CAN WE AVOID THE INTRUDER-STATE PROBLEMS IN THE STATE-UNIVERSAL COUPLED-CLUSTER APPROACHES WHILE PRESERVING SIZE EXTENSIVITY?

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It is our great pleasure to dedicate this paper to Professor Rudolf Zahradník on the occasion of his 75th birthday and to wish him only the best in both his personal and scientific life. I (senior author) will never forget our enduring friendship that lasted over more than four decades despite the political upheavals that separated us for a long time in geography, but not in spirit. We are all grateful for his continued kind advice and support, and admire his selfless and zealous efforts on behalf of Czech and Slovak Science after the collapse of the Communist regime. We wish him much success and happiness in the years to come.

Following the analysis of principal bottlenecks in the extension of the single-reference (SR) coupled-cluster (CC) methodology to the multireference (MR) case, we review and discuss some recent developments that facilitate the use of general model spaces (GMSs) within the state universal (SU) or Hilbert space MR CC formalism. The use of a GMS improves our ability to avoid the intruder state problems. This feature is further enhanced by generalizing the idea of the externally corrected (ec) SR CC formalism to the MR situations. In this latter approach we employ the cluster analysis to extract the most important higher-than-pair cluster amplitudes from a suitable set of known wave functions. Similarly to the SR case, the most convenient external source is represented by wave functions that are obtained *via* a modest size MR configuration interaction (CI), which employs an *N*-dimensional reference space. The resulting higher-than-pair cluster amplitudes are subsequently used in the SU CCSD method that is based on an *M*-dimensional GMS avoiding intruders. We discuss general aspects of these developments from various viewpoints and provide selective illustrations of the key concepts and ideas.

Keywords: Coupled-cluster methodology; Multireference state-universal formalism; Intruder states; Connectivity conditions; Externally-corrected formalism.

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Much work has been expended in pursuit of the multireference (MR) version of the standard single-reference (SR) coupled-cluster (CC) theory[1,2] (*cf.* refs[3,4] for an overview) leading eventually to the so-called valence universal (VU) or Fock space[5,6] and state universal (SU) or Hilbert space[7] formalism (for an overview, see, *e.g.*, refs[8–12]). Yet, to this very day, no general-purpose set of MR CC codes has been designed and various *ad hoc* applications remain rather limited (*cf.*, *e.g.*, refs[13–15]). Indeed, with the exception of applications to atomic systems (see, *e.g.*, refs[8,16]), particularly at the relativistic level (see, *e.g.*, refs[17–19]), there have been very few exploitations of the MR CC methods.

The very *raison d'être* why we have two, radically different, MR CC formalisms is related to the fact that the MR generalization of the SR CC Ansatz is far from being unambiguous. The complexity of the resulting MR formalisms, implying considerable computational demands, also certainly contributes to the limited exploitation of the existing MR CC theories. The latter obstacle is closely related to the fact that both formalisms require the use of the complete model space (CMS) if the size-extensivity is to be preserved, since the dimension of the CMS rapidly increases with the increasing number of active orbitals and electrons, not unlike the dimension of the corresponding full configuration interaction (FCI) problem (*cf.*, *e.g.*, ref.[20]). Moreover, one of the greatest impediments that is enhanced by the use of a CMS is the occurrence of the so-called intruder states, which invariably sneak in when we explore the potential energy surfaces (PESs) or curves (PECs) over a wide range of geometries. Indeed, the larger the model space, the more likely we are to encounter intruders.

For the reasons just outlined there has been numerous attempts to adapt the MR CC theory – or, in fact, the closely related many-body perturbation theory (MBPT) – employing the effective Hamiltonian formalism to incomplete model spaces (IMSs), or even to completely arbitrary general model spaces (GMSs), the latter ones being spanned by a freely chosen set of configurations.

In the context of VU theories, the use of the IMS was thoroughly examined by Lindgren and Mukherjee[21] (*cf.* also ref.[9]), who showed that in order to warrant the size-extensivity when using a truncated CMS, one has to abandon the intermediate normalization of the wave operator and replace it with the so-called size-extensive normalization[22]. An important step in this direction was made by Lindgren[23], who introduced the so-called quasi-CMS. Another approach was formulated by Kutzelnigg *et al.*[24], who suggested the use of the so-called isolated IMS. We should also note that the necessary and sufficient conditions for the connectivity of the effective

Hamiltonian when a GMS is employed were formulated by Lindgren and Mukherjee[21].

In the context of the SU CC theory, the use of IMSs has been discussed in a considerable detail already in the original paper of Jeziorski and Monkhorst[7]. A specific formulation of the SU CC theory for special classes of IMSs was later given by Meissner *et al.*[25] This formulation was then extended to GMSs by Meissner and Bartlett[26], and was again achieved by abandoning the intermediate normalization of the wave operator. The shortcomings of these formulations and a possible remedy[27] will be outlined later on. Finally, we should also point out that a similar problem of the CMS truncation arose first in the context of the effective Hamiltonian formalism-based MR MBPT and was extensively discussed by Brandow[28], Hose and Kaldor[29], and others.

Unfortunately, the use of various special IMSs just mentioned only further complicates the already intricate MR CC formalism. Consequently, the exploitation of these formulations has been very limited. In fact, most of these theoretical developments have not been even tested in actual computations and we are certainly not aware of any general-purpose codes that would be based on these formalisms.

Another alternative that enables one to overcome the intruder state problem is to exploit the Brillouin–Wigner (BW)-type formulation of the CC theory[30]. Unfortunately, just as in BW MBPT, the size-extensivity property is completely lost in these approaches and is only partially recovered in the last iteration[30,31]. We would like to believe that this approach could also benefit from some of the developments that will be outlined below.

Yet another useful strategy that avoids the problems of intruders and the requirement of the complete model space exploits the so-called intermediate Hamiltonian formalism[32]. This approach seems to be particularly amenable in the context of the VU CC methodology. For an excellent exposition and relevant literature see the recent work by Meissner and Gryniaków[33].

In this paper we first try to provide a general outlook that exposes the principal bottlenecks of the MR CC theories and to lay bare the sources of these difficulties. We then sketch how to overcome these obstacles by introducing certain new concepts that enable us to formulate a fully connected SU CC theory based on a GMS while preserving the intermediate normalization, as well as how to extend the externally corrected (ec) SR CC methods[34–36], in particular the so-called reduced MR (RMR) CCSD method[37–39], to the MR SU CC case (*cf.* also ref.[4]). We shall also expound how the latter extension is hardly avoidable in truncated (to singles and doubles) MR CC

approaches, which should help to conciliate some preconceived objections or scruples concerning the ec-type methods.

Following the general outline given below, we succinctly compile the essence of the effective Hamiltonian formalism in order to fix our notation, and skim over the most recent developments[27] that address the above mentioned problems. In doing so we shall emphasize the most important facets of these advances as viewed from a broader perspective and assess some alternative venues that were proposed earlier.

GENERAL OUTLINE

In the SR CC formalism, the energy E is fully determined by one- and two-body clusters T_1 and T_2, respectively, namely

$$E = \langle \Phi_0 | H(1 + T_1 + T_2 + \frac{1}{2} T_1^2) | \Phi_0 \rangle . \qquad (1)$$

However, in the SR CC chain of equations, the k-body clusters are generally coupled to the ℓ-body clusters, where $k - 2 \le \ell \le k + 2$ (ignoring negative ℓ-values). Thus, to obtain the CCSD formalism, we have to neglect the three- and four-body clusters by setting $T_3 = T_4 = 0$ in order to decouple the standard CCSD equations from the rest of the CC chain. In a similar way one arrives at higher-level approximations, such as CCSDT, CCSDTQ, *etc.*

Clearly, when we evaluate the energy, Eq. (*1*), using the CCSD cluster amplitudes, we obtain the CCSD energy approximating the true FCI energy for a given *ab initio* model. As long as the effect of higher-than-pair clusters is negligible, the CCSD result represents an excellent approximation. The basic assumption for the SR CC method to yield a good approximation is the nondegeneracy of the reference (usually the Hartree–Fock) configuration $|\Phi_0\rangle$. This assumption is usually reasonably well satisfied in the vicinity of the ground state equilibrium geometry and the small corrections (amounting normally to about 1–3% of the correlation energy) due to the three-body connected clusters can be taken care of perturbatively *via* the CCSD(T) method[40]. Unfortunately, when breaking true chemical bonds, as when computing the entire PESs or PECs, this basic assumption is invariably violated to the extent that the three- and four-body – or even higher-order – connected cluster amplitudes become essential and can no longer be handled perturbatively. Likewise, an explicit account of these clusters *via* the CCSDT or CCSDTQ becomes soon computationally unaffordable. A proper way to overcome these difficulties is to employ the MR formalism.

As already alluded to above, however, the extension of the SR CC formalism to the MR case is far from being unambiguous and neither of the existing formulations is free of shortcomings. This is also reflected in the fact that no general-purpose MR CC codes have yet been developed. For this reason, much attention has been recently devoted to the so-called state-selective or state-specific approaches that focus on one state at a time (*cf.*, *e.g.*, ref.[4]). Here also belong the ec versions of the CCSD method of either the energy[41] or amplitude[34,35,37–39] correcting types. The latter kind exploits some external source of the information about the higher-than-pair clusters and employs these clusters for a physically more meaningful decoupling of the CC chain. Indeed, if we determine the three- and four-body cluster amplitudes from the full CI (FCI) wave function, representing the exact solution for a given *ab initio* model (as defined by the chosen atomic orbital basis set), and employ them to evaluate the T_3- and T_4-dependent terms that have been neglected in the CCSD formalism, we obtain the corrected CCSD equations that have the same algebraic form as the standard ones, but their solution returns the exact T_1 and T_2 clusters, which in turn yield back the FCI energy when employed in Eq. (*1*). The question thus arises which external source wave function is most suitable and at the same time most affordable for this purpose.

Generally speaking, we desire such an external source wave function that is easily accessible and provides a good description of the static and nondynamic correlation effects. By analyzing a number of possible sources, we have found out that the most suitable source is provided by a modest size MR CISD (CI with singles and doubles) wave function, which is also exploited in the RMR CCSD method[37–39].

The suitability of a CI-type wave function for this purpose is understandable in view of the complementarity of the CI and CC approaches in their handling of the nondynamic and dynamic correlations, respectively. Moreover, there is a simple relationship between the CI and CC amplitudes, as implied by the exponential CC Ansatz. Consequently, it is easy to transform any MR CISD wave function into the SR CISDTQ··· form and to carry out the cluster analysis. Most importantly, a modest size MR CISD involves only a very small subset of the three- and four-body cluster amplitudes, namely those that play the decisive role. At the same time, these three- and four-body amplitudes implicitly account for the T_5, T_6, and higher-body clusters that are present in the MR CISD wave function. Finally, in the limiting case, the FCI results are equivalent to the full CC (FCC) ones. In view of these facts, it is not only appropriate, but in fact decidedly expedient, to

exploit the advantages of both the CI and CC methodologies simultaneously.

Now, the quasidegeneracy problem that we encounter in SR approaches is not unlike the intruder state problem of MR theories: both are due to a strong interaction with states that are not included in the model space $\mathcal{M}_0$ (which, in the SR case, is one-dimensional). The above given outline indicates that there are at least two avenues opened to us to eliminate, or at least moderate, the detrimental role of intruder states in the MR CC approaches that are based on the effective Hamiltonian formalism. First, by allowing the model space $\mathcal{M}_0$ to be an arbitrary GMS, we can not only avoid possible intruders but, by choosing as small a model space as feasible, we can greatly reduce the computational effort. Second, we can exploit external source wave functions. Guided by our RMR CCSD experience, our preferred choice is a modest-size MR CISD. The external corrections are even more essential in the MR case than in the SR one since, generally, the off-diagonal elements of the effective Hamiltonian involve higher-than-pair clusters[42].

Thus, considering an M-dimensional GMS for SU CCSD, we exploit an N-dimensional reference space MR CISD wave functions that account for eventual intruders. We refer to this approach as the (N,M)-CCSD method. Using the MR CISD three- and four-body cluster amplitudes we then carry out ec SU CCSD. In this way we can account – at least approximately – for the effect of intruders, but also for the T_3- and T_4-dependent terms in the SU CCSD equations and in the effective Hamiltonian. In the following sections we briefly adumbrate the required formalism leading to the (N,M)-CCSD method.

EFFECTIVE HAMILTONIAN FORMALISM

Let $\mathcal{M}_0$ designate an M-dimensional GMS that is spanned by M arbitrary configurations $|\Phi_i\rangle$ and $\mathcal{M}$ the corresponding M-dimensional target space spanned by M exact eigenstates $|\Psi_i\rangle$ of the electronic Hamiltonian H of interest,

$$H|\Psi_i\rangle = E_i|\Psi_i\rangle\,, \quad (i = 1, \ldots, M)\,. \tag{2}$$

These exact (*i.e.*, FCI) wave functions may thus be expressed in the form

$$|\Psi_i\rangle = \sum_{j=1}^{M} c_{ij}|\Phi_j\rangle + \sum_{|\Xi_j\rangle \in \mathcal{M}_0^{\perp}} d_{ij}|\Xi_j\rangle\,, \tag{3}$$

where $|\Xi_j\rangle$ span the orthogonal complement $\mathcal{M}_0^{\perp}$ of $\mathcal{M}_0$ in the N-electron space $\mathcal{H}_{\mathcal{N}}$ of the model employed.

Clearly, $\mathcal{M}$ is not unique, since we only require that the projections $|\tilde{\Phi}_i\rangle$ of $|\Psi_i\rangle$ onto $\mathcal{M}_0$,

$$|\tilde{\Phi}_i\rangle = P|\Psi_i\rangle\,, \quad P = \sum_{i=1}^{M} |\Phi_i\rangle\langle\Phi_i| \tag{4}$$

span again $\mathcal{M}_0$. One then introduces the wave operator U which accomplishes the "inverse" mapping (for details, see, *e.g.*, refs[10,12])

$$|\Psi_i\rangle = U|\tilde{\Phi}_i\rangle\,, \quad |\tilde{\Psi}_i\rangle = U|\Phi_i\rangle, \quad \text{and} \quad U = \sum_{i=1}^{M} |\tilde{\Psi}_i\rangle\langle\Phi_i| = U\,P\,. \tag{5}$$

Using the intermediate normalization $\langle\Phi_i|\tilde{\Psi}_j\rangle = \delta_{ij}$, so that $P\,U = P$, we have that

$$|\tilde{\Psi}_i\rangle = |\Phi_i\rangle + \sum_{|\Xi_j\rangle \in \mathcal{M}_0^{\perp}} b_{ij}|\Xi_j\rangle\,, \tag{6}$$

where

$$\boldsymbol{B} \equiv ||b_{ij}|| = \boldsymbol{C}^{-1}\,\boldsymbol{D}\,, \quad \boldsymbol{C} \equiv ||c_{ij}||\,, \quad \boldsymbol{D} \equiv ||d_{ij}||\,. \tag{7}$$

Finally, projecting Eq. (*2*) onto $\mathcal{M}_0$ we can write

$$H^{(\mathrm{eff})}|\tilde{\Phi}_i\rangle = E_i|\tilde{\Phi}_i\rangle\,, \quad (i = 1, \ldots, M)\,, \tag{8}$$

where

$$H^{(\mathrm{eff})} = P\,H\,U = P\,H\,U\,P\,. \tag{9}$$

Diagonalizing $H^{(\mathrm{eff})}$ within $\mathcal{M}_0$ we thus find the energies E_i (i = 1, ..., M), and the transformation matrix $\boldsymbol{C}$ since $\langle\Phi_j|\tilde{\Phi}_i\rangle = c_{ij}$.

STATE-UNIVERSAL COUPLED-CLUSTER THEORY

Generalizing the SR CC Ansatz to the MR case following Jeziorski and Monkhorst[7], we write

$$U = \sum_j \mathrm{e}^{T(j)} |\Phi_j\rangle\langle\Phi_j| , \tag{10}$$

so that

$$|\tilde{\Psi}_i\rangle = \mathrm{e}^{T(i)}|\Phi_i\rangle \quad \text{and} \quad |\Psi_i\rangle = \sum_{j=1}^{M} c_{ij}\mathrm{e}^{T(j)}|\Phi_j\rangle , \tag{11}$$

where

$$T(i) = \sum_k T_k(i) , \quad T_k(i) = \sum_j t_j^{(k)}(i) G_j^{(k)}(i) . \tag{12}$$

Here $G_j^{(k)}(i)$ designates a k-fold excitation operator (spin-adapted or not) acting on the reference $|\Phi_i\rangle$. Note that different $G_j^{(k)}(i)|\Phi_i\rangle \equiv |\Phi_{i,j}^{(k)}\rangle$ may represent the same configuration state, *i.e.*, $G_j^{(k)}(i)|\Phi_i\rangle = G_m^{(k)}(\ell)|\Phi_\ell\rangle$ for some i, j and ℓ, m.

The cluster amplitudes $t_j^{(k)}(i)$ are then given by the generalized Bloch equations

$$\Lambda_i(k;\ell) = \sum_{j(\neq i)} \Gamma_{ij}(k;\ell) H_{ji}^{(\mathrm{eff})} , \tag{13}$$

where

$$\Lambda_i(k;\ell) = \langle G_\ell^{(k)}(i)\Phi_i|\bar{H}(i)|\Phi_i\rangle , \quad \bar{H}(i) = \mathrm{e}^{-T(i)} H \mathrm{e}^{T(i)} , \tag{14}$$

$$\Gamma_{ij}(k;\ell) = \langle G_\ell^{(k)}(i)\Phi_i|\mathrm{e}^{-T(i)}\mathrm{e}^{T(j)}|\Phi_j\rangle , \tag{15}$$

and

$$H_{ij}^{(\mathrm{eff})} = \langle\Phi_i|H\,\mathrm{e}^{T(j)}|\Phi_j\rangle . \tag{16}$$

Note that Λ_i has the form of the left-hand side of the SR CC equation (right-hand side being zero) that is associated with the reference $|\Phi_i\rangle$ and Γ_{ij}'s represent the coupling coefficients.

Once the amplitudes $t_j^{(k)}(i)$ are found, we recompute the effective Hamiltonian matrix $\boldsymbol{H}^{(\mathrm{eff})} \equiv ||H_{ij}^{(\mathrm{eff})}||$ and find its eigenvalues and eigenvectors (*cf.* Eq. (*8*)).

GMS-BASED SU CC METHOD[27]

In order to preserve as much as possible the connected character of the theory when using an arbitrary GMS for $\mathcal{M}_0$, we distinguish the internal and external excitation operators $G_\ell^{(k)}(i)$. The former ones simply transform the references among themselves, while the external ones accomplish excitations to $\mathcal{M}_0^\perp$. Since $|\tilde{\Psi}_i\rangle$ involves only the reference $|\Phi_i\rangle$, Eq. (*6*), the cluster amplitudes constituting $T(i)$, Eq. (*11*), must be such that the coefficients in $|\tilde{\Psi}_i\rangle$ that are associated with references $|\Phi_j\rangle$, $j \neq i$, must vanish. Writing generally

$$|\tilde{\Psi}_i\rangle = \sum_{j=1}^{M} \tilde{c}_{ij}|\Phi_j\rangle + \sum_{|\Xi_j\rangle \in \mathcal{M}^\perp} \tilde{b}_{ij}|\Xi_j\rangle , \qquad (17)$$

we thus require that

$$\tilde{c}_{ij} = \delta_{ij} , \qquad (18)$$

so that Eq. (*6*) holds. This then implies the constraints that we refer to as the C-conditions that are imposed on the cluster amplitudes $t_j^{(k)}(i)$ that are associated with the internal excitations. In fact, the C-conditions can also be called "connectedness" conditions, since they can be shown to eliminate the disconnected terms from both the effective Hamiltonian matrix elements and coupling coefficients[27].

Thus, the amplitudes that are associated with one-body internal excitation operators $G_\ell^{(1)}(i)$, $G_\ell^{(1)}(i)|\Phi_i\rangle \in \mathcal{M}_0$, must vanish, *i.e.*

$$t_\ell^{(1)}(i) = 0 . \qquad (19)$$

However, the amplitudes associated with two-body internal excitation operators, say $G_\ell^{(2)}(i) \equiv G_{P_1P_2}^{Q_1Q_2}(i)$, are given by the C-conditions

$$t_{P_1P_2}^{Q_1Q_2}(i) = -t_{P_1}^{Q_1}(i)\,t_{P_2}^{Q_2}(i) + t_{P_1}^{Q_2}(i)\,t_{P_2}^{Q_1}(i) , \qquad (20)$$

and, similarly, for higher-order amplitudes. In general, if $G^{Q_1 \dots Q_k}_{P_1 \dots P_k}(i)$ represents an internal excitation, so that

$$G^{Q_1 \dots Q_k}_{P_1 \dots P_k}(i)|\Phi_i\rangle = |\Phi_j\rangle, \tag{21}$$

the corresponding cluster amplitude is given by

$$t^{Q_1 \dots Q_k}_{P_1 \dots P_k}(i) = -\sum_{\mathcal{P}_k} \prod_{\ell=1}^{p} \langle \Phi_j | (n_\ell\,!)^{-1} [T_\ell(i)]^{n_\ell} | \Phi_i \rangle, \tag{22}$$

where the sum extends over all nontrivial partitions $\mathcal{P}_k$ of k, *i.e.*, $k = \sum_{\ell=1}^{p} \ell \cdot n_\ell$, with $0 \le n_\ell \le k$ and $1 \le p < k$. It is then easy to rewrite the right-hand side of Eq. (*22*) in terms of the $t^\ell(i)$ amplitudes defining $T_\ell(i)$, $\ell = 1, 2, \dots, (k-1)$.

Thus, in a GMS-based SU CC formalism, the internal amplitudes are given by the C-conditions, while the external ones are again determined by the SU CC equations, Eq. (*13*). The C-conditions must be implemented in every iteration when solving the SU CC equations. It may be shown that when the C-conditions hold, the entire formalism remains connected[27]. The explicit expressions and the demonstration of the connectivity property of both the effective Hamiltonian and of the coupling coefficients will be presented elsewhere[27].

EXTERNALLY CORRECTED SU CCSD METHOD: (*N*,*M*)-CCSD

In order to extend the RMR CCSD method to the MR case, we have to determine higher-than-pair cluster amplitudes *via* the cluster analysis of the MR CISD wave functions. In view of the fact that the transformed mixed wave functions $|\tilde{\Psi}_i\rangle$, i = 1, ..., M (be they of the FCI or MR CISD kind) involve only a single reference $|\Phi_i\rangle$, Eq. (*6*), we can proceed with the cluster analysis as in the SR case once the transformation defined by $\boldsymbol{C}^{-1}$ is applied to the set of chosen states that correspond to the M model-space references[42]. In this way the desired subset of three- and four-body amplitudes may be easily determined as explained in detail in ref.[42]

Once the higher-than-pair clusters have been determined, they are used to evaluate the T_3- and T_4-dependent terms in all three components of the SU CC equations, namely in the left-hand sides $\Lambda_i(k; \ell)$, Eq. (*14*), in the coupling coefficients $\Gamma_{ij}(k; \ell)$, Eq. (*15*), and in the effective Hamiltonian $H^{(\mathrm{eff})}_{ij}$, Eq. (*16*). The role of these terms in the effective Hamiltonian was already

explored in ref.[42] and recently also in the Λ_i' and Γ_{ij}'s by relying on simple H4 and H8 models[27b]. We find that individually all three effects are of roughly the same importance. The simultaneous account of the T_3 and T_4 terms in Λ_i's and in $H^{(\mathrm{eff})}$ gives already very good results. Of course, by far the superior results are obtained when these clusters are accounted for in all three components. Needless to say that when we employ the FCI amplitudes for this purpose, we again recover the FCI result, regardless of the GMS employed. This provides not only a numerical verification of the proposed formalism, but also serves to check the correctness of our codes, similarly to the SR case[35,37].

When there is no serious intruder state problem, we can use the same reference space for both MR CISD and SU CCSD, resulting in the (M,M)-CCSD method. We also note that (0,M)-CCSD corresponds to the standard SU CCSD method, while (N,1)-CCSD is equivalent to the SR RMR CCSD approach.

CONCLUSIONS

The principal effect of the CMS truncation is the appearance of disconnected terms that arise from the products of lower-order external excitations. If these terms are simply neglected, the consistency of the SU CC equations is violated and the theory does not become exact in the limit when all the relevant clusters are accounted for.

In this paper, we provide a brief outline of a proper GMS-based SU CC formalism, while preserving the property of the intermediate normalization. The key to this formulation is the introduction of the so-called C-conditions that eliminate the undesirable disconnected terms from the effective Hamiltonian as well as from the coupling coefficients, and warrant the exact behavior in the limiting case when all the clusters are accounted for. Moreover, it can be shown[27] that with the exception of coupling coefficients, all the terms in the resulting formalism can be computed by exploiting the expressions for the standard SR CC theory.

The importance of the CMS truncation was already pointed out in the General Outline section above. It is instructive to compare our approach to this problem with the earlier ones. In the first proposal by Meissner *et al.*[25], the restriction was made to the special incomplete model spaces which, nonetheless, were general enough to include the quasi-complete model spaces proposed by Lindgren[23] in the context of VU theories. The defining requirement for such a special IMS is that all excitation operators be uniquely classified into the internal and external ones not only with re-

spect to a particular reference function, but with respect to the entire reference space[25]. This requirement implies that for all references we have (see Eq. (*1*) of ref.[26])

$$PT(i)|\Phi_i\rangle \equiv 0\,, \quad (i = 1, \ldots, M)\,. \tag{23}$$

In the subsequent paper by Meissner and Bartlett[26] this formalism was extended to a GMS by relaxing the above requirement to (see Eq. (*7*) of ref.[26])

$$P(i)\,T(i)|\Phi_i\rangle \equiv 0\,, \quad (i = 1, \ldots, M) \tag{24}$$

where

$$P(i) = 1 - Q(i)\,, \quad Q(i) = Q + \sum_j^{(i)} P_j\,, \tag{25}$$

with the sum $\sum_j^{(i)}$ extending over those $P_j \equiv |\Phi_j\rangle\langle\Phi_j|$ for which there exists at least one reference $|\Phi_\ell\rangle$, $1 \le \ell \le M$, such that $G_j(i)|\Phi_\ell\rangle \in \mathcal{M}_0^\perp$, where $G_j(i)$ represents an internal (or "transfer") operator such that $G_j(i)|\Phi_i\rangle = |\Phi_j\rangle$. Thus $P(i)$ can be rewriten as

$$P(i) = P - \sum_j^{(i)} P_j = \sum_j^{(\tilde{i})} P_j\,, \tag{26}$$

where the sum $\sum_j^{(\tilde{i})}$ extends over those P_j that were excluded above from the sum $\sum_j^{(i)}$.

In contrast to these formulations, our C-conditions can be stated as follows

$$P\,\mathrm{e}^{T(i)}|\Phi_i\rangle \equiv |\Phi_i\rangle\,, \quad (i = 1, \ldots, M) \tag{27}$$

or

$$P(\mathrm{e}^{T(i)} - 1)|\Phi_i\rangle \equiv 0\,, \quad (i = 1, \ldots, M)\,. \tag{28}$$

In this way, the intermediate normalization is preserved, since Eq. (*27*) implies that $\tilde{c}_{ij} = \delta_{ij}$, Eq. (*18*).

To illustrate the difference in conditions (*23*) or (*24*) and (*27*), consider, *e.g.*, the off-diagonal matrix element $H_{ij}^{(\mathrm{eff})}$, $(i \neq j)$, assuming that $|\Phi_i\rangle$ and $|\Phi_j\rangle$ differ in two molecular spin orbitals, so that $|\Phi_i\rangle = G_{P_1P_2}^{Q_1Q_2}|\Phi_j\rangle$, where $G_{P_1P_2}^{Q_1Q_2} = (X_{Q_1}^{\dagger} X_{P_1})(X_{Q_2}^{\dagger} X_{P_2})$. One then finds

$$\begin{aligned} H_{ij}^{(\mathrm{eff})} &= \Lambda_2(P_1P_2:Q_1Q_2;j) \\ &+ \boldsymbol{P}_{Q_1Q_2}\boldsymbol{P}_{P_1P_2} t_{P_1}^{Q_1}(j)\Lambda_1(P_2:Q_2;j) \\ &+ [t_{P_1P_2}^{Q_1Q_2}(j) + \boldsymbol{P}_{Q_1Q_2} t_{P_1}^{Q_1}(j) t_{P_2}^{Q_2}(j)] H_{jj}^{(\mathrm{eff})} . \end{aligned} \qquad (29)$$

Here $\boldsymbol{P}_{XY} = 1 - (XY)$ is the antisymmetrizer of X and Y, with (XY) designating the transposition of X and Y. Now, the last term in Eq. (*29*) vanishes when the C-conditions, Eq. (*20*), hold. However, the requirement (*23*) implies that $t_{P_1P_2}^{Q_1Q_2} = 0$, while at least one of the products, $t_{P_1}^{Q_1} t_{P_2}^{Q_2}$ or $t_{P_1}^{Q_2} t_{P_2}^{Q_1}$, may be, in general, different from zero. In fact, in a particularly adverse case, this may dramatically change the correct value of $H_{ij}^{(\mathrm{eff})}$, as will be shown elsewhere[27].

The evaluation of the effective Hamiltonian matrix elements and of the coupling coefficients is further facilitated by the introduction of the concept of local active molecular spin orbitals (MSOs). This concept enables us to treat any M-dimensional model space as a collection of $M(M-1)/2$ two-dimensional model spaces. Moreover, for all such two-dimensional model spaces that involve the same number of local active MSOs, we can employ the same algorithm and codes.

Finally, we have outlined how to extend the amplitude-corrected RMR CCSD method to the MR case, which in turn is helpful in overcoming the intruder-state problem. The detailed account of these developments will be given elsewhere[27].

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