Reappraisal of the Role of Size-Extensive Normalization for Multireference Coupled Cluster (MRCC) Theory Using General Model Space: A Valence Universal MRCC Approach†

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We present a brief description of a valence-universal multireference coupled cluster (VU-MRCC) theory that can handle completely general incomplete model spaces, remaining close to the intermediate normalization (IN) condition for Ω as much as possible without violating extensivity and without the use of a post facto correction. In this formalism, the connectedness of the cluster operators as well as effective Hamiltonian and hence the extensivity of the corresponding roots is achieved by invoking *appropriate decoupling conditions* on the special type of wave operator $\Omega = \{\exp(S + X_{cl})\}$ satisfying the Bloch equations in the Fock-space S in an excitation operator and X is a closed operator (denoted by cl). This special type of wave-operator leads to a unique partition of the excitations from the model space into those generated by the cluster operators (open and quasi-open) and those generated by the effective Hamiltonian (closed). In this formulation, for every X_{cl}, there is a counterterm from $\{\exp(S)\}_{cl}$ canceling each other. This leads to a connected expressions for cluster amplitudes, using the constraint $\Omega_{cl} = 1$. The new form of the effective Hamiltonian preserves the extensivity of the target energies. Our analysis implies that IN for Ω is a valid size-extensive normalization for certain special IMS such as the quasi-complete model space and the isolated incomplete model space.

I. Introduction

Prompted by the conspicuous success of the single-reference coupled cluster (SRCC) method,[1−4] its generalization to encompass open-shell and quasi-degenerate cases has been attempted by several authors. Diverse methodologies have been put forward, which emphasize different physical aspects of electron correlation in the quasi-degenerate situations. This difference in emphasis is reflected in the use of different ansatzes for the wave-operator, Ω, and/or in the span of the model functions in the quasi-degenerate space, which can involve model spaces with varying numbers of active electrons or a fixed number of active electrons. Most of the earlier formalisms were built on the concept of effective Hamiltonians and used a complete model space (also called a complete active space). Using the customary and convenient intermediate normalization (IN) for Ω, all these developments arrived at connected (size-extensive) cluster-operators, which led to a connected effective Hamiltonian. The target energies were obtained via the diagonalization of the effective Hamiltonian defined over the complete model space (CMS). Size-extensivity of the energies thus obtained were guaranteed by the completeness of the active space. Another approach is to abandon the concept of the effective Hamiltonian altogether and either focus on only one state of interest (usually termed as state-specific approach[5−9]) or target only those roots that are of interest (the intermediate Hamiltonian approach[10−14]).

As emphasized above, the two main classes of effective Hamiltonian-based multireference coupled cluster (MRCC) methods are designed to address different aspects of the correlation problem for quasi-degenerate systems The state-universal (SU) multireference coupled cluster (SU-MRCC) approach[15] focuses on the description of a system with a fixed number of electrons, making it the method of choice for states with a fixed number of electrons, and in the study of potential energy surfaces (PES). The valence-universal (VU) multireference coupled cluster (VU-MRCC) approach,[16−22] on the other hand, targets states with varying numbers of valence electrons through the use of a single wave operator, akin to the single-reference (SR) case, such that it correlates not only the reference functions of interest with a definite valence occupancy but also reference functions of all the lower valence (subduced) sectors, obtained by deleting the occupancies systematically. Thus to define this operator uniquely, one needs to simultaneously consider not only the system of interest but also the corresponding ions that result from the successive removal of the electrons occupying the active orbitals. The method thus becomes the natural method of choice for computing energy differences of spectroscopic interest such as ionization potential, electron affinity, double ionization potential and excitation energy.[17−22] The increased computational requirements for VU-MRCC is offset by the increased information content of the formalism, allowing one to take care of the differential correlation energy attendant upon deletion or addition of electrons or excitations, which is needed for a balanced description of energy differences.

Despite their rigor and elegance, applicability of the MRCC theories using a CMS has been somewhat restricted until today owing to the perennial problem of intruders.[23] This arises from

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string mixing of some low-lying virtual functions with some high-lying model functions spanning the complete model space. One may imagine that the problem of intruders can be avoided using incomplete model space (IMS) instead of CMS, where the offending model functions mixing strongly with the virtual functions are deliberately kept out of the model space. Generally, the reference functions that dominate the wave functions corresponding to the low-lying excited states span an *incomplete model space*, because in most chemically interesting systems, these low-lying excited states are likely to be associated with single and double excitations from the ground state instead of attributing a given number of active electrons and active orbitals to all possible excitations. If one shifts the high-lying functions of the CMS to the virtual space (thereby making the model space incomplete in nature), this seems like a natural starting point from the physical point of view, where one may avoid intruders and at the same time target the low-lying states of interest.

Such a straightforward development, however, is fraught with the theoretical difficulty of ensuring extensivity of the computed target energies. All the standard versions of MR theories with effective Hamiltonians exploit the use of CMS to maintain the connectedness of the effective Hamiltonian, which automatically ensures the extensivity of energies. Such, unfortunately, is not the case in an IMS-based theory. Even if it were possible to get a connected effective Hamiltonian in an IMS, the computed state energies on diagonalization would still have been inextensive, just as in a CI in an IMS. The theoretical constraints on the effective Hamiltonian, which would guarantee the size-extensivity of the energies, is obviously somewhat more intricate.

The reason size-inextensivity appears in a diagonalization of even a connected operator in an IMS can be traced by looking at the diagonalization problem as an infinite order perturbation theory, thereby monitoring all the connected and disconnected terms that are generated at each order of perturbation.[24] Let us briefly recapitulate the analysis here, because this forms the starting point of generating a size-extensive MRCC theory in an IMS. If we start from one of the model functions as the unperturbed function for one of the target energies, and take care of other model functions in an IMS, interacting via the matrix elements of a connected operator by a Rayleigh−Schrödinger (RS) perturbation, then at each order there will be two kinds of terms: (i) the so-called direct term, which involves a sum over states involving transitions from the starting model function to all the other model functions, eventually returning to the starting model function itself, and (ii) the so-called normalization term, which involves a product of a norm-correction involving the perturbation correction of the wave function and energy shifts with various orders of perturbation, with a negative sign. The normalization term gives rise to two distinct types of entities. In one, there are no common orbitals among the norm factor and the energy shift factor. They are, therefore, algebraically disconnected, and size-inextensive. By adding certain sets of similar such terms together and by using what is known as the Franz−Mills identity,[25] we can rewrite these disconnected terms as a sum over states expression just like as in the direct term. The intermediate states entering the sum in this expression are generated by the same excitations from the unperturbed functions as are involved in each factor of the disconnected normalization term, but the intermediate states are produced by the action of these excitations on some other model function generated by these excitations, rather than on the starting unperturbed function itself. If these intermediate functions thus generated belong to the IMS, then they would be exactly canceled at the same order of perturbation stemming from a direct disconnected term, which necessarily involves only the sum over the model functions in the IMS. If, on the other hand, an intermediate state generated does not belong to the IMS (this will always happen for some terms, when the model space is incomplete), then such disconnected normalization terms will never get canceled by the analogous disconnected counterterms from the direct term, simply because there is no such intermediate state in this term. This is the real reason behind the appearance of disconnected terms at each order of perturbation while following the diagonalization procedure in an IMS as an infinite order perturbation theory. It should be mentioned here that there is another set of normalization term where there are common orbitals in the two factors. These so-called EPV (exclusion principle violating) terms are thus algebraically connected and, hence are harmless as far as size-extensivity is concerned. Because in a CMS, excitation on any model function to another involves only active orbitals, they lead only to excitations involving the functions in the CMS itself, and hence, all the disconnected terms from the normalization term get canceled by a corresponding direct term. In contrast, although the excitations from the starting model function to another model function in a perturbation still involves only active orbitals, the intermediate states generated come from the action of these excitations on model functions other than the starting one, and these may belong to the complementary active space which, together with the starting IMS, span the CMS. Because the intermediate states appearing in the direct term never involve the functions of the complementary active space, these disconnected normalization terms never get canceled by any of the direct terms. This analysis holds as much for a diagonalization on a connected effective Hamiltonian in an IMS as for a CI in an IMS.

From what has been discussed above, it is clear that if one could ensure that excitation from the starting model function could be confined to only those whose action on other model functions restrict the excitation also only within the IMS, then there would not have been any disconnected term in the perturbation involving intermediates lying outside the IMS, and the problem of inextensivity would go away for the perturbative diagonalization of the matrix of the connected operator in an IMS. Because one can start with any model function as the starting unperturbed function, it follows that it is necessary that the effective operator should be such that any excitation involving this operator should not lead to excitations outside the IMS by its action on any model function. Following the earlier works of Mukherjee,[26] we want to call such types of excitations connecting the model functions as “closed”. In contrast, types of excitations where their action on some functions in the IMS generates functions in the IMS, but their action on some other model function takes them to the complementary active space, are called “quasi-open”. As we have just now emphasized, the effective Hamiltonian should be both connected and “closed” for ensuring extensivity of the target energies on diagonalization in an IMS.

It was shown by Mukherjee,[26] that this can be ensured by including in cluster operators in the wave-operator Ω not only excitations leading to virtual functions (via excitations which we will call “open”) but also all the quasi-open excitations. The latter involves excitations only active orbitals but, in contrast to the closed operators, may or may not lead to excitations to the complementary active space. The cluster amplitudes for the quasi-open operators should be determined from the “decoupling conditions” that the matrix elements of all the quasi-open

components of the transformed operator $L = \Omega^{-1}H\Omega$ should vanish. This can be accomplished in a straightforward manner via the use of Bloch equation[27] in an IMS. Mukherjee showed that, if one includes in Ω only open and quasi-open operators (which is the minimal decoupling conditions), then it can generally so happen that the customary intermediate normalization for Ω would have to be abandoned. This comes about because the quasi-open operators can lead to excitations within the IMS and also because products of quasi-open cluster operators can be closed as well. By including only open and quasi-open operators in Ω, extensive MRCC formalisms have been developed both for VU[21,26,28] and for SU[29,30] MRCC formalisms. Using the same idea, state-specific MRCC theory has also been developed.[7]

It should be recognized at this stage that the decoupling conditions implicit in the Bloch equation for an IMS impose vanishing amplitudes for all the open and quasi-open operators of the transformed Hamiltonian L. Clearly, this still leaves open the possibility of choosing the closed component of Ω, viz $\Omega_{\rm cl}$. The normalization that comes closest to the IN for Ω would be to choose $\Omega_{\rm cl} = 1_{\rm cl}$. The more desirable choice $P\Omega P = P$ would be incompatible with the decoupling conditions $L_{\rm q-op} = 0$, because these conditions, rather than certain arbitrary conditions imposed on $\Omega_{\rm q-op}$, determine $\Omega_{\rm q-op}$.

From now on, we refer to both open and quasi-open operators generically as "external", and label all such operators as $A_{\rm ext}$. Similarly, both quasi-open and closed operators would henceforth be collectively termed as internal, labeled as $A_{\rm int}$.

Of course, it is desirable to look for a size-extensive method for IMS using IN for Ω, because, for one, this would generate a simpler expression for $H_{\rm eff}$ just as in a corresponding theory using CMS and, for other IN, allows a straightforward generation of the cluster amplitudes from a knowledge of the CI coefficients for an exact function.[31] However, the situation is rather tricky. One may imagine that, once a size-extensive formalism is developed with a cluster ansatz for Ω containing open and quasi-open operators, it is possible to introduce at the final stage of the formalism to impose the IN on the wave operator via the transformation

$$\tilde{\Omega} = \Omega[P\Omega P]^{-1} \tag{1}$$

which generates a new effective Hamiltonian $\tilde{H}_{\rm eff}$, given by

$$\tilde{H}_{\rm eff} = P\Omega P H_{\rm eff}[P\Omega P]^{-1} \tag{2}$$

Being a similarity-transformed operator of the original $H_{\rm eff}$ and $\tilde{H}_{\rm eff}$ produces the same roots. Such an approach was indeed suggested long ago by Chaudhuri et al.,[24] who also pointed out the attendant difficulties. Though this stratagem does produce size-extensive energies, despite the use of IN for the wave-operator, it is a *post facto restoration* of IN after having generated a connected $H_{\rm eff}$ without the IN. A straightforward generation of the modified wave-operator $\tilde{\Omega}$ without the intermediary of the Ω is not theoretically possible.

We pursue in this paper the idea that the only feasible direct approach to generate an MRCC theory with IMS, which is manifestly size-extensive and which uses a normalization condition on Ω that is as close as is possible to IN, is to impose $\Omega_{\rm cl} = 1_{\rm cl}$ as the natural choice of normalization. As it turns out, the above condition on $\Omega_{\rm cl}$ also leads to the same type of simple expression for $H_{\rm eff}$ as for the CMS, though (unlike the use of IN) it is not possible to generate the cluster coefficients from the knowledge of CI coefficients from a FCI alone. There have been attempts to generate a SU-MRCC theory where IN on Ω via the use of additional internal cluster operators was imposed disregarding the attendant inextensivity of the target energies.[31] It was shown, however, that with choice of the product separable IMS, such energies are additively separable in the limit of noninteracting subsystems, and the theory is size consistent. Our major concern in this paper is, however, to ensure size-extensivity and we want size consistency to naturally follow for a product separable IMS.

We present in this paper precisely such a formulation via the use of an alternative cluster ansatz for Ω, which imposes the condition $\Omega_{\rm cl} = 1_{\rm cl}$ through the inclusion of additional "closed" cluster operators. We develop a VU-MRCC theory for IMS using this new ansatz.

The paper is organized as follows. In section 2 we will present the theoretical developments of our VU-MRCC theory for an arbitrary model space. Section 3 summarizes the main contents of the paper and concluding remarks.

II. Theoretical Developments

Before embarking on the theoretical developments of our new VU-MRCC theory using IMS, it is pertinent to introduce certain concepts and certain notations that will set the scenario.

A. Preliminaries. In VU formulation of the MRCC theory, one defines a wave-operator Ω, which generates exact functions $\Psi_k^{(n_{\rm v})}$ by its action on the starting MR functions $\Psi_{0k}^{(n_{\rm v})}$, given by

$$\Psi_{0k}^{(n_{\rm v})} = \sum_{\mu} \phi_{\mu}^{(n_{\rm v})}\, c_{\mu k}^{(n_{\rm v})} \;\forall\; n_{\upsilon} \tag{3}$$

where $n_{\rm v}$ is the number of valence electrons of the model functions $\phi_{\mu}^{(n_{\rm v})}$. In a VU-MRCC theory, one simultaneously considers model spaces with different numbers of valence occupancies, so that $n_{\rm v}$ runs over a range $n_{\rm v} = 0, m_{\rm v}$, where $m_{\rm v}$ is the number of valence electrons of our interest. Because Ω generates exact functions for all model space MR combinations $\Psi_{0k}^{(n_{\rm v})}$, Ω is valence universal. Clearly, Ω contains many more cluster operators than are needed to construct target states $\Psi_k^{(m_{\rm v})}$.

In the traditional VU-MRCC formulations using an IMS, it is customary to define both the actual IMS with $n_{\rm v}$ active electrons by the projector $P^{(n_{\rm v})}$ and the complementary active space characterize by the projector $R^{(n_{\rm v})}$. The union PUR forms the CMS.

The Bloch equation for the various $n_{\rm v}$ valence problems is given by

$$H\Omega P^{(^{n_{\rm v}})} = \Omega P H_{\rm eff}^{(n_{\rm v})} P \tag{4}$$

It is also useful to define valence rank $n_{\rm v}$ of an operator as the number of valence destruction operators contained in it. To have enough flexibility to generate exact functions from all $n_{\rm v}$ valence model functions, it is imperative to include in Ω excitation operators of various valence ranks $n_{\rm v} = 0, m_{\rm v}$. The simplest set of CC equations for a VU-MRCC results if one uses a *normal ordered exponential ansatz* for Ω as

$$\Omega = \{\exp(S)\}$$
$$S = \sum_{n_{\upsilon}=0}^{m_{\rm v}} S^{(n_{\rm v})} \tag{5}$$

$S^{(n_{\rm v})}$ are the set of $n_{\rm v}$ valence cluster operators. The normal ordering is done with respect to the zero valence SR model function ϕ_0, taken as the vacuum. Owing to the normal ordering,

there is a hierarchical decoupling of the equations for the cluster amplitudes for various valence ranks in the following sense: for an n_v valence Bloch equation no cluster operators of valence rank greater than n_v can appear. Thus, one can start for the zero valence problem upward all the way to the m_v valence problem where at each valence level the only unknowns are the cluster amplitudes of the same valence rank, with the frozen cluster amplitudes of all the lower valence ranks. This has been termed a subsystem embedding condition (SEC) by Mukherjee and others.[16,17,19] We also define an operator in normal order $A^{[n_v]}$ as

$$A^{[n_v]} = \sum_{l_v=0}^{n_v} A^{(l_v)} \tag{6}$$

With this notation

$$\Omega = \{\exp(S^{[m_v]})\} \tag{7}$$

We also note that, owing to normal ordering

$$\Omega P^{(n_v)} \equiv \Omega^{[n_v]} P^{(n_v)} = \{\exp(S^{[n_v]})\} P^{(n_v)} \tag{8}$$

which is a compact representation of SEC.

If one starts from an m_v valence CMS, deletes one electron from each model function $\phi_\mu^{(m_v)}$ in all possible manners and collects all the distinct $(m_v - 1)$ valence model functions thus generated; the resulting *subduced* model space is also a CMS for the $(m_v - 1)$ valence problems. One can go all the way down to the zero valence problem by successive deletion of electrons, thereby generating all the lower valence CMS in the process. For an IMS, however, the model spaces generated by the subduction process depend on the actual starting IMS.[26] Thus, for an m_v valence IMS deletion of one electron from all model functions of IMS and collection of distinct $(m_v - 1)$ valence model functions will generate the corresponding subduced IMS with $(m_v - 1)$ valence electrons. Again, the process can be repeated all the way down to the zero valence levels, producing successively IMS of the lower valence ranks. By construction, the one valence subduced model space is always complete, and so also is the MS for the zero valence problem, which is spanned by just the model function ϕ_0, the vacuum.

In the original size-extensive formulation of Mukherjee[26] for an IMS Ω was chosen to be of the form

$$\Omega = \{\exp(S)\} \equiv \{\exp(S_{op}^{[n_v]} + S_{q-op}^{[n_v]})\} \tag{9}$$

As discussed in section I, this choice guarantees size-extensivity of the target state energies, which is predicated both to the connectedness of the H_{eff} and to its closed nature. Owing to the appearance of the quasi-open cluster operators in Ω, there is no intermediate normalization, and $P\Omega P \neq P$ as well as $\Omega_{cl} \neq 1_{cl}$ in general. Substituting eq 7 in eq 4, and using the generalized Wick's theorem,[33] it follows that

$$\{\overbrace{H\exp(S)}\exp(S)\}P^{(n_v)} = \{\exp(S)\,\overbrace{\exp(S)H_{eff}}\}P^{(n_v)} \;\forall\; n_v \tag{10}$$

where the symbols $\{\overbrace{A\exp(S)}\}$ and $\{\overbrace{\exp(S)B}\}$ stand respectively for all connected composites obtained by joining all possible powers of S with A and B, excluding contractions among the various S. Using SEC, proceeding upward in valence ranks from the valence rank zero, and equating the external operators of both sides of the Bloch equation with a given valence rank, one arrives at

$$\{\overbrace{H\{\exp(S^{[n_v]})\}}\}_{ext}^{(n_v)} P^{(n_v)} = \{\overbrace{\{\exp(S^{[n_v]})\}H_{eff}^{[n_v]}}\}^{(n_v)} P^{(n_v)} \;\forall\; n_v \tag{11}$$

Equation 11 is valid for each external operator (open or quasi-open, as the case may be) of each particle rank of the composites appearing in the equation, and for each valence rank. Similarly, equating the closed components of the Bloch equation, written in normal order for each valence rank, and using generalized Wick's theorem, one obtains

$$\{\overbrace{H\{\exp(S^{[n_v]})\}}\}_{cl}^{(n_v)} P^{(n_v)} = \{\overbrace{\{\exp(S^{[n_v]})\}_{cl}H_{eff}^{[n_v]}}\}^{(n_v)} P^{(n_v)} \;\forall\; n_v \tag{12}$$

which defines H_{eff} of various valence ranks.

In more compact form, using $\Omega^{[n_v]}$ for $\{\exp(S^{[n_v]})\}$, the working equations for determining the cluster amplitudes are given by

$$\{\overbrace{H\Omega^{[n_v]}}\}_{ext}^{[n_v]} P^{(n_v)} = \{\overbrace{\Omega_{ext}^{[n_v]}\, H_{eff}^{[n_v]}}\}^{[n_v]} P^{(n_v)} \tag{13}$$

and the effective Hamiltonians are found from the expression

$$\{\overbrace{H\Omega^{[n_v]}}\}_{cl}^{[n_v]} P^{(n_v)} = \{\overbrace{\Omega_{cl}^{[n_v]}\, H_{eff}^{[n_v]}}\}^{[n_v]} P^{(n_v)} \tag{14}$$

Equations 11 and 13 are entirely equivalent to the decoupling conditions on the transformed Hamiltonian L, with minimal normalization constrains imposed on Ω ensuring the following property of L:

$$L_{op}^{(n_v)} = 0 \;\forall\; n_v = 0, m_v$$
$$L_{q-op}^{(n_v)} = 0 \;\forall\; n_v = 0, m_v \tag{15}$$

As was shown by Mukherjee, the above choice of Ω leads to an $H_{eff}^{[n_v]}$, as the closed part of L:

$$H_{eff}^{[n_v]} = L_{cl}^{(n_v)} \tag{16}$$

which is equivalent to its implicit definition via eq 12 or (14). Equation 12 or 14 indicates that H_{eff} is both *connected and closed*, which ensures the size-extensivity of the computed energies.

Because a large class of chemically interesting states are qualitatively well-described by model functions spanning a set of various m-hole−n-particle excited functions generated from ϕ_0, it becomes useful at this stage to generalize the concept of active orbitals to encompass both holes and particles and use superscripts (m, n) to indicate in an operator A the hole and particle valence ranks separately, as, for example, by $A^{(m,n)}$. With this generalized notation, the working equations stemming from Bloch equation would look like

$$\{\overbrace{H\Omega^{[k,l]}}\}_{ext}^{[k,l]} P^{(k,l)} = \{\overbrace{\Omega_{ext}^{[k,l]}\, H_{eff}^{[k,l]}}\}^{(k,l)} P^{(k,l)}$$

and

$$\{\overbrace{H\Omega^{[k,l]}}\}_{cl}^{(k,l)} P^{(k,l)} = \{\overbrace{\Omega_{cl}^{[k,l]}\, H_{eff}^{[k,l]}}\}^{(k,l)} P^{(k,l)} \tag{17}$$
$$\forall\; (k, l) = (0, 0) - (m, n)$$

We emphasize again here that, owing to the lack of intermediate normalization, the customary expression for H_{eff} no longer remains valid, and one must use eq 12 to iteratively solve for it. Thus, it makes sense to look for an alternative normalization of the operator Ω, which makes H_{eff} take the same simple expression as $\{H\Omega\}_{\text{cl}}$, as in a CMS, but maintaining the size-extensivity of the target energies. We show in the next subsection that such a choice is indeed possible by the inclusion of additional closed operators in Ω.

B. Imposition of $\Omega_{\text{cl}} = 1_{\text{cl}}$ in a Size-Extensive VU-MRCC Formulation with IMS. As indicated in the Introduction and the subsection above, we now present a formulation where we impose the normalization condition

$$\Omega_{\text{cl}} = 1_{\text{cl}} \tag{18}$$

on Ω, to arrive at the much simpler expression $H_{\text{eff}} = \{\overbrace{H\Omega}\}_{\text{cl}}$ even for an IMS, while ensuring the size-extensivity of the target energies. We will achieve this, following the earlier ideas of Chaudhuri et al.,[24] by including in Ω certain closed cluster operators X of various valence ranks (k, l). Thus we introduce a new cluster wave-operator Ω, given by

$$\Omega \equiv \{\exp(S + X)\} = \{\exp(S^{[m,n]} + X^{[m,n]})\} \tag{19}$$

The cluster amplitudes of these operators would be determined from the condition that, for each hole−particle valence rank (k, l), the closed component of Ω would satisfy eq 18:

$$\{\Omega_{\text{cl}}\}^{(k,l)} = 1_{\text{cl}}^{(k,l)} \tag{20}$$

or,

$$\{\exp(S + X)\}_{\text{cl}}^{(k,l)} = 1_{\text{cl}} \tag{21}$$

This leads to

$$X_{\text{cl}}^{(k,l)} = -\{\exp(S)\}_{\text{cl}}^{(k,l)} \; \forall \; k, l \tag{22}$$

Because we are imposing a normalization condition on just the closed portion of Ω, leaving its external (open and, in particular, quasi-open) components to be determined by the decoupling conditions eq 17, there is no conflict between them, and one would expect size-extensivity of the computed energies would remain unaffected. As we show below, such is indeed the case, though a demonstration of this for any arbitrary model space (which can involve valence holes as well as valence particles) requires a careful exposition and analysis of the structure of the Bloch equation in the VU-MRCC theory using IMS.

To make our presentation clear, we proceed in two steps, by taking first the set of IMS covering most of the common choices (where the proof of size-extensivity of the energies in more or less straightforward), and take up the second set of IMS where the proof becomes somewhat more involved. The proof used in the second set of IMS is the more general, which subsumes the first set of IMS, so ultimately the proof for the second would have been enough. But, as we just indicated above, we proceed stepwise for the ease of following the proofs.

Let us first consider such IMS where the valence universal Ω has always some creation operators in the S. This is always the case either when the vacuum ϕ_0 itself is contained in the IMS or when the IMS contains electrons differing in the number of electrons as compared to ϕ_0. For such IMS, one can arrive

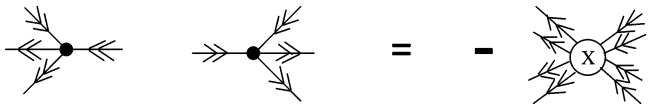

Figure 1. Diagrammatic depiction of cancelation of products of quasi-open ($S_{\text{q-op}}$) operators producing a closed composite by a term containing closed X operators.

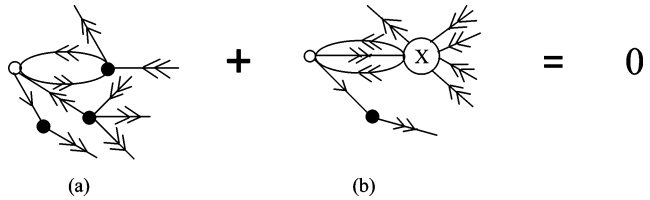

Figure 2. Diagrammatic depiction of mutual elimination of all those diagrams in the working equation of VU-MRCC when, for any X operators (Figure 1a) appearing in a connected term, there is counterterm (Figure 1b) produced byproducts of $S_{\text{q-op}}$ operators that are closed. The filled circles denote the vertexes for the cluster operators, and the open circle denotes an H vertex.

at the working equations for the various cluster amplitudes of S of different valence ranks via SEC as

$$\{\overbrace{H\{\exp(S + X)\}^{[k,l]}}\}^{(k,l)}P^{(k,l)} = \{\overbrace{\{\exp(S + X)\}^{[k,l]}H_{\text{eff}}^{[k,l]}}\}_{\text{ext}}^{(k,l)}P^{(k,l)} \tag{23}$$

Because there are always creation as well as destruction operators in each S, for every composite on either side of eq 23 containing an X_{cl} of a given valence rank, there are always powers of $S_{\text{q-op}}$ operators forming a closed entity of the same valence rank, joined from right or left of, respectively, H and H_{eff}. From now on, for brevity, we drop the subscript "q-op" for S and also refer to the powers of $S_{\text{q-op}}$ that are closed as "closed powers". Owing to the imposition of the normalization condition, eq 20 on Ω, all such closed powers of S would cancel the corresponding X, via eq 22. In the final working equations, there would thus not remain any X operators at all! Also, there would not be any closed powers of S operators connected to H or H_{eff}. Figures 1 and 2 indicate such cancelations.

The final form of the working equations then become

$$\{\overbrace{H\{\exp(S)\}'^{[k,l]}}\}^{(k,l)}P^{(k,l)} = \{\overbrace{\{\exp(S)\}'^{[k,l]}H_{\text{eff}}^{[k,l]}}\}_{\text{ext}}^{(k,l)}P^{(k,l)} \tag{24}$$

The expression for H_{eff} is given by

$$\{\overbrace{H\{\exp(S)\}'^{[k,l]}}\}_{\text{cl}}^{(k,l)} = H_{\text{eff}}^{(k,l)} \tag{25}$$

where the prime on $\{\exp(S)\}$ indicates that all the closed powers of S are to be excluded from eqs 24 and 25.

One should note that the counterterms coming from the closed powers of S canceling X is possible only because all the S operators forming a closed power can appear in the connected composites on either side of eq 23. In the case of the vacuum, ϕ_0 itself is not a part of the model space, it is essential to include in S some de-excitation operators as shown in Figure 3, which have no lines to the left, indicating that there are no hole−particle creation operators in such S. In such situations, it is entirely possible that there are some composites in eq 23 containing X for which a counterterm stemming from closed powers of S does not exist simply because such closed powers cannot exist in the connected composites on either the right or left sides of the equation.[32] Figure 4 indicates such a situation

Figure 3. Pure de-excitation operators in S_{q-op} when it is possible to reach a function with fewer valence occupancy.

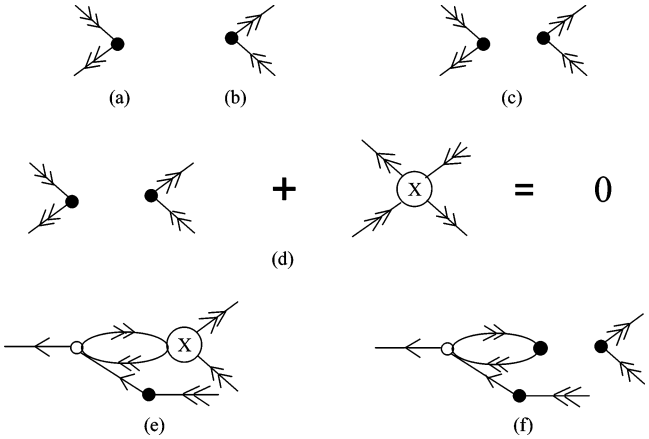

Figure 4. (a) A zero valence excitation operator S_{q-op}. (b) A de-excitation operator with no lines to the right. (c) The product of two producing a closed operators for one-hole one-particle IMS. (d) Constraint on X canceling the closed product of two S_{q-op} in (c). (e) A typical term where X appears. (f) The possible counterterm, which could have canceled (e), but cannot because the diagram is disconnected. This is why the diagram in (e) remains uncancel if one uses eq 24. On the other hand, using eq 29, the sum of (e) and (f) generate one of the entities of $\{H\{\exp(S+X)\}\}$ and the mutual cancelation can then be effected.

where the IMS consists of all one-hole−one-particle excited functions generated from ϕ_0. The operators shown in Figure 4a,b are each quasi-open in this case, because the excitation operator in Figure 4a leads to an excitation to a two-hole−two-particle excited state, which is outside the IMS, and the de-excitation shown in Figure 4b leads to ϕ_0, which is also outside the IMS. Their product, however, is closed, as shown in Figure 4c, which can be eliminated by introducing a closed operator X satisfying the equation shown diagrammatically in Figure 4d. Although this does restore the normalization condition, eq 21, in the connected composites of eq 23 there is no such cancellation of the operator X because the closed power of Figure 4c cannot appear in a composite entity as shown in Figure 4e,f. Figure 4e is a valid diagram whereas Figure 4f is not and it does not appear in eq 23. Hence, the term containing X of Figure 4e survives, because X is negative of two disconnected operators of S; as shown in Figure 4d, X itself is disconnected and hence the presence of an X in eq 23 spells a breakdown of the connectivity of the working equations. This is an unwarranted and awkward situation. To cover such cases, we suggest a somewhat more involved proof, as delineated below.

We start from the original Bloch equation with Ω defined in eq 19 and rewrite it in normal order using generalized Wick'stheorem. Equating the external components for each valence rank and excitation rank on both sides of the equation, we have

$$\overline{\{H\{\exp(S+X)\}\exp(S+X)\}}_{ext}P = \{[\exp(S+X)]_{ext}\,\overline{\exp(S+X)H_{eff}}\}P \quad (26)$$

where we have omitted the superscripts showing the valence rank of the associated operators for brevity. Canceling all the X operators in the portion of $\{\exp(S+X)\}$ present on both sides via eq 22, we have

$$\overline{\{H\{\exp(S+X)\}'\exp(S)'\}}_{ext}P = \overline{\{\exp(S)'\,\exp(S+X)'_{ext}H_{eff}\}}P \quad (27)$$

where all the primed quantities indicate that all the closed powers of S have been canceled by the counterterm containing X. Because we are considering the most general IMS, where not all X operators connected to H or H_{eff} may have a counterpart from some closed power of cluster operators S_{q-op}, some X operators in the connected parts will remain uncanceled.

If we now introduce a new composite obtained by bringing in some quasi-open powers of S_{q-op} operators alongside the connected terms in the Bloch equation (eq 26) such that the missing closed counterpart with S_{q-op} for each X can be generated, then the proof of the connectivity of the operators S and consequently H_{eff} can be accomplished. We denote composites thus generated from two mutually disconnected quantities A and B as $\{\overline{AB}\}$. To illustrate this procedure of generating the composite, let us consider the diagram in Figure 4f. The entity containing two S_{q-op} operators connected to H is the analogue of the operator A. The excitation operator requires a de-excitation operator as another factor to generate a closed power of S_{q-op}. Thus the de-excitation operator unconnected to A is the entity B, and the two terms unconnected to each other but generating a closed power of S in the normal ordered product can be denoted as $\overline{AB}$. This disconnected composite of Figure 4f gets exactly canceled by the connected-looking counterterm containing X, as appears in Figure 4e. Thus, generally speaking, we can rewrite eq 27 in terms of the composites just defined as

$$\overline{\{H\{\exp(S+X)\}\exp(S)'\}}_{ext}P = \{\exp(S)'\,\overline{\exp(S+X)H_{eff}}\}_{ext}P \quad (28)$$

where we have brought in those quasi-open powers of S on both sides of the equation, that generate the composites which together with the quasi-open powers of S in the connected quantities such as $\{H\{\exp(S+X)\}\}$ or $\{\overline{\exp(S+X)'_{ext}H_{eff}}\}$, to generate a closed term under the bar. We note here that the term $\{\exp(S)\}'$ gets regenerated in eqs 26 and 27 even after we have removed from it the powers of cluster operators that are quasi-open because of the exponential structure of the infinite series $\{\exp(S)\}'$.

Using the SEC as before, we then have

$$\overline{\{H\{\exp(S+X)\}^{[k,l]}\}}^{(k,l)}_{ext}P^{(k,l)} = \overline{\{\exp(S+X)^{[k,l]}_{ext}\,H^{[k,l]}_{eff}\}}^{(k,l)}_{ext}P^{(k,l)} \quad (29)$$

where we now show explicitly the hole-particle valence rank (k, l) for the first time, which we omitted earlier for brevity. Equation 29, unlike the eq 28, contains only the composites with bar, and no other factors such as $\{\exp(S)\}'$.

Obviously, now we can cancel all the terms with X in eq 29 with the corresponding closed powers of S in the composites under the bar, and hence get

$$\overline{[H\{\exp(S)\}'^{[k,l]}]}^{(k,l)}_{ext}P^{(k,l)} = \overline{[\exp(S)'^{[k,l]}_{ext}H^{[k,l]}_{eff}]}^{(k,l)}_{ext}P^{(k,l)} \quad (30)$$

where we have brought back the contracted quantities again, because all the closed entities under the bar with X and powers

of S have been canceled, leaving only connected terms. Similarly, the corresponding expression for H_{eff} is given by

$$H_{\text{eff}}^{(k,l)} = \{\overbrace{H\{\exp(S)\}^{\prime[k,l]}}\}_{\text{cl}}^{(k,l)} \tag{31}$$

The above analysis completes the proof of the connectivity of the cluster operators in S as well as of the closed operator H_{eff} and hence of the computed energies. Because this proof is also trivially valid for first set of IMS where all the X operators in a connected term do have the corresponding closed counterpart coming from powers of S, this subsumes the situation involving the first set of IMS as well.

We conclude this section with the interesting observation that follows from our analysis for certain special class of IMSs as the quasi-complete model space (QMS)[18,34] and isolated IMS (IIMS).[35] A QMS is where one classifies the active orbitals in various groups a, b, c, etc. and allocates specific numbers of electrons n_a, n_b, n_c, etc. in these groups in all possible manner. An m-hole$-n$-particle IMS containing certain active holes and particles is an example of QMS. An IIMS is generated when one starts with an IMS where one of the groups a is completely filled in with then required number of electrons n_a and fills in the group b, c, etc. with suitable electrons n_b, n_c, etc. The union of these IMS and all those obtained by exciting electrons from group a to b and or c, etc. and/or also from b to c, etc., where one excites from a up to a fixed number of electrons constitutes an IIMS. An example of IIMS is the union of ϕ_0 and all (n-hole$-n$-particle) IMS for $n = 1$, m, where m is some integer ≥ 1. For QMS no quasi-open operator can have nonvanishing model space projection, i.e., $PA_{\text{q-op}}P = 0$. Thus, for a QMS, the use of the additional operators X ensuring $\Omega_{\text{cl}} = 1_{\text{cl}}$ would automatically imply the use of IN for Ω. For an IIMS, also $P\Omega P = P$ if $\Omega_{\text{cl}} = 1_{\text{cl}}$.

III. Concluding Remarks

In this paper, we have looked at certain specific aspects of the choice of size-extensive normalization of Ω in relation to maintence of extensivity of the computed energies from an H_{eff} using an IMS. Following the earlier analysis of Mukherjee[26] that, in general, the use of IN for Ω is incompatible with the size-extensivity of the target state energies, our intention has been to look for a normalization of Ω that is as close as possible to IN. The desire to effect this modification of the formalism is to generate an H_{eff} that has exactly the same expression as one would have obtained using IN for Ω. In the context of the VU-MRCC IMS we have used the concept of the quasi-open and closed operators, tracing the origin of the size-inextensivity of the computed energies to the appearance of the quasi-open matrix elements of H in a CI with IMS. It has been emphasized that the size-extensivity of the energies is predicated by the use of a connected H_{eff} which is closed. Because the quasi-open components of Ω are fixed by the requirement of the vanishing quasi-open matrix elements of H_{eff}, we have no flexibility in fixing them by any other auxiliary conditions. The only flexibility left is for Ω_{cl} only. We have shown in this paper that Ω_{cl} can be chosen to be equal to 1_{cl}, which leads to the same type of expression for H_{eff} a one would have using IN for Ω. By including closed cluster operators X in addition to the usual open and quasi-open cluster operators S in a normal ordered Ansatz of a VU$-$ wave operator, and by determining X from the condition $\Omega_{\text{cl}} = 1_{\text{cl}}$, a closed connected H_{eff} can be obtained with the expression $H_{\text{eff}} = \{\overbrace{H\{\exp(S)'\}}\}_{\text{cl}}$. The prime in this expression implies that there are no powers of cluster operators S in this expression that is closed. In this formalism there is no need to determine X explicitly, because all terms containing X gets canceled by some powers of $S_{\text{q-op}}$ that are closed. We have also discussed two special IMS-QMS and IIMS-where our choice of normalization Ω automatically implies IN.

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Note Added in Proof. After the completion of this paper, we found an alternative and simpler solution to the problem, where the closed powers of only those quasi-open valence operators are removed which can appear on both sides of eq 24 via suitable X_{cl}. It leaves out the closed powers of $S^{(0,0)}$ and the de-excitation operators but leads again to the simpler expression, eq 25, for the valence part of H_{eff}. A detailed discussion of this formalism will be presented in a forthcoming paper.

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