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Multireference self-consistent size-consistent singles and doubles configuration interaction for ground and excited states

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One proposes a state-specific self-consistent dressing of the configuration interaction (CI) matrix built on a multireference space and all the singly and doubly substituted determinants. The dressing insures size consistency [and separability when localized molecular orbitals (MOs) are used]. In the here-proposed solution, which generalizes a previous single reference method [(SC)²CI, *J. Chem. Phys.* **99**, 1240 (1993)] valid only for the research of the ground state, all the reference determinants play an *equal* role and the method is applicable to *excited* states. The implementation will be simpler if the reference space is a complete active space, but this restriction is not compulsory.

I. INTRODUCTION

There exist three main types of methods to treat the electronic many-body problem, namely perturbation theory, coupled cluster expansions, and variational configuration interactions. For the ground state the former provides the main information about the logical structure of the problem through the linked cluster theorem,¹ but in practice it is weakly convergent and of poor accuracy at low orders. The second method² is theoretically grounded and efficient. The third one gives upper bounds to the energy, but it is only practicable in general when one proceeds to a truncation in the vectorial space of Slater determinants and then it is size-inconsistent. We have recently found a procedure to insure the size consistency of any truncated configuration interaction (CI),³ and illustrated its practical efficiency through a series of tests.^{3,4} The method, named self-consistent size-consistent CI [(SC)²CI], proceeds through a self-consistent dressing of the diagonal elements of the CI matrix and may be viewed as an exact and flexible coupled electron pair approximation (CEPA),⁵ of which the version CEPA-O is identical to the linear coupled cluster. It insures the separability of the energy of an (*A*···*B*) supersystem into the energy of two closed shell fragments

$$E_{A+B} \rightarrow E_A + E_B \quad \text{when } R_{AB} \rightarrow \infty$$

provided that localized molecular orbitals (MOs) are used. The method may be applied in particular to a CI built from a multireference space and all the determinants resulting from single and double substitutions (MRDCI) but (i) it is only valid for the ground state eigenvector and energy and (ii) one determinant of the reference space [usually the Hartree-Fock (HF) determinant] plays a special role.

When one breaks a (multiple) bond, a near degeneracy occurs between the ground state determinant and one (or several) doubly (or multiply) excited determinants. For excited states with $S_2=0$, several determinants play an equal

role and one has to move to multireference (MR) procedures. Perturbation theory must be considered in its (quasi) degenerate version. Actually a generalized linked cluster theorem⁶ has been demonstrated when the model space is a complete active space (CAS), but then perturbation theory will diverge, due to intruder state problems⁷ and becomes useless. Multireference coupled cluster formalisms have been found recently⁸ but they are very complex, computationally expensive, and less efficient for excited states than for the ground state. CI techniques are of course applicable without restrictions but their lack of size-consistency cannot be repaired by the generalized Davidson's correction.⁹ This correction does not behave properly for the single-reference problem when the number of particles increases and its generalization to multireference situations is not firmly grounded. So that it would be very helpful to find a size-consistent dressing for excited and/or real multireference problems, as it was done for the ground state. This is the purpose of the present paper, which will proceed along the same method by insuring the cancellation of unlinked contributions through an appropriate dressing (i.e., change) of the Hamiltonian matrix elements.

The method will use twice the concept of intermediate Hamiltonian proposed by us some years ago in a perturbative approach.¹⁰ Here, as in a recent series of papers,^{3,4} the intermediate Hamiltonians are used in a self-consistent formulation. The intermediate Hamiltonians are effective Hamiltonians built in an *N*-dimensional model space, but which only provide *n* (<*N*) relevant roots. In this work we shall consider the search of a single root, which is not necessarily the lowest one, and the resulting intermediate Hamiltonian is state-specific. The process must be repeated to obtain another state.

The derivation of the fundamental equation will proceed as follows. We shall first recall the principle of the self-consistent size-consistent dressing for the single reference case which assumes the effect of the triples and quadruples

on the singles and doubles to be the same as the effect of the singles and doubles on the reference configuration, except for exclusion effects, which are determinant specific. Then one analyzes the effect of the singly and doubly substituted determinants for the multireference problem, showing that their effect may be seen as specific diagonal energy dressing for each reference determinant. Then for each determinant interacting with the reference space, one establishes a genealogic weight on each reference determinant. Finally the dressing of the diagonal energies of these determinants is obtained as a weighted combination of the dressings of the reference determinants, avoiding all exclusion effects and possible redundancy.

II. FORMALISM

A. Brief recall of the single-reference (SC)²CI

For the ground state and the single-reference (ϕ_0) problem, if the wave function is written in the basis of determinants as

$$\psi = C_0 \phi_0 + \sum_i C_i \phi_i \quad (1)$$

the correlation energy may be written

$$E_c = \left(\sum_i C_i \langle \phi_0 | H | \phi_i \rangle \right) C_0^{-1} \quad (2)$$

The determinants which contribute to this summation are only singles and doubles with respect to ϕ_0 . Then it was shown that whatever the CI space S (of projector P_S) the cancellation of all unlinked contributions is insured when the diagonal matrix elements of the CI matrix are shifted by a quantity

$$\Delta_{ii} = \langle \phi_i | \Delta | \phi_i \rangle = \left(\sum_j \langle \phi_0 | H | \phi_j \rangle C_j \right) C_0^{-1}, \quad (3)$$

$$D_j^+ \phi_i \neq 0, \notin S$$

where D_k^+ is a single or double excitation operator. This means that one defines a diagonal dressing operator Δ ,

$$\Delta_{ij} = 0 \text{ for } i \neq j$$

and that the diagonalization of the dressed CI matrix

$$P_S (H + \Delta) P_S \psi = \epsilon \psi \quad (4)$$

furnishes a size-consistent solution, provided that the dressing of Eq. (3) is self-consistent. It is clear that in this process one determinant, ϕ_0 , plays a special role. Even if the so-proposed (SC)²CI happens to give perfectly reliable results for bond breaking when the selected space is a CAS-SDCI space,^{3,4} we would like to leave this single-reference constraint.

Notice that one may write the dressing matrix elements in an alternative manner

$$\Delta_{ii} = E_c + \text{EPV}(i) + R(i), \quad (5)$$

where E_c is the correlation energy [Eq. (2)],

$$\text{EPV}(i) = - \left(\sum_{j, D_j^+ \phi_i = 0} C_j \langle \phi_0 | H | \phi_j \rangle \right) C_0^{-1} \quad (5\text{bis})$$

takes care of the exclusion-principle effects (EPV diagrams) and

$$R(i) = - \left(\sum_{j, D_j^+ \phi_i \in S} C_j \langle \phi_0 | H | \phi_j \rangle \right) C_0^{-1} \quad (5\text{ter})$$

takes care of possible redundancy effects when the CI space contains more than singles and doubles. The basic idea is that in the single-reference case the main information reduces to one number (the correlation energy), reflecting the effect of the singles and doubles on ϕ_0 , and the dressing consists in assuming that the effect of the triples and quadruples gives the same energy shift on the singles and doubles (except for exclusion effects) as the singles and doubles produce on the effective energy of ϕ_0 . This dressing insures a rigorous size extensivity, i.e., the cancellation of all unlinked contributions to the energy, and thus the strict separability for $A \cdots B$ problem splitting into noninteracting closed shell subsystems when localized MOs are used.

B. Formulation of the effect of a MR-SDCI

Here we shall transpose that strategy to a multireference case. The reference space S defines a projector P_S and the reference determinants will be labeled ϕ_I, ϕ_J, \dots ,

$$P_S = \sum_{I \in S} |\phi_I\rangle \langle \phi_I| \quad (6)$$

The other determinants of the MRSDCI will be labeled ϕ_i, ϕ_j and define a space s of projector P_s ,

$$P_s = \sum_{i \in s} |\phi_i\rangle \langle \phi_i| \quad (7)$$

Now the role of ϕ_0 is played by the space S . While the effect of the interaction of ϕ_0 with the singles and doubles was only an energy shift, the interaction of the determinant of the space S with those of the space s is more complex. The relevant eigenvector of the CI matrix truncated to the S space,

$$P_S H P_S |\psi'_m\rangle = E'_m |\psi'_m\rangle \quad (8)$$

may be written

$$|\psi'_m\rangle = \sum_{I \in S} C'_{Im} \phi_I \quad (9)$$

Consider now the corresponding eigenvector ψ_m of the MR-SDCI

$$(P_S + P_s) H (P_S + P_s) \psi_m = E_m \psi_m \quad (10)$$

and if we project ψ_m into the reference space S , and normalize this projection

$$\mathcal{N}P_S\psi_m = \sum_{I \in S} C_{Im}\phi_I, \quad (11)$$

\mathcal{N} being a normalization factor,

$$\|\mathcal{N}P_S\psi_m\| = 1,$$

then $C_{Im} \neq C'_{Im}$, which means that $P_S\psi_m$ and ψ'_m are not collinear. The effect of the interaction between S and s is not only the energy shift from E'_m to E_m , it also concerns the change of the components of the eigenvector on the reference space. If N_S is the dimension of the reference space, the information for a single root consists in N_S numbers (one energy and N_S-1 ratios between the components, the last one being arbitrary or defined by normalization). It has been shown elsewhere^{3,12} that the most compact and simplest procedure to introduce this information consists in the definition of a diagonal energy shift on the reference space determinants. If we define for each determinant ϕ_I a quantity

$$h_{II}^m = \left(\sum_{i \in s} C_{im} \langle \phi_I | H | \phi_i \rangle \right) C_{Im}^{-1} \quad (12)$$

and consider the diagonal operator h ($h_{IJ}=0$ for $I \neq J$), then the diagonalization of $P_S(H+h)P_S$ provides a root of correct energy and an eigenstate having the correct components on the reference space (i.e., those resulting of the diagonalization of the MRSDCI matrix),

$$P_S(H+h)P_S\psi_m = E_m P_S\psi_m. \quad (13)$$

This is evident from the comparison of the eigenequations for the line ϕ_I in both problems. Noting for instance $\langle \phi_k | H | \phi_L \rangle = H_{kL}$, one has

$$P_S(H+h)P_S \rightarrow \left[H_{II} + \left(\sum_{i \in s} C_{im} H_{Ii} \right) C_{Im}^{-1} - E_m \right] C_{Im} + \sum_{J \neq I \in S} H_{IJ} C_{Jm} = 0, \quad (14)$$

$$(P_S + P_s)H(P_S + P_s) \rightarrow (H_{II} - E_m)C_{Im} + \sum_{J \neq I \in S} H_{IJ} C_{Jm} + \sum_{i \in s} H_{Ii} C_{im} = 0. \quad (15)$$

If we are interested in ψ_m and E_m only, the whole information regarding the effect of the singly and doubly substituted determinants is contained in the N_S numbers h_{II} , i.e., in single determinantal energy-shifts, and this is the information which we shall use to incorporate the dominant effect of the triples and quadruples on the singles and doubles. Notice that Eq. (12) is a generalization of Eq. (2).

C. Weighted genealogy

A priori, a given determinant ϕ_i of the space s may interact with several determinants ϕ_I , ϕ_J of the reference space S (although, as will be discussed later, most of the

determinants ϕ_i only interact with *one* determinant ϕ_I). We propose to define a "genealogic weight" of the determinant ϕ_i on their parents ϕ_I belonging to S by the relation giving the amplitude of the weight,

$$\rho_{iIm} = \frac{H_{iI} C_{Im}}{\sum_{J \in S} (H_{iJ} C_{Jm})}. \quad (16)$$

This relation insures the normalization of the weights ρ_{iIm}

$$\sum_{I \in S} \rho_{iIm} = 1. \quad (17)$$

The definition of ρ_{iIm} is physically dictated by the eigenequation for ϕ_i ,

$$(H_{ii} - E_m)C_{im} + \sum_{j \neq i \in s} H_{ij} C_{jm} + \sum_{I \in S} H_{iI} C_{Im} = 0, \quad (18)$$

i.e.,

$$C_{im} = - \left(\sum_{I \in S} H_{iI} C_{Im} \right) \left[(H_{ii} - E_m) + C_{im}^{-1} \sum_{j \neq i \in s} H_{ij} C_{jm} \right]^{-1}. \quad (19)$$

This genealogy establishes a quantitative correspondence between the determinants ϕ_i and the determinants of the main model space S . Notice that the weight distribution is state-dependent and is self-consistent since it depends on the coefficients C_{Im} of the eigenvector of the dressed matrix. It must be noted that with the definition of the weight given in Eq. (16), numerical problems that could occur in the evaluation of h_{II}^m for very small C_{Im} coefficients can be avoided.

D. The weighted dressing

We want to transpose the basic statement used in the single-reference problem, namely,

"The effect of the triples and quadruples on the effective energies of the singles and doubles is the same, except for exclusion effects, as the effect of the singles and doubles on the reference energy."

This is the key point of the (SC)²CI method. Here we shall shift the energy of the determinants ϕ_i , i.e., the determinants obtained from the references by a single or a double substitution, in an analogous manner.

Let us consider first the case where ϕ_i has only one parent, ϕ_I in the reference space. It seems clear that the energy shift must be equal to h_{II}^m except for exclusion and redundancy effects

$$\Delta_{ii}^m = h_{II}^m + \text{EPV}(i, I)^m + R(i, I)^m, \quad (20)$$

where $\text{EPV}(i, I)^m$ and $R(i, I)^m$ will be defined as follows. If one calls D_k^+ the single and double substitutions, we define

$$\text{EPV}(i, I)^m = - \left[\sum_{\substack{D_k^+ \\ D_k^+ \phi_i = 0}} C_{(k)Im} \langle \phi_I | H | D_k^+ \phi_I \rangle \right] C_{Im}^{-1}, \quad (21)$$

TABLE I. The full CI matrix of the model problem.

Determ.	Coeff.		Matrix elements of H							
$\phi_{00} = \sigma_0^2 s_0^2$	1	0								
$\phi_{10} = \sigma_1^2 s_0^2$	λ	K_{01}	Γ_1							
$\phi_{01} = \sigma_0^2 s_1^2$	l	k_{01}	0	g_1						
$\phi_{11} = \sigma_1^2 s_1^2$	λl	0	k_{01}	K_{01}	$\Gamma_1 + g_1$					
$\phi_{20} = \sigma_2^2 s_0^2$	μ	K_{02}	K_{12}	0	0	Γ_2				
$\phi_{02} = \sigma_0^2 s_2^2$	m	k_{02}	0	k_{12}	0	0	g_2			
$\phi_{12} = \sigma_1^2 s_2^2$	λm	0	k_{02}	0	k_{12}	0	K_{01}	$\Gamma_1 + g_2$		
$\phi_{21} = \sigma_2^2 s_1^2$	μl	0	0	K_{02}	K_{12}	k_{01}	0	0	$\Gamma_2 + g_1$	
$\phi_{22} = \sigma_2^2 s_2^2$	μm	0	0	0	0	k_{02}	K_{02}	k_{12}	k_{12}	$\Gamma_2 + g_2$

$$R(i, I)^m = - \left[\sum_{D_k^+} C_{(kI)m} \langle \phi_I | H | D_k^+ \phi_I \rangle \right] C_{Im}^{-1}, \tag{22}$$

where $C_{(kI)m}$ is the coefficient of $D_k^+ \phi_I$ in the eigenvector ψ_m . Thus $EPV(i, I)^m$ is the contribution to h_{II}^m of all the single and double substitutions D_k^+ which are possible on ϕ_I and which are impossible on ϕ_i , due to exclusion effects, while $R(i, I)^m$ sums the contributions to h_{II}^m resulting from operations D_k^+ which may be applied to ϕ_i but which send to determinants of the MRSDCI space and whose effect should not be counted twice.

One sees that Eq. (20) is the transposition of the basic equation [Eq. (3)] of the (SC)²CI method, and that Eqs. (21) and (22) generalize Eqs. (5 bis) and (5 ter). However in general ϕ_i has several parent determinants in the MR space. Then we propose to write the general equation for the dressing

$$\Delta_{ii}^m = \sum_{I \in S} [h_{II}^m + EPV(i, I)^m + R(i, I)^m] \rho_{iIm}, \tag{23}$$

i.e., a weighted combination of the dressings from the different parents of ϕ_i . Of course the method must be iterated to the self-consistency of the coefficients, dressings and energy, as was the case for the (SC)²CI method.

III. SEPARABILITY

A. Illustration on a model problem

The size-consistent character of a method may be analyzed on a model problem concerning two noninteracting electron pairs on two subsystems A and B. One may consider for instance two H₂ molecules, and suppose that one is more strongly correlated than the other. For simplicity consider that we have only three MOs $\sigma_0, \sigma_1, \sigma_2$ and three relevant determinants $\sigma_0^2, \sigma_1^2, \sigma_2^2$ on system A and three MOs s_0, s_1, s_2 and three determinants s_0^2, s_1^2, s_2^2 on system B. For the supersystem $\phi_{00} = |\sigma_0^2 s_0^2\rangle, \phi_{10} = |\sigma_1^2 s_0^2\rangle, \phi_{01} = |\sigma_0^2 s_1^2\rangle, \text{ etc.}$ Then the full matrix is written in Table I with the following notation:

$K_{01} = \langle \sigma_0 \sigma_1, \sigma_0 \sigma_1 \rangle, K$ (resp. k) concerning system A (resp. B) integrals, and

$$\Gamma_1 = \langle \phi_{10} | H | \phi_{10} \rangle - \langle \phi_{00} | H | \phi_{00} \rangle,$$

$$g_1 = \langle \phi_{01} | H | \phi_{01} \rangle - \langle \phi_{00} | H | \phi_{00} \rangle$$

are excitation energies on system A and B, respectively.

Notice that a separable solution is written as

$$\psi = (\sigma_0^2 + \lambda \sigma_1^2 + \mu \sigma_2^2)(s_0^2 + l s_1^2 + m s_2^2)$$

so that the separable coefficients are also given in Table I. Then it is possible to know what should be the exact dressing using the exact relationship¹²

$$\Delta_{ii} = \left[\sum_{\alpha \in (S+s)} H_{\alpha i} C_{\alpha} \right] C_i^{-1}. \tag{24}$$

We shall select different reference spaces and compare our dressings of the doubly substituted determinants with the exact ones.

Consider *first* the case where the reference determinants are ϕ_{00} and ϕ_{10} . This is a complete active space σ_0 and σ_1 being the active MOs. Then the determinants to be dressed are $\phi_{01}, \phi_{11}, \phi_{20}, \phi_{02}$, and ϕ_{12} and the outer space determinants are ϕ_{21} and ϕ_{22} . The exact dressings are, applying Eq. (24) for

$$\phi_{01}, \Delta_{01,01} = K_{02} \frac{\mu l}{l} = K_{02} \mu,$$

$$\phi_{11}, \Delta_{11,11} = K_{12} \frac{\mu l}{\lambda l} = K_{12} \mu / \lambda,$$

$$\phi_{20}, \Delta_{20,20} = (k_{01} \mu l + k_{02} \mu m) / \mu = k_{01} l + k_{02} m,$$

$$\phi_{02}, \Delta_{02,02} = K_{02} \frac{\mu m}{m} = K_{02} \mu,$$

$$\phi_{12}, \Delta_{12,12} = K_{12} \frac{\mu m}{\lambda m} = K_{12} \mu / \lambda.$$

To apply our dressing we must first establish

$$h_{00,00} = k_{01} l + K_{02} \mu + k_{02} m,$$

$$h_{10,10} = k_{01} l + K_{12} \mu / \lambda + k_{02} m.$$

Then ϕ_{01}, ϕ_{02} have only one parent ϕ_{00} , ϕ_{11} and ϕ_{12} have one parent ϕ_{10} , and ϕ_{20} has two parents ϕ_{00} and ϕ_{10} . Applying Eq. (23) one finds

$$\Delta_{01,01} = \Delta_{02,02} = K_{02} \mu \text{ since the excitations } (s_0 \rightarrow s_1)^2 \text{ and } (s_0 \rightarrow s_2)^2,$$

possible on ϕ_{00} , are impossible on ϕ_{01} and ϕ_{02}

$\Delta_{11,11} = \Delta_{12,12} = K_{12}\mu/\lambda$ since the excitations $(s_0 \rightarrow s_1)^2$ and $(s_0 \rightarrow s_2)^2$,

possible on ϕ_{10} ,

are impossible on ϕ_{11} and ϕ_{12} .

Regarding ϕ_{20} , which has two parents, one gets

$$\Delta_{20,20} = (k_{01}l + k_{02}m)(\rho_{20,00} + \rho_{20,10}) = k_{01}l + k_{02}m$$

so that the dressing are the correct ones. The dressing will make the CAS SDCI size-consistent and separable.

This was a case where the MR space is (i) a CAS and (ii) located on a subsystem. As a *second* case one may consider a reference space which is still complete but involves excitations on both subsystems, considering ϕ_{00} , ϕ_{01} , ϕ_{10} , and ϕ_{11} as references. Then the outer space is reduced to ϕ_{22} and the exact dressing energies are $\Delta_{20,20} = k_{02}m$, $\Delta_{02,02} = K_{02}\mu$, $\Delta_{12,12} = K_{12}\mu/\lambda$, and $\Delta_{21,21} = k_{12}m/l$. One may verify that

$$h_{00,00} = K_{02}\mu + k_{02}m,$$

$$h_{10,10} = K_{12}\mu/\lambda + k_{02}m,$$

$$h_{01,01} = k_{12}m/l + K_{02}\mu,$$

$$h_{11,11} = k_{12}m/l + K_{12}\mu/\lambda.$$

All the determinants ϕ_i have two parents, namely

ϕ_{00} and ϕ_{10} for ϕ_{20} ,

ϕ_{00} and ϕ_{01} for ϕ_{02} ,

ϕ_{10} and ϕ_{11} for ϕ_{12} ,

ϕ_{01} and ϕ_{11} for ϕ_{21} .

Then,

$$\Delta_{20,20} = (k_{02}m)(\rho_{20,00} + \rho_{20,10}) = k_{02}m,$$

$$\Delta_{12,12} = (K_{12}\mu/\lambda)(\rho_{12,10} + \rho_{12,11}) = K_{12}\mu/\lambda$$

and similarly $\Delta_{02,02}$ and $\Delta_{21,21}$ are correct.

As a *third* case one may imagine that the reference space is no longer complete, and composed of ϕ_{00} , ϕ_{10} , and ϕ_{01} . Then ϕ_{11} belongs to the intermediate space s , together with ϕ_{20} , ϕ_{02} , ϕ_{12} , and ϕ_{21} , the outer space being again reduced to ϕ_{22} . One may check again that the dressing matrix elements are the correct ones, namely,

$$\Delta_{11,11} = 0, \quad \Delta_{20,20} = k_{02}m, \quad \Delta_{02,02} = K_{02}\mu,$$

$$\Delta_{12,12} = K_{12}\mu/\lambda \quad \text{and} \quad \Delta_{21,21} = k_{12}m/l.$$

It is worth analyzing why $\Delta_{11,11} = 0$ in our dressing procedure. ϕ_{11} has two reference parents ϕ_{10} and ϕ_{01} , for which

$$h_{10,10} = k_{01}l + K_{12}\mu/\lambda + k_{02}m,$$

$$h_{01,01} = K_{01}\lambda + k_{12}m/l + K_{02}\mu,$$

$$h_{00,00} = K_{02}\mu + k_{02}m,$$

but the substitutions $(\sigma_1 \rightarrow \sigma_2)^2$ and $(s_1 \rightarrow s_2)^2$ on ϕ_{11} send to the determinants ϕ_{21} and ϕ_{12} , respectively, which belong to the model space and they are excluded by the quantity $R_{11,10}$

and $R_{11,01}$, respectively in Eq. (23). So that one sees that the reference space does not need to be complete to obtain the separability.

B. Proof of separability for a localized reference space

One may consider a supersystem, made of two noninteracting systems A and B , and one will suppose that the MOs are localized on either A or B . Let us assume that the reference determinants are obtained by excitations on system A . Let us call ϕ_{0B} the ground state configuration of B and ϕ_{iA} the reference configurations for the *separate* problems. For the supersystem the reference space S is composed of determinants

$$\phi_{i_A 0_B} = \phi_{i_A} \cdot \phi_{0_B} \quad (25)$$

and the s space is made of two types of determinants, namely

$$\phi_{i_A 0_B} = \phi_{i_A} \cdot \phi_{0_B} \quad (26)$$

and

$$\phi_{i_A j_B} = \phi_{i_A} \cdot \phi_{j_B} \quad (27)$$

The MR-SDCI is not size consistent, the energy is not additive. For a state which should be the product of a state ψ_{m_A} and of ψ_{0_B} ,

$$E_m \neq E_{m_A} + E_{0_B}$$

and

$$P_{S+s}\psi_m \neq P_{S+s}(\psi_m^A \psi_0^B)$$

due to the size-inconsistence of the variational truncated CI. The spectrum of the system A is affected by the inclusion of the system B in the AB supersystem, which is meaningless.

We want to demonstrate that the here-proposed dressing will restore the correct behavior.

For the system A only, the MR-SDCI dressing of the determinant ϕ_{i_A} is

$$\Delta_{i_A i_A}^m = \sum_{I_A} [h_{i_A I_A}^m + \text{EPV}(i_A, I_A)^m] \rho_{i_A I_A}^m \quad (28)$$

and its coefficient is $C_{i_A m}$.

For the system B alone, the dressing would be that of a single reference (SC)²SDCI. If E_{CB} is the ground state correlation energy for B ,

$$\Delta_{j_B j_B}^0 = E_{CB} + \text{EPV}(j_B), \quad (29)$$

we shall demonstrate that the expected values of the coefficients for the supersystem, namely,

$$C_{i_A 0_B}^m = C_{i_A m} C_{0_B}, \quad (30)$$

$$C_{i_A j_B}^m = C_{i_A m} C_{j_B} \quad (31)$$

and the additivity of the energies

$$E_m = E_{m_A} + E_{0_B}$$

satisfy the eigenequations of the dressed MR-SDCI matrix. One must consider the two types of determinants belonging to s . The determinant $\phi_{I_A j_B}$ has only one parent determinant, namely $\phi_{I_A 0_B}$. For compactness of notation, the subscript in parentheses will indicate a diagonal matrix element,

$$\Delta_{(I_A j_B)}^m = h_{(I_A 0_B)}^m + \text{EPV}(I_A j_B, I_A 0_B)^m, \quad (32)$$

$$h_{(I_A 0_B)}^m = h_{(I_A)}^m + E_{0_B}, \quad (33)$$

since all excitations on B are possible on $\phi_{I_A 0_B}$ and the substitutions on A possible on ϕ_{I_A} are the same as those possible on $\phi_{I_A 0_B}$,

$$\text{EPV}(I_A j_B, I_A 0_B)^m = \text{EPV}(j_B), \quad (34)$$

$\phi_{I_A j_B}$ interacts only with determinants of the types $\phi_{J_A j_B}$ and $\phi_{I_A k_B}$,

$$\langle \phi_{I_A j_B} | H | \phi_{J_A j_B} \rangle = H_{I_A J_A}, \quad (35)$$

$$\langle \phi_{I_A j_B} | H | \phi_{I_A k_B} \rangle = H_{j_B k_B}. \quad (36)$$

So that the eigenequation for the line $\phi_{I_A j_B}$ in the dressed supersystem is

$$\begin{aligned} & [H_{(I_A j_B)} + h_{(I_A)}^m + E_{CB} + \text{EPV}(j_B) - E_m] C_{I_A m} C_{j_B} \\ & + \sum_{\substack{J_A \\ \neq I_A}} H_{I_A J_A} C_{J_A m} C_{j_B} + \sum_{\substack{k_B \\ \neq j_B}} H_{j_B k_B} C_{I_A m} C_{k_B} = 0. \end{aligned} \quad (37)$$

It should be compared with the dressed eigenequations for the subsystems. For ϕ_{I_A} ,

$$[H_{(I_A)} + h_{(I_A)}^m - E_{m_A}] C_{I_A m} + \sum_{\substack{J_A \\ \neq I_A}} H_{I_A J_A} C_{J_A m} = 0 \quad (38)$$

and for ϕ_{j_B} ,

$$[H_{(j_B)} + E_{CB} + \text{EPV}(j_B) - E_{0_B}] C_{j_B} + \sum_{\substack{k_B \\ \neq j_B}} H_{j_B k_B} C_{k_B} = 0. \quad (39)$$

Multiplying the Eq. (38) by C_{j_B} and Eq. (39) by C_{I_A} and adding them one obtains Eq. (37) provided that

$$E_m = E_{m_A} + E_{0_B} \quad (40)$$

and that

$$H_{(I_A j_B)} = H_{(I_A)} + H_{(j_B)}. \quad (41)$$

The determinant $\phi_{i_A 0_B}$ may have several parent determinants $\phi_{I_A 0_B}$. It is possible to demonstrate that

$$\Delta_{(i_A 0_B)}^m = \Delta_{(i_A)}^m + E_{0_B} \quad (42)$$

since $\rho_{(i_A 0_B)(J_A 0_B)m} = \rho_{i_A J_A m}$, as evident from Eq. (16). $\phi_{i_A 0_B}$ interacts with $\phi_{J_A 0_B}$ through $H_{i_A J_A}$ and the eigenequation for the dressed supersystem is

$$[H_{(i_A 0_B)} + \Delta_{(i_A)}^m + E_{0_B} - E_m] C_{i_A} C_{0_B} + \sum_{\substack{J_A \\ \neq i_A}} H_{i_A J_A} C_{J_A} C_{0_B} = 0 \quad (43)$$

which is satisfied for the solution of the system A since C_{0_B} is factorized

$$[H_{(i_A)} + \Delta_{(i_A)}^m - E_{m_A}] C_{i_A m} + \sum_{\substack{J_A \\ \neq i_A}} H_{i_A J_A} C_{J_A m} = 0. \quad (44)$$

Then the effect of B is simply a shift of the energies of states of system A by the quantity E_{0_B} , as it must be.

Notice that if S is a CAS and if D_k^+ is a double excitation involving only inactive orbitals, our procedure does not assume that

$$C_{(D_k^+ I_A)^m} = d_k C_{I_A m}, \quad (45)$$

where d_k is a state-independent amplitude of the double excitation D_k^+ . This condition would of course insure the separability in the preceding problem, and we have obtained it when D_k^+ concerns a system B noninteracting with the system A bearing the active orbitals. But as we have seen, this relation was satisfied in our method provided that the

$$H_{(D_k^+ I_A)} = H_{(I_A)} + \Delta E_{D_k^+}, \quad (46)$$

i.e., that the excitation energies are additive. This is not true in general and we have no reason to impose Eq. (45), which is a sufficient but non-necessary condition for the size consistency of our CAS-SDCI dressed algorithm, as discussed in the Appendix.

So far we have only been able to prove the separability of the here-proposed method for a reference model space which is entirely located on one subsystem. We want to point out here an important *remark* concerning our previous work [Ref. 3(b)] i.e., the (SC)²CI method which uses a dressing with respect to a single reference ϕ_0 . The method may be applied to any CI involving more than singles and doubles, but contrarily to what is said in Ref. 3(b) (Sec. IV D), the separability is only satisfied when the more than doubly-excited determinants are located on *one* subsystem. The demonstration for a general selected CI space was *incorrect* since we had not proved that the eigenequation for a determinant $\phi_{i_A j_B}$, excited on both A and B subsystems, is satisfied when $E_{AB} = E_A + E_B$ and $C_{i_A j_B} = C_{i_A} \cdot C_{j_B}$. This eigenequation is *not* satisfied in the (SC)²CI single reference dressing while it becomes satisfied in the present multireference procedure.

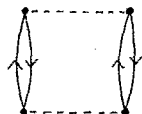
C. Physical content of the dressing

The dressing of course incorporates effects of the triple and quadruple excitations from the references, and since it is a self-consistent procedure it also incorporates the effect of higher excitations, as necessary to restore the size-consistency. This mechanism was extensively analyzed for the single reference problem in Ref. 3. Here it is impossible

to proceed to such a deduction for the general multireference case, for which a diagrammatic expansion does not even exist. One may thus refer to some extreme situations such as a CAS-multireference space or a multireference involving all singly-excited determinants. One may also consider first a ground-state problem in which one configuration, ϕ_0 is dominant, and trace the effects included by the dressing from the non degenerate perturbative expansion.

For sake of simplicity we shall consider the case where the CI is a CAS-SDCI with four active electrons and we shall distinguish the ground state closed shell leading determinant ϕ_0 ; $\phi_0 = |\text{core } a\bar{a}b\bar{b}|$ taken as the vacuum state in the nondegenerate expansion from ϕ_1 . We shall give downward double arrows to the active MOs a and b and upward double arrows to the virtual active MOs c, d, \dots . The inactive occupied MOs (i, j, \dots) and virtual MOs (r, s, \dots) will bear upward and downward single arrows.

The single reference (SC)² procedure simply dresses any determinant ϕ_i by the effect of the double excitations on ϕ_0 possible on ϕ_i , i.e., at the 2nd order level by the diagrams

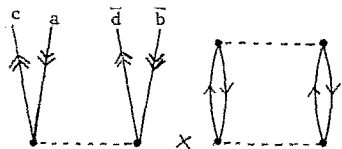


where at least one propagation line was inactive. These contributions appear now in the quantity h_{00} relative to ϕ_0 . If ϕ_K is a doubly excited reference determinant, for instance

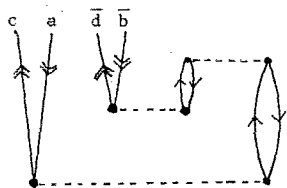
$$\phi_K = |\text{core } c\bar{a}b\bar{d}|,$$

the quantity h_{KK} incorporates the effect of a series of interactions

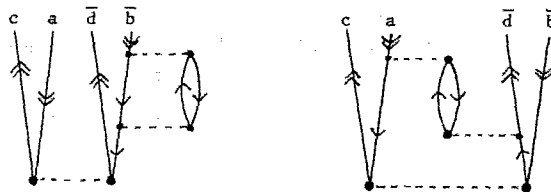
(i) between ϕ_K and quadruples, through unlinked or linked contributions,



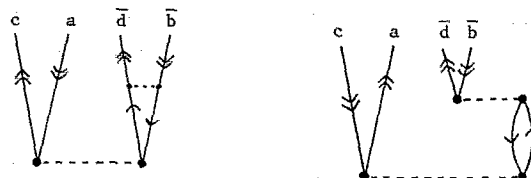
where the symbol X indicates the relative positions of the two lowest interaction lines are free, and



(ii) between ϕ_K and triples,

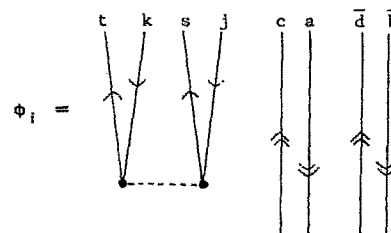


and (iii) between ϕ_K and nonreference doubles,



Now the quantity h_{KK} will be used to dress the energy of a nonreference determinant ϕ_i interacting with ϕ_K , for instance a quadruple obtained from ϕ_K by the double excitation

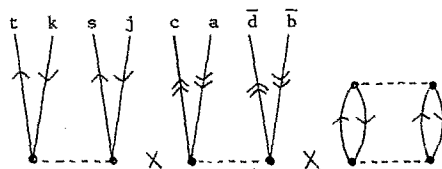
$$D_i^+ = a_i^+ a_s^+ a_j a_k$$



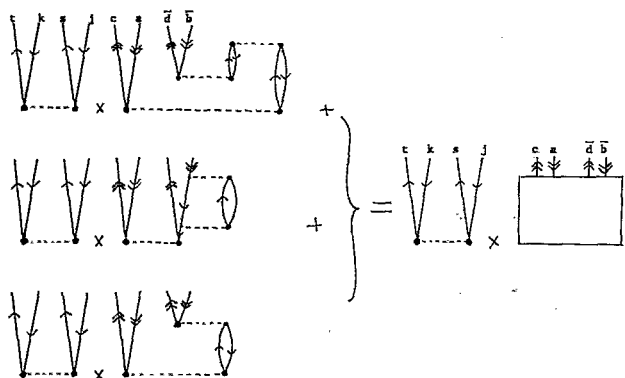
we have demonstrated that if the active MOs are on a system A and if the MOs $j, k, s,$ and t belong to a noninteracting system B,

$$C_{i_B k_A} = C_{i_B} C_{k_A}$$

which means that the dressing incorporates, besides the unlinked contribution which already appeared in the single reference (SC)²CI dressing

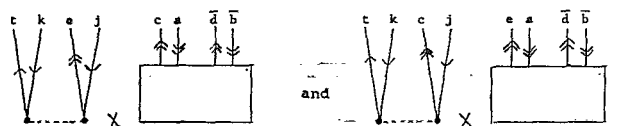


the new contributions such as

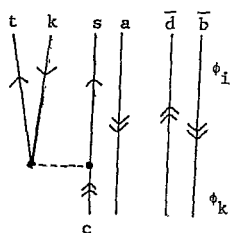


which are linked and incorporate the effect of hexa-, penta-, and inactive quadruply excited determinants, which do not belong to the CI space.

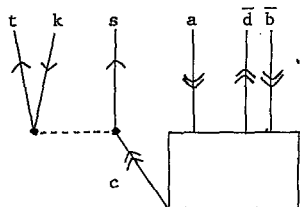
The determinant ϕ_i may interact with several reference determinants, for instance $\phi_i = \phi(k^t e^c \bar{d}^a \bar{b})$ interacts with both $\phi_K = \phi(a^c \bar{b})$ and $\phi_2 = (e^a \bar{b})$. Then the dressing combines



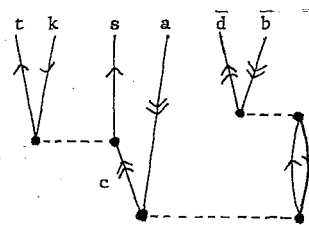
If one considers a triply excited determinant ϕ_i , interacting with ϕ_K through a connecting interaction



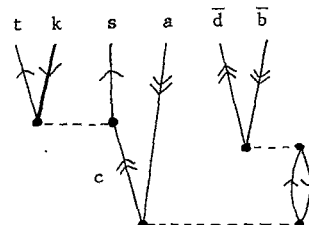
the dressing Δ_{ii} only retains the part of h_{KK} which concerns the processes leaving untouched the propagation line (here c) implied in $\langle \phi_i | H | \phi_K \rangle$; it sums the diagrams which act on the other propagation lines of ϕ_K , which may be symbolized as



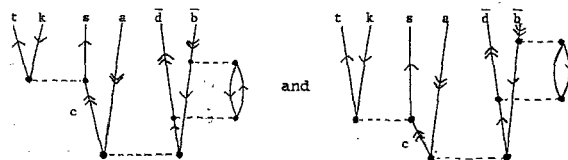
and which implies



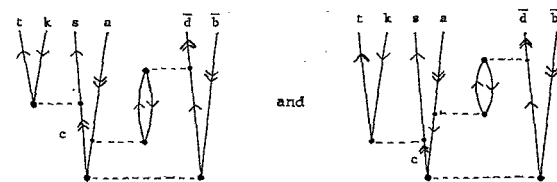
(and not



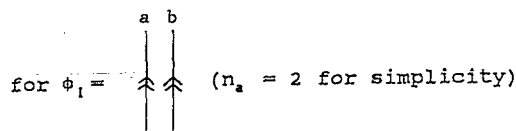
already taken into account in the CI) and both



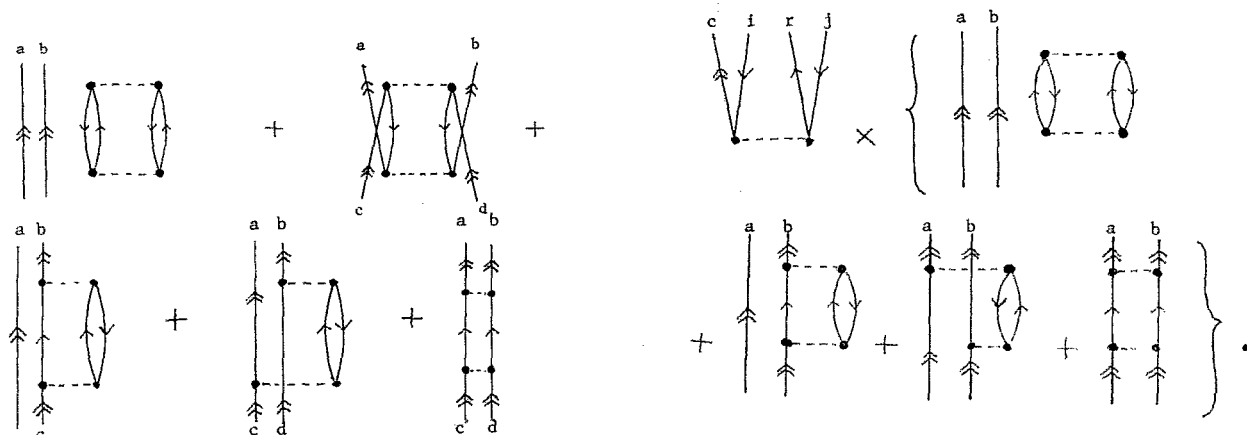
or



Let us consider then a more general CAS reference space from a more general point of view and for a state which may be an excited one. The core will be taken as the new vacuum; if n_a is the number of active electrons, the reference determinants are now defined by n_a propagation lines (labeled a, b, c) with upward double arrows. The downward and upward single arrows symbolize inactive holes (labeling i, j, \dots) and particles (labeled r, s, \dots), respectively. The unlabeled propagation lines will be implicitly upward and may bear active or virtual MOs. Now one must first consider the quantities h_{II} which incorporate at least the effect of the following 2nd order diagrams (and higher order corrections)

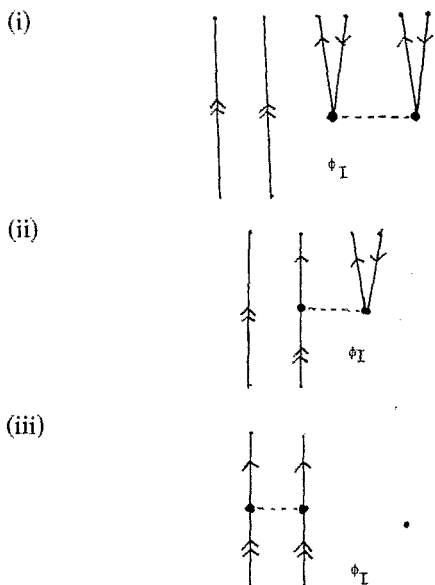


h_{II}



i.e., the effect of the interaction between ϕ_I and the determinants $\phi_i \in S$. Notice that the reference determinant in the lowest part of these diagrams may be different from ϕ_I .

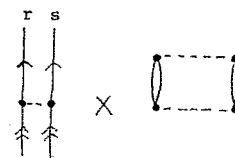
A nonreference determinant $\phi_i \in s$ interacting with ϕ_I may be of three different types,



Of course the labels of the downward propagation lines must be different from i and j , and the upward lines cannot bear the labels r and c . This is managed by the $EPV(i, I)^m$ correction to h_{II}^m . This dressing will be weighted by the quantity ρ_{ilm} since ϕ_i interacts with other reference determinants such as $\phi_j = ac$. From that origin the same determinant ϕ_i will receive another dressing $[h_{JJ}^m + EPV(i, J)^m] \rho_{iJm}$. If one considers a determinant of type (iii), for instance,

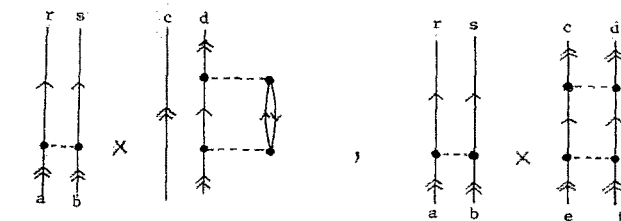
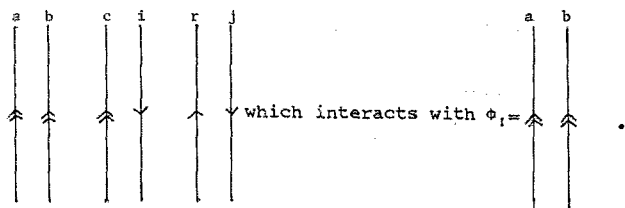
$$\phi_i = \begin{array}{cc} r & s \\ \uparrow & \uparrow \end{array}, \quad \text{which interacts with } \phi_I = \begin{array}{cc} a & b \\ \uparrow & \uparrow \end{array}$$

the dressing that it receives from ϕ_I reduces to the following type:



when $n_a = 2$. This will no longer be true when $n_a > 2$; when $n_a = 4$ for instance one incorporates in the dressing of $|cdrs|$ diagrams of the type

Let us consider a determinant of the first type for instance



coming from the dressing h_{II} , $\phi_i = |abcd|$.

If the reference space is the set of all singly excited configurations, taking the closed shell ground state determi-

It will be dressed partly by contributions of h_{II} , reflecting the following corrections:

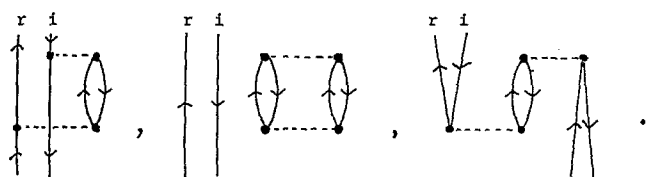
nant as the vacuum, the references are written as

$$\phi_I = \begin{array}{c} i \quad r \\ | \quad | \\ \text{---} \\ | \quad | \end{array} = \phi \begin{pmatrix} r \\ i \end{pmatrix}$$

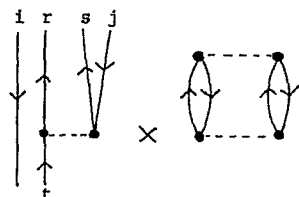
while ϕ_i is either a doubly or a triply excited determinant

$$\phi_i = \begin{array}{c} | \quad | \\ \text{---} \\ | \quad | \end{array}, \quad \begin{array}{c} | \quad | \\ \text{---} \\ | \quad | \end{array}$$

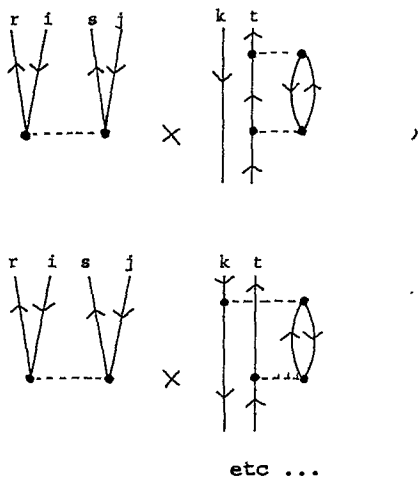
Then the quantities h_{II} report the effects of the doubles and triples on the singles, for instance



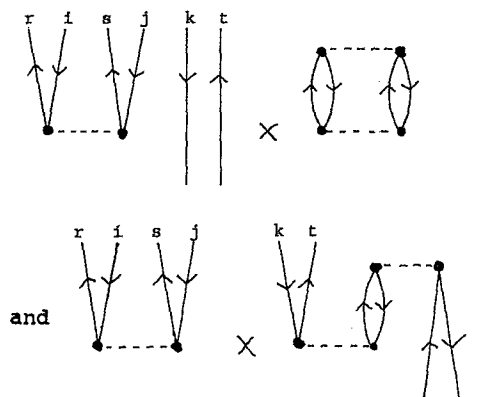
The dressing of a doubly excited determinant $\phi_i = \phi(i^r s_j)$ coming from $\phi_j = \phi(i)$ only incorporates the effect of the quadruples



with specific exclusion effects. The part of the dressing h_{II} coming from the doubles is excluded by the redundancy correction, as explained in the next section. For a triply excited determinant $\phi_i = \phi(i^r s_j k)$ the dressing coming from $\phi_j = \phi(k)$ incorporates effects from quadruples

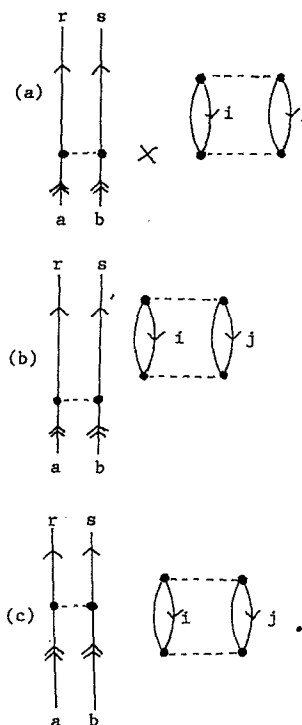


and from pentuples



It may be interesting to notice that in the above diagrams the conditions $l, m \neq k$ and $u, v \neq t$ are already managed by h_{II} [$\phi_i = \phi(i^r s_j)$] while the conditions $l, m \neq i, j$ and $u, v \neq r, s$ are ruled by the $EPV(i, I)^m$ correction.

There are some problematic exclusions. For instance in diagram (a) we exclude the labels a and b on the unlabeled propagation lines of the right part, although diagram (b) might be considered. This exclusion is due to the fact that the counterpart (c) does not exist if a and/or b appear on the unlabeled lines



IV. PRACTICAL CONSIDERATIONS

A. The EPV terms

The main problem, from a computational point of view, concerns the rapid evaluation of the EPV terms $EPV(i, I)^m$

and the redundant terms $R(i, I)^m$. Let us move back to the single reference case and recall the solution used for the EPV terms.

For a doubly excited determinant $\phi_{gh \rightarrow rs}$ where g, h and r, s are occupied and virtual MOs, respectively, one cannot repeat excitations involving at least one of the MOs g, h, r or s . For instance the excitations $df \rightarrow ts$ are forbidden, but the indexes d, f , and t are free and the calculation of the EPV terms for a determinant ϕ_i would require triple summations. This would lead to an n^7 increase of the computation time of the dressing. The computation of the EPV corrections was made direct using a trick first proposed for an infinite summation of EPV diagrams in a perturbative approach.¹³ The idea consists in storing partial summations relative to the orbitals, the pairs of orbitals and the sets of three orbitals. For the spin orbital g ,

$$e(g) = \left(\sum_j C_j H_{0j} \right) C_0^{-1} \quad (D_j^+ \phi_0 = \phi_j) \quad (47)$$

for the pair of spin orbitals g and h ,

$$e(g, h) = \left(\sum_j C_j H_{0j} \right) C_0^{-1} \quad D_j^+ \text{ involving } g \text{ and } h, \quad (48)$$

and the same for the $e(g, h, r)$. [As will be discussed later the storage of the three-index array $e(g, h, r)$ can be avoided.] Then for a determinant $\phi_i = D_i^+ \phi_0$, the EPV terms are given by

$$\begin{aligned} \text{EPV}(i) = & - \sum_{\substack{g \\ \in D_i^+}} e(g) + \sum_{\substack{g, h \\ \in D_i^+}} e(g, h) - \sum_{\substack{g, h, r \\ \in D_i^+}} e(g, h, r) \\ & + C_i H_{0i}. \end{aligned} \quad (49)$$

We may generalize these one-, two-, and three-index arrays for each reference determinant ϕ_I , so that they become two-, three- and four-index arrays.

If D_{jI}^+ is the operator such that $\phi_j = D_{jI}^+ \phi_I$,

$$e(g, I) = \left(\sum_j C_{jI} H_{jI} \right) C_{I0}^{-1} \quad D_{jI}^+ \text{ involving } g \quad (50)$$

One may define as well three- and four-index arrays $e(g, h, I)$ and $e(g, h, r, I)$ for each reference determinant ϕ_I ,

$$\begin{aligned} \text{EPV}(i, I)^m = & - \sum_{\substack{g \\ \in D_{iI}^+}} e(g, I)^m + \sum_{\substack{g, h \\ \in D_{iI}^+}} e(g, h, I)^m \\ & - \sum_{\substack{g, h, r \\ \in D_{iI}^+}} e(g, h, r, I)^m + C_{iI} H_{iI} C_{I0}^{-1}. \end{aligned} \quad (51)$$

A priori the three-orbital arrays $e(g, h, r, I)$ might become memory consuming, especially when the number of references increases. However one must notice that it is possible to consider the reference determinants ϕ_I in the outer loop of

the dressing and to calculate h_{jI}^m and the arrays $e(g, \dots, I)^m$. Then one shall dress the determinants ϕ_i interacting with ϕ_j for their fraction ρ_{iIm} . Going to the next reference determinant ϕ_j one may redefine h_{jI}^m and the $e(g, \dots, I)^m$ arrays. So that the memory required for the computation of the EPV terms is not larger than for the single-reference case.

Moreover one may notice that one can avoid the three-index arrays without introducing a bottleneck in the computation time. Actually the summation over the MOs,

$$e(g, h, r, I)^m = \left[\sum_s C_{(a_s^+ a_r^+ a_g a_h \phi_I)^m} \langle rs | gh \rangle \right] C_{Im}^{-1} \quad (52)$$

may be repeated for each ϕ_i . The cost is a single summation over n spin orbitals, and if N is the dimension of the $(S+s)$ MRSDCI space, this summation only requires a time proportional to $N \cdot n$, negligible compared to the HC product in the diagonalization step, which scales as $N \cdot n^4$.

B. The redundancy correction

For the single-reference problem the redundancy correction $R(i)$ [Eq. (5 ter)] is zero when the CI is restricted to singles and doubles. When the selected CI space involves determinants of higher degrees of excitation, it is easy to calculate $R(i)$ by considering the effect of the double desexcitations which occur inside the selected CI space during the proper building of the CI matrix in our direct selected CI algorithms.^{14,15} Here the problem is more difficult.

For a completely arbitrary reference space and during the computation of $P_{(S+s)} H P_{(S+s)}$, for each interaction between two determinants of the s space $\phi_j = D_k^+ \phi_i$ (where D_k^+ is a single or double substitution), one must in principle check whether for each parent ϕ_l of ϕ_i the D_k^+ operation is possible or not, and if it is, one should subtract the quantity $C_{(D_k^+ \phi_l)} \langle \phi_l | H | D_k^+ \phi_l \rangle \rho_{il}$ from the dressing matrix element Δ_{ii} of ϕ_i . This would significantly slow the diagonalization step if the number of reference determinants is large. However one may easily find some conditions which restrict the number of D_k^+ substitutions for which the test of redundancy must be performed. To illustrate this statement we shall first consider several extreme cases.

In the first case the references are *all* the singly excited determinants (singles CI), an approximation sometimes used for spectroscopy studies. Then all MOs are active. The s space is composed of the doubles and triples.

The dressing matrix elements h_{II} of the singles, obtained from the $S+s$ space, i.e., the SDTCI, may be decomposed into a part coming from the doubles and a part coming from the triples,

$$h_{II} = h d_{II} + h t_{II}.$$

Now when we transfer the dressing to the triples we take into account effects of quadruples and quintuples which do not belong to the SDTCI, and there is no redundancy to be feared. In the dressing of the doubles one should only dress by the contribution $h t_{II}$ of their parents which reflects effect of the quadruples, and not by the contribution $h d_{II}$ which would introduce effects of the triples, already present in the $(S+s)$ CI space.

As an other limit, one may consider the case where the references define a complete active space (CAS).

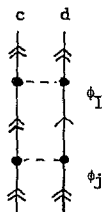
One must discriminate the operations D_{il}^+ such that $H_{il} \neq 0$ according to the number of inactive holes and inactive particles appearing in D_{il}^+ and which vary from 0 to 2. The total dressing matrix element h_{il} of ϕ_I may be partitioned into eight terms, depending on the number of inactive holes and inactive particles involved in the D_{il}^+ operators,

$$h_{II} = (h_{22} + h_{21} + h_{12} + h_{20} + h_{11} + h_{02} + h_{01} + h_{10})_{II},$$

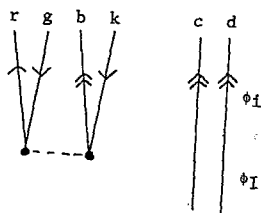
where in hpq p is the number of inactive holes and q the number of inactive particles. The determinants belonging to s have at most 2 inactive holes and 2 inactive particles. One must avoid to report their effect in the dressing of the determinants $\phi_i \in s$. If ϕ_i involves 2 inactive holes and 2 inactive particles, the dressing must be $h_{II}\rho_{ilm}$ since there is no risk of redundancy. If the determinant ϕ_i involves two inactive holes and one inactive particle only, the dressing should be

$$(h - h_{01})_{II}\rho_{ilm}$$

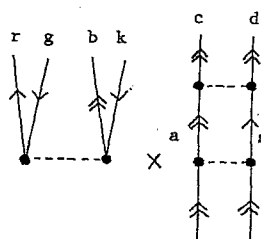
in order to avoid the redundancy with the determinants having 2 inactive holes and 2 inactive particles (included in s). The term h_{01} involve diagrams of the type



while we are considering the dressing of ϕ_i obtained from ϕ_I by the following interaction:



and it is clear that the dressing by h_{01}_{II}



would involve a determinant belonging to s . The same logics lead to the following dressing rules for ϕ_i according to the

number of inactive holes and particles involved in this determinant

number of inactive holes	number of inactive particles	dressing from the parent ϕ_I (to be multiplied by ρ_{ilm})
2	2	h
2	1	$h - h_{01}$
1	2	$h - h_{10}$
2	0	$h - h_{01} - h_{02}$
1	1	$h - h_{01} - h_{10} - h_{11}$
0	2	$h - h_{10} - h_{20}$
1	0	$h - h_{01} - h_{10} - h_{11} - h_{02} - h_{12}$
0	1	$h - h_{01} - h_{10} - h_{11} - h_{20} - h_{21}$

So that the method is easily applicable to a CAS-SDCI. For an arbitrarily selected MR-SDCI space the avoidment of redundancies is certainly more difficult.

V. CONCLUSION

The starting point of the present work is a recently proposed method [(SC)²CI] to make size-consistent any CI. This method only applies to the ground state. It is valid for a selected CI, for instance to a multireference singles and doubles CI, but the dressing is performed from a single reference. So that the term of multireference only concerned the selected CI space, not the dressing. The present work eliminates the two limits of our previous work since (i) it is a real multireference procedure; (ii) it works on excited states as well as on the ground state.

Of course it contains the preceding (SC)²CI algorithm as a special case and it tends to it when all coefficients on the reference space except one tend to zero.

The cost of the dressing should be negligible with respect to the research of the desired roots of the MRSDCI matrix at least for well-behaved reference spaces (sufficiently close to a CAS or to singles CI for instance) and the storage of intermediate informations for the dressing should need much less memory than the eigenvector itself. The practical implementation of this procedure in direct CI algorithms is under work.

We would like to point out that the method is *uncontracted*. The dressing modifies the coefficients of all the MRSDCI space in a self-consistent manner. Of course it is superior to a generalized Davidson's correction since it insures the cancellation of unlinked effects. Our experience is that (SC)²SDCI gives practically the same result as CCSD with great simplicity and better convergence behavior. So that we expect that the here-proposed method [which we shall label MR* (SC)²CI] will parallel the results of MRCC-SD methods (when available) through a much smaller computational effort. The present method manages carefully the exclusion and redundancy effects which are neglected in the linear multireference coupled cluster approximation.¹⁶ Recently, an improvement of this method has been proposed by Szalay and Bartlett,¹⁷ introducing EPV terms on occupied orbitals in an averaged way. In our procedure the EPV terms concern both occupied and virtual MOs, without averaging. These methods, as the average

coupled pair functional of Gdanitz and Ahlrichs,¹⁸ are size-extensive but they are not strictly separable.

As noticed in the Appendix our method does not have to assume, for a CAS reference space, that if D_k^+ is an inactive double excitation the coefficient of the determinant $D_k^+ \phi_l$ is a simple product

$$C_{(D_k^+ \phi_l)^m} = d_k C_{lm},$$

d_k being a state-independent and ket-independent amplitude. This condition is sufficient to insure the separability but is not necessary and may be erroneous when the diagonal energy differences are not additive.

The here proposed method can be compared with the quasidegenerate variational perturbation theory (QDVPT) of Cave and Davidson.¹⁹ Their method consists in a dressing of the diagonal energies of the determinants of our space s . They are dressed by a unique quantity

$$E_{\text{corr}}^m = E^m - \langle P_s \psi_m | H | P_s \psi_m \rangle$$

supposed to mimic the effect of the outer space determinants. This dressing is state specific but it is the same for all the determinants of s , while we discriminate them in order to take into account the specific coupling of ϕ_i with the reference determinants and the exclusion and redundancy effects. The situation of QDVPT with respect to the here-proposed MR* (SC)²CI may be compared to as the situation of the CEPA-O version of the coupled electron pair approximation (or linear coupled cluster) with respect to our (SC)²CI for singles and doubles.

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APPENDIX: NONFACTORIZATION OF THE COEFFICIENT OF THE DETERMINANTS OBTAINED BY INACTIVE DOUBLE EXCITATIONS

The fact that the coefficients of the determinants obtained by a given inactive double excitation D_k^+ on the CAS determinants ϕ_l are not products of a unique coefficient d_k by the coefficients C_l of ϕ_l [cf. Eq. (45)] is easily seen on the following model problem. Let us consider an $A \cdots B$ system, as active MOs all the MOs of A , as reference space the CAS on A (i.e., the full CI on A). Suppose that the system B only involves one occupied and one virtual MO (b and b^*) and that for symmetry reasons only the $D_b^+ = (b \rightarrow b^*)^2$ closed shell excitation is possible on B . Then the full CI is composed of products $\phi_{I_A} \cdot b^2$, where ϕ_{I_A} is a determinant located on A and of products $\phi_{I_A} \cdot b^{*2}$. The first ones belong to the reference space S , the second ones to the space s , and there is no outer space. Then the two spaces S and s are isodimensional and the full CI matrix structure is given below

	determinants	matrix
S	$\phi_{I_A} b^2$	$\langle I_A b^2 \rangle$
	$\phi_{J_A} b^2$	$H_{J_A I_A} \langle J_A b^2 \rangle$
s	$\phi_{I_A} b^{*2}$	$K_{bb^*} \quad 0 \quad \langle I_A b^{*2} \rangle$
	$\phi_{J_A} b^{*2}$	$0 \quad K_{bb^*} \quad H_{J_A I_A} \langle J_A b^{*2} \rangle$

The square off-diagonal block between S and s is "diagonal" with a unique value (K_{bb^*}) of its elements, while the off-diagonal parts of the two blocks H_{SS} and H_{ss} are identical.

If the diagonal matrix elements may be written as

$$\langle \phi_{I_A b^{*2}} | H | \phi_{I_A b^{*2}} \rangle - \langle \phi_{I_A b^2} | H | \phi_{I_A b^2} \rangle = \Delta_b, \quad \forall I_A \quad (\text{A1})$$

then it is easy to show that one may diagonalize the two blocks H_{SS} and H_{ss} and that the two eigenvectors are identical (in two orthogonal spaces),

$$H_{SS} \psi_m^s = E_m \psi_m^s,$$

$$H_{ss} \psi_m^s = (E_m + \Delta_b) \psi_m^s,$$

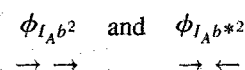
and that

$$\langle \psi_m^s | H | \psi_n^s \rangle = K_{bb^*} \delta_{mn}.$$

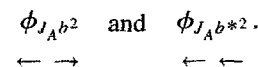
Then actually Eq. (50) is satisfied

$$C_{I_A b^{*2}} = d_b C_{I_A b^2},$$

where d_b is a unique factor, characteristic of the $b \rightarrow b^{*2}$ amplitude. But this will no longer be true if Eq. (46) is not satisfied. Even for an intermolecular problem, if A and B no longer overlap but are in a range of distances where electrostatic effects between the supposed polar systems A and B are not negligible, the energy difference between



(the arrows representing the direction of the dipoles on A and B) will be different from the energy difference between



If ϕ_{I_A} and ϕ_{J_A} have two opposite dipole moments μ_A and $(-\mu_A)$ and b^2 and b^{*2} have two opposite dipole moments μ_B and $-\mu_B$ parallel to μ_A , then the first energy difference is

$$\Delta_b - 2 \mu_A \cdot \mu_B r_{AB}^{-3},$$

while the second one is $\Delta_b + 2 \mu_A \cdot \mu_B r_{AB}^{-3}$.

These effects are much stronger for molecular problems, for instance when the b MO is a "core" MO in the same region of space as the active MOs. So that one has no reason to impose a condition which is only valid asymptotically for remote sets of MOs.

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