Elementary presentation of self-consistent intermediate Hamiltonians and proposal of two totally dressed singles and doubles configuration interaction methods

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Intermediate Hamiltonians are effective Hamiltonians which are defined on an N-dimensional model space but which only provide $n < N$ exact eigenvalues and the projections of the corresponding eigenvectors onto the model space. For a single root research, the intermediate Hamiltonian may be obtained from the restriction of the Hamiltonian to the model space by an appropriate, uniquely defined dressing of the diagonal energies or of the first column. Approximate self-consistent dressings may be proposed. The simplest perturbative form gives the same result as the original 2nd order intermediate Hamiltonian or the "shifted B_k" technique but it is of easier implementation. Self-consistent inclusion of higher order exclusion principle violating corrections greatly improves the results, especially for nearly degenerate problems, as shown on several illustrative applications. Possible generalizations to enlarged or reduced model spaces are discussed.

I. INTRODUCTION

The basic structure of the electronic many-body problem has been formulated through the Rayleigh–Schrödinger (RS) perturbative expansion starting from the independent-particle approximation, and has led to the fundamental linked cluster theorem.[1] These results make clear the origin of the size-inconsistency of truncated variational configuration interaction (CI) calculations, and the physical likeliness of coupled cluster expansions[2] of the wave function

$$\psi = \exp S \phi_0,$$

where S keeps a simple form [linear combination of single and double excitations for instance (CC-SD)]. Both RS perturbative expansion and the CC one are based on a single reference, at this stage. In molecular physics, the Hartree–Fock (HF) ϕ_0 determinant becomes degenerate with some doubly (and eventually more) excited determinant when chemical bonds are broken, and these near degeneracies induce divergences of the perturbation series and question the validity of the CC expansion. It is in principle possible to move to quasidegenerate perturbation theory (QDPT) and a generalized linked cluster theorem has actually been established by Brandow[3] for a very special type of model space. The model space must be complete, i.e., accept all possible distributions of a fixed number of active electrons n_a into a fixed set of active monoelectronic functions Na, thus generating $C_{Na}^{n_a}$ determinants, some of which are very exotic and high in energy. The chemists call this space a valence complete active space (CAS) which is unvariant under unitary transformations of valence spin orbitals and complete for the symmetry species considered. They have immediately noticed

that QDPT had no chance to converge, in general, due to the occurrence of near degeneracies between some determinants of the outer space (acting as "intruder states") and some determinants of the model space.[4] These near degeneracies are unavoidable in practice, and condemn the use of a size-consistent QDPT for the computation of reliable potential energy surfaces (PES). On the other hand multireference coupled cluster theories have been the subject of an intense collective effort,[5] but the solutions are very difficult and their implementation is not straightforward.

In this context, a new tool has been proposed some years ago by one of us (J.P.M.) and co-workers, namely, the intermediate effective Hamiltonians.[6] The N-dimensional model space is partitioned into a main model space, of dimension n_a, and an intermediate model space, of dimension $n_i = N - n_a$, and the intermediate Hamiltonian $\tilde{H}$, built onto the whole model space, only delivers n_m exact eigenvectors onto the whole model space. A perturbative expansion (generalized degenerate perturbation theory) was proposed at this time, and other variants have been suggested by different authors,[7] since, as explained below, the intermediate Hamiltonians are not uniquely defined.

The strength of intermediate Hamiltonians is their ability to accept near-degeneracies between the intermediate model space and the outer space, thus solving the intruder state problem.[8]

The present paper proposes in Sec. II a very simple presentation of intermediate Hamiltonians dedicated to the research of a single root. It shows that they are obtained by changing (or dressing) the elements of the truncated Hamiltonians matrix PHP, where P is the projector on the

model space. We briefly discuss the flexibility of the dressing, and propose an elementary formulation of the dressing in terms of the coefficients of the eigenstate on the outer space determinants. This trivial expression is in principle academic, but will receive a large series of applications, beyond the present work. In Sec. III, we concentrate on a fourth-order variation/perturbation combination, which, for CI problems, consists in an iterative dressing of the SDCI matrix by the effect of the triples and quadruples. This dressing may be of perturbative type or inspired by coupled cluster expansions, but the presented work is limited to the perturbative aspect.

The simplest version gives the same solution than the so-called shifted B_k approximation[9] (which is a 2nd order intermediate Hamiltonian, with a full dressing of the CI matrix) but is less memory consuming. A sophisticated version takes into account high-order EPV corrections in a self-consistent manner and this addition makes possible to treat accurately single bond breaking, despite the monodeterminantal character of the main model space, as shown through a few test calculations (Sec. IV). Possible generalizations to enlarged or reduced model spaces are discussed in Sec. V.

II. THE SELF-CONSISTENT INTERMEDIATE HAMILTONIANS

A. Generalities

Let us suppose that one has defined an n-dimensional model space S of projector P

$$P = \sum_{\substack{i=0 \\ i \in S}}^{n-1} |\phi_i\rangle\langle\phi_i|, \tag{1}$$

the functions ϕ_i being orthonormal single determinants or configurations. Also assume that one only searches one eigenvalues ϵ_0 and the corresponding eigenvector ψ_0

$$H\psi_0 = \epsilon_0\psi_0 \tag{2}$$

or more precisely its projection into the model space, $P\psi_0$. This means that one desires to build an intermediate Hamiltonian (according to a previous definition[6]) built on S,

$$\bar{H} = P\bar{H}P, \tag{3}$$

such that

$$\bar{H}\bar{\psi}_0 = \epsilon_0\bar{\psi}_0, \tag{4a}$$

$$\bar{\psi}_0 = P\psi_0. \tag{4b}$$

Of course this condition fixes one energy and $(n-1)$ coefficients, and does not determine $\bar{H}$ uniquely, while the effective Hamiltonians are entirely defined by their spectral definition, for instance, for Bloch's Hamiltonians,[10]

$$H^{\text{eff}} = \sum_{k=1,n} |P\psi_k\rangle\epsilon_k\langle P\psi_k^\perp|. \tag{5}$$

One has a great flexibility in the definition of $\bar{H}$. The partitioning technique[11] proposes one choice

$$\bar{H} = PHP + PHQ(\epsilon_0 - QHQ)^{-1}QHP, \tag{6}$$

which presents the difficulty of the inversion of QHQ, Q being the projector on the outer space $(Q = 1-P)$, and which modifies all the matrix elements of the truncated matrix

$$\langle\phi_i|\bar{H}|\phi_j\rangle \neq \langle\phi_i|H|\phi_j\rangle \quad \forall i,j.$$

Now we shall assume that one of the basis functions, ϕ_0, is a good approximation to ψ_0. By that we do not assume that $\langle\psi_0|\phi_0\rangle$ is large, which is not compulsory (even for the convergence of a nondegenerate perturbation from ϕ_0), but simply that ψ_0 is the eigenvector having the largest component on ϕ_0,

$$|\langle\psi_0|\phi_0\rangle| > |\langle\psi_i|\phi_0\rangle| \quad \forall i \neq 0 \tag{7}$$

and reciprocally

$$|\langle\psi_0|\phi_0\rangle| > |\langle\psi_0|\phi_i\rangle| \quad \forall i \neq 0,$$

which is a very weak condition. Then, ϕ_0 will define our main model space, of projector P_m,

$$P_m = |\phi_0\rangle\langle\phi_0| \tag{8}$$

and the other determinants of our model space define the intermediate model space, of projector P_i,

$$P_i = P - P_m = \sum_{\substack{k \neq 0 \\ \in S}} |\phi_k\rangle\langle\phi_k|. \tag{9}$$

It is evident that if one knows the exact eigenergy E_0 and the components of the exact eigenvector on the model space, i.e., in the intermediate normalization

$$P\psi_0 = \phi_0 + \sum_{i \in S} C_i\phi_i, \tag{10}$$

it is always possible to define a diagonal operator Δ defined on S, which we shall call the diagonal dressing operator,

$$\langle\phi_k|\Delta|\phi_l\rangle = 0 \quad \text{if } k \neq l,$$

such that

$$P(H + \Delta)P\psi_0 = \epsilon_0\psi_0. \tag{11}$$

This eigenequation becomes, for the line i,

$$\langle\phi_i|H|\phi_0\rangle + \sum_{\substack{j \in S \\ \neq i,0}} C_j\langle\phi_i|H|\phi_j\rangle + C_i(\langle\phi_i|H|\phi_i\rangle$$

$$+ \langle\phi_i|\Delta|\phi_i\rangle - \epsilon_0) = 0 \tag{12}$$

and uniquely defines

$$\langle\phi_i|\Delta|\phi_i\rangle = \epsilon_0 - \langle\phi_i|H|\phi_i\rangle - \sum_{j \neq i} \langle\phi_i|H|\phi_j\rangle \frac{C_j}{C_i} \tag{13}$$

(if $C_i \neq 0$; if $C_i = 0$, $\langle\phi_i|\Delta|\phi_i\rangle$ may be kept to zero). This is an academic view, although it may be used to define "dressed energies" for instance to analyze in a pictorial manner the effect of the nondynamical correlation as a change of the effective energies of the valence compo-

nents.[12] In general we do not know the exact eigenvector, which we are trying to approach, and the preceding remark is simply a proof of unique existence of the diagonal dressing operator, analogous to the spectral definition of H^{eff} in the quasidegenerate perturbation theory.

An alternative solution would consist in the definition of a "column" dressing, modifying the matrix elements between ϕ_0 and the ϕ_i's, i.e., of the first column of the Hamiltonian matrix

$$\langle \phi_k | \Delta' | \phi_i \rangle = \langle \phi_k | \Delta' | \phi_0 \rangle \delta_{i0}. \tag{14}$$

Referring to the eigenequations for H and $H + \Delta'$ one obtains

$$\langle \phi_i | \Delta' | \phi_0 \rangle = - \left[\langle \phi_i | H | \phi_0 \rangle + \sum_{j \in S \neq i,0} C_j \langle \phi_i | H | \phi_j \rangle \right.$$
$$\left. + C_i (\langle \phi_i | H | \phi_i \rangle - \epsilon_0) \right]. \tag{15}$$

This approach has two drawbacks (1) it is non-Hermitian; (2) it will introduce matrix elements between ϕ_0 and all ϕ_i's even if they differ by a large number of spin–orbitals.

Other dressings have been evoked in a more specialized context.[13]

B. The basic equation

Actually the exact eigenequation, $H\psi_0 = \epsilon_0 \psi_0$, is written, for line i,

$$\langle \phi_i | H | \phi_0 \rangle + \sum_{\substack{j \neq i,0 \\ \in S}} C_j \langle \phi_i | H | \phi_j \rangle + C_i (\langle \phi_i | H | \phi_i \rangle - \epsilon_0)$$
$$+ \sum_{\alpha \notin S} C_\alpha \langle \phi_i | H | \phi_\alpha \rangle = 0. \tag{16}$$

Comparison of Eq. (16) with Eq. (13) immediately gives another definition of the dressing matrix element

$$\langle \phi_i | \Delta | \phi_i \rangle = (C_i)^{-1} \sum_{\alpha \notin S} C_\alpha \langle \phi_i | H | \phi_\alpha \rangle. \tag{17}$$

This equation still looks academic since one does not know the coefficients C_α outside of the model space. But there are cases where one may have good guesses of the coefficients C_α, relative to the determinants ϕ_α interacting with at least one determinant of the model space. In general the coefficients C_α are functions of the coefficients C_k, plus additional information. Then, if one knows a function f such that

$$\{C_\alpha\} = f\{C_k\},$$

the dressing Δ may formally be written

$$\{\Delta\} = g\{C_k\}$$

i.e., the dressing is a function of the coefficients and the intermediate Hamiltonian $\bar{H}$ becomes a self-consistent Hamiltonian satisfying the matrix equation

$$\bar{H}(C) = P[H + \Delta(C)]PC = \epsilon_0 C. \tag{18}$$

The problem is then nonlinear.

An alternative formulation consists in introducing a vector $\Delta'(C)$ the ith component of which is

$$\Delta'_i = \langle \phi_i | \Delta | \phi_i \rangle C_i = \sum_{\alpha \notin S} C_\alpha \langle \phi_i | H | \phi_\alpha \rangle \tag{19}$$

and the problem becomes a vectorial equation

$$(PHP - \epsilon_0) C + \Delta'(C) = 0. \tag{20}$$

Notice that this procedure may be considered as a non-Hermitian dressing of PHP by addition of extra terms on the first column matrix elements $\langle \phi_i | H | \phi_0 \rangle$,

$$\langle \phi_i | \bar{\Delta} | \phi_0 \rangle = \sum_\alpha C_\alpha \langle \phi_i | H | \phi_\alpha \rangle, \tag{21}$$

and solution of the resulting self-consistent equation

$$\{P[H + \bar{\Delta}(C)]P - \epsilon_0\}C = 0. \tag{22}$$

This formulation has the advantage that the dressing $\langle \phi_i | \bar{\Delta} | \phi_0 \rangle$ is always possible while $\langle \phi_i | \Delta | \phi_i \rangle$ cannot be defined if $C_i = 0$ (or exceedingly small), at least at the first iteration of the process (for instance, in the configuration interaction problem if ϕ_0 is the ground state determinant and ϕ_i is a triply or quadruply excited determinant in the configuration interaction problem).

Also remark that the method is not restricted to the ground state, and it may be applied to an excited state as well, changing the reference function ϕ_0. But it is restricted to a state-by-state dressing, with the intermediate Hamiltonians being different for the different roots of the same model space.

III. PERTURBATIVE FORMULATION

A. The simplest scheme

Let us assume that the model space S involves, besides ϕ_0, all the determinants interacting with ϕ_0 through H,

$$P\phi_i = \phi_i \quad \text{if} \quad \langle \phi_i | H | \phi_0 \rangle \neq 0.$$

This means that the components of the first-order wavefunction belong to S. Then if one considers the second-order perturbed wave-function $\psi^{(2)}$, using a yet unspecified zeroth-order Hamiltonian,

$$H_0 = \sum_{i \in S} E_i^0 |\phi_i\rangle\langle\phi_i| + \sum_{\alpha \notin S} E_\alpha^0 |\phi_\alpha\rangle\langle\phi_\alpha|$$

its components in the outer space are given by

$$Q\psi^{(2)} = \frac{Q_0}{E_0^0 - H_0} V\psi^{(1)}$$
$$= \sum_{\alpha \notin S} (E_0^0 - E_\alpha^0)^{-1} \sum_{k \in S} \langle \phi_\alpha | H | \phi_k \rangle C_k^{(1)} \tag{23}$$

so that one may write, to a better approximation, replacing $C_k^{(1)}$ by C_k,

$$C_\alpha = \left(\sum_{k \in S} C_k \langle \phi_\alpha | H | \phi_k \rangle \right) (E_0^0 - E_\alpha^0)^{-1} \tag{24}$$

and

$$\langle \phi_i | \Delta | \phi_i \rangle = C_i^{-1} \sum_{\alpha \notin S} \frac{\langle \phi_i | H | \phi_\alpha \rangle}{E_0^0 - E_\alpha^0} \sum_{k \in S} \langle \phi_\alpha | H | \phi_k \rangle C_k.$$

(25)

In practice one sees that the evaluation of the coefficients C_α, and therefore of the dressing of the diagonal energies, combines variation and perturbation (for the last step, going from the model space to the outer space). Thus it is an iterative process since the coefficients depend on the dressing and the dressing depends on the coefficients.

As briefly mentioned before, the division by the coefficients C_i, some of which may be very small, may be considered as a source of troubles despite the fact that (i) C_i^{-1} multiplies small quantities (namely a part of the third order energy); (ii) the division by C_i may be avoided since one proceeds later to a multiplication by C_i [see Eq. (20) or (22)]. And actually it may happen that the ground state physically relevant root is not the lowest eigenvalue of the dressed matrix.

The first column dressing

$$\langle \phi_i | \bar{\Delta} | \phi_0 \rangle = \sum_{\alpha \notin S} \frac{\langle \phi_i | H | \phi_\alpha \rangle}{E_0^0 - E_\alpha^0} \sum_{k \in S} \langle \phi_\alpha | H | \phi_k \rangle C_k$$

(25 bis)

avoids these difficulties but is non-Hermitian.

B. Comparison with previous formulations

At this stage, the method should be related to the application of the original version of intermediate Hamiltonians to this particular definition of the main and intermediate model spaces. In that version the second-order dressing concerned all the matrix elements between functions belonging to the model space and was given by

$$\langle \phi_i | \Delta'' | \phi_j \rangle = \sum_{\alpha \notin S} \frac{\langle \phi_i | H | \phi_\alpha \rangle \langle \phi_\alpha | H | \phi_j \rangle}{E_0^0 - E_\alpha^0}$$

$$\forall \phi_i, \quad \phi_j \in S,$$

(26)

E_0^0 being the zeroth order energy for the functions of the main model space. Of course $P(H+\Delta)P \neq P(H+\Delta'')P$ but one may verify that the two dressed matrices have a common root and eigenvector since the eigenequation for lines i are identical. For Δ'' it gives

$$\langle \phi_i | H | \phi_0 \rangle + \sum_{j \neq i} \left(\langle \phi_i | H | \phi_j \rangle \right.$$

$$+ \sum_{\alpha \notin S} \frac{\langle \phi_i | H | \phi_\alpha \rangle \langle \phi_\alpha | H | \phi_j \rangle}{E_0^0 - E_\alpha^0} \right) C_j + \left(\langle \phi_i | H | \phi_i \rangle \right.$$

$$+ \sum_{\alpha \notin S} \frac{\langle \phi_i | H | \phi_\alpha \rangle \langle \phi_\alpha | H | \phi_i \rangle - \epsilon_0}{E_0^0 - E_\alpha^0} \right) C_i = 0$$

(27)

while for Δ it is written

$$\langle \phi_i | H | \phi_0 \rangle + \sum_{j \neq i} \langle \phi_i | H | \phi_j \rangle C_j + \left[\langle \phi_i | H | \phi_i \rangle + C_i^{-1} \right.$$

$$\times \sum_{\alpha \notin S} \frac{\langle \phi_i | H | \phi_\alpha \rangle}{E_0^0 - E_\alpha^0} \left(\sum_j \langle \phi_\alpha | H | \phi_j \rangle C_j \right) - \epsilon_0 \left] C_i = 0. \right.$$

(28)

Therefore, at this stage the present self-consistent diagonal dressing is identical to our previously proposed nondiagonal noniterative dressing, when the intermediate model space involves all the components interacting with the main function ϕ_0. Such a formulation had been proposed a long time ago by Davidson as a "shifted-B_k approximation,"[9] by reference to a previous work by Shavitt et al.[14] derived from the partitioning technique. The interest of our present self-consistent diagonal version is twofold.

(i) It does not require a significant memory in the computation. In the original version one had to store all $\langle \phi_i | \Delta' | \phi_j \rangle$ elements, and while the undressed matrix was sparce, the dressed matrix was full. For instance one can consider the electronic correlation problems, ϕ_0 being the HF approximation. The intermediate model space is spanned by all the doubly excited configuration $\phi\binom{ab}{rs}$ where r and s are occupied MOs, a and b are virtual MOs. Then most pairs of doubly excited determinants $\phi\binom{ab}{rs}$ and $\phi\binom{cd}{tu}$ do not interact, $\langle \phi_i | H | \phi_j \rangle = 0$, while there is always at least a quadruply excited determinant $\phi\binom{abcd}{rstu}$ which interacts with both determinants and contribute to $\langle \phi_i | \Delta'' | \phi_j \rangle$.

(ii) It is much more rapid, as noticed and exploited by Maynau and Heully,[15] to perform an outer loop on the triples and quadruples ϕ_α and to determine their coefficient C_α than to generate the appropriate ϕ_α's for all couples ϕ_i, ϕ_j (i.e., the ϕ_α's interacting with both ϕ_i and ϕ_j) as done in the diagrammatic version of the CIPSI algorithm.[16] This question will be addressed more in detail in a forthcoming work.

The cost to pay is the iterative character of the dressing, but the convergence is so rapid that the present formulation is much more convenient.

The nondiagonal noniterative 2nd order intermediate Hamiltonian built on the SDCI model space has been demonstrated to be qualitatively size-extensive, i.e., to give a correlation energy proportional to the number of particles.[17] So that we may assert that the here-proposed iterative diagonal dressing insures the size-extensivity. However, at this stage the method is not strictly separable, i.e., does not give exactly the energy of an AB supersystem where A and B do not interact as the sum of the energies of A and B.

The method should also be compared to the self-consistent size-consistent singles and double CI, recently proposed by one of us (J.P.M.) and co-workers.[13,18] In this method, which may be seen as an improved coupled electron pair approximation[19] (CEPA), the dressing of the excited determinants is given by

$$\langle\phi_i|\Delta|\phi_i\rangle= \sum_{\substack{j \\ D_j^+\phi_i\neq0}} C_j\langle\phi_0|H|\phi_j\rangle, \qquad (29)$$

where D_j^+ is a (single or) double excitation and $\phi_j = D_j^+\phi_0$. This simple dressing insures the size-consistence and the strict separability of the energy of a supersystem $A...B$ into the sum of the energies of A and B when the MOs localize on systems A or B. It is worthwhile comparing Eqs. (17) and (29). Equation (29) is obtained from Eq. (17) by simply (a) reducing ϕ_α to the quadruples when dressing the doubles. ϕ_i actually interacts with all the quadruples ϕ_α which are obtained from ϕ_i by another (disjoint) double excitation. If ϕ_α is a quadruple interacting with ϕ_i ($\langle\phi_\alpha|H|\phi_i\rangle\neq0$) then one may find a double excitation D_j^+ such that

$$D_j^+\phi_i=\phi_\alpha$$

and

$$\langle\phi_\alpha|H|\phi_i\rangle=\langle D_j^+\phi_0|H|\phi_0\rangle.$$

(b) Reducing then C_α to a single term when dressing ϕ_i,

$$C_\alpha=C_iC_j \quad \text{if} \quad \phi_\alpha=D_j^+ D_i^+\phi_0$$

instead of its complete expansion (see below Sec. V).

The (SC)^2 SDCI algorithm dresses each excited determinant by the unlinked effects of the outer space only, while we here propose a *full dressing* involving *both linked and unlinked contributions from the triples and quadruples.*

C. Improved version: Addition of higher orders EPV corrections

A slightly better evaluation of the coefficient C_α (and therefore a better dressing) may be obtained as follows. One might have added ϕ_α to the intermediate model space, and the eigenequation would have been written for the line ϕ_α,

$$\sum_{k\in S} C_k\langle\phi_\alpha|H|\phi_k\rangle + (\langle\phi_\alpha|H|\phi_\alpha\rangle - E$$
$$+ \langle\phi_\alpha|\Delta|\phi_\alpha\rangle)C_\alpha=0. \qquad (30)$$

Of course one does not know $\langle\phi_\alpha|\Delta|\phi_\alpha\rangle$. But one may approximate it by considering the above-mentioned self-consistent size-consistent CIs.[18] In this method and for that CI, the dressing would be [cf. Eq. (29)],

$$\langle\phi_\alpha|\Delta|\phi_\alpha\rangle = E - \langle\phi_0|H|\phi_0\rangle + \text{EPV}_\alpha, \qquad (31)$$

where E is the exact energy and EPV_α represent the exclusion principle violating corrections

$$\text{EPV}_\alpha = - \sum_i C_i\langle\phi_0|H|\phi_i\rangle,$$
$$D_i^+\phi_\alpha=0. \qquad (32)$$

Equation (31) is obtained by noticing that in Eq. (29) the right-hand member is equal to the correlation energy plus the EPV_i contribution for ϕ_i.

This last term sums the effect of all the single and double excitations which cannot act on ϕ_α, due to the Pauli principle. Then it comes out from Eqs. (30) and (31) that

$$C_\alpha= \sum_{k\in S} C_k\langle\phi_\alpha|H|\phi_k\rangle/[\langle\phi_0|H|\phi_0\rangle$$
$$- (\langle\phi_\alpha|H|\phi_\alpha\rangle + \text{EPV}_\alpha)]. \qquad (33)$$

The derivation naturally induces the choice of the Epstein–Nesbet definition of the zeroth-order Hamiltonian

$$H_0\phi_I=\langle\phi_I|H|\phi_I\rangle\phi_I \quad \forall I=0,k,\alpha \qquad (34)$$

but we now have added higher order effects through the EPV corrections. The practical implementation of the EPV corrections through the introduction of one-, two-, and three-dimensional arrays takes benefit of a previous work on the infinite summation of EPV diagrams[20] and has been explicited when presenting the (SC)^{2}CI algorithms.[18]

Finally,

$$\langle\phi_i|\Delta|\phi_i\rangle$$

$$= C_i^{-1} \sum_{\alpha\in S} \frac{\langle\phi_i|H|\phi_\alpha\rangle}{\langle\phi_0|H|\phi_0\rangle - (\langle\phi_\alpha|H|\phi_\alpha\rangle + \text{EPV}_\alpha)}$$

$$\times \sum_{k\in S} C_k\langle\phi_\alpha|H|\phi_k\rangle \qquad (35)$$

or

$$\langle\phi_i|\bar\Delta|\phi_0\rangle = \langle\phi_i|\Delta|\phi_i\rangle C_i.$$

The practical advantage of this formulation will be illustrated below, but it is clear that the EPV corrections slow the possible divergence when ϕ_α and ϕ_0 tend to become too close in energy. If one of the doubles ϕ_k becomes degenerate with ϕ_0 some triples and quadruples ϕ_α involving the double excitation D_k^+ become low in energy, but the effect of this double excitation D_k^+ is impossible on these ϕ_α's so that the energy denominator increases. Even if two doubly excited determinants $D_k^+\phi_0$ and $D_i^+\phi_0$ tend to become degenerate with ϕ_0, the quadruply excited determinant $\phi_\alpha=D_k^+ D_i^+\phi_0$, which also tend to become degenerate with ϕ_0, will not lead to a zero-energy denominator, due to the large EPV_α corrections.

Notice that here, if the EPV terms are calculated from the variational coefficients [cf. Eq. (32)] the method is really self-consistent, and it might not be transformed, as occurred for the simplest version, into a noniterative full-matrix dressing.

One may easily demonstrate the following statements.
Statement 1: If Q is the projector on the outer space ($1=P+Q$), and if QHQ is diagonal in the basis of the ϕ_α's, then the self-consistent diagonal dressing including the EPV terms gives the exact energy.

The proof goes through the following remark.
(i) if QHQ is diagonal it means that $\langle\phi_\alpha|H|D_j^+\phi_\alpha\rangle = 0$, $\forall j$ and therefore that $D_j^+\phi_\alpha=0$. Hence $\text{EPV}_\alpha = -\Sigma_j C_j\langle\phi_0|H|\phi_j\rangle = -x$, where x is the searched correlation energy. Then,

$$\langle \phi_i | \Delta | \phi_i \rangle = C_i^{-1} \sum_{\alpha \notin S} \sum_{j \in S} \frac{\langle \phi_i | H | \phi_\alpha \rangle \langle \phi_\alpha | H | \phi_j \rangle C_j}{E - E_\alpha^0} .$$

(ii) This is equivalent, according to a preceding remark to a nondiagonal dressing

$$\langle \phi_i | \Delta' | \phi_i \rangle = \sum_{\alpha \notin S} \frac{\langle \phi_i | H | \phi_\alpha \rangle \langle \phi_\alpha | H | \phi_i \rangle}{E - E_\alpha^0} ,$$

$$\langle \phi_i | \Delta' | \phi_j \rangle = \sum_{\alpha \notin S} \frac{\langle \phi_i | H | \phi_\alpha \rangle \langle \phi_\alpha | H | \phi_j \rangle}{E - E_\alpha^0} ,$$

which is exactly the partitioning technique dressing [Eq. (6)] for the case where QHQ is diagonal in the basis of the ϕ_α's. The partitioning technique equation is exact, therefore E is exact. This is a rather special case. It implies that the problem concerns four electrons only, otherwise there is no reason that all $\langle \phi_\alpha | H | D_j^+ \phi_\alpha \rangle$ are zero. But we shall mention an amazing application of that statement in the next section.

Statement 2: For the problem of n H_2 molecules in a minimal basis set, the self-consistent dressing including the EPV terms gives the exact energy.

The undressed matrix may be written in a new basis

$$\begin{array}{c} \phi_0 \\ n^{-1/2} \sum_i \phi_i \end{array} \begin{pmatrix} 0 & \sqrt{n}h \\ \sqrt{n}h & \Delta E \end{pmatrix} ,$$

where h is the interaction between the HF determinant and any doubly excited determinant, if all molecules are identical. The simplest perturbation will give a dressed matrix

$$\begin{pmatrix} 0 & \sqrt{n}h \\ \sqrt{n}h & \Delta E - (n-1) \dfrac{h^2}{\Delta E} \end{pmatrix}$$

whose eigenvalue behaves as $-(n-1)(h^2/\Delta E)$, which means that the energy per molecule becomes $-h^2/\Delta E$. In that case the variational step becomes asymptotically useless, and the correlation energy evaluation behaves as purely perturbative. On the contrary if one introduces the EPV correction, the equation becomes

$$\begin{pmatrix} 0 & \sqrt{n}h \\ \sqrt{n}h & \Delta E - (n-1) \dfrac{h^2}{\Delta E - Ch} \end{pmatrix}$$

where C is the coefficient on each doubly excited determinant, and the eigenvalue is nCh, as desired.

Statement 3: However this dressing does not give the exact separability for independent electron pairs $(1,...,i,...,n)$ when nonminimal basis sets are used. It only gives the sum of the self-consistent 2nd order energies, as calculated according to Ref. 24, for the separate subsystems.

$$E(1,...,i,...,n) = \sum_{i=1,n} \epsilon^2_{(SC)^2}(i).$$

We let the reader demonstrate this result.

All these statements lead to the conclusion that the presently proposed total dressing of the SDCI matrix insures the correct behavior of the energy with the number of particles, although the strict separability is not insured.

IV. ILLUSTRATIVE EXAMPLES

We shall only give a few numerical examples, with special attention to difficult situations where a degeneracy tends to occur between ϕ_0 and one of the doubly excited configurations. One might believe that since our method is basically a single-reference scheme, it will be unable to manage that (near) degeneracy. We want to illustrate the ability of our totally-dressed SDCI algorithm to treat correctly such physical situations.

A. The H_4 model problem: The rectangle into square deformation

This model problem has been the critical test-ground for a series of methods, especially for coupled cluster algorithms.[21] If a rectangular H_4 conformation is distorted towards the square $(R=r)$,
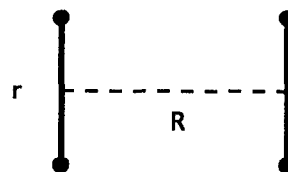
a degeneracy occurs between the b_1 and b_2 MOs

b 1   b 2
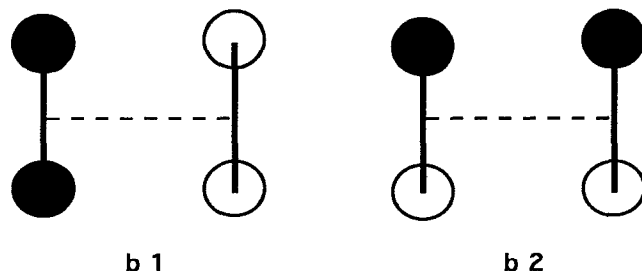
and the determinant $\phi_0 = |a_1^2 b_1^2|$ becomes degenerate with a doubly excited determinant $\phi_i = |a_1^2 b_2^2|$. This is a case where in the minimal basis set the singles and triples are not of the relevant symmetry so that the outer space reduces to a unique quadruply excited configuration $|b_2^2 a_2^2|$. Then as it has been demonstrated above, QHQ being diagonal, the total-dressing with EPV gives the exact solution. This will no longer be true for nonminimal basis sets and we have performed a similar calculation in a double zeta basis set.

The results appear in Table I and Fig. 1. The r value was kept at 1.401 58 a.u. Starting from large R values where the SDCI error is small but non-negligible, the error increases when R decreases. The self-consistent size-consistent SDCI scheme, which only adds the unlinked effects of the triples and quadruples reduces the error by a factor 2 at most. The incorporation of the linked effects in our perturbative total dressing (TD1) reduces the error by one order of magnitude at least, even for $R \leqslant r$, and the incorporation of the EPV in the dressing (TD1EPV) re-

TABLE I. Rectangular H_4 system in a double zeta basis set as a function of R (a.u.) for $r=1.401\,58$ a.u. FCI energies (in a.u.), and errors to FCI.

R	FCI	FCI-SCF	FCI-SDCI	FCI-(SC)^{2}CI	FCI-TD1	FCI-TD1EPV
1.2	−1.793 989	−0.058 914	−0.001 472	−0.000 984	0.000 011	0.000 016
1.24	−1.802 647	−0.061 854	−0.001 891	−0.001 266	0.000 022	0.000 016
1.28	−1.810 103	−0.065 750	−0.002 597	−0.001 744	0.000 043	0.000 018
1.32	−1.817 366	−0.071 340	−0.003 868	−0.002 607	0.000 101	0.000 008
1.36	−1.826 048	−0.079 990	−0.006 193	−0.004 168	0.000 230	0.000 020
1.4	−1.838 21	−0.093 570	−0.009 926	−0.006 563	0.000 487	0.000 083
1.401 58	−1.838 784	−0.094 227	−0.010 096	−0.006 668	0.000 499	8.6E-05
1.42	−1.846 002	−0.088 08	−0.008 235	−0.005 493	0.000 364	4.8E-05
1.44	−1.854 827	−0.082 82	−0.006 576	−0.004 415	0.000 248	1.5E-05
1.46	−1.864 44	−0.078 775	−0.005 302	−0.003 571	0.000 166	−7E-06
1.48	−1.874 579	−0.075 666	−0.004 356	−0.002 938	0.000 11	−2.3E-05
1.5	−1.885 016	−0.073 248	−0.003 658	−0.002 468	7.2E-05	−3.2E-05
1.52	−1.895 58	−0.071 337	−0.003 141	−0.002 12	4.6E-05	−3.8E-05
1.54	−1.906 151	−0.069 797	−0.002 793	−0.001 859	2.8E-05	−4.2E-05
1.56	−1.916 645	−0.068 533	−0.002 457	−0.001 659	1.5E-05	−4.4E-05
1.58	−1.927 007	−0.067 476	−0.002 227	−0.001 505	6E-06	−4.5E-05
1.6	−1.937 201	−0.066 578	−0.002 046	−0.001 419	−1E-06	−4.6E-05
1.8	−2.027 364	−0.061 597	−0.001 303	−0.000 88	−2.7E-05	−5E-05
2	−2.096 821	−0.059 056	−0.001 088	−0.000 73	−3.4E-05	−5.2E-05
2.2	−2.149 662	−0.057 225	−0.000 979	−0.000 652	−3.8E-05	−5.2E-05
2.4	−2.189 66	−0.055 767	−0.000 911	−0.000 603	−3.9E-05	−5.2E-05
2.6	−2.219 768	−0.054 576	−0.000 864	−0.000 569	−3.8E-05	−5.1E-05
2.8	−2.242 283	−0.053 601	−0.000 828	−0.000 544	−3.7E-05	−4.9E-05
20.	−2.303 002	−0.049 850	−0.000 701	−0.000 446	−4.7E-05	−5.6E-05

duces the error by another order of magnitude for $R<1.1r$ (the errors are negligible for both TD1 and TD1 EPV for $R>1.1r$). The ability of our procedure to go through the avoided crossing $R=r$ is nicely demonstrated.

Table I also reports the energies for two H_2 noninteracting molecules. The error to full CI is the deviation to additivity since for each subsystems SDCI gives the exact energy. One sees that in this case, due to the use of delocalized MOs, the (SC)^2 SDCI procedure deviates from the strict additivity (by about half of the error of SDCI). Let us remember that (SC)^2 SDCI is strictly additive when localized MOs are used, but is not unvariant under unitary transformation of MOs. The deviation to additivity is reduced by one order of magnitude when the total dressing by triples and quadruples is performed. In order to check whether this behavior remained true for more correlated systems we have repeated the calculation for $R=20$ u.a., $r=2.0$ u.a. The total correlation energy is then 0.068 552 a.u., and the errors of SDCI and (SC)^2 SDCI are 0.002 147 and 0.001 499 a.u., respectively, and the total dressing again reduces the error by a factor 10 (0.000 143 a.u. for TD1, 0.000 206 a.u. for TD1+EPV). These errors (~ 0.1 kcal mol^{-1}) are below what is considered to be the chemical accuracy.

B. Breaking of a single bond in a four-electron problem

As a test example we have studied the T-shaped Li_4 problem, fixing an atom on the top of a Li_3 isosceles triangle and studying the dependance of the energy on the length R of the axial $Li\cdots Li$ bond. The geometry may be characterized as follows $x_1=3$ a.u., $y_1=0$, $x_2=3$ a.u., y_2
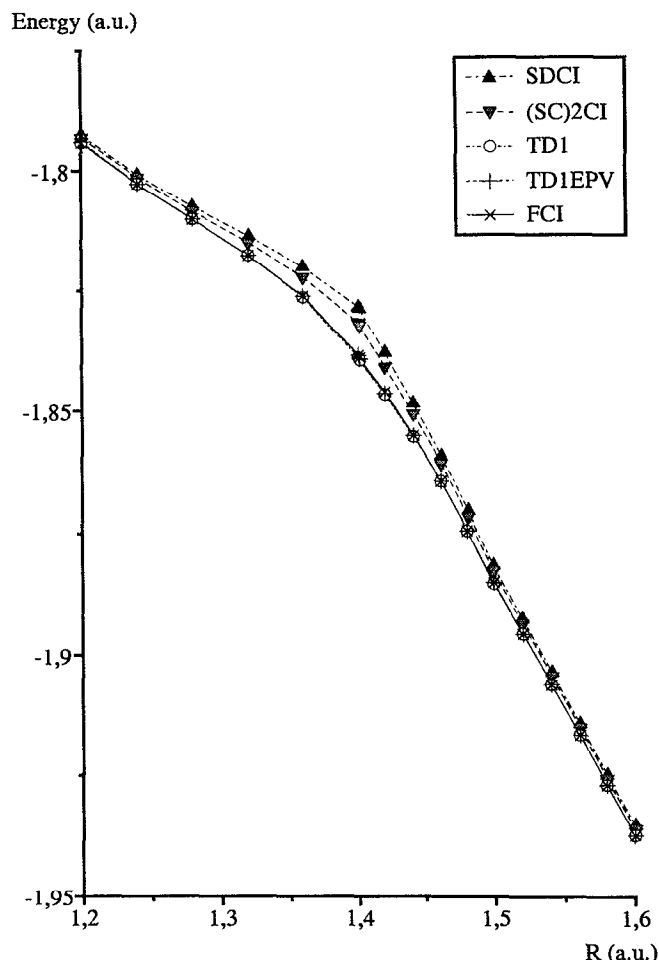

FIG. 1. Evolution of the energy in the rectangular H_4 problem in a double zeta basis set, as a function of R for $r=1.401\,58$ a.u.

TABLE II. Characteristics of the T-shaped Li_4 potential curve (fixed Li_3 isoceles triangle, lengthening of the axial Li–Li bond) in a double zeta basis set. All quantities are in cm^{-1}, except R_e (a.u.).

	SCF	SDCI	$(SC)^2SDCI$	TD1	TD1-EPV	FCI
R_e	5.359	5.544	5.576	5.620	5.605	5.611
ω_e	257	206	193	184	187	186
$\omega_e x_e$	0.878	2.034	2.290	2.968	2.401	2.576
α_e	0.000 68	0.001 10	0.001 31	0.001 56	0.001 37	0.001 40
D_e	22 598	4 643	3 069	1 554	2 732	2 649

$=0$, $x_3=0$, $y_3=7$ a.u., $x_4=0$, $y_4=7$ a.u. This may be seen as a model for a single bond in the presence of other electron pair(s). The calculations have been performed with various basis sets $(1s)$ $(1s,1p)$, and $(2s)$ which give similar behaviors so that we only report those relative to the last basis set. The results appear in Tables II and III and in Fig. 2. Comparison is made between SDCI, the size consistent self-consistent SDCI, the perturbative total dressing without and with EPV, and the full CI results.

The first element of comparison concerns the potential well region, which may be analyzed by its "spectroscopic constants" if the Li_3 triangle is considered as a pseudoatom (cf. Table II). It is clear that going from SDCI to $(SC)^2$ SDCI, then to our total dressings without and with EPV corrections systematically improves all the characteristics, the equilibrium distance the curvature (ω_e) and the anharmonicity. The effect of the EPV corrections is not negligible. Regarding the total energies one sees from Table III that at short interatomic distances the $(SC)^2$ SDCI energies were not significantly better than those of SDCI. The total dressing brings the energy very close to the exact one ($|error| < 10^{-4}$ a.u. for 4 bohr $< R < 6.2$ bohr), but below it. The EPV correction pushes the energy above the exact one, with a somewhat larger but constant error of $\sim 2.10^{-4}$ a.u.

When the bond is broken (large R values) the SDCI energies become much too high, with an asymptotic error of 1.1×10^{-2} a.u. The $(SC)^2$ SDCI method repairs the major part of that defect since the asymptotic error falls down to 3.8×10^{-3} a.u. The proposed total dressing here does not diverge, despite its perturbative character, but it gives energies that are too low, with an asymptotic error of 4.1×10^{-3} a.u. The inclusion of the EPV correction is sufficient to give an accurate behavior in the asymptotic region since the error remains 0.7×10^{-3} a.u. The dissociation energies D_e reported in Table II reflect these differences in the asymptotic behaviors and show the ability of our total dressing with EPV to treat the bond breaking to a high accuracy despite (i) its single reference nature and (ii) its perturbative character.

V. DISCUSSION

The present work has proposed a very simple presentation of self-consistent intermediate Hamiltonians for the research of a single root. This root is not necessarily the lowest one, but it is the eigenvector which has the largest component on the determinant chosen as main model space or reference. Since the choice of that determinant is

TABLE III. T-shaped Li_4 problem with an increase of the axial bond length R (in a.u.). FCI energy and errors to FCI (in a.u.).

| R	FCI	FCI-SCF	FCI-SDCI	FCI-$(SC)^2$CI	FCI-TD1	FCI-TD1EPV
5	−0.800 14	−0.026 99	−0.001 83	−0.001 42	7E-06	−0.000 142
5.2	−0.802 142	−0.027 808	−0.001 988	−0.001 524	1.5E-05	−0.000 155
5.4	−0.803 485	−0.028 671	−0.002 156	−0.001 628	2.6E-05	−0.000 169
5.6	−0.804 296	−0.029 58	−0.002 332	−0.001 729	4E-05	−0.000 184
5.8	−0.804 687	−0.030 539	−0.002 519	−0.001 83	5.5E-05	−0.000 2
6	−0.804 745	−0.031 547	−0.002 716	−0.001 928	7.5E-05	−0.000 217
6.2	−0.804 548	−0.032 607	−0.002 923	−0.002 024	9.8E-05	−0.000 234
6.4	−0.804 158	−0.033 721	−0.003 141	−0.002 119	0.000 125	−0.000 253
6.6	−0.803 627	−0.034 889	−0.003 369	−0.002 211	0.000 156	−0.000 273
6.8	−0.802 999	−0.036 111	−0.003 607	−0.002 302	0.000 193	−0.000 294
7	−0.802 307	−0.037 386	−0.003 853	−0.002 39	0.000 237	−0.000 315
7.2	−0.801 582	−0.038 714	−0.004 108	−0.002 477	0.000 287	−0.000 337
7.4	−0.800 846	−0.040 092	−0.004 37	−0.002 562	0.000 344	−0.000 36
7.6	−0.800 117	−0.041 518	−0.004 638	−0.002 646	0.000 408	−0.000 383
7.8	−0.799 409	−0.042 988	−0.004 911	−0.002 727	0.000 481	−0.000 407
8	−0.798 731	−0.044 497	−0.005 187	−0.002 807	0.000 562	−0.000 431
9	−0.795 98	−0.052 452	−0.006 552	−0.003 16	0.001 09	−0.000 551
10	−0.794 315	−0.060 57	−0.007 769	−0.003 426	0.001 814	−0.000 652
20	−0.792 69	−0.101 112	−0.011 178	−0.003 793	0.003 431	−0.000 73
40	−0.792 69	−0.113 498	−0.011 511	−0.003 784	0.004 146	−0.000 627
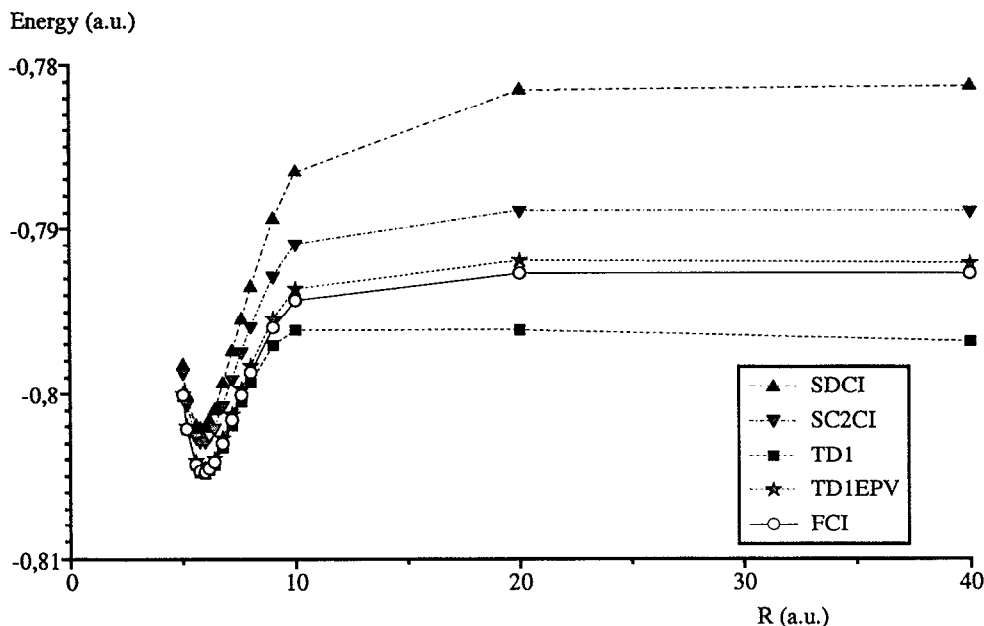
FIG. 2. Evolution of the energy in the T-shaped Li_4 problem in a double zeta basis set, as a function of the length R of the axial bond.

free, the method might equally be applied to excited states, at least when one may have a single reference zeroth-order description, as for most triplet states.

The dressing may take several forms. It may be concentrated on the first column, on the diagonal, or concern the full matrix, and the two first solutions have the advantage of economy of the information storage. The dressing may be expressed from the coefficients of the eigenvector on the outer space determinants, which have to be estimated. A further paper will proceed to a coupled-cluster type evaluation of these amplitudes, while the present work uses a perturbative evaluation, easily applicable to excited states.

We have essentially considered the case where the intermediate model space spanned the first order wave function (singles and doubles), and the useful outer space involved the space spanning the 2nd order correction (triples and quadruples). Since the interaction between the outer-space determinants was not considered explicitly in our formulations, the method must be compared to the 4th order perturbative evaluation of the energy. The cost of our proposals should be similar to MP4 and the accuracy should be much better since the amplitude on the doubly excited state are variational, and actually our proposals do not diverge when a (near) degeneracy occurs in the model space.

The simplest perturbative scheme may be seen as a convenient reformulation of the so-called shifted-B_k approximation or of the non-self-consistent 2nd order intermediate Hamiltonians and therefore behaves correctly when the number of particles increases. In order to obtain this property, one must proceed to the diagonalization *after* dressing, instead of perturbing a multireference vector obtained by diagonalizing a bare matrix, as done in CIPSI (Ref. 22) and most of the related MRMP2 methods.[23]

The addition of EPV corrections greatly improves the behavior in case of strong degeneracies within the model space, at a low computational extra-cost when one stores the summation of the effect of double (and single) excitations in terms of one MO, two-MOs, three-MOs partial contributions, as previously proposed[20] and used in the self-consistent size-consistent CI method.[18] The numerical tests have shown the efficiency of the method.

The method is of single-reference character. However one must notice (i) that the choice of the reference is free. It may be an excited configuration as discussed above, and in case of avoided crossing, it may change, as shown on the H_4 problem where one goes from $\phi_0=a^2$, b^2 to ϕ_0' $= a_1^2 b_2^2$. (ii) When the EPV contributions are considered, the method is able to treat the situations where one of the intermediate determinants has an amplitude equal to that of ϕ_0.

That striking ability of the TD1-EPV algorithm to treat near degeneracies has been illustrated on $4e^-$ problems only, but it should remain valid for systems involving more electrons, since the amplitudes of the triples and quadruples are evaluated perturbatively in the intermediate normalization, avoiding size-consistency defects.

Of course one should consider the following generalizations: (i) The intermediate model space might be larger than the set of determinants interacting with ϕ_0. As an extreme case it might also involve all the determinants belonging to the 2nd order wave function $\psi^{(2)}$, and the method would then provide an improved evaluation of the sixth-order corrected energy. More reasonably, the intermediate model space might include a limited number of triples, quadruples, etc. If, for instance, one breaks a double bond, a valence quadruply excited configuration be-

comes degenerate with ϕ_0, and more generally the intermediate model space might include a CAS plus all the doubles. Of course the generation of the ϕ_α's has to be revised. (ii) On the contrary the intermediate space might be shorter than the whole set of all singles and doubles, containing only those of largest amplitudes. Then the contributing outer space will also concern the other singles and doubles, not all quadruples. The dressing will also concern the main model space determinant ϕ_0,

$$\langle \phi_0 | \Delta | \phi_0 \rangle = \sum_{i \notin S} C_i \langle \phi_0 | H | \phi_i \rangle,$$

the coefficients C_i being evaluated to the first order, or preferably by the recently proposed nondivergent self-consistent 2nd order technique[24] which proceeds by diagonalizing 2×2 matrices spanned by ϕ_0 and ϕ_i after a minimal dressing by EPV. Then the vector on S and D is complete and the dressing of the S and D diagonal energies by the T and Q configurations may be performed according to the same technique.

In practice the implementation rests on the efficient algorithm recently proposed by Maynau and Heully for the perturbation of the SDCI vector by all triples and quadruples.[15] But instead of perturbing this MR vector, one dresses the S and D configurations diagonal energies, in an iterative manner. The computation time per iteration is the same; a few iterations are necessary but while the SD(TQ) algorithm was not size-extensive, the present one is. A preliminary work by Maynau and two of us[25] had given an approximate version of the present proposal; in that work the total-dressing energy was calculated as a mean-value of the diagonal dressing

$$\epsilon = \langle \tilde{\psi} | \Delta | \tilde{\psi} \rangle$$

on a vector resulting from the $(SC)^2$SDCI method. The $(SC)^2$SDCI method is size extensive and iterative, the vector $\tilde{\psi}$ is certainly very close to the eigenvector of $P(H + \Delta)P$. So that the iterations concerned an algorithm the cost of which is only that of SDCI, and not the long loops generating all triples and quadruples. But the present formulation is much clearer and certainly more reliable.

ACKNOWLEDGMENTS

[1] J. Goldstone, Proc. R. Soc. London, Ser. A 239, 267 (1957).

[2] F. Coester, Nucl. Phys. 1, 421 (1958); F. Coester and H. Kummel, ibid. 17, 477 (1960).

[3] B. H. Brandow, Rev. Mod. Phys. 39, 771 (1967).

[4] See, for instance, Ph. Durand and J. P. Malrieu, in Ab-initio Methods in Quantum Chemistry, edited by K. P. Lawley (Wiley, New York, 1986), Vol. 1, p. 321; D. Mukherjee and S. Pal, Adv. Quantum Chem. 20, 291 (1989); G. Hose and U. Kaldor, Chem. Phys. 62, 469 (1981); J. Phys. Chem. 86, 2133 (1982).

[5] B. Jeziorski and H. J. Monkhorst, Phys. Rev. A 24, 1668 (1981); L. Z. Stolarczyk and H. J. Monkhorst, ibid. 32, 725, 743 (1985); W. D. Laidig and R. J. Bartlett, Chem. Phys. Lett. 104, 424 (1984); L. Meissner, S. A. Kucharski, and R. J. Bartlett, J. Chem. Phys. 91, 6187 (1989); B. Jeziorski and J. Paldus, ibid. 90, 2714 (1989); L. Meissner and R. J. Bartlett, ibid. 92, 561 (1990); A. Balková, S. A. Kucharski, L. Meissner, and R. J. Bartlett, ibid. 95, 4311 (1991); D. Mukhopadhyay and D. Mukherjee, Chem. Phys. Lett. 163, 171 (1989); 177, 441 (1991); V. Kaldor, Theor. Chim. Acta 80, 427 (1991); J. Paldus, P. Piecuch, L. Pylypow, and B. Jeziorski, Phys. Rev. A 47, 2738 (1993), and references therein.

[6] J. P. Malrieu, Ph. Durand, and J. P. Daudey, J. Phys. A 18, 809 (1985).

[7] A. V. Zaitsevski and J. L. Heully, J. Phys. B 25, 603 (1992); see also, D. Mukherjee, Int. J. Quantum Chem. 20, 409 (1986); S. Koch, Theor. Chim. Acta 81, 169 (1991).

[8] S. Evangelisti, J. P. Daudey, and J. P. Malrieu, Phys. Rev. A 35, 4930 (1987).

[9] L. E. Nietsche and E. R. Davidson, J. Chem. Phys. 68, 3103 (1978); J. Am. Chem. Soc. 100, 7201 (1978); E. R. Davidson, L. B. McMurchie, and S. J. Day, J. Chem. Phys. 74, 5491 (1981).

[10] C. Bloch, Nucl. Phys. 6, 329 (1958).

[11] H. Feschbach, Ann. Phys. (NY) 5, 357 (1958); 19, 287 (1962); Ann. Rev. Nucl. Sci. 8, 49 (1958); P. O. Löwdin, J. Math. Phys. 3, 969 (1962).

[12] See, for instance, K. F. Freed, Acc. Chem. Res. 16, 137 (1983), and references herein; P. Westhaus, J. Chem. Phys. 73, 5197 (1980); S. Pal, M. D. Prasad, and D. Mukherjee, Theor. Chim. Acta 66, 311 (1984), and references herein; J. Y. Metz and J. Lievin, ibid. 67, 369, 391 (1985); B. Lam, M. W. Schmidt, and K. Ruedenberg, J. Phys. Chem. 89, 2221 (1985); F. Spiegelmann, J. P. Malrieu, D. Maynau, and J. P. Zurru, J. Chem. Phys. 83, 69 (1986); M. M. Goodgame and W. A. Goddard III, Phys. Rev. Lett. 54, 66 (1985); A. Clotet, J. P. Daudey, J. P. Malrieu, J. Rubio, and F. Spiegelmann, Chem. Phys. 147, 293 (1990).

[13] J. L. Heully and J. P. Malrieu, Chem. Phys. Lett. 199, 545 (1992).

[14] Z. Gershgorn and T. Shavitt, Int. J. Quantum Chem. 2, 751 (1968).

[15] D. Maynau and J. L. Heully, Chem. Phys. Lett. 211, 625 (1993).

[16] R. Cimiraglia, J. Chem. Phys. 83, 1746 (1985); R. Cimiraglia and M. Persico, J. Comput. Chem. 8, 39 (1987).

[17] J. P. Malrieu, Theor. Chim. Acta 62, 163 (1982).

[18] J. P. Daudey, J. L. Heully, and J. P. Malrieu, J. Chem. Phys. 99, 1240 (1993).

[19] H. P. Kelly and M. A. Sessler, Phys. Rev. 132, 2091 (1963); Phys. Rev. A 134, 1450 (1964); W. Meyer, Int. J. Quantum Chem. Symp. 5, 341 (1971); R. Alrichs, H. Lishka, V. Staemmler, and W. Kutzelnigg, J. Chem. Phys. 62, 1225 (1975).

[20] M. B. Lepetit and J. P. Malrieu, J. Chem. Phys. 87, 5937 (1987).

[21] K. Jankovski and J. Paldus, Int. J. Quantum Chem. 18, 1243 (1980); K. Jankovski, J. Paldus, and J. Wasilewski, J. Chem. Phys. 95, 3549 (1991); K. Jankovski, J. Paldus, I. Grabowski, and K. Kowalski, ibid. 97, 1600 (1992).

[22] B. Huron, P. Rancurel, and J. P. Malrieu, J. Chem. Phys. 58, 5745 (1973); S. Evangelisti, J. P. Daudey, and J. P. Malrieu, Chem. Phys. 75, 91 (1983).

[23] R. J. Harrison, J. Chem. Phys. 94, 5021 (1991).

[24] M. B. Lepetit and J. P. Malrieu, Chem. Phys. Lett. 208, 503 (1993).

[25] J. Sanchez-Marin, D. Maynau, and J. P. Malrieu, Theor. Chim. Acta (in press).