

State-specific Coupled Cluster type dressing of Multireference Singles and Doubles Configuration Interaction matrix

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Abstract

Using the theory of state-specific self-consistent intermediate Hamiltonians one proposes a new dressing of a Multireference (MR) Singles and Doubles Configuration Interaction Hamiltonian matrix, which insures size-consistency. The method is based on a Coupled Cluster (CC) type factorization of the coefficients of the triples and quadruples and can be considered as leading to a dressed CI formulation of a state-specific MRCC method. Preliminary application of the new procedure to H_4 model and comparison with other MRCC schemes are presented.

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1 Introduction

The linear and exponential expansions of the N -electron wave function generate two distinct approaches to electron correlation problem. The Configuration Interaction (CI) method as conceptually simpler was proposed and used to go beyond the one particle approximation already in the fifties [1]. The Coupled Cluster (CC) approach was primarily introduced in nuclear physics and then proposed for quantum chemistry by Čížek [2]. Due to its exponential form of the wavefunction the method is not only highly accurate but is also extensive (i.e. scales correctly with the number of particles) when truncated at a given level of excitations [2]. The lack of the latter property is one of the major drawbacks of the CI method and makes it inadequate for description of large systems.

The description of chemical reactivity (e.g. dissociation) and of some open shell and excited states inevitably requires multiconfigurational approaches. Generalization of the CI method for multireference cases is straightforward and the multireference configuration interaction (MRCI) method has been the most popular tool in molecular spectroscopy during a long time. In the MRCI method one may in principle remove an essential part of the extensivity error (due to mixing of different categories of excitations), but it still suffers from the lack of rigorous extensivity, which is crucial when we deal with extended systems. The usual a posteriori Davidson-type corrections that take into account to some extent the unlinked contributions which should be removed [4] can only partially solve the problem and many attempts have been made to modify the method to obtain nearly extensive results (for recent review see ref. [5]).

On the other hand the coupled cluster approach is more difficult to generalize to the multireference situations than the CI method. The impressive development of Multireference Coupled Cluster (MRCC) methods has led to mature formalisms and tractable approximations [3]. An increasing number of applications to atomic [6] and molecular [6] [13] [27] systems can be encountered in the recent literature. However the computational complexity of these methods is very high and there are still many specific problems that have to be overcome (as for instance the generalization of the Fock space methods to an arbitrary open shell reference state [7]) in order to reach the 'black box' level.

One should also mention another very active and rapidly growing field, namely research on multireference perturbation theory (MRPT) [9]. Unfortunately MRPT methods become expensive already at third order, although second order results on huge CAS reference spaces are routinely available [10] and offer an interesting alternative to those of MRCC and MRCI. Nevertheless these methods are irrelevant in our present considerations.

Additional complexity that inevitably occurs in MRCC theories follows from the lack

of the unambiguously specified separation of hole and particle states. One can in general introduce a fixed vacuum state (e.g. one of the references) for all the reference functions or a reference-dependent one with independent (although conjugated) expansions with respect to each reference. As a result the genuine MRCC theories may be classified according to the above distinction, imposing different definitions of the wave operator $\hat{\Omega}$ [3]. Moreover both schemes are inherently of the multistate character. In the so-called Fock space approach (referred also as valence universal CC approach - VUCC) one has to consider a manifold of states having different number of valence electrons [8], while in the Hilbert space approach (state universal CC approach - SUCC) all states (with a constant number of valence electrons) corresponding to the different linear combinations of reference functions must be simultaneously handled [12].

In light of the above remarks the research of single state or state-specific approximations is of great practical meaning. Several such MRCC schemes have been originally proposed (see ref. [22]). They employ in general the state-specific wave operator acting on a single reference state but of the multideterminantal form.

Aforementioned procedures that rely on the underlying configuration space and try to modify MRCI method in order to obtain extensive results form another group, which may be viewed as group of approximate MRCC methods of the MRCEPA type [11] [5]. All those schemes are grounded on the cluster assumption and inherently use the CC factorization of triples and quadruples coefficients, reproducing to some extent the hierarchy of single reference CEPA methods. They are state specific as the CI method.

Here we are aiming at this goal (i.e. obtaining a general state-specific MRCC theory) starting from the recently proposed MR 'dressed' CI method (MR(SC)²CI) [14], which may be considered as an exact state-specific MRCEPA procedure. The previously formulated single reference counterpart referred to as size-consistent self-consistent CI method ((SC)²CI) [15] insures the extensivity by a proper cancellation of unlinked effects. It was shown [19] that adding the linked effects (arising from the triples and quadruples as in CCSD method) one may eventually end up with a 'dressed' CI formulation of the corresponding SRCCSD approximation. As in the single reference case we want to include the linked contributions of triples and quadruples as well, obtaining 'dressed' CI formulation of a state-specific MRCCSD type approximation.

In Sec. 2 we formally develop such an attempt, starting from the brief recall of the self-consistent, state-specific, intermediate Hamiltonians theory [16], which is then used to introduce a CC type dressing of MRCI matrix. The content of the new method is compared to other MRCC schemes and its size-consistency is demonstrated. In Sec. 3 the results of application of the prototype implementation of the newly proposed CC type dressing to

H_4 model are presented.

2 Theory

In the following we shall consider a multireference space S spanned by reference determinants I . We shall also consider the determinants i obtained by the single and double substitutions D_k^+ on the references and which do not belong to S . These determinants span a space s . The corresponding projectors are

$$\hat{P}_S = \sum_{I \in S} |I\rangle\langle I| \quad (1)$$

$$\hat{P}_s = \sum_{i \in s} |i\rangle\langle i| \quad (2)$$

The determinants i may interact with one or several reference determinants, depending on their nature and the structure of the reference space. Hereafter the model space will be chosen as the union $S \oplus s$ and the associated projector will be labeled $\hat{P}_{S \oplus s}$.

A) Self-consistent state-specific intermediate Hamiltonians

Let us recall briefly the proposition, first formulated in ref. [16], which defines a state-specific intermediate Hamiltonian built in a model space. For the state $|\Psi_m\rangle$ (ground or excited state) one can write its expansion in terms of N -electron basis $\{|I\rangle, |i\rangle, |\alpha\rangle\}_{I \in S, i \in s, \alpha \notin S \oplus s}$

$$|\Psi_m\rangle = \sum_{I \in S} C_I^m |I\rangle + \sum_{i \in s} c_i^m |i\rangle + \sum_{\alpha \notin S \oplus s} c_\alpha^m |\alpha\rangle \quad (3)$$

Now, we would like to define an intermediate effective Hamiltonian $\hat{P}_{S \oplus s}(\hat{H} + \hat{\Delta}^m)\hat{P}_{S \oplus s}$, where $\hat{\Delta}^m$ is a dressing operator, such that

$$\hat{P}_{S \oplus s}(\hat{H} + \hat{\Delta}^m)\hat{P}_{S \oplus s}|\Psi_m\rangle = E_m \hat{P}_{S \oplus s}|\Psi_m\rangle \quad (4)$$

$|\Psi_m\rangle$ and E_m being the exact eigenstate and eigenvalue

$$\hat{H}|\Psi_m\rangle = E_m|\Psi_m\rangle \quad (5)$$

As usually for effective Hamiltonians, we demand the exact energy when acting on the projection of the exact eigenvector onto the model space, but contrarily to the effective Hamiltonians built in d dimensional model space (giving d roots), the state-specific intermediate Hamiltonians are only required to give one exact root.

Consider now the exact eigenequation for the line I

$$\sum_{\substack{J \in S \\ J \neq I}} H_{IJ} C_J^m + (H_{II} - E_m) C_I^m + \sum_{i \in s} H_{Ii} c_i^m = 0 \quad (6)$$

This equation is the same for \hat{H} and for $\hat{P}_{S \oplus s} \hat{H} \hat{P}_{S \oplus s}$, so that there is no dressing to introduce in the $P_S H P_{S \oplus s}$ block of the matrix

$$\hat{P}_S \hat{\Delta}^m \hat{P}_{S \oplus s} = 0 \quad (7)$$

If one moves to the singles and doubles, the eigenequation for the line i is

$$\sum_{I \in S} H_{iI} C_I^m + \sum_{\substack{j \in s \\ j \neq i}} H_{ij} c_j^m + (H_{ii} - E_m) c_i^m + \sum_{\alpha \notin S \oplus s} H_{i\alpha} c_\alpha^m = 0 \quad (8)$$

To obtain a correct dressing one has simply to transform the last summation of the above equation into a proper matrix element of a dressing operator, included in one of the first three terms (i.e. effectively shift the last summation to the model space). One may for instance define a diagonal dressing [18]

$$\Delta_{ii}^m = \left(\sum_{\alpha \notin S \oplus s} H_{i\alpha} c_\alpha^m \right) (c_i^m)^{-1} \quad (9)$$

$$\Delta_{ii}^m = 0 \quad \text{if } i \neq j \quad (10)$$

such that $\hat{P}_{S \oplus s} (\hat{H} + \hat{\Delta}^m) \hat{P}_{S \oplus s}$ accepts $\hat{P}_{S \oplus s} |\Psi_m\rangle$ as eigenvector with the energy E_m .

Assuming that one can write the coefficients of the outer space determinants as a sum over references

$$c_\alpha^m = \sum_{J \in S} c_{\alpha J}^m \quad (11)$$

then it is possible to define a dressing of the first columns of the matrix (more precisely of the $P_{S \oplus s} H P_S$ block)

$$\Delta'_{iJ}{}^m = \left(\sum_{\alpha \notin S \oplus s} H_{i\alpha} c_{\alpha J}^m \right) (C_J^m)^{-1} \quad (12)$$

$$\Delta'_{ij}{}^m = 0 \quad (13)$$

The two dressings lead to a common eigenvector of $\hat{P}_{S \oplus s} (\hat{H} + \hat{\Delta}^m) \hat{P}_{S \oplus s}$ and $\hat{P}_{S \oplus s} (\hat{H} + \hat{\Delta}'^m) \hat{P}_{S \oplus s}$, namely $|\tilde{\Psi}_m\rangle = \hat{P}_{S \oplus s} |\Psi_m\rangle$ with the eigenvalue E_m , but all other eigenstates are different.

B) Coupled Cluster type dressing

The above proposal is purely academic if one does not have a reasonable evaluation of the coefficients c_α^m of the outer space determinants. Remember that these determinants are here triples and quadruples with respect to at least one reference $I \in S$ and singles or doubles with respect to some of the singles and doubles $i \in s$.

Our strategy to approximate the outer space coefficients is grounded on the CC assumption saying that higher many-body effects may be reasonably described in terms of two-body (and one-body) cluster amplitudes. In the following we shall assume a separate cluster expansion for every reference determinant $I \in S$, implying for the wave operator

$$\hat{\Omega}^m = \sum_I \hat{\Omega}_I^m \quad (14)$$

where $\hat{\Omega}_I^m$ has the form

$$\hat{\Omega}_I^m = e^{\hat{T}_I^m} \hat{P}_I; \quad \hat{T}_I^m = \sum_k d_I^{m,k} D_k^+ \quad (15)$$

where we restrict D_k^+ to single and double excitations with respect to $|I\rangle$ only ($\hat{T}_I^m = \hat{T}_{1,I}^m + \hat{T}_{2,I}^m$). The index m means that we shall try to define a state-specific ansatz. It means that we have for the coefficients of determinants belonging to s space (for simplicity we forget the disconnected part coming from $(\hat{T}_{1,I}^m)^2$ for doubles, which might be introduced without significant increase of complexity; for a discussion see Sec. D)

$$c_i^m = \sum_{\substack{I \\ |i\rangle = D_k^+ |I\rangle}} d_I^{m,k} C_I^m \quad (16)$$

whereas for the outer space determinants we shall assume

$$c_\alpha^m = \sum_{I \in S} \sum_{\substack{(k,l) \\ |\alpha\rangle = D_l^+ D_k^+ |I\rangle}} d_I^{m,l} d_I^{m,k} C_I^m \quad (17)$$

where the second sum runs over all possible decompositions of $|\alpha\rangle$ with respect to a given reference determinant.

Using the last eq. one is able to introduce a column dressing according to eq. (12). Thus the partitioning of the outer space coefficients with respect to references is given by

$$c_{\alpha J}^m = \sum_{\substack{(k,l) \\ |\alpha\rangle = D_l^+ D_k^+ |J\rangle}} d_J^{m,k} d_J^{m,l} C_J^m \quad (18)$$

leading to the column dressing of the form

$$\Delta'_{iJ}{}^m = \sum_{\substack{(k,l) \\ |\alpha\rangle=D_l^+D_k^+|J}} H_{i,D_k^+D_l^+J} d_J^{m,k} d_J^{m,l} \quad (19)$$

with $H_{i,D_k^+D_l^+J}$ matrix element, which may be always expressed as a proper matrix element between some reference and double (or single) substitution on it.

The crucial thing is here the definition of the state-specific cluster amplitudes $d_I^{m,k}$. In next section we shall partition the dressed MRCI coefficients c_i with respect to references to obtain pseudoamplitudes d_{iI}^m . Then, they will be labeled according to the reference and the nature of the substitution D_k^+ such that, if

$$|i\rangle = D_k^+|I\rangle \quad (20)$$

then we shall write

$$d_I^{m,k} = d_{iI}^m = d_{(D_k^+I)I}^m \quad (21)$$

It should be emphasized that a given substitution D_k^+ will receive a different amplitude depending on the reference determinants J , on which it acts.

Our procedure will be iterative: starting from undressed CI coefficients (weighted to obtain initial pseudoamplitudes) we shall dress the MRCI matrix and diagonalize it. Using the new pseudoamplitudes (defined from the new coefficients) the new dressing may be evaluated. The process is repeated until self-consistency is achieved. As a matter of fact the new procedure is a generalization of the MR(SC)²CI scheme [14] to a 'total' dressing that includes also linked effects of triples and quadruples (which are present in CCSD method) with respect to the reference determinants.

C) Reference-specific state-specific amplitudes

As can be seen from the previous subsection, we actually have in common with the state universal (or Hilbert space) approach that we employ separated cluster ansätze for references [12] (for more detailed comparison see Sec. 2D). In this approach a given determinant $i \in s$ is associated with a set of excitations with respect to its parents, by which it is obtainable, and the corresponding set of amplitudes coming from expansions for the parent references. All these amplitudes 'enter' the corresponding CI coefficient (as in eq. (16)).

Consider now the reference space of the CAS type. In such a case the most numerous inactive double excitations generate determinants having one parent only. The corresponding reference-specific amplitudes are thus uniquely defined by proper coefficients. The semi-active excitations introduce determinants which might have many parents. One may hope

that for such determinants an appropriate scheme of partitioning of their (dressed) MRCI coefficients will provide a reasonable definition of the reference-dependent amplitudes.

Let us try now to define state-specific and reference-specific pseudoamplitudes for all substitutions leading from S to s space. Let us remark that the coefficients of the eigenvector $|\tilde{\Psi}_m\rangle$ of the dressed matrix $\tilde{H} = H + \Delta'^m$ satisfy the eigenequation (we shall omit the tilde accents for the actual coefficients)

$$\sum_{I \in S} \tilde{H}_{iI} C_I^m + \sum_{\substack{j \in s \\ j \neq i}} \tilde{H}_{ij} c_j^m + (\tilde{H}_{ii} - E_m) c_i^m = 0 \quad (22)$$

In the following we shall only dress the H_{iI} columns ($\tilde{H}_{iI} \neq H_{iI}$). This suggests two possibilities. One may either

- i) consider the second sum of eq. (22) as negligible in front of the first one (since the C_I are supposed to be larger than c_i , being respectively of order zero and one if one thinks in terms of a perturbative expansion from $|\tilde{\Psi}_m^0\rangle = \sum_{I \in S} C_I^m |I\rangle$) and write

$$c_i^m \simeq \frac{\sum_{I \in S} \tilde{H}_{iI} C_I^m}{E_m - H_{ii}} \quad (23)$$

This suggests to write an amplitude

$$d_{iI}^m = \frac{\tilde{H}_{iI}}{\Delta \varepsilon_i^m} \quad (24)$$

where $\Delta \varepsilon_i^m$ is an effective energy difference. In order to obey strictly the basic eq. (22), one is led to the following definition of $\Delta \varepsilon_i^m$

$$\Delta \varepsilon_i^m = (E_m - H_{ii}) - \left(\sum_{\substack{j \in s \\ j \neq i}} H_{ij} c_j^m \right) (c_i^m)^{-1} = \sum_{J \in S} \tilde{H}_{iJ} C_J^m (c_i^m)^{-1} \quad (25)$$

- ii) or consider the full eq. (22) and write

$$c_i^m = \frac{\sum_{I \in S} \tilde{H}_{iI} C_I^m + \sum_{\substack{j \in s \\ j \neq i}} H_{ij} c_j^m}{(E_m - H_{ii})} = \frac{\sum_{I \in S} (\tilde{H}_{iI} + \sum_{\substack{j \in s \\ j \neq i}} H_{ij} d_{jI}^m) C_I^m}{(E_m - H_{ii})} \quad (26)$$

Hence the set of linear equations (assuming that one may replace \tilde{H}_{iJ} by H_{iJ})

$$d_{iI}^m = \frac{\tilde{H}_{iI} + \sum_{\substack{j \in s \\ j \neq i}} H_{ij} d_{jI}^m}{E_m - H_{ii}} \quad (27)$$

Although the second definition avoids the denominators of eq. (24), which may be problematic when some ratios c_j^m/c_i^m (see eq. (25)) become large, it is less practical, since it introduces M -body dressing operator (d_{iI} will not disappear even if $H_{iI} = 0$). Regarding the first possibility, for practical proposals one may be tempted to replace \tilde{H}_{iJ} in the definition of eqs. (24) and (25) by H_{iJ} . So that we shall assume that reference-specific amplitudes are given by

$$d_{iI}^m = \frac{H_{iI}c_i^m}{\sum_{J \in S} H_{iJ}C_J^m} \quad (28)$$

The above definition corresponds to the weighting of MRCI coefficients proposed for MRCEPA type dressing (see ref. [14]). If one postulates that pseudoamplitudes d_{iI} 's come from a normalized, reference dependent partitioning of c_i coefficient

$$c_i^m = \sum_I \varrho_{iIm} c_i^m; \quad \sum_I \varrho_{iIm} = 1 \quad (29)$$

and on the other hand $c_i^m = \sum_I d_{iI}^m C_I^m$ and the definition of eq. (28) is employed, one is led to

$$\varrho_{iIm} = \frac{H_{iI}C_I^m}{\sum_{J \in S} H_{iJ}C_J^m} \quad (30)$$

which is the natural partitioning suggested by eq. (22), proposed already in ref. [14]. However, as mentioned before, the resulting d_{iI} 's may become undesirably large (or even infinite) when the quantity $\sum_{J \in S} H_{iJ}C_J^m$ becomes small (or even zero) due to interferences of contributions with different signs.

In MR(SC)²CI (see ref. [20]) procedure the amplitudes are traced and when some of them become large, the underlying determinants are removed from the MRCI space. As the numerical tests show, such a selection concerns only very small part (usually much less than 1%) of all determinants, and insuring nice convergence, does not influence practically the final results, which are very encouraging [20]. Therefore we decided to keep this definition as a basic one, although several other definitions may be also proposed. One might use the equal weights approximation for instance, for the rare determinants governed by the second sum of eq. (22).

Another possibility, which scales the quantities d_{iI} not only on the strength of the interaction H_{iI} but also on the energy gap between H_{ii} and H_{II} , is to start from amplitudes optimized variationally in 2 dimensional CI between $|I\rangle$ and $|i\rangle$ and then normalize them, in order to satisfy eq. (16)

$$d_{iI}^m = d_{iI}^{1,m} c_i^m / C_I^m; \quad d_{iI}^{1,m} = \frac{|d_{iI}^{0,m}|}{\sum_J |d_{iJ}^{0,m}|}; \quad d_{iI}^{0,m} = \frac{c_i^0}{C_I^0} \quad (31)$$

where C_I^0, c_i^0 are variationally optimized coefficients. The primitive amplitudes $d_{iI}^{0,m}$ depend on both H_{iI} and $H_{ii} - H_{II}$ (with the latter one in the numerator), remain (in absolute values) smaller than one, provided that we always take the root with C_I^0 larger than c_i^0 and never diverge (if one refers to Quasi Degenerate Perturbation Theory [16] the wave operator $\Omega_I^{(1)}$ at first order defines $d_{iI} = H_{iI}/(H_{II} - H_{ii})$, which diverges when $H_{II} = H_{ii}$). The c_i/C_I ratios, might introduce problems when $c_i \gg C_I$. In such a case however, if a shift of the resulting large amplitudes on parent K , such that $C_K \simeq c_i$, is not possible, i might be treated as having no parents. With this special status i would be dressed according to (SC)²CI scheme, with respect to a reference determinant K chosen such that $C_K > c_i$, i being triple or quadruple from K .

D) Comparison with MRCC formalisms

The so-dressed MRCISD matrix may be considered as furnishing an eigenvalue (pseudoeigenvalue, due to the dependence on the coefficients) formulation of a state-specific Multireference Coupled Cluster Singles and Doubles (MRCCSD) method. To remain closer to the rigorous CC approaches one may distinguish the amplitudes of the single substitutions

$$a_I^{m,k} = d_I^{m,k} \quad (32)$$

if D_k^+ is a single substitution with respect to I ($\hat{T}_{1,I}^m = \sum_k a_I^{m,k} D_k^+$) and introduce the proper amplitudes of the double substitutions D_l^+

$$b_I^{m,l} = d_I^{m,l} - \sum_{\substack{(l_1,l_2) \\ D_l^+ = D_{l_1}^+ D_{l_2}^+}} a_I^{m,l_1} a_I^{m,l_2} \quad (33)$$

Eq. (19) only takes into account $\hat{T}_1 \hat{T}_2$ and \hat{T}_2^2 . In order to strictly obey the assumed exponential form of $\hat{\Omega}$ one should also introduce the amplitudes of the triples coming from the third power of single substitutions (\hat{T}_1^3) and the amplitudes of quadruples coming from $\hat{T}_1^2 \hat{T}_2$ and \hat{T}_1^4 . However, one may notice that this rigorous formulation differs from the simplest one only by effects of orders higher than two on the wave function and higher than four on the energy. In fact the restriction of \hat{T} to \hat{T}_1 and \hat{T}_2 is an approximation which omits some important 4th order corrections on the energy (i.e. the linked contributions of the triples) and the exact treatment of 5th (resp. 6th) order corrections coming from $\hat{T}_1^2 \hat{T}_2$ and \hat{T}_1^3 (resp. \hat{T}_1^4) is not compulsory in view of this lower order error, except if some \hat{T}_1 terms have very large amplitudes.

Our state-specific formulation differs deeply from the dominant trends in the MRCC research. Most of them (as mentioned in the introduction) belong to two families which

assume a very universal structure of the wave operator. The first one (VUCC or Fock space CC) exploits the Valence Universal wave operator [17] and is less important in our considerations. The second family (SUCC or Hilbert space CC) is based on the reference dependent choice of the vacuum. The wave operator is just defined as a sum of independent wave operators defined with respect to reference determinants

$$\hat{\Omega} = \sum_K^d e^{\hat{T}_K} \hat{P}_K \quad (34)$$

Such an ansatz was originally proposed by Jeziorski and Monkhorst [12]. Its basic feature is that we have as many independent amplitudes as the number of references times the number of amplitudes in the single reference case. As a result we have to consider the manifold of all d states simultaneously to build enough equations. The so-obtained amplitudes are reference-dependent but they are state universal i.e. they are solutions of the whole system of equations (for all roots in the model space).

Our philosophy is a very modest one, since we define a state-specific expansion for the wave operator $\hat{\Omega}$. The ansatz we exploit here has a form similar to that of SUCC approach

$$\hat{\Omega}^m = \sum_{I \in S} e^{\hat{T}_I^m} \hat{P}_I \quad (35)$$

where the summation over I is restricted to S space only (and does not concern the whole model space $S \oplus s$) and \hat{T}_I^m denote state-specific operators with reference-dependent pseudoamplitudes obtained by a proper partitioning (different for different states) of dressed CI coefficients with respect to reference determinants.

In the theory of traditional effective Hamiltonians the effect of outer space determinants is first included in the effective Hamiltonian (via the wave operator), which is then diagonalized in the model space to provide d exact roots. Here, we not only restrict (as usually for the intermediate effective Hamiltonians) the manifold of states to be reproduced to the main model space. Another basic difference follows from the fact that the wave operator of eq. (35) is not built explicitly. However the self-consistent dressing of MRCISD matrix, as defined in Sec. 2B, is equivalent to the traditional scheme

$$\hat{H}_{eff} \hat{P}_S |\Psi_m\rangle = \hat{P}_S \hat{H} \hat{\Omega}^m \hat{P}_S |\Psi_m\rangle = E_m \hat{P}_S |\Psi_m\rangle \quad (36)$$

$$\hat{P}_{S \oplus s} (\hat{H} + \hat{\Delta}^m) \hat{P}_{S \oplus s} |\Psi_m\rangle = E_m \hat{P}_{S \oplus s} |\Psi_m\rangle \quad (37)$$

From the practical point of view it means that instead of a set of non-linear equations we may use the CI machinery for the pseudoeigenvalue problem, which is hoped to be much less troublesome. On the other hand, as the model space is now formally much larger,

one has to take care of redundancy effects coming from $\hat{T}_1\hat{T}_2, \hat{T}_2^2 \dots$, since for instance some quadruples with respect to one of the references may still belong to the s space, being doubles from other references. This may complicate the algorithm, especially for incomplete reference spaces.

Several other state-specific MRCC schemes have been originally proposed (see ref. [22]). In the very beginning of the MRCC story Sinanoglu and Silverstone [23] proposed a state-specific expansion, but it was rapidly recognized that their formulation introduced an exceedingly large number of amplitudes which could not be defined. Linearized version of MRCC Hilbert space method (LMRCC) with prediagonalization, proposed by Laidig and Bartlett in the early 80's [21], in which the manifold of states is decoupled, also belongs to this category. Recently Piecuch and Adamowicz [22] have formulated another practical proposal referred to as State Selective (SS) CC method, which employs the single reference formalism with a state-specific selection of higher rank excitations introduced by model space determinants. Li and Paldus [22] have proposed another, spin-adapted SSCC method using unitary group approach. Our scheme is truly multireference (the amplitudes are reference dependent and there is no determinant playing distinguished role) and it does not need prediagonalization (what may be important [24]).

E) Size-consistency

Starting from the the MRCISD coefficients, which are not size-extensive, one repeats the dressing procedure until self-consistency is achieved. We shall demonstrate that the method is size-consistent (by size-consistency we mean that the supermolecule energy is a sum of subsystem energies obtained with the same method i.e. the correct separation of the energy when a separable model space is used) i.e. at convergence the desired eigenstate of the dressed MRCISD matrix furnishes size-consistent energy. The proof consists in showing that the method satisfies the separability condition for a supersystem $A \cdots B$ composed of two non-interacting systems A and B .

The MO's are supposed to be localized on subsystems A and B . Let us label I_A and J_B the reference determinants for the independent description of A and B , S_A and S_B the corresponding reference spaces. A separable reference space for the supersystem is a space built of *all* determinants $I_A J_B$

$$S_{AB} = S_A \otimes S_B \quad (38)$$

The SD space s_{AB} may be then written as a direct sum

$$s_{AB} = (s_A \otimes S_B) \oplus (S_A \otimes s_B) \quad (39)$$

i.e. it is composed of determinants of the forms $i_A J_B$ and $I_A j_B$, where $i_A \in s_A$, $j_B \in s_B$. Notice that the determinants $i_A j_B$ do not appear in the SD space for the supersystem. Although $i_A j_B$ determinants, where i_A and j_B are single substitutions on subsystems are formally doubles, but they do not interact with any reference $I_A J_B$ for the supersystem $A \cdots B$). In case of logical selection they would anyway appear. Then the full exponentialization of outer space coefficients with $\hat{T}_{1,I}^m$ taken into account is necessary to restore size-consistency. In the following we shall assume that the reference space is separable and eq. (39) holds.

Consider now two eigenstates Ψ_p^A and Ψ_q^B of the dressed subsystems corresponding to the p th and q th roots, with E_p^A and E_q^B respectively, and let us form their product Ψ_m^{AB} (projected onto the supersystem model space $M_{AB} = S_{AB} \oplus s_{AB}$)

$$\Psi_m^{AB} = P_{M_{AB}} \Psi_p^A \Psi_q^B \quad (40)$$

We shall prove that this function, with coefficients satisfying (in the future we shall omit the upper indices for subsystems)

$$C_{I_A J_B, m}^{AB} = C_{I_A, p}^A C_{J_B, q}^B; \quad c_{i_A J_B, m}^{AB} = c_{i_A, p}^A C_{J_B, q}^B; \quad c_{I_A j_B, m}^{AB} = C_{I_A, p}^A c_{j_B, q}^B \quad (41)$$

is an eigenfunction of the dressed supersystem MRCISD matrix with an additively separable energy

$$E_m^{AB} = E_p^A + E_q^B \quad (42)$$

Hence, we shall prove that Ψ_m^{AB} corresponds to a certain (size-consistent) root m (with E_m^{AB}) of the supersystem eigenvalue problem.

The demonstration might follow the proof of separability of MR(SC)²CI method [14], in which the dressing operator is factorized into non-interacting subsystems contributions. It is possible however to prove a more general statement which may be applied to both methods (and other similar procedures) in order to show their size-consistency.

Definition 2.1 *We shall say that an intermediate effective Hamiltonian $\hat{H} + \hat{\Delta}^m$ is **separable**, if it accepts the function Ψ_m^{AB} as an eigenfunction with an additive eigenvalue $E_m^{AB} = E_p^A + E_q^B$.*

Let now the indices ρ , τ refer to localized determinants belonging to S , s or outer spaces.

Definition 2.2 *The outer space coefficients are **factorizable** if for each supersystem determinant $\alpha_{AB} = \rho_A \tau_B$*

$$c_{\alpha_{AB}}^m = c_{\rho_A}^p c_{\tau_B}^q$$

Statement 2.1 *If the outer space coefficients are factorizable the $\hat{H} + \hat{\Delta}^m$ is separable.*

Proof Let, according to our assumptions, the coefficients of determinants belonging to the model space M_{AB} be factorized as specified in eq. (41) and those of the outer space determinants be factorizable according to def. (2.2). $\hat{H} + \hat{\Delta}^m$ is diagonalized in the model space, so that we have to consider eqs. for two types of determinants, namely $I_A J_B$ and $i_A J_B$. For the latter one we have (for simplicity of notation we shall write the diagonal matrix elements with a unique index between square brackets - e.g. $h_{[I]} \equiv h_{II}$)

$$\begin{aligned} (H_{[i_A J_B]} - E_m^{AB}) c_{i_A J_B, m}^{AB} + \sum_{I_A K_B} H_{i_A J_B, I_A K_B} C_{I_A K_B, m}^{AB} + \sum_{\alpha} H_{i_A J_B, \alpha} c_{\alpha, m}^{AB} + \\ + \sum_{K_B \neq J_B} H_{J_B K_B} C_{i_A K_B, m}^{AB} + \sum_{j_A \neq i_A} H_{i_A j_A} c_{j_A J_B, m}^{AB} = 0 \end{aligned} \quad (43)$$

where α may represent two types of outer space determinants, namely those which are triples or quadruples on A (resp. B) i.e. of the type $\alpha_A J_B$ (resp. $I_A \alpha_B$) and those which are singles or doubles on both A and B , i.e. of the type $i_A j_B$. Eq. (43) is satisfied for $E_m^{AB} = E_p^A + E_q^B$ when the assumed factorization of the inner and outer space coefficients holds

$$\begin{aligned} [(H_{[i_A]} - E_p^A) c_{i_A}^p + \sum_{I_A} H_{i_A I_A} C_{I_A}^p + \sum_{\alpha_A} H_{i_A \alpha_A} c_{\alpha_A}^p + \sum_{j_A \neq i_A} H_{i_A j_A} c_{j_A}^p] C_{J_B}^q + \\ [(H_{[J_B]} - E_q^B) C_{J_B}^q + \sum_{K_B \neq J_B} H_{J_B K_B} C_{K_B}^q + \sum_{k_B} H_{J_B k_B} c_{k_B}^q] c_{i_A}^p = 0 \end{aligned} \quad (44)$$

since the quantities in the large square brackets $[]$ are zero (the eigenequations for i_A and J_B respectively, in the dressed separated subsystems). For the lines corresponding to the reference functions $I_A J_B$ analogous derivation is straightforward. \square

So that, as long as we approximate the c_{α} 's in a separable manner, the method is size-consistent and statement (2.1) provides a universal tool, which enables to check size-consistency of dressing procedures. We shall prove now that our definition of outer space determinants coefficients used for CC type dressing has the desirable property. The proof goes through the following steps

i) notice that

$$d_{i_A J_B, I_A J_B}^m = d_{i_A I_A}^p \quad (45)$$

This is a direct consequence of the definition of the amplitudes (28) and of the fact that $i_A J_B$ only interacts with references of the type $K_A J_B$

$$d_{i_A J_B, I_A J_B}^m = \frac{H_{i_A I_A} \cdot c_{i_A}^p C_{J_B}^q}{\sum_{K_A} H_{i_A K_A} \cdot C_{K_A}^p C_{J_B}^q} \quad (46)$$

It is easy to show that amplitudes resulting from variationally optimized primitives (see eq. (31)) satisfy eq. (45) as well.

ii) as pointed out previously there are two types of outer space determinants, namely $\alpha_A J_B$ (resp. $I_A \alpha_B$) and $i_A j_B$. Using the definition of the c_α 's (eq. (17)) and eqs (45), (16) one may show for both types the desired factorization

$$c_\alpha^m = \sum_{I_A K_B} \sum_{\substack{(k,l) \\ |\alpha\rangle = D_k^+ D_l^+ |I_A K_B\rangle}} d_{(D_k^+ I_A J_B) I_A K_B}^m d_{(D_l^+ I_A J_B) I_A K_B}^m C_{I_A K_B}^m =$$

for $\alpha_A J_B$

$$\begin{aligned} &= \sum_{I_A} \sum_{\substack{(k,l) \\ |\alpha_A J_B\rangle = D_{k_A}^+ D_{l_A}^+ |I_A J_B\rangle}} d_{(D_{k_A}^+ I_A J_B) I_A J_B}^m d_{(D_{l_A}^+ I_A J_B) I_A J_B}^m C_{I_A J_B}^m = \\ &\sum_{I_A} \sum_{\substack{(k,l) \\ |\alpha_A\rangle = D_{k_A}^+ D_{l_A}^+ |I_A\rangle}} d_{(D_{k_A}^+ I_A) I_A}^p d_{(D_{l_A}^+ I_A) I_A}^p C_{I_A}^p C_{J_B}^q = c_{\alpha_A}^p C_{J_B}^q \end{aligned} \quad (47)$$

and for $i_A j_B$

$$\begin{aligned} &= \sum_{I_A K_B} \sum_{\substack{(k,l) \\ |i_A j_B\rangle = D_{k_A}^+ D_{l_B}^+ |I_A K_B\rangle}} d_{(D_{k_A}^+ I_A K_B) I_A K_B}^m d_{(D_{l_B}^+ I_A K_B) I_A K_B}^m C_{I_A K_B}^m = \\ &\sum_{I_A} d_{i_A I_A}^p C_{I_A}^p \sum_{K_B} d_{j_B K_B}^q C_{K_B}^q = c_{i_A}^p c_{j_B}^q \end{aligned} \quad (48)$$

So that, the dressing is separable and our trial function (eq. (40)) is an eigenfunction of the dressed supersystem hamiltonian with the eigenvalue $E_m^{AB} = E_p^A + E_q^B$.

3 Numerical example

The H_4 model has been extensively used in studies on single and multireference coupled cluster methods [25]. Already in the minimal basis set it represents an example of non-trivial system owing to near degeneracies occurring in various geometrical arrangements. Here we use the rectangular arrangement called in ref. [25] P4, consisting of two parallel H_2 molecules with a fixed bond length, stretched to 2 bohr. The distance R between the two molecules is varied in this model, changing the degree of quasidegeneracy [25].

Using the minimal basis set and the (2,2) CAS corresponding to two active electrons in the *homo*, *lumo* active orbitals makes the dressing irrelevant. There is nothing left out of CASCISD space. Therefore we decided to modify the model slightly, adding four

additional $1s$ atomic orbitals: two bond centered and two located between H_2 molecules, forming a rectangular shape with $1s$ orbitals in the middle of every side. Such a system has the same properties as the original one - at square geometry the exact degeneracy occurs. The same modifications were used in ref. [14] to illustrate the efficiency of the MR(SC)²CI method. So that we can compare the present results of CC type dressing with those of the MRCEPA type.

Certainly, comparing to the original model of ref. [25], the precise values of energies are slightly different. It makes the direct comparison impossible but in this case we are rather interested in the qualitative observations as the percentage of the correlation energy reproduced and the general behavior (stability) of the method near degeneracy and in other regions. As in ref. [14] we consider only distances R larger than 2 and we start from HF triplet MOs. Then MRCI calculations with determinants $(\psi_1)^2(\psi_2)^2$ and $(\psi_1)^2(\psi_3)^2$ (ψ_i , $i = 1, \dots, 8$ corresponds to the increasing orbital energy) as references are performed.

The results are given in Table 1. The MRCI results are already quite good in this case and the dressings do not contribute too much. As one can see the MRCC method adds from 0.07 mH (at 2.001 and 10.0) to 0.17 (at $R = 5.0$) to the corresponding MRCI energy and finally gives almost constant (99.64-99.98 %) part of the correlation energy independently on the degree of quasidegeneracy. This is an important message. The MRCC results remain between MRCI and FCI ones in the whole region: for strong and weak quasidegeneracy as well. Near square geometry the MRCC correction is about 1/5 of the difference between MRCI and FCI, whereas for large geometries it reaches 4/5. However, the difference between MRCC and MR(SC)²CI is biggest in the intermediate region (it is equal to 0.96 mH at $R = 5.0$) where the total contribution of MRCC method (with respect to MRCI) is biggest as well.

At infinite separation (with both references localized on one H_2) both dressings give just the sum of single H_2 FCI energies (including the presence of bond centered orbitals), confirming separability (notice that CISD is equivalent to FCI for this 2-electron system). Two or three dressing iterations were sufficient to insure the convergence in all cases without any screening of large amplitudes (the definition of eq. (28) for d_{iI} 's were employed).

The VUCC (valence universal coupled cluster) or SUCC (state universal coupled cluster) results on the original P4 model have been recently reported [26] [27]. The exact values of correlation energies for the original P4 model are very similar to those presented here (the difference is not larger than 3.5 mH at all geometries). Anyway one observes qualitative differences in behavior of VUCC and SUCC results, comparing to our procedure. The valence universal method gives 106.9, 107.9, 97.4, 64.8 and 50.3 (VU-CCSD/A of ref. [26]) percent of the correlation energy respectively at $R = 2.002, 2.1, 3.0, 5.0, 10.0$. In the

case of SUCC (MRCCSD-3 of ref. [27]) one obtains 100.5, 100.0, 100.9, 107.0 and 109.9 percent of the correlation energy at the same geometries. As discussed in ref. [27] the linear MRCC theory (L-MRCCSD) has singularities at two geometries.

As one can see, using a two determinantal reference space one is not able to describe properly various degrees of quasidegeneracy (it concerns especially large geometries where the second and third determinants become relatively close) in both cases (i.e. using VUCC or SUCC). Our approximated scheme does not face similar difficulties. As one can be seen from Table 1 there is no problem with stability of our multireference method in the whole region: for strong and weak quasidegeneracy as well. The error with respect to FCI results never exceeds 0.4 mH.

4 Conclusion

The present work proposes a partition of the coefficients of the Singles and Doubles from a multireference space, as obtained from a MRCISD wave function. This partition makes possible the definition of state-specific reference-dependent amplitudes for the single and double excitations. The MRCISD wave function is then written as

$$|\Psi_m\rangle = \sum_{I \in S} (1 + \hat{T}_I^m) |I\rangle \langle I | \Psi_m^0 \rangle \quad (49)$$

where S stands for the reference space, compatible with a partition of the state-specific operator $\hat{\Omega}^m$ into a sum of reference-specific state-specific operators

$$\hat{\Omega}^m = \sum_{I \in S} \hat{\Omega}_I^m \quad (50)$$

Then it is possible to assume an exponential form to each of the $\hat{\Omega}_I^m$'s

$$\hat{\Omega}_I^m = e^{\hat{T}_I^m \hat{P}_I} \quad (51)$$

and one obtains directly a coupled cluster expansion of the multireference wave function. The so-obtained leading contributions to the coefficients of the Triples and Quadruples (i.e. of \hat{T}^2 type) are used to dress the CISD matrix according to the state-specific intermediate Hamiltonians formalism, in the iterative self-consistent manner. Our proposal may be viewed as a dressed CISD formulation of the CCSD method for the multireference case, as previously proposed for the single reference [19]. One may also consider that this procedure decouples the Jeziorski-Monkhorst multistate ansatz [12] into a state-specific decontracted expansion. The results of a pilot application on the H_4 problem, which

happens to be difficult for VU and SU MRCC approaches, are very encouraging, although work is certainly desirable to refine the definition of the reference dependent state-specific amplitudes within the here proposed general frame.

This work was inspired by a previous formulation of the MRCEPA problem [14]. The weighted genealogy of this reference is logically connected to the here exploited partition of the coefficients of single and double excitations with respect to their parent references. A further work will clarify this point and will propose an alternative formulation of the state-specific MRCEPA method.

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SS-CCdCI and MR(SC)²CI results for H_4 .

Modified P4 model (minimal basis set with additional $1s$ atomic orbitals located between H atoms). Two determinantal reference space. Energy differences in millihartrees, with respect to the SCF energy given in the first column - all signs reversed (except SCF energies).

$R[au]$	SCF[H]	MRCI	MR(SC) ² CI	SSCCdCI ($\%E_{corr}$)	FCI
2.001	-1.947095	115.754	115.806	115.826 (99.70)	116.178
2.01	-1.947978	113.230	113.282	113.302 (99.70)	113.655
2.1	-1.955194	95.153	95.208	95.233 (99.64)	95.574
2.5	-1.961392	73.125	73.184	73.233 (99.68)	73.467
3.0	-1.937631	66.150	66.215	66.292 (99.78)	66.438
4.0	-1.866259	60.346	60.418	60.510 (99.87)	60.586
5.0	-1.806237	57.896	57.973	58.073 (99.94)	58.107
6.0	-1.765281	56.706	56.778	56.866 (99.97)	56.885
10.0	-1.708607	55.254	55.286	55.327 (99.98)	55.339

At $R = 2.001$ the coefficients of references are respectively $C_0 = 0.692$ and $C_{22}^{33} = -0.688$.