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Size-consistent self-consistent truncated or selected configuration interaction

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Based on the principle of intermediate effective Hamiltonians, a simple procedure is proposed in order to eliminate the unlinked contributions of any truncated or selected configuration interaction (CI). The corrections are diagonal energy shifts, easily calculated. A self-consistent version is proposed, which insures separability if localized molecular orbitals (MO) are used. In the special case of double CI, the present method is an improved version of the coupled electron pair approximation (CEPA), but it may be applied to *any* selected model space, involving configurations of various degrees of excitation. The efficiency of the proposed algorithms is illustrated on a series of test calculations performed on Be_2 , F_2 , N_2 , and NH_3 .

I. INTRODUCTION

Calculations of correlated electronic wave functions face qualitative difficulties regarding the dependance of the correlation energy upon the number of electrons (size consistency) and the additivity for system splittings into separated fragments (separability).¹ Despite major recent progress,² full configuration interaction calculations (FCI) are only possible for small numbers of electrons and limited basis sets. The linked cluster theorem³ insures the correctness (size consistency and separability into closed-shell fragments) of the perturbative expansion from a single determinant, but this expansion diverges when bonds are broken. Moving to quasidegenerate perturbation theory (to insure convergence in such cases) reintroduces qualitative difficulties, since a generalization of the linked cluster theorem is only possible for complete model spaces,⁴ which, due to intruder states problems, are in practice unusable.

Correct behavior is obtained in coupled cluster expansions⁵ of the wave function, at least for a single reference, but the method is rather demanding. Approximate size consistency and separability are recovered at low computational cost through the coupled electron pair approximation, originally proposed by Kelly,⁶ which has received various improvements.⁷ This method cancels the *unlinked diagrams* of the so-called double CI (CI of all doubly excited configurations) and omits most of the linked diagrams going through the quadruple excitations, which are sometimes important and which are included in the coupled cluster expansion.

One advantage of selected CI's is that they include all low orders effects involving the most important components of the wave function even if some of them are highly excited, provided that the selection has been made rationally (i.e., iteratively) as occurs in the CIPSI algorithm⁸ (CI from an iteratively selected zeroth-order space) and other multireference double CI (MRDCI) algorithms.^{9,10} The problem with selected CI's, as with all truncated CI's, is that they are not size consistent and, of course, not separable. Unless one goes very close to exact wave functions through the variational solution of selected spaces of over

10^5 determinants (a size which is now available through recently proposed direct selected CI algorithms^{11,12}), this problem is of considerable consequence and must be resolved. Corrections to the normalization of the wave function have long been proposed by Davidson and others,¹³ for the double CI from a single reference. They do not behave correctly when the number of particles increases and generalizations to multireference cases tend to give rather unreliable results.¹⁴

The present work offers an answer to this problem. It is based on the strategy of a recent generalization of effective Hamiltonians theory.¹⁵ Intermediate Hamiltonians¹⁶ are built on a N -dimensional model space, but they only produce n ($n < N$) significant eigenvectors and eigenvalues. In the present work we shall concentrate on the case where only one root is sought ($n=1$). The changes from the truncated to the effective Hamiltonian matrix (i.e., its dressing) will be minimal: It will only consist in a cancellation of all *unlinked* contributions. For the single state case, we shall show that this dressing of the CI matrix may be written through diagonal energy shifts, the expression of which is quite easy, and which may be calculated at a very low computational cost. A self-consistent version of this dressing is presented, since it depends on the eigenenergy and eigenvector coefficients of the matrix itself. It is shown that for the special case where the CI is limited to doubly excited configurations, the method provides an improved version of the coupled electron pair approximation, correctly including all the fourth-order exclusion-principle-violating (EPV) diagrams. In all cases the method is size consistent and strictly separable if localized MOs are used. Numerical illustrations are given and the strategy of implementation in direct selected CI algorithms is discussed.

II. PRINCIPLES

A. Intermediate effective Hamiltonians for a single-reference main model space

Let us consider an arbitrary space of configurations ϕ_i (the model space) of dimension $N+1$, and containing among them a special configuration ϕ_0 , which has a large

overlap with the eigenstate of H which we are interested in. In this case ϕ_0 defines the main model space associated with the projector $P_m = |\phi_0\rangle\langle\phi_0|$ and the ϕ_i 's ($i \neq 0$) define the so-called intermediate model space (projector $P_i = \sum_{i=1,N} |\phi_i\rangle\langle\phi_i|$). We want to build an intermediate Hamiltonian \tilde{H} onto the model space such that

$$\tilde{H}\tilde{\psi}_0 = \varepsilon_0\tilde{\psi}_0, \tag{1}$$

where, if $P = P_m + P_i$,

$$\tilde{\psi}_0 = P\psi_0, \tag{2}$$

ψ_0 being the exact eigenstate and ε_0 the exact eigenenergy of the full Hamiltonian

$$H\psi_0 = \varepsilon_0\psi_0. \tag{3}$$

The eigenenergy of \tilde{H} is exact and the eigenvector $\tilde{\psi}_0$ is the projection of the exact eigenvector onto the model space. The characteristics of the intermediate Hamiltonians have been discussed elsewhere¹⁶ and different variants have been proposed.¹⁷ They are all based on a power expansion in terms of λ^n ,

$$H = H_0 + \lambda V \tag{4}$$

from a zeroth order Hamiltonian H_0 , as usual in the quasidegenerate perturbation theory which leads to effective Hamiltonians. But while an N -dimensional model space effective Hamiltonian delivers N exact roots and N projected exact eigenvectors, the intermediate Hamiltonians provide only n (here one) exact roots.

Since we only consider one single root, one may notice that Eqs. (1)–(3) could be satisfied by an appropriate change of the diagonal matrix elements. The dressing matrix

$$\tilde{V} = \tilde{H} - PHP \tag{5}$$

may be purely diagonal

$$\langle\phi_i|\tilde{V}|\phi_j\rangle = \langle\phi_i|\tilde{V}|\phi_i\rangle\delta_{ij}, \tag{6}$$

since we seek only one eigenvalue ε_0 and the N components of $\tilde{\psi}_0$ on the intermediate model space determinants

$$\tilde{\psi}_0 = \phi_0 + \sum_{i=1,N} \tilde{C}_i\phi_i. \tag{7}$$

Knowledge of the eigenenergy ε_0 and of the coefficients \tilde{C}_i entirely defines the value of the diagonal energy shifts through Eq. (1). The ϕ_i component of this equation is written as

$$\langle\phi_0|H|\phi_i\rangle + \sum_{j \neq i} \langle\phi_j|H|\phi_i\rangle\tilde{C}_j + [\langle\phi_i|H|\phi_i\rangle + \langle\phi_i|\tilde{V}|\phi_i\rangle - \varepsilon_0]\tilde{C}_i = 0.$$

Hence,

$$\langle\phi_i|\tilde{V}|\phi_i\rangle = \varepsilon_0 - \langle\phi_i|H|\phi_i\rangle - \left[\langle\phi_0|H|\phi_i\rangle + \sum_{j \neq i} \langle\phi_j|H|\phi_i\rangle\tilde{C}_j \right] \tilde{C}_i^{-1}. \tag{8}$$

This result is valid only when a single root is sought. If one is interested in several roots, one may either change the

one-dimensional main model space and define another intermediate Hamiltonian, or change the dressing procedure. The original versions¹⁶ of intermediate Hamiltonians proposed perturbative definitions of \tilde{V} which concerned either the column(s) associated with the main model space PVP_m or the whole matrix PVP . A forthcoming paper will give the corresponding nondiagonal transpositions of the present work, which will be important for the simultaneous search of several roots. For the sake of simplicity we shall concentrate here on the purely diagonal dressing.

One should immediately notice that Eq. (8) is, in some sense, a self-consistent equation, the dressing being a function of the eigenenergy and of the eigenvector of the dressed matrix. But so far ε_0 and $\tilde{\psi}_0$ are not known and will be approached through the usual many-body perturbation development of E_0 and ψ from ϕ_0 . We shall use the Møller–Plesset definition of H_0 in terms of mono-electronic energies ε_r (Ref. 18)

$$H_0 = \sum_r \varepsilon_r a_r^+ a_r \tag{9}$$

and the Rayleigh–Schrödinger expansion which leads to the diagrammatic expansion of the energy and of the wave function. Our strategy in order to define \tilde{V} will be the following: We shall perform two perturbation expansions,

(i) the usual perturbation expansion with respect to $V = H - H_0$ and ϕ_0 ,

(ii) the perturbative development of ε_0 and $\tilde{\psi}_0$ from \tilde{H} and the same H_0 operator, now restricted to PH_0P , and the same zeroth order wave function ϕ_0 . This development is made inside the model space only and we shall proceed to a term by term identification of the two series.

Hence, we have, on one side, the usual expansion

$$H = H_0 + \lambda V, \tag{10}$$

$$\psi_0 = \Omega\phi_0, \tag{11}$$

$$\Omega = P_0 + \sum_{k=1,\infty} \lambda^k \Omega^k, \tag{12}$$

and on the other side

$$\tilde{H} = P(H_0 + \mu V)P + \mu\tilde{V} = PH_0P + \mu(PVP + \tilde{V}), \tag{13}$$

$$\tilde{\psi}_0 = \tilde{\Omega}\phi_0, \tag{14}$$

$$\tilde{\Omega} = P_0 + \sum_{l=1,\infty} \mu^l \tilde{\Omega}^l. \tag{15}$$

$\tilde{\Omega}$ must incorporate all the contributions of $P\Omega$ (and only them). The process will consist in assigning the Ω contributions to some well-defined contributions of $\tilde{\Omega}$. The correspondence is not order by order, but will obey the following requirement: A contribution to Ω^k must appear as a contribution of $\tilde{\Omega}^l$ with $l \leq k$.

The original publication on intermediate Hamiltonians presented in detail the expansion of $\tilde{\Omega}$ and \tilde{V} in the case of a full dressing.¹⁶ A forthcoming paper will present the full low-order expressions of the dressing for the case of a single root and diagonal dressing. Here our purpose is rather

modest: We simply want to incorporate the low-order corrections which will restore size consistency, i.e., which cancel the unlinked diagrams introduced by the diagonalization of *PHP*.

B. Suppression of unlinked contributions: A simple view

1. Perturbative approach

Let us suppose that the model space contains two doubly excited determinants ϕ_i and ϕ_j

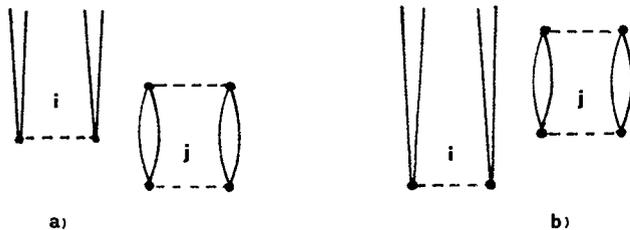
$$\phi_i = D_i^+ \phi_0,$$

$$\phi_j = D_j^+ \phi_0,$$

and that these two excitations are disconnected, i.e., they have neither holes nor particles in common. Then the quadruple excitation which combines D_i^+ and D_j^+ exists and gives a quadruply excited determinant

$$\phi_{i+j} = D_i^+ \phi_j = D_j^+ \phi_i = D_i^+ D_j^+ \phi_0.$$

Let us suppose that ϕ_{i+j} has not been included in the model space. Then the third order unlinked diagrams of the wave function ($P\Omega^{(3)}\phi_0$)



have not been considered in the diagonalization of *PHP*, since they go through the quadruply excited configuration ϕ_{i+j} . They would give rise to two contributions to the third order perturbed wave function

$$Xa = \frac{|\phi_i\rangle\langle\phi_i|H|\phi_{i+j}\rangle\langle\phi_{i+j}|H|\phi_j\rangle\langle\phi_j|H|\phi_0\rangle}{(E_0-E_i)(E_0-E_{i+j})(E_0-E_j)}, \quad (16)$$

$$Xb = \frac{|\phi_i\rangle\langle\phi_i|H|\phi_{i+j}\rangle\langle\phi_{i+j}|H|\phi_i\rangle\langle\phi_i|H|\phi_0\rangle}{(E_0-E_i)(E_0-E_{i+j})(E_0-E_i)}. \quad (17)$$

So

$$Xa + Xb = \frac{|\phi_i\rangle\langle\phi_i|H|\phi_0\rangle\langle\phi_0|H|\phi_j\rangle\langle\phi_j|H|\phi_0\rangle}{(E_0-E_i)(E_0-E_{i+j})} \times \left(\frac{1}{E_0-E_i} + \frac{1}{E_0-E_j} \right).$$

Notice that

$$Xa + Xb = \frac{|\phi_i\rangle\langle\phi_i|H|\phi_0\rangle\langle\phi_0|H|\phi_j\rangle\langle\phi_j|H|\phi_0\rangle}{(E_0-E_i)^2(E_0-E_j)} \quad (18)$$

if $E_0 - E_{i+j} = E_0 - E_i + E_0 - E_j$, as is the case for a Møller-Plesset definition of H_0 [Eq. (9)].

However, the diagonalization of *PHP* introduces unlinked third-order corrections to the wave function

$$Xc = \frac{|\phi_i\rangle\langle\phi_i|H|\phi_0\rangle\langle\phi_0|H|\phi_j\rangle\langle\phi_j|H|\phi_0\rangle}{(E_0-E_i)^2(E_0-E_j)} \quad (19)$$

through the term

$$-\frac{Q_0}{a} \psi^{(1)} \epsilon^{(2)},$$

where $Q_0 = 1 - P_0$,

$$\frac{Q_0}{a} = \sum_{i \neq 0} \frac{|\phi_i\rangle\langle\phi_i|}{E_0 - E_i}.$$

In a complete perturbation expansion, the three unlinked contributions should cancel out,

$$Xa + Xb + Xc = 0. \quad (20)$$

Since Xc is necessarily present in the diagonalization of *PHP* we should add contributions Xa and Xb through an adequate dressing of the matrix. There are several appropriate dressings as will be shown in detail elsewhere; here we shall concentrate on a diagonal dressing.

Contribution Xb is easily incorporated as a diagonal contribution since it could be expressed as

$$Xb = \frac{|\phi_i\rangle\langle\phi_i|\tilde{V}_1|\phi_i\rangle\langle\phi_i|H|\phi_0\rangle}{(E_0-E_i)^2} \quad (21)$$

with

$$\begin{aligned} \langle\phi_i|\tilde{V}_1|\phi_i\rangle &= \frac{\langle\phi_i|H|\phi_{i+j}\rangle\langle\phi_{i+j}|H|\phi_i\rangle}{(E_0-E_{i+j})} \\ &= \frac{\langle\phi_0|H|\phi_j\rangle\langle\phi_j|H|\phi_0\rangle}{(E_0-E_{i+j})}. \end{aligned} \quad (22)$$

This expression illustrates our strategy: a contribution to $\Omega^{(3)}$ appears as a contribution to $\tilde{\Omega}^{(2)}$ through the inclusion of λ^2 , a term (of second order) as a first order correction \tilde{V} .

In the original formulation,¹⁶ contribution Xa was incorporated through the definition of an off-diagonal element $\langle\phi_i|\tilde{V}|\phi_j\rangle$. Here it will be incorporated through a diagonal dressing

$$Xa = \frac{|\phi_i\rangle\langle\phi_i|\tilde{V}_2|\phi_i\rangle\langle\phi_i|H|\phi_0\rangle}{(E_0-E_i)(E_0-E_i)} \quad (23)$$

which implies

$$\begin{aligned} \langle\phi_i|\tilde{V}_2|\phi_i\rangle &= \frac{\langle\phi_i|H|\phi_{i+j}\rangle\langle\phi_{i+j}|H|\phi_j\rangle\langle\phi_j|H|\phi_0\rangle}{(E_0-E_{i+j})(E_0-E_j)} \\ &\times \frac{E_0-E_i}{\langle\phi_i|H|\phi_0\rangle}. \end{aligned} \quad (24)$$

Noting that

$$\langle\phi_i|\tilde{V}|\phi_{i+j}\rangle = \langle\phi_0|H|\phi_j\rangle,$$

$$\langle\phi_{i+j}|\tilde{V}|\phi_j\rangle = \langle\phi_i|H|\phi_0\rangle,$$

one obtains

$$\langle\phi_i|\tilde{V}_2|\phi_i\rangle = \frac{\langle\phi_0|H|\phi_j\rangle\langle\phi_j|H|\phi_0\rangle}{(E_0-E_{i+j})} \left(\frac{E_0-E_i}{E_0-E_j} \right). \quad (25)$$

Thus

$$Xa + Xb = \frac{|\phi_i\rangle\langle\phi_i|\tilde{V}|\phi_i\rangle\langle\phi_i|H|\phi_0\rangle}{(E_0 - E_i)(E_0 - E_i)}$$

with

$$\begin{aligned} \langle\phi_i|\tilde{V}|\phi_i\rangle &= \langle\phi_i|\tilde{V}_1 + \tilde{V}_2|\phi_i\rangle \\ &= \frac{\langle\phi_0|H|\phi_j\rangle\langle\phi_j|H|\phi_0\rangle}{(E_0 - E_{i+j})} \left[1 + \frac{(E_0 - E_i)}{(E_0 - E_j)} \right]. \end{aligned} \quad (26)$$

In the case of additivity of the energy denominators

$$E_0 - E_{i+j} = E_0 - E_i + E_0 - E_j,$$

one may re-express $\langle\phi_i|\tilde{V}|\phi_i\rangle$ as

$$\langle\phi_i|\tilde{V}|\phi_i\rangle = \frac{\langle\phi_0|H|\phi_j\rangle\langle\phi_j|H|\phi_0\rangle}{(E_0 - E_j)}. \quad (27)$$

[Otherwise it would be written as

$$\langle\phi_i|\tilde{V}|\phi_i\rangle = \frac{\langle\phi_0|H|\phi_j\rangle\langle\phi_j|H|\phi_0\rangle}{(E_0 - E_j)} \left(\frac{E_0 - E_i + E_0 - E_j}{E_0 - E_{i+j}} \right).]$$

This is a perturbative dressing of *PHP* which will cancel all the unlinked diagrams where the closed part involving the double excitation D_j^+ would appear.

2. Self-consistent approach

Of course the correction

$$\frac{\langle\phi_0|H|\phi_j\rangle\langle\phi_j|H|\phi_0\rangle}{E_0 - E_j}$$

will diverge when ϕ_j tends to be degenerate with ϕ_0 ($E_0 - E_j$ tending to zero). This is why one may be tempted to use an alternative expression; noting that in the intermediate normalization

$$\tilde{C}_j = \frac{\langle\phi_j|H|\phi_0\rangle}{E_0 - E_j} + \text{higher order terms}, \quad (28)$$

one may write the dressing of ϕ_i under the effect of ϕ_{i+j} as

$$\langle\phi_i|\tilde{V}|\phi_i\rangle = \langle\phi_0|H|\phi_j\rangle\tilde{C}_j \quad (29)$$

[or eventually

$$\langle\phi_i|\tilde{V}|\phi_i\rangle = \langle\phi_0|H|\phi_j\rangle\tilde{C}_j \left(\frac{E_0 - E_i + E_0 - E_j}{E_0 - E_{i+j}} \right)$$

if the energy denominators additivity is not verified].

This self-consistent formulation will avoid divergence problems and will include higher order corrections, as discussed later. It will also insure strict separability, as shown below for localized MO treatments.

We have considered so far an elementary problem, with two disconnected double excitations $\phi_i = D_i^+ \phi_0$, $\phi_j = D_j^+ \phi_0$ and the effect of the quadruply excited configuration $\phi_{i+j} = D_i^+ D_j^+ \phi_0$. Let us now consider real problems and various choices of model spaces.

III. APPLICATION TO SINGLE AND DOUBLE CI

A. Derivation

Let us consider the case where the intermediate model space includes *all* the doubly excited configurations and *only* them. Then in the self-consistent version of the diagonal dressing, the diagonal energy of the determinant ϕ_i will be shifted under the effect of all the possible quadruply excited determinants $\phi_{i+j} = D_j^+ \phi_i$, where a double excitation D_j^+ is possible on ϕ_i if and only if D_j^+ and D_i^+ are disconnected. In the following, $\mathcal{D}(i)$ will be used to characterize the set of double substitutions which are disconnected with respect to D_i^+ . The dressing will be expressed as

$$\langle\phi_i|\tilde{V}|\phi_i\rangle = \sum_{j \in \mathcal{D}(i)} \langle\phi_0|H|D_j^+ \phi_0\rangle \tilde{C}_j, \quad (30)$$

where \tilde{C}_j is the coefficient of $\phi_j = D_j^+ \phi_0$ in the eigenvector $\tilde{\psi}$ in the intermediate normalization [Eq. (7)].

It is possible to express Eq. (30) by noting that, if the Brillouin theorem is satisfied, the exact correlation energy is

$$\tilde{E} = \sum_j \langle\phi_0|H|D_j^+ \phi_0\rangle \tilde{C}_j. \quad (31)$$

(This simply reflects the well-known perturbative equations

$$E = \sum_n E^{(n)},$$

$$E^{(n)} = \langle\phi_0|V|\psi^{(n-1)}\rangle = \langle\phi_0|V|P_{\text{Doubles}}\psi^{(n-1)}\rangle).$$

Then

$$\langle\phi_i|\tilde{V}|\phi_i\rangle = \tilde{E} - \sum_{j \notin \mathcal{D}(i)} \langle\phi_0|H|D_j^+ \phi_0\rangle \tilde{C}_j. \quad (32)$$

The exact dressing of the $\langle\phi_i|\tilde{H}|\phi_i\rangle$ term can be expressed as the exact correlation energy minus the contributions of the double excitations which are outside $\mathcal{D}(i)$ and which are much less numerous than the total number of double excitations. Actually

$$D_j^+ \phi_i = D_j^+ D_i^+ \phi_0 = 0$$

if and only if the operation D_j^+ implies at least one hole or one particle already created in ϕ_i .

B. Strict separability of the energy

We should notice that we now have a self-consistent Hamiltonian, which is itself a function of both its eigenenergy $\langle\phi_0|H|\phi_0\rangle + \tilde{E}$ and its eigenvector \tilde{C}

$$\tilde{H} = \tilde{H}(\tilde{E}, \tilde{C}), \quad (33)$$

$$\tilde{H}\tilde{C} = (\langle\phi_0|H|\phi_0\rangle + \tilde{E})\tilde{C}. \quad (34)$$

Expressions (30)–(32) lead to the cancellation of the unlinked fourth-order corrections, and thus *size-extensivity* is guaranteed. We shall demonstrate that strict *separability* is also assured if the system under study is composed of two noninteracting *A* and *B* fragments and if one uses *localized*

molecular orbitals, located either on A or on B . Then one may split the double excitations into double excitations on A (say i_A) and double excitations on B (say i_B). For fragment A alone, Eq. (34) will be written, for the line i_A ,

$$\begin{aligned} &\langle \phi_{i_A} | H | \phi_{0_A} \rangle + \sum_{k_A \neq i_A} \langle \phi_{i_A} | H | \phi_{k_A} \rangle \tilde{C}_{k_A} \\ &+ \left(\langle \phi_{i_A} | H | \phi_{i_A} \rangle + \tilde{E}_A - \sum_{j_A \in \mathcal{D}(i_A)} \langle \phi_0 | H | \phi_{j_A} \rangle \tilde{C}_{j_A} \right. \\ &\left. - \langle \phi_{0_A} | H | \phi_{0_A} \rangle - \tilde{E}_A \right) \tilde{C}_{i_A} = 0, \end{aligned}$$

i.e.,

$$\begin{aligned} &\langle \phi_{i_A} | H | \phi_{0_A} \rangle + \sum_{k_A \neq i_A} \langle \phi_{i_A} | H | \phi_{k_A} \rangle \tilde{C}_{k_A} \\ &+ \left(\langle \phi_{i_A} | H | \phi_{i_A} \rangle - \langle \phi_{0_A} | H | \phi_{0_A} \rangle \right. \\ &\left. - \sum_{j_A \in \mathcal{D}(i_A)} \langle \phi_0 | H | \phi_{j_A} \rangle \tilde{C}_{j_A} \right) \tilde{C}_{i_A} = 0. \quad (35) \end{aligned}$$

(Notice the nonlinear character of the equation.) For the supersystem ($A+B$) the corresponding eigenvalue equation

$$[\tilde{H}' - (\langle \phi'_0 | H | \phi'_0 \rangle + \tilde{E}')] \tilde{C}' = 0$$

will be written for the line i_A

$$\begin{aligned} &\langle \phi'_{i_A} | H | \phi'_0 \rangle + \sum_{k_A \neq i_A} \langle \phi'_{i_A} | H | \phi'_{k_A} \rangle \tilde{C}'_{k_A} + \sum_{j_B} \langle \phi'_{i_A} | H | \phi'_{j_B} \rangle \tilde{C}'_{j_B} \\ &+ \left(\langle \phi'_{i_A} | H | \phi'_{i_A} \rangle + \tilde{E}' - \sum_{j_A \in \mathcal{D}(i_A)} \langle \phi'_0 | H | \phi'_{j_A} \rangle \tilde{C}'_{j_A} \right. \\ &\left. - \sum_{l_B \in \mathcal{D}(i_A)} \langle \phi'_0 | H | \phi'_{l_B} \rangle \tilde{C}'_{l_B} - \tilde{E}' - \langle \phi'_0 | H | \phi'_0 \rangle \right) \tilde{C}'_{i_A} = 0. \quad (36) \end{aligned}$$

For separated fragments,

$$\langle \phi_{i_A} | H | \phi_{j_B} \rangle = 0 \quad \forall j_B,$$

$$l_B \in \mathcal{D}(i_A) \quad \forall l_B,$$

$$\langle \phi'_{i_A} | H | \phi'_0 \rangle = \langle \phi_{i_A} | H | \phi_{0_A} \rangle,$$

$$\langle \phi'_{i_A} | H | \phi'_{k_A} \rangle = \langle \phi_{i_A} | H | \phi_{k_A} \rangle,$$

$$\langle \phi'_{i_A} | H | \phi'_{i_A} \rangle - \langle \phi'_0 | H | \phi'_0 \rangle = \langle \phi_{i_A} | H | \phi_{i_A} \rangle - \langle \phi_{0_A} | H | \phi_{0_A} \rangle.$$

Hence, Eq. (36) may be written as

$$\begin{aligned} &\langle \phi_{i_A} | H | \phi_{0_A} \rangle + \sum_{k_A \neq i_A} \langle \phi_{i_A} | H | \phi_{k_A} \rangle \tilde{C}'_{k_A} \\ &+ \left[\langle \phi_{i_A} | H | \phi_{i_A} \rangle - \langle \phi_{0_A} | H | \phi_{0_A} \rangle \right. \\ &\left. - \sum_{j_A} \langle \phi_{0_A} | H | \phi_{j_A} \rangle \tilde{C}'_{j_A} \right] \tilde{C}'_{i_A} = 0, \end{aligned}$$

which is identical to Eq. (35) when $\tilde{C}'_{i_A} = \tilde{C}_{i_A}$. Equation (36) is automatically satisfied when the amplitudes of the (localized) double excitations in the supersystem are those of the isolated systems. Then

$$\tilde{C}'_{i_A} = \tilde{C}_{i_A} \quad \text{and} \quad \tilde{C}'_{j_B} = \tilde{C}_{j_B} \quad \text{imply} \quad \tilde{E}' = \tilde{E}_A + \tilde{E}_B$$

and so the strict additivity of the correlation energy or exact separability is verified.

Theorem: Provided that localized molecular orbitals are used, the self-consistently dressed double CI matrix insures the exact additivity of energy, i.e., the correlation energy for a supersystem $A+B$ when the interaction between A and B vanishes is exactly equal to the sum of correlation energies for the systems A and B calculated separately with the same procedure as long as the double CI matrix is dressed according to Eq. (27).

Exact separability insures size extensivity (which is a weaker requirement). For independent electron pairs (n He atoms or H_2 molecules), the proposed self-consistent size-consistent double CI [(SC)²DCI] algorithm gives the exact energy since for each subsystem the double CI is the full CI.

C. Practical implementation

Let us call no and nv the number of occupied and virtual MO's of the problem ($2no$ = number of electrons, $no + nv$ = size of the basis set). The number of doubly excited determinants increases in proportion to $(no \cdot nv)^2$. Equation (30) would require approximately the same number of double excitations to be performed on each doubly excited configuration, and the computation time of the dressing would increase in proportion to $(no \cdot nv)^4$. Equation (31) reduces the computing time to $no \cdot nv^2$ (one hole appears in both D_i^+ and D_j^+) + $no^2 nv$ (one particle in both D_i^+ and D_j^+). The dressing may, however, be performed much more rapidly by a preliminary calculation. The summation

$$= \sum_{j \in \mathcal{D}(i)} \langle \phi_0 | H | \phi_j \rangle \tilde{C}_j$$

in Eq. (32) is the summation of the exclusion-principle-violating (EPV) diagrams of order 4 (and higher degrees incorporated by the self-consistency). For a purely perturbative infinite summation of EPV diagrams¹⁹ M. B. Lepetit and one of the present authors (J.P.M.) have proposed a practical method which may be used here. It consists in storing partial correlation energies, for each spin orbital p (occupied or virtual)

$$e_1(p) = \sum_j \langle \phi_0 | H | D_j^+ \phi_0 \rangle \tilde{C}_j$$

$$D_j^+ \text{ implying } p; \quad (37)$$

—all pairs of spin orbitals (p, q)

$$e_2(p, q) = \sum_j \langle \phi_0 | H | D_j^+ \phi_0 \rangle \tilde{C}_j$$

$$D_j^+ \text{ implying } p \text{ and } q; \quad (38)$$

—all triplets of spin-orbitals (p, q, r)

$$e_3(p, q, r) = \sum_j \langle \phi_0 | H | D_j^+ \phi_0 \rangle \tilde{C}_j$$

$$D_j^+ \text{ implying } p, q \text{ and } r. \quad (39)$$

Notice that in the $e_2(p, q)$ arrays p and q may be occupied or virtual MOs, of the same or different spins. In the three-index array $e_3(p, q, r)$, either one of the three indexes must be an occupied MO and the two others virtual MOs, or the reverse (two holes, one particle). These arrays are not very large since they are shorter ($\sim nonv^2$) than the \tilde{C} vector.

It is now easy to see that if the doubly excited determinant is

$$\phi_i = a_a^+ a_b^+ a_v a_t \phi_0 = \phi \begin{pmatrix} a, b \\ t, v \end{pmatrix}$$

($v, t =$ occupied MOs, $a, b =$ virtual MOs), Eq. (32) may be expressed as

$$\langle \phi_i | \tilde{V} | \phi_i \rangle = \tilde{E} - e_1(t) - e_1(v) - e_1(a) - e_1(b) + e_2(t, v)$$

$$+ e_2(a, b) + e_2(t, a) + e_2(t, b) + e_2(v, a)$$

$$+ e_2(v, b) - e_3(t, v, a) - e_3(t, v, b) - e_3(t, a, b)$$

$$- e_3(v, a, b) + \tilde{C}_i \langle \phi_0 | H | \phi_i \rangle. \quad (40)$$

$$\langle \phi_i | H | \phi_0 \rangle + \sum_j \langle \phi_i | H | \phi_j \rangle \tilde{C}_j + (\langle \phi_i | H | \phi_i \rangle - \langle \phi_0 | H | \phi_0 \rangle - e_1(t) - e_1(v) - e_1(a) - e_1(b) + e_2(t, v) + e_2(a, b) + e_2(t, a)$$

$$+ e_2(t, b) + e_2(v, a) + e_2(v, b) - e_3(t, v, a) - e_3(t, v, b) - e_3(t, a, b) - e_3(v, a, b) + \tilde{C}_i \langle \phi_0 | H | \phi_i \rangle) \tilde{C}_i = 0. \quad (41)$$

This equation is surprisingly similar to a coupled electron pair approximation (CEPA) equation. The CEPA-O⁶ equation simply omits all e quantities [and is invariant under the unitary transformations of occupied (or virtual) MOs]. The CEPA-2²² version simply considers $-e_2(t, v)$. The CEPA-3²³ version, although it is frequently expressed in terms of orbital contributions rather than in terms of spin orbitals, may be seen as considering only $-e_1(t) - e_1(v) + e_2(t, v)$ in Eq. (40). It is the closest version to our proposal, which may be considered as a correct CEPA formulation, dealing exactly with all EPV diagrams. In fact, holes and particles play a symmetrical role in the many-body problem and the usual CEPA formulations break that symmetry, which is crucial for EPV conditions (the violation concerning particles as well as holes). In the perturbative tradition that symmetry was maintained, as is

This equation simply takes into account the successive double countings. The e arrays are calculated for each iteration; using Eq. (40) the calculation of the diagonal dressing is of negligible computational cost.

D. Comparison with other methods

One may first discuss the connection between our proposal and usual Davidson corrections. Since these corrections involve the SDCI wave function ψ_{SD} , one should consider the first iteration of our procedure. If one uses Eq. (32) and neglects the EPV terms

$$\langle \phi_i | \tilde{V} | \phi_i \rangle = \tilde{E}.$$

Then

$$\langle \psi | \tilde{V} | \psi \rangle = \sum_i \tilde{C}_i^2 \langle \phi_i | \tilde{V} | \phi_i \rangle = \tilde{E} \sum_i \tilde{C}_i^2$$

in the intermediate normalization. Hence,

$$\Delta E_{\text{corr}} = \frac{1 - C_0^2}{C_0^2} E_{\text{corr}},$$

which is the so-called renormalized Davidson correction.^{20,21} At the first iteration, our energy differs by the consideration of all EPVs. The following iterations change the content of the wave function.

Let us consider now the connexion with the CEPA algorithms. Combining Eq. (34) and (40) one obtains for each configuration

$$\phi_i = \phi \begin{pmatrix} a, b \\ t, v \end{pmatrix},$$

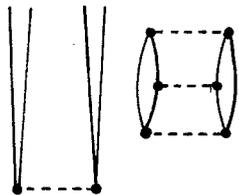
evident in Ref. 19 or in previous proposals by Kelly^{6,24} which have not received the attention they deserved. The exact separability condition required to include all terms from Eqs. (32) or (40), and CEPA deviates from strict additivity (but it is size extensive in all its forms). The relation between the Davidson correction and the CEPA methods has been thoroughly studied in a series of papers by Dykstra *et al.*²⁵ The coupled pair functional (CPF),²⁶ the relation of which with CEPA-1 has been clarified by its authors, goes through a modification of the norm in the SDCI functional in order to achieve size extensivity. The weights of the determinants in the norm are not uniform but they again essentially depend on the *holes*. Some conditions have been introduced to obtain the unitary invariance with respect to occupied orbitals for identical pairs.

Our formulation of course is not invariant under rota-

tion of the orbitals, neither of the occupied nor of the virtuals ones. The partition between the EPV and the other linked diagrams is not invariant. This is one defect of our (SC)²DCI with respect to the coupled cluster formalism, since that method includes all the linked fourth-order diagrams which we have omitted. However our proposal offers a much lower computational cost, since it basically reduces to a (S)DCI algorithm. Inclusion of the predominant fourth-order diagrams will be the subject of Sec. IV.

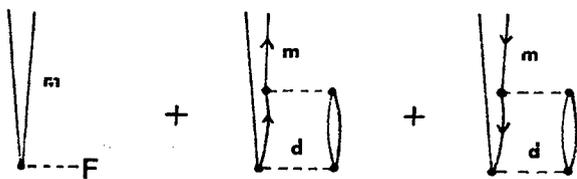
Compared to the many-body perturbation expansion the present proposal includes all the third-order diagrams and all infinite order contributions staying within the model space. The contribution of triply (*vide infra*) and quadruply excited determinants is reduced to the EPV diagrams. The normal linked contributions involving triples and quadruples are lacking. Of course this is a defect to be rectified. One advantage of our approach is its nonperturbative character and its ability to treat nearly degenerate situations where perturbation treatments diverge. It is to be noted that for physically noninteracting electron pairs the (SC)²DCI result is exact.

The substitution of the second order dressing of a determinant ϕ_i by a self-consistent expression $\langle \phi_0 | H | \phi_j \rangle \tilde{C}_j$ introduces higher-order corrections, as already mentioned (i.e., closed diagrams of the energy in which the determinant ϕ_j appears between the last two interaction lines). One should, however, notice that the exclusion principle is only dealt with correctly for the second-order contribution through Eq. (40), since other holes and particles appear on the lower parts of the closed diagram, and their incompatibility with the holes and particles of ϕ_i would be difficult to fully take care of.

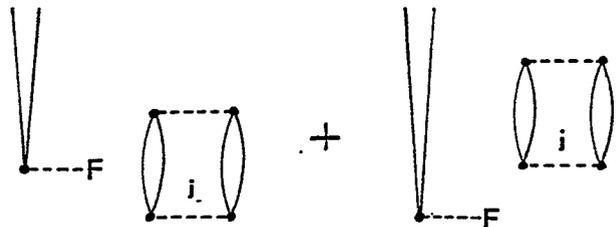


E. Inclusion of single determinants

In practice, all the calculations presented in the next section (III F) concern single and double CI's, and include a dressing of the energies of the singly excited determinants. The low order contributions to the coefficients on these singly excited determinants ϕ_m are



The first contribution is zero when ϕ_0 is the Hartree-Fock determinant. It is now clear that one must introduce the third-order effect of unlinked contributions caused by the triply excited configuration $\phi_{m+j} = D_j^+ \phi_m$



in order to cancel the undesired unlinked contribution

$$-\frac{Q_0}{a} |\phi_m\rangle \langle \phi_m | \psi^{(1)} \rangle \epsilon^{(2)}.$$

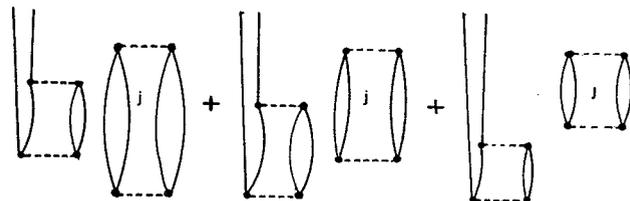
If

$$\phi_m = \phi \begin{pmatrix} a \\ t \end{pmatrix}$$

implies the t hole and the a particle, this effect may be obtained by defining

$$\langle \phi_m | \tilde{V} | \phi_m \rangle = \tilde{E} - e1(t) - e1(a) + e2(t,a). \quad (42)$$

For the second order contribution $C_m^{(2)}$ to C_m , one should again add three contributions,



where j concerns a double excitation D_j^+ . The numerators are identical and could be factorized. The energy denominators are

$$\frac{1}{\Delta j(\Delta d + \Delta j)(\Delta j + \Delta m)} + \frac{1}{\Delta d(\Delta d + \Delta j)(\Delta j + \Delta m)} + \frac{1}{\Delta d \Delta m(\Delta j + \Delta m)}$$

$$= \frac{1}{(\Delta m + \Delta m)\Delta j \Delta d} + \frac{1}{(\Delta m + \Delta j)\Delta d \Delta m} = \frac{1}{\Delta m \Delta j \Delta d},$$

where $\Delta m, \Delta d, \Delta j$ are energy differences relative to the single excitation $M_m^+ = a_t^+ a_p$, D_d^+ appearing in the open part of the above diagrams and D_j^+ , respectively. Then the contribution of the three last disconnected diagrams will give

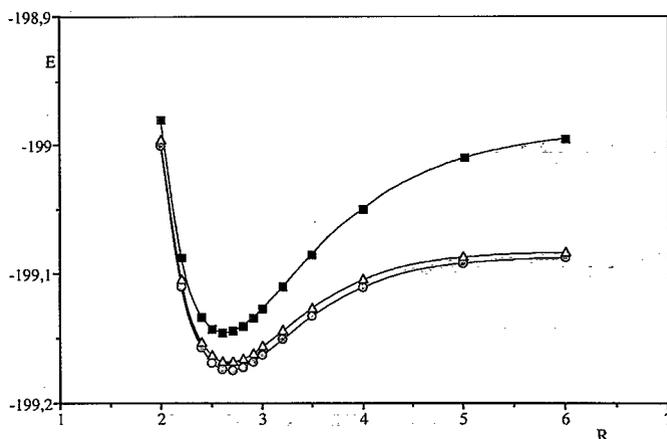


FIG. 1. Potential curve of F_2 : ■ SDCI, Δ (SC)²DCI, \circ CC-SD (Ref. 27).

TABLE I. Comparison of correlation energies obtained for F_2 at different levels. The first column contains the HF values, the second one the SDCI contribution to correlation and the third one the SDCC value (Ref. 27). The last two columns give the results obtained with shifted diagonal elements at iteration zero ($\langle \psi | \tilde{H} - E_{\text{SCF}} | \psi \rangle$) or at convergence ($\Delta \tilde{E}$). In column five and seven are given in parentheses (in 10^{-4} a.u.) the differences with column three.

R (bohr)	E_{SCF}	ΔE_{SDCI}	ΔE_{SDCC}	$\langle \psi \tilde{H} - E^0 \psi \rangle$	$\Delta \tilde{E}_{(\text{SC})^2\text{CI}}$
2.0	-198.5973	-0.3829	-0.4034	-0.3984 (50)	-0.3989 (49)
2.2	-198.6599	-0.3912	-0.4138	-0.4083 (55)	-0.4088 (50)
2.4	-198.7331	-0.4003	-0.4237	-0.4193 (44)	-0.4200 (37)
2.5	-198.7374	-0.4050	-0.4317	-0.4252 (65)	-0.4259 (58)
2.6	-198.7357	-0.4098	-0.4381	-0.4312 (69)	-0.4321 (60)
2.7	-198.7297	-0.4146	-0.4446	-0.4375 (71)	-0.4385 (61)
2.8	-198.7208	-0.4195	-0.4513	-0.4438 (75)	-0.4450 (63)
2.9	-198.7098	-0.4243	-0.4581	-0.4504 (77)	-0.4518 (63)
3.0	-198.6977	-0.4292	-0.4650	-0.4570 (80)	-0.4587 (63)
3.5	-198.6316	-0.4536	-0.5016	-0.4924 (92)	0.4954 (62)
4.0	-198.5718	-0.4778	-0.5391	-0.5298 (93)	-0.5335 (56)
5.0	-198.4897	-0.5209	-0.6032	-0.5980 (52)	-0.5985 (47)
6.0	-198.4433	-0.5519	-0.6489	-0.6453 (36)	-0.6404 (85)
10.0	-198.3905	-0.5951		-0.7052	-0.6922

$$\frac{\langle \phi_m | \langle \phi_m | H | D_d^\dagger \phi_0 \rangle \langle D_d^\dagger \phi_0 | H | \phi_0 \rangle \cdot \langle \phi_0 | H | D_j^\dagger \phi_0 \rangle \langle D_j^\dagger \phi_0 | H | \phi_0 \rangle}{\Delta m \Delta d \Delta j}$$

i.e., $C_m^{(2)} \langle \phi_0 | H | D_j^\dagger \phi_0 \rangle \tilde{C}_j$.

The dressing of the singly excited determinants to cancel the unlinked effect of the triples (but also of intermediate quadruples) follows the same logic as that of the doubly excited determinants. In the above procedure, in principle, the summation of the D_j^\dagger processes should include the processes which are possible on both ϕ_m and ϕ_d , if one wants to benefit from the summation without omitting EPV diagrams. In fact, for the sake of simplicity, we have used Eq. (33) even when Brillouin's theorem is satisfied, which means that a few fifth-order EPV diagrams on the energy are missing. Since $C_m^{(2)}$ remains small, this should not introduce significant errors.

F. Results

Strict additivity is, of course, verified (it is a test of the correctness of the program) when self-consistency of the dressing is achieved. In general, 3–5 iterations are sufficient to insure self-consistency. The importance of self-consistency increases with the number of particles and the degree of correlation, since the change from ψ (eigenfunction of $P_0 H P_0$) to $\tilde{\psi}$ increases. For many weakly correlated systems with a small number of electrons, the inclusion of the dressing at the first order would already be sufficient

$$\Delta E_{\text{sc}} = \langle \tilde{\psi} | \tilde{V} | \tilde{\psi} \rangle = \sum_i C_i^2 \langle \phi_i | \tilde{V} | \phi_i \rangle$$

once the coefficients are written in the intermediate normalization. However, little is gained if one stops at this step, which merely represents an improved Davidson correction.

Three examples will be given, namely, three potential curves corresponding to a single bond (F_2),²⁷ a dispersion

interaction—at the SDCI level at least—(Be_2),²⁸ and a triple bond (N_2).²⁷ The first of these should be dealt with correctly by our (SC)²SDCI description. Figure 1 and Table I compare the SDCI results with our results and the SD coupled cluster values. One immediately sees that the (SC)²SDCI only differs from the CC values by a small and almost constant energy difference (0.006 ± 0.002 a.u.). The spectroscopic constants (Table II) of CC and (SC)²SDCI are nearly identical while the SDCI values were very different. It should be noticed that our procedure converges nicely at large interatomic distances, while the CC algorithm apparently diverges for R larger than 6 bohr. The value for 10 bohr was obtained without any difficulty. The difference between $\langle \tilde{\psi} | H - E_{\text{SCF}}^0 | \tilde{\psi} \rangle$ and \tilde{E} (i.e., the effect of self-consistency) is small ($\sim 1.10^{-3}$ a.u.), but increases and changes its sign when the bond lengthens, i.e., when the correlation is stronger and when the quality of ψ becomes poorer and poorer.

For Be_2 neither the SDCI nor the SDCC approaches are able to reproduce the experimental curve, which requires introducing triples and quadruples. At this step it becomes interesting to see how far the (SC)²SDCI deviates from the SD-CC,²⁸ at least when localized MOs are used. The (SC)²SDCI energies are above the SD-CC values by

TABLE II. Spectroscopic constants of F_2 calculated at the SDCI, (SC)²SDCI, and SD-CC (Ref. 27) levels.

	R_e (Å)	D_e (eV)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)
SDCI	1.385	4.491	1052	9.90
(SC) ² SDCI	1.407	2.306	947	10.87
SD-CC	1.410	2.362	945	12.6
Expt.	1.41	1.66	871	14.3

TABLE III. Potential energy values obtained for N₂. Same comments than for Table I.

R (bohr)	E _{SCF}	ΔE _{SDCI}	ΔE _{SDCC} ^a	⟨ψ $\tilde{H}-E^0$ ψ⟩	Δ $\tilde{E}_{(SC)^2SDCI}$
1.500	-108.437 26	-0.262 79	-0.275 43	-0.272 37	(31) -0.272 52 (29)
1.800	-108.904 55	-0.283 39	-0.300 17	-0.295 87	(43) -0.296 11 (41)
1.900	-108.951 42	-0.291 18	-0.309 73	-0.304 88	(48) -0.305 14 (46)
2.000	-108.968 01	-0.299 39	-0.319 96	-0.314 40	(56) -0.314 74 (52)
2.068	-108.966 62	-0.305 20	-0.327 26	-0.321 19	(61) -0.321 56 (57)
2.500	-108.835 61	-0.344 93	-0.379 43	-0.369 00	(104) -0.370 15 (93)
2.750	-108.726 23	-0.368 77	-0.412 96	-0.399 02	(139) -0.401 41 (115)
3.000	-108.618 85	-0.392 07	-0.448 17	-0.429 34	(188) -0.434 60 (136)
4.000	-108.289 43	-0.472 28	-0.639 83	-0.551 84	(878) -0.686 33 (465)

^aReference 21.

32×10^{-6} a.u. at 4.5 bohr and 36×10^{-6} a.u. at 8.5 bohr, which is a surprisingly low difference.

Application of a procedure based on doubles only to a triple bond (N₂) is somewhat paradoxical, since some quadruples and hexaexcited determinants become degenerate with ϕ_0 at long distances. The calculation has been performed in order to compare with the results of CC-SD presented by Laidig *et al.*²⁷ Table III and Fig. 2 again show the similarity between the two methods. The difference between them is less constant than for F₂, it increases from 3×10^{-3} a.u. at $R=1.5$ bohr to 14×10^{-3} a.u. at $R=3$ bohr. The effect of iterating the coefficients also increases rapidly while the bond breaks. At 4 bohr, our procedure gives signs of divergence, as does CC-SD at 5 bohr. The spectroscopic characteristics of the potential well (Table IV) are then very similar to those of the CC-SD.²⁷

IV. GENERALIZATION TO ARBITRARY MANY REFERENCE APPROACHES AND TO SELECTED CI'S

The main defect of the (SC)²SDCI is the lack of the most important linked fourth-order diagrams going through triples and quadruples. It is tempting to see whether one could generalize our proposal to *selected* CI's involving, for instance, the triples and quadruples of major amplitude in the wave function which could first be selected through a perturbative process such as in the CIPSI algorithm. However, we shall first consider the case where

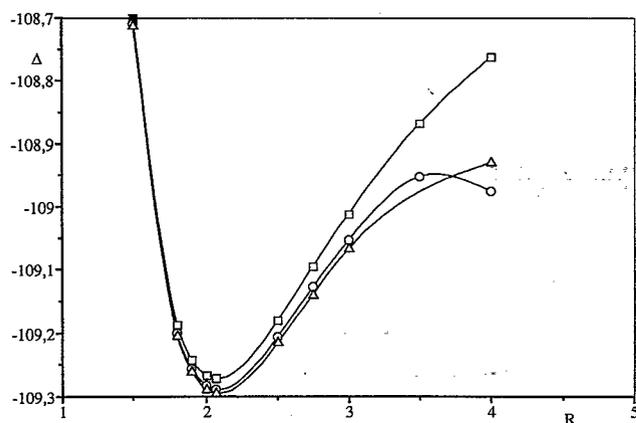


FIG. 2. Potential curves of N₂: □ SDCI, ○ (SC)²SDCI, Δ CC-SD (Ref. 27).

all configurations up to the quadruples (or hexaexcited ones) are included, to generalize the dressing. Then we shall consider the case where the model space involves, besides the doubles, a fraction of the triples, quadruples, or determinants of higher degree of excitation. Finally, we shall propose a procedure to dress *any selected* CI. A few illustrative results will be presented.

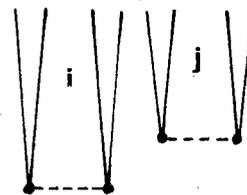
A. Dressing of an SDTQCI

One may imagine that for a small enough problem, a variational CI including all configurations up to the quadruples (or up to the six-times excited determinants) is possible. Then it is clear that

—the singles and doubles should not be dressed since their double excitations cause a return to model space configurations,

—the triples and quadruples (or more generally the most excited configurations) should be dressed by the double excitations acting on them and leading to penta- and hexa-excited determinants. In the previous section only two unlinked diagrams had to be considered to cancel the effect of normalization. Here if we consider a perturbative second order contribution to the coefficient of a quadruply excited configuration

$$\phi_{i+j} = D_j^+ D_i^+ \phi_0$$

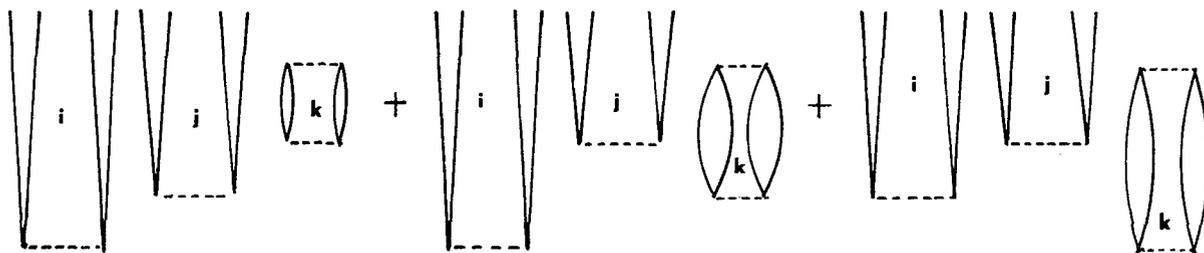


the action of hexaexcited configurations $D_k^+ \phi_{i+j}$ produces three different diagrams

TABLE IV. Spectroscopic constants of N₂ (cm⁻¹ and Å).

	SD-CI	(SC) ² SD-CI	SD-CC ^a	Expt. ^a
r_e	1.0958	1.1012	1.1037	1.0977
ω_e	24.63	24.02	23.76	23.59
$\omega_e x_e$	11.74	12.41	12.67	14.3
β_e	2.005	1.985	1.976	1.998
$10^{-3} \alpha_e$	15.45	16.18	16.42	17.3

^aReference 27.



where the last interaction is contained within the closed part. These diagrams differ by the position of the first interaction of the closed part. The numerators are always identical and the energy denominators must be added together as occurred in the case of the singly excited determinants. If we call

$$h_i = \langle \phi_0 | H | D_i^+ \phi_0 \rangle$$

$$\Delta i = \langle \phi_0 | H_0 | \phi_0 \rangle - \langle D_i^+ \phi_0 | H_0 | D_i^+ \phi_0 \rangle$$

(and similarly for j and k), the three diagrams give

$$\frac{h_i h_j h_k^2}{(\Delta i + \Delta j)(\Delta i + \Delta j + \Delta k)} \{ [\Delta i(\Delta i + \Delta j)]^{-1} + [\Delta i(\Delta i + \Delta k)]^{-1} + [\Delta k(\Delta i + \Delta k)]^{-1} \} = \frac{h_i h_j h_k^2}{\Delta i(\Delta i + \Delta j)^2 \Delta k},$$

which cancels the contribution of

$$-\frac{Q_0}{a} |\phi_{i+j}\rangle \langle \phi_{i+j} | \psi^{(2)} \rangle \frac{\langle \phi_0 | H | \phi_k \rangle \langle \phi_k | H | \phi_0 \rangle}{E_0 - E_k}$$

concerning the component $\{(h_i h_j)/[\Delta i(\Delta i + \Delta j)]\}$ of ϕ_{i+j} in $\psi^{(2)}$.

The same phenomenon occurs for the other components of ϕ_{i+j} in $\psi^{(2)}$ and one has thus to dress the determinant ϕ_{i+j} by the quantity $h_k^2/\Delta k$. In a size-consistent formulation one may write

$$\langle \phi_{i+j} | \tilde{V} | \phi_{i+j} \rangle = \sum_{k \in \mathcal{D}(i+j)} \langle \phi_0 | H | D_k^+ \phi_0 \rangle \tilde{C}_k.$$

For the quadruply excited configurations this formulation is rigorous and does not introduce any spurious sixth-order EPV diagram on the energy. For the triply excited determinants the exclusion is less rigorously dealt with by using the general formula

$$\langle \phi_L | \tilde{V} | \phi_L \rangle = \sum_{k \in \mathcal{D}(L)} \langle \phi_0 | H | D_k^+ \phi_0 \rangle \tilde{C}_k \quad (43)$$

since the exclusion rule is not the same for the different diagrams implied in the summation (as was already noticed for the singly excited determinants) but this is a rather weak defect.

From a practical point of view one may again use the previously defined e arrays and define the dressing vector as

$$\begin{aligned} \langle \phi_L | \tilde{V} | \phi_L \rangle = & \tilde{E} - \sum_{t \in L} e_1(t) - \sum_{p \in L} e_1(p) + \sum_{t \in L} \sum_{t' \in L} e_2(t, t') \\ & + \sum_{p \in L} \sum_{p' \in L} e_2(p, p') + \sum_{t \in L} \sum_{p \in L} e_2(t, p) \\ & - \sum_{t \in L} \sum_{t' \in L} \sum_{p \in L} e_3(t, t', p) \\ & - \sum_{t \in L} \sum_{p \in L} \sum_{p' \in L} e_3(t, p, p') \\ & + \sum_{t \in L} \sum_{t' \in L} \sum_{p \in L} \sum_{p' \in L} \tilde{C} \begin{pmatrix} pp' \\ tt' \end{pmatrix} \langle tt' | | pp' \rangle, \quad (44) \end{aligned}$$

where t (respectively, p) $\in L$ means that t (respectively, p) is a hole (respectively, a particle) present in ϕ_L . Despite this quadruple summation the evaluation of Eq. (44) is not a long one since it only concerns the set of double excitations which contributes to the operator O_L , creating ϕ_L from ϕ_0

$$\phi_L = O_L \phi_0.$$

One is therefore able to insure size consistency of any truncated CI involving all determinants up to a certain degree of excitation. However, this approach is, in practice, unusable for most problems and one should consider selected CI alternatives.

B. Dressing of a CI including all doubles and selected higher excitations

Let us consider a CI including, besides all doubles (and singles), the most important triples and quadruples or determinants of a higher degree of excitation. The selected quadruples will, in general, be a small fraction of the total number of quadruples. Now the doubles should be dressed by the quadruples which do not belong to the selected list, and one should, in principle, check whether $D_k^+ \phi_L$ belongs or not to S before dressing ϕ_L under the effect of $D_k^+ \phi_L$. This would be a long process. The best procedure consists of

- (i) first, dressing each determinant ϕ_L (except ϕ_0) according to Eq. (44);
(ii) then, undressing in a second step, the determinants ϕ_k such that

$$\phi_L = D_l^+ \phi_k \quad (\phi_k \neq \phi_0)$$

by the quantity $-\tilde{C}_l \langle \phi_0 | H | D_l^+ \phi_0 \rangle$. Notice that for highly excited determinants ϕ_L the number of couples D_l^+ and ϕ_k may be large and this will be a practical limitation to the efficiency of the present method.

This undressing step may be done in the normal course of building the CI matrix. When one considers the determinants ϕ_L of excitation m larger than two, and considers their interaction with the determinants of a level of excitation $m-2$, the undressing of the less excited determinant is straightforward.

The whole process is easily implemented in the direct selected CI algorithm using hole-particle formalism (SCIEL) as has recently been proposed¹¹ by Caballol and one of the present authors (J.P.M.). In this program the deexcitation processes are explicitly identified and so the undressing can then be easily performed.

C. Completely general model spaces

So far we have assumed that all doubles have been considered in the model space. For systems with a large number of electrons and/or large basis sets, the number of doubles may be exceedingly large. One may then—either omit the small doubles; this is relevant for instance for differential studies. If the MOs keep a physically constant character one may work with a stable selected set for the CI (for instance, for the study of force constants). Then Eq. (44) will be used considering only the doubles within the model space for the dressing. The undressing remains identical to the preceding one;—or add the perturbative effect of the small Doubles. The simplest way to do this is to write

$$E = \tilde{E} + \epsilon_{\text{small}}^{(2)}. \quad (45)$$

More sophisticated perturbative dressing of arbitrary selected CIs will be presented in the near future. The numerical results of the next section will use both possibilities.

D. Separability in the general case

It is possible to demonstrate the separability of our size-consistent self-consistent selected CI [(SC)²SCI] for any physically meaningful selection, provided that *localized orbitals* are used. The demonstration is straightforward if the selection implies configurations which are excited *either* on system *A* or on system *B*. The equation $(\tilde{H} - \tilde{E})\tilde{C} = 0$ relative to the separate system *A* may be written for the configuration ϕ_{i_A}

$$\left(\langle \phi_{i_A} | H | \phi_{i_A} \rangle - \tilde{E}_A + \sum_{j_A \in \mathcal{D}(i_A)} \tilde{C}_{j_A} \langle \phi_{0_A} | H | \phi_{j_A} \rangle \right) \tilde{C}_{i_A} + \sum_{k_A} \langle \phi_{i_A} | H | \phi_{k_A} \rangle \tilde{C}_{k_A} = 0. \quad (46)$$

In the supersystem problem, for the same configuration, the equation is written as

$$\left(\langle \phi'_{i_A} | H | \phi'_{i_A} \rangle - \tilde{E}'_{A+B} + \sum_{j_A \in \mathcal{D}(i_A)} \tilde{C}'_{j_A} \langle \phi'_0 | H | \phi'_{j_A} \rangle + \sum_{k_B \in \mathcal{D}(i_A)} \tilde{C}'_{k_B} \langle \phi'_0 | H | \phi'_{k_B} \rangle \right) \tilde{C}'_{i_A} + \sum_{k_A} \langle \phi'_{i_A} | H | \phi'_{k_A} \rangle \tilde{C}'_{k_A} + \sum_{l_B} \langle \phi'_{i_A} | H | \phi'_{l_B} \rangle \tilde{C}'_{l_B} = 0. \quad (47)$$

For separate systems

$$-\langle \phi_{i_A} | H | \phi_{l_B} \rangle = 0 \quad \forall i_A, l_B;$$

—all excitations $D_{k_B}^+$ are possible on any ϕ_{i_A} . So that putting $\tilde{E}'_{A+B} = \tilde{E}_A + \tilde{E}_B$, $\tilde{C}'_{i_A} = \tilde{C}_{i_A}$, $\tilde{C}'_{j_B} = \tilde{C}_{j_B}$ satisfies the equation of the supersystem.

Even more surprisingly, the property of additivity is maintained when the selected space involves *composite* excitations concerning both systems. Asymptotically, the nonvanishing composite configurations can only be of the type

$$\phi_{i_A+j_B} = L_{j_B}^+ \phi_{i_A} = L_{i_A}^+ \phi_{j_B},$$

where $\phi_{i_A} = L_{i_A}^+ \phi_0$, $\phi_{j_B} = L_{j_B}^+ \phi_0$ (we use L^+ instead of D^+ , since it is not necessarily a double excitation but it may be single, triple, or whatever). The decomposition of $\phi_{i_A+j_B}$ is necessarily unique for a vanishing interaction. We shall simply assume that if $\phi_{i_A+j_B}$ has been selected, ϕ_{i_A} and ϕ_{j_B} have also been selected; assuming the contrary would mean that the selection was physically meaningless. If we now simply add, for the sake of simplicity, $\phi_{i_A+j_B}$ to the set $\{\phi_{i_A}, \phi_{j_B}\}$ previously discussed, in Eq. (46)

$$\sum_{k_B \in \mathcal{D}(i_A)} \tilde{C}'_{k_B} \langle \phi'_0 | H | \phi'_{k_B} \rangle = \sum_{\text{all } k_B} \tilde{C}'_{k_B} \langle \phi'_0 | H | \phi'_{k_B} \rangle - \tilde{C}'_{j_B} \langle \phi'_0 | H | \phi'_{j_B} \rangle,$$

Eq. (46) becomes

$$\left(\langle \phi'_{i_A} | H | \phi'_{i_A} \rangle - \tilde{E}'_{A+B} + \sum_{j_A \in \mathcal{D}(i_A)} \tilde{C}'_{j_A} \langle \phi'_0 | H | \phi'_{j_A} \rangle + \sum_{\text{all } k_B} \tilde{C}'_{k_B} \langle \phi'_0 | H | \phi'_{k_B} \rangle \right) \tilde{C}'_{i_A} - \tilde{C}'_{j_B} \langle \phi'_0 | H | \phi'_{j_B} \rangle \tilde{C}'_{i_A} + \sum_{k_A} \langle \phi'_{i_A} | H | \phi'_{k_A} \rangle \tilde{C}'_{k_A} + \langle \phi'_{i_A} | H | \phi'_{i_A+j_B} \rangle \tilde{C}'_{i_A+j_B}. \quad (48)$$

Since $\langle \phi'_{i_A} | H | \phi'_{i_A+j_B} \rangle = \langle \phi_{0_B} | H | \phi_{j_B} \rangle$ and $\tilde{C}'_{i_A+j_B} = \tilde{C}'_{i_A} \tilde{C}'_{j_B}$, Eq. (47) reduces again to Eq. (45) when $\tilde{E}'_{A+B} = \tilde{E}_A + \tilde{E}_B$

$$\tilde{C}'_{i_A} = \tilde{C}_{i_A}, \quad \tilde{C}'_{j_B} = \tilde{C}_{j_B} \quad (\text{Q.E.D.}).$$

TABLE V. NH_3 correlation energies from a selected CI approach. The full CI energy^a is -0.2099 a.u. \tilde{E} refers to the $(\text{SC})^2\text{SCI}$ energy.

Dimension of the selected CI	(Number of generators)	Number of selected determinants				Energies			
		<i>S</i>	<i>D</i>	<i>T</i>	<i>Q</i>	E_{var}	$E_{\text{var}+\epsilon^{(2)}}$	\tilde{E}	$\tilde{E}+\epsilon^{(2)}$
1 440	(97)	16	1414	0	9	-0.1800	-0.1973	-0.1850	-0.2023
2 807	(97)	40	2671	28	109	-0.1944	-0.1987	-0.1997	-0.2041
3 381	(97)	47	3045	90	199	-0.1969	-0.1992	-0.2022	-0.2045
4 953	(97)	96	3943	346	607	-0.2001	-0.2005	-0.2051	-0.2055
13 588	(97)	78	4892	4364	4253	-0.2032	-0.2032	-0.2073	-0.2073
16 313	(104)	78	4874	5362	5998	-0.2036	-0.2036	-0.2076	-0.2076
22 927	(389)	70	4848	8342	9666	-0.2046	-0.2046	-0.2082	-0.2082
SDCI	(1)	108	6336	0	0	-0.1973		-0.2033	

^aReference 35.

E. Comparison with other multireference methods

Several generalizations of the Davidson correction for the multireference case have been proposed.^{29,30} If one considers a problem where besides the ground state ϕ_0 determinant several other reference determinants ϕ_R have been introduced, and all singles and doubles ϕ_i with respect to the reference determinants are treated, the dressing will only concern the determinants ϕ_i (a point which will be discussed further on). If one neglects the EPV contributions, the dressing at the first iteration reduces to

$$\langle \phi_i | \tilde{V} | \phi_i \rangle = E_{\text{corr}}$$

and the first order correction in the intermediate normalization will be

$$\Delta \tilde{E} = \langle \tilde{\psi} | \tilde{V} | \tilde{\psi} \rangle = E_{\text{corr}} \sum_i \tilde{C}_i^2,$$

which may be rewritten, using the normalized coefficients ($\langle \psi | \psi \rangle = 1$), as

$$\Delta E = E_{\text{corr}} \frac{(1 - C_0^2 - \sum_{R \neq 0} C_R^2)}{C_0^2},$$

which is slightly different from the previous formulations^{29,30} and may be seen as the correct generalization of the renormalized Davidson's correction.^{20,21} Of course, these corrections working with an unchanged wave function cannot behave correctly for a large number of particles. It is easy to see that for n independent subsystems the correction proposed here above doubles the correlation energy, which is far from being sufficient and shows the importance of the iterations.

The original MRLCC formalism³⁰ (or MRCEPA-O) is restricted to a complete reference space and introduces a unique energy shift of the configurations of the outer space without iterating the wave function which is kept contracted in the reference space. It is equivalent to our procedure to the first iteration only and without consideration of the EPV contributions. An improved formulation, also restricted to complete reference spaces, has been recently

proposed by Ruttink *et al.*³¹ The dressing is not uniform but only depends on the excitation class and EPV problems are also disregarded.

One should also discuss the connection with the recently proposed quasidenerate variational perturbation theory (QDVARPT) of Cave and Davidson³² and the multireference averaged coupled pair functional (MRACPF) of Gdanitz and Ahlrichs.³³ The relation between these two proposals and an improvement of the former have been clarified in Ref. 34. As appears clearly in Eq. (4) of Ref. 34, these methods proceed through two different dressings of the reference determinants $\phi_R (\neq \phi_0)$, and the nonreference determinants ϕ_i , but the dressing is unique for each class. The choice of the normalization factor entering in the dressing rests on arguments based on the number of particles. One advantage is that the weights of the references are revised and the reference space does not need to be complete.

Our method also proceeds through (self-consistent) dressing but (i) the dressing is different for each determinant due to the exclusion principle effects and its amplitude

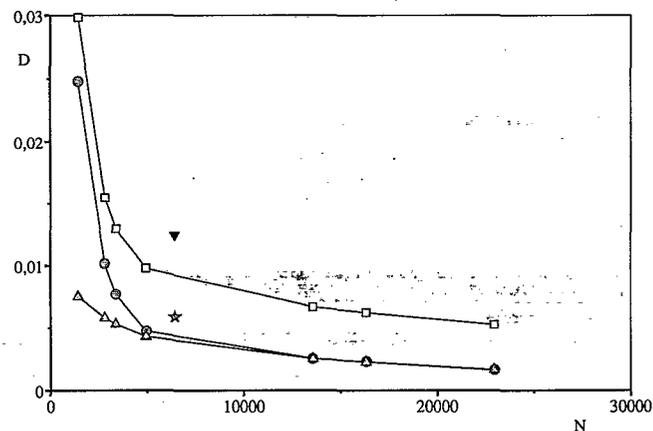


FIG. 3. Convergence of $(\text{SC})^2$ selected CI for NH_3 . Energy error (a.u.) as a function of the number of selected determinants: \square selected CI; \circ $(\text{SC})^2$ selected CI; \triangle $(\text{SC})^2$ selected CI + perturbative remainder [Eq. (45)]; ∇ SDCI; \star $(\text{SC})^2$ SDCI.

do not refer to the number of particles, (ii) one may see that according to our method for an MRSDCI, including all singles and doubles, none of the reference diagonal energies should be dressed, (iii) the inclusion of all singles and Doubles on all the reference determinants is not compulsory, (iv) there is no need for the reference space to be complete.

F. Numerical illustrations of the (SC)² selected CI algorithm

1. Comparison with full CI: NH₃

Since the full CI energy of NH₃ in a moderate size basis set has been evaluated with reasonable accuracy³⁵ despite the large number (2×10^8) of determinants, we have tried to check the precision of our algorithm. Figure 3 and Table V present the results. The selection was performed in two steps. Starting from the ground state determinant a certain number *ns* of doubly excited determinants were first selected as having a coefficient larger than a certain threshold (*ns*=97, 104, or 389). Perturbing, to the first order, the multireference function resulting from the corresponding diagonalization, a second selection was performed with a lower threshold, introducing thus the triples and quadruples of larger weight and most doubles and singles.

The benefit of the CIPSI-type selection is well documented;³⁶ from 22×10^3 determinants, i.e., a fraction 10^{-4} of the total CI space, the error is only 5.3×10^{-3} a.u. (the total correlation energy being -0.2099 a.u.). When we apply our self-consistent dressing to that CI space the error falls to 1.7×10^{-3} a.u. (1 kcal/mol). The selection involved all non-negligibly contributing doubles (4900) and about 8×10^3 triples and 9×10^3 quadruples. The error is within chemical accuracy with a very small fraction of the total number of determinants. Without dressing the same energy (-56.4219 a.u.) would be obtained by selecting 171×10^3 determinants,¹¹ i.e., *the dressing saves 1 order of magnitude in CI size*. The importance of having added the most important fourth-order linked contributions may be seen by comparing our best value to the ones given by SDCI before and after dressing. After dressing the error was still 6×10^{-3} a.u., which means that from 18×10^3 triples and quadruples among 25×10^6 , we have picked 2/3 of the linked fourth-order effect.

The error at the MP2 level was 18×10^{-3} a.u. The size-consistent variational treatment of only 1400 determinants plus its MP2 counterpart reduces the error to

7×10^{-3} a.u., which indicates the possible interest of Eq. (45) for very large systems, where a complete treatment of all doubles and singles is not possible.

2. The CAS-SDCI: potential well of Be₂ and F₂

For Be₂, the valence CAS implies the 2s and 2p orbitals. Starting from that CAS space all singles and doubles have been generated (14 992 determinants). The potential well depth has been evaluated by comparing the energies at 5 and 8 bohr. The CAS-SDCI energy difference is $-0.000 390$ a.u.; the dressing increases the well depth by 18% to $-0.000 461$ a.u., which compares satisfactorily with the value obtained by the single-double-triple coupled cluster [Ref. 28(b)], $-0.000 494$ a.u., in which all triples are freely determined (the quadruples being products of doubles) while we have 6×10^3 triple and 7.5×10^3 quadruple independent coefficients.

For F₂ (cf. Table VI) we first performed an SDCI upon the two-configuration CAS reference space, for the region of the equilibrium distance and for 6 bohr (for the sake of comparison with Ref. 25). The size-consistency correction is very large (~ 0.5 eV). Our (SC)² SCI result from the 2-reference SDCI is already lower than the 32-reference SDCI value of Ref. 27, but slightly above the value of the linear coupled cluster estimate from a 10- or 32-reference CAS space.

V. DISCUSSION AND CONCLUSION

The present work has proposed a very simple procedure to make *truncated or selected CI's* not only size extensive but even separable (provided that localized MOs are used). The procedure simply consists in a dressing of the diagonal energies of the excited determinants. This dressing is expressed in terms of the coefficients of the doubly excited determinants and of their matrix elements with the ground state determinant. If one simply uses the coefficients of the undressed CI, the dressing is expressed as a first-order correction

$$\sum_i C_i^2 \langle \phi_i | \tilde{V} | \phi_i \rangle$$

which may be seen as a well justified Davidson correction. For a large number of particles however this correction becomes less and less accurate since the coefficients of the truncated CI become meaningless.¹⁴

This is why we have proposed a self-consistent version of the dressing thereby improving on the amplitudes of the

TABLE VI. F₂ total energies for various procedures introducing all single and double excitations on CAS spaces.

R (bohr)	Ref. 27				This work			
	10-config. CAS		32-config. CAS		2-config. CAS		Selected CI	
	MR-CISD	MR-LCCM	MR-CISD	MR-LCCM	MR-CISD	(SC) ² SCI	SCI	(SC) ² SCI
2.65			-199.1719	-199.1905	-199.1594	-199.1765		
2.70	-199.1665	-199.1883	-199.1725	-199.1905	-199.1600	-199.1771		
2.75			-199.1723	-199.1899	-199.1600	-199.1771	-199.1652	-199.1813
6	-199.1231	-199.1434			-199.1168	-199.1322	-199.1212	-199.1356

wave function for the doubly excited determinants. Such self-consistent CI's then become separable (and therefore size extensive). Although of little numerical effect in problems with small numbers of particles or weakly correlated systems, the impact of self-consistency is crucial. It does not represent a practical difficulty since the dressing does not require significant memory nor additional computation time, in particular when the dressing is calculated within the iteration of the diagonalization procedure. The method should be easily implemented in the direct selected CI algorithm,¹¹ for any selection scheme.

When applied to single and double CI, the method may be seen as an improved CEPA algorithm correctly treating all the EPV diagrams, insuring strict additivity and giving exact results for separated electron pairs. The numerical results appear to be surprisingly close to the SD coupled cluster results, despite the fact that the only linked fourth-order diagrams going through triples and quadruples included in the treatment are the EPV ones. The fields of application of this method are numerous. It would be especially relevant for the calculation of intermolecular energies or core-valence effects. In such problems the quantity to calculate is a small difference between large correlation energies (the total correlation energy of $A + B$, or of the core-valence electrons) concerning large numbers of electrons, and size consistency is absolutely necessary. It is certain that the method will give reliable results for the ground state structural properties of well-behaved closed-shell molecules.

The generalization to selected CIs is an important step. It will first of all enable the treatment of multiple bonds, since it will make it possible to treat multireference (and in particular valence CAS) single and double CI without size-consistency errors and therefore to study bond breaking and chemical reactions. As many others, our proposal proceeds through energy shift, but it follows a very different logic (intermediate Hamiltonians); it is very general, includes the EPV diagrams, and contrarily to most of the efficient multireference CI schemes,³⁷ it is an uncontracted procedure: The weights of the components of the wave function on the reference space, for instance the valence CAS space, are changed under the interaction with the other determinants, as is inevitable since for instance the different dressings of the ionic and neutral valence components must affect the ratio of the ionic/neutral coefficients.

The selected and dressed CI is a completely flexible and open tool and this is its main advantage. It approaches the full CI limit by increasing the size of the selected space; it is possible for instance to incorporate the largest fourth-order (or higher order) linked contributions by appropriate enlargement of the model space. In that direction, the use of quasinatural orbitals would be useful. On the other hand, if the number of electrons and/or the size of the basis set lead to an exceedingly large number of doubles, it is possible to treat the effect of the smallest ones in a perturbative mode. A simple partition has already been proposed here but in the near future, we shall propose a combination of self-consistent and perturbative dressings of higher accuracy.

So far the main limitation of our method is that it concerns a single state and uses a reference determinant. If one goes to another state, the reference should change and the dressed Hamiltonians should be different. We are currently building a non-Hermitian dressing which will be valid for the simultaneous investigation of several states.

Note added in proof. Since the submission of the present work, alternative nondiagonal self-consistent dressings have been proposed by two of us³⁸ and the efficiency of the dressing of selected CI have been illustrated by larger test calculations.³⁹

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