_\nu$ enhances both the rank and the order by $\nu-1$. Inserting the Baker-Hausdorff expansion (A4) in the matrix element (A2), we see that all contributions must vanish for which the rank of $[\ldots[\hat{\boldsymbol{A}}_{(\mu)},\hat{\boldsymbol{T}}_i],\ldots\hat{\boldsymbol{T}}_j]$ is smaller than the residual rank $|[I]-[J]|$ of the respective excitation operators $\hat{\boldsymbol{C}}_I,\hat{\boldsymbol{C}}_J$. The rank of physical excitation operators $\hat{\boldsymbol{C}}_I$ is given by the respective class, $[I]$. This allows us to conclude the order relation

$$\langle\Psi_I^{\perp}|\hat{\boldsymbol{A}}_\mu|\Psi_J^0\rangle=O(|[I]-[J]|-\mu)\quad\text{for }|[I]-[J]|\geqslant\mu. \tag{A5}$$

This result may readily be applied to the matrix elements of the Hamiltonian $\hat{\boldsymbol{H}}=\hat{\boldsymbol{H}}_0+\hat{\boldsymbol{H}}_I$. While being an operator of rank $\mu=2$, $\hat{\boldsymbol{H}}_I$ itself is of first order of perturbation theory; hence

$$\langle\Psi_I^{\perp}|\hat{\boldsymbol{H}}|\Psi_J^0\rangle=O(|[I]-[J]|-1)\quad\text{for }[I]-[J]\geqslant 2. \tag{A6}$$

We note that the diagonal matrix elements are of the order zero, while for $|[I]-[J]|=1$ the matrix elements are of order 1.

For the matrix elements with $[I]\geqslant[J]$ (lower left triangle) the more stringent canonical order relations (as shown in Fig. 3) can be deduced. To see this we consider a matrix element of $\hat{\boldsymbol{H}}-E_0^N$,

$$\langle\Psi_I^{\perp}|\hat{\boldsymbol{H}}-E_0^N|\Psi_J^0\rangle=\langle\Phi_0^N|\hat{\boldsymbol{C}}_I^{\dagger}\exp(-\hat{\boldsymbol{T}})[\hat{\boldsymbol{H}},\hat{\boldsymbol{C}}_J]\exp(\hat{\boldsymbol{T}})|\Phi_0^N\rangle. \tag{A7}$$

The commutator $[\hat{\boldsymbol{H}},\hat{\boldsymbol{C}}_J]$ has a contribution that is of rank $[J]+1$ and is of first order of perturbation theory. As above we may conclude that

$$\langle\Psi_I^{\perp}|\hat{\boldsymbol{H}}-E_0^N|\Psi_J^0\rangle=O([I]-[J])\quad\text{for }[I]\geqslant[J]. \tag{A8}$$

Since $\langle\Psi_I^{\perp}|E_0^N|\Psi_J^0\rangle=E_0^N\delta_{IJ}$, this result also holds for the representation of $\hat{\boldsymbol{H}}$ itself.

With the help of this result for the biorthogonal representation one may easily prove the canonical order relations (23) for the ECO intermediate states. For this purpose we decompose an arbitrary matrix element $\tilde{H}_{IJ}$ as follows by inserting twice the biorthogonal resolution of the identity:

$$\langle\tilde{\Psi}_I|\hat{\boldsymbol{H}}|\tilde{\Psi}_J\rangle=\sum_{K,L}\langle\tilde{\Psi}_I|\Psi_K^0\rangle\langle\Psi_K^\perp|\hat{\boldsymbol{H}}|\Psi_L^0\rangle\langle\Psi_L^\perp|\tilde{\Psi}_J\rangle. \tag{A9}$$

Since $\underline{\underline{\tilde{H}}}$ is a Hermitian matrix we may confine ourselves to the case $[I]\geqslant[J]$. By construction, the intermediate states $|\tilde{\Psi}_J\rangle$ are orthogonal to the correlated excited states $|\Psi_J^0\rangle$ of lower classes, $[K]<[I]$. Thus the summation over K on the right-hand side of Eq. (A9) is restricted by $[K]\geqslant[I]$. Similarly, we may conclude a restriction $[L]\leqslant[J]$ for the summation over L. This follows from

$$\langle\Psi_L^\perp|\tilde{\Psi}_J\rangle=\langle\Phi_0^N|\hat{\boldsymbol{C}}_L^\dagger\exp(-\hat{\boldsymbol{T}})\tilde{\boldsymbol{C}}_J|\Psi_0^N\rangle \tag{A10}$$

$$=\langle\Phi_0^N|\hat{\boldsymbol{C}}_L^\dagger\tilde{\boldsymbol{C}}_J|\Phi_0^N\rangle. \tag{A11}$$

Since $\tilde{\boldsymbol{C}}_J$ is a linear combination of excitation operators of classes $\mu\leqslant[J]$, this matrix element vanishes if $[L]>[J]$. Altogether, the summation on the right-hand side of Eq. (A9) is restricted according to $[K]\geqslant[I]\geqslant[J]\geqslant[L]$. Using the order relations (A8) for $\langle\Psi_K^\perp|\hat{\boldsymbol{H}}|\Psi_L^0\rangle$ we may conclude that every summation term and thus the hole sum is at least of the order $[I]-[J]$. We note that the minimum value is indeed adopted, since for $[K]=[I]$ and $[L]=[J]$ the overlap matrix elements $\langle\tilde{\Psi}_I|\Psi_K^0\rangle$ and $\langle\Psi_L^\perp|\tilde{\Psi}_J\rangle$ are of zeroth order.

APPENDIX B: COMPACTNESS OF THE UNITARY TRANSFORMATION RELATING THE ECO AND THE UCC REPRESENTATIONS

Let us consider an arbitrary matrix element of the unitary matrix $\underline{\underline{U}}$ with $[I]\geqslant[J]$:

$$U_{IJ}=\langle\Phi_0^N|\hat{\boldsymbol{C}}_I^\dagger\exp(-\hat{\boldsymbol{\sigma}})\tilde{C}_J\exp(\hat{\boldsymbol{\sigma}})|\Phi_0^N\rangle. \tag{B1}$$

Here we use the form of Eqs. (20,21) for $|\tilde{\Psi}_J\rangle$ and the UCC ground state (74). Similar to the considerations in Appendix A, we may now argue as follows: The unitary coupled cluster operator is given by a sum $\hat{\boldsymbol{\sigma}}=\Sigma_{\nu=1}^N\hat{\boldsymbol{\sigma}}_\nu$ of νp-νh contributions $\hat{\boldsymbol{\sigma}}_\nu$ (also referred to as contributions of rank ν). As in the case of the usual CC operator $\hat{\boldsymbol{T}}$ [see Eq. (A1)], one may show by perturbation theory that the order relation

$$\hat{\boldsymbol{\sigma}}_\nu=O(\nu-1) \tag{B2}$$

holds for these parts. Using the Baker-Hausdorff formula we obtain

$$\exp(-\hat{\boldsymbol{\sigma}})\hat{\boldsymbol{C}}_J\exp(\hat{\boldsymbol{\sigma}})=\hat{\boldsymbol{C}}_J+[\hat{\boldsymbol{C}}_J,\hat{\boldsymbol{\sigma}}]+\frac{1}{2}[[\hat{\boldsymbol{C}}_J,\hat{\boldsymbol{\sigma}}],\hat{\boldsymbol{\sigma}}]+\cdots. \tag{B3}$$

A commutator $[\hat{\boldsymbol{B}},\hat{\boldsymbol{\sigma}}_\nu]$ increases both the rank of a given operator $\hat{\boldsymbol{B}}$ and its perturbation theoretical order (at least) by $\nu-1$ (see Appendix A). For example, each commutator involving $\hat{\boldsymbol{\sigma}}_2$ increases the rank by 1, concomittantly adding one order of perturbation theory. In the overlap matrix element U_{IJ} only those terms from the expansion (B3), for which the rank increment is at least $[I]-[J]$, may contribute. This means that the nonvanishing contributions are at least of the order $[I]-[J]$. Thus we have shown the relations (80) for the lower left triangle ($[I]\geqslant[J]$) of $\underline{\underline{U}}$. Since $\underline{\underline{U}}$ is unitary they must also hold for the remaining part $[I]<[J]$, as shown in Appendix C.

APPENDIX C: ORDER RELATIONS IN A UNITARY MATRIX

Let us consider a unitary matrix $\underline{\underline{U}}$ with a block structure $\underline{\underline{U}}_{\mu,\nu}$, $\mu,\nu=1,2\ \ldots$, and assume that the block of the lower left triangle fulfills the canonical order relations (81):

$$\underline{\underline{U}}_{\mu,\nu}\equiv O(\mu-\nu)\quad\text{for}\quad\mu\geqslant\nu. \tag{C1}$$

We will prove that, as a consequence of unitarity, the canonical order relations hold for the entire matrix:

$$\underline{\underline{U}}_{\mu,\nu}\equiv O(|\mu-\nu|). \tag{C2}$$

Let $\underline{U}_k$, $k=1,2,\ \ldots,$ denote the columns of blocks of $\underline{\underline{U}}$. From the orthogonality of $\underline{U}_1$ and $\underline{U}_2$ one may readily conclude that $\underline{\underline{U}}_{1,2}\equiv O(1)$. This means that the canonical order relations hold for the first two columns $\underline{U}_1$ and $\underline{U}_2$. Now their orthogonality to $\underline{U}_3$ can only be fulfilled if $\underline{\underline{U}}_{1,3}\equiv O(2)$ and $\underline{\underline{U}}_{2,3}\equiv O(1)$. Proceeding in such a way one may successively show the canonical order relations for all columns of $\underline{\underline{U}}$. The proof can be completed in a formally correct manner as follows. Assume that j refers to the first column for which the canonical order relation is violated, that is,

$$\underline{\underline{U}}_{ij}=O(j-i-d)\quad\text{for}\quad i<j \tag{C3}$$

and let i be a row for which the deviation d, $0<d\leqslant j-i$ is maximal. If the maximal deviation occurs in more than one column, then i is assumed to be the largest row index. Now consider the product of the columns $\underline{U}_i$ and $\underline{U}_j$:

$$\underline{U}_i^\dagger\underline{U}_j=\sum_k\underline{\underline{U}}_{ki}^\dagger\ \underline{\underline{U}}_{kj} \tag{C4}$$

$$=\underline{\underline{U}}_{ii}^\dagger\underline{\underline{U}}_{ij}+\sum_{\substack{k<j\\k\neq i}}\underline{\underline{U}}_{ki}^\dagger\ \underline{\underline{U}}_{kj}$$

$$+\sum_{k\geqslant j}\underline{\underline{U}}_{ki}^\dagger\ \underline{\underline{U}}_{kj}\,. \tag{C5}$$

The first term (T1) on the right-hand side is of order $j-i-d$ [since $\underline{\underline{U}}_{ii}=\underline{\underline{1}}+O(1)$]. The last term (T3) on the right-hand side is of the order $j-i$, since all blocks involved fulfill the canonical order relations; the minimal order is adopted for $k=j$. The order analysis of the second term (T2) on the right-hand side is easily performed by partitioning the summation into two contributions corresponding to $k<i$ and $k>i$, respectively:

$$(T2)\equiv\sum_{\substack{k<i\\k<j}}O(i-k)O(j-k-d_{jk})+\sum_{\substack{k>i\\k<j}}O(k-i)$$

$$\times O(j-k-d_{jk}). \tag{C6}$$

Here $d_{jk}\leqslant j-k$ denotes the deviation of the block $\underline{\underline{U}}_{kj}$ from the canonical order relation. In the first contribution the d_{jk}

may assume the value d; the lowest possible order would arise from $k=i-1$ and $d_{ji-1}=d$. By assumption, $d_{jk}<d$ for the second contribution. Thus we arrive at the following result for the order of (T2):

$$\begin{aligned}(T2)&=O(1)O(j-i+1-d)+O(j-i-d')\\&=O(j-i+2-d)+O(j-i-d'),\end{aligned}\tag{C7}$$

where $d'<d$. This shows that neither (T2) nor (T3) can compensate for the lowest-order contribution of (T1). From the orthogonality of $\underline{U}_i$ and $\underline{U}_j$ we must conclude that $\underline{\underline{U}}_{ij}$ is at least of the order $j-i-d+1$ in contradiction to the assumption (C3).

The proof given here can be readily generalized to the following assertion. Let $\underline{\underline{U}}$ and $\underline{\underline{V}}$ be two (quadratic) matrices with a block structure as considered above for which the orthogonality relation

$$\underline{\underline{U}}^{\dagger}\underline{\underline{V}}=\underline{\underline{V}}^{\dagger}\underline{\underline{U}}=\underline{\underline{1}}\tag{C8}$$

holds. If the canonical order relations are fulfilled for the lower left triangle of blocks of $\underline{\underline{U}}$ and $\underline{\underline{V}}$ they hold for the entire matrices.

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