

# Four self-consistent dressings to achieve size-consistency of singles and doubles configuration interaction

Jean-Louis Heully and Jean-Paul Malrieu

*IRSAMC, Laboratoire de Physique Quantique, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France*

Received 7 July 1992; in final form 10 September 1992

Benefitting from the flexibility of intermediate effective Hamiltonians, we define four different dressings of the singles and doubles CI matrix which take into account the dominant effect of triple and quadruple excitations. Self-consistent versions of the dressing insure the strict separability of the energy for a system splitting into separate fragments (and therefore size-extensivity) provided that localized MOs are used. The relative advantages of the different versions are discussed.

## 1. Introduction

Although it incorporates the leading interactions responsible for electron correlation in atoms and molecules, the configuration interaction (CI) restricted to the singly and doubly excited determinants (singles and doubles) suffers a major defect, namely its lack of size-consistency [1,2]. For a system built of  $n$  independent subsystems, that truncated CI only brings a part of the correlation energy which increases as  $\sqrt{n}$  (instead of a linear dependence). The defect, linked to the non-exponential structure of the wavefunction, is not satisfactorily corrected by the denormalization of the wavefunction and the resulting variety of Davidson type corrections [3].

The present Letter introduces a series of dressings of the CISD matrix which, provided that they are self-consistent, insure a correct behavior of the ground state eigenenergy, i.e. a linear increase of the correlation energy with the number of particles (size-extensivity) and even insure an additivity of the energy for a system built of two non-interacting subsystems, if localized molecular orbitals are used. Two of these dressings are Hermitian, the two others

are non-Hermitian but are equivalent as regard the ground-state energy and eigenvector.

The so-dressed CISD matrices are intermediate effective Hamiltonians, a recently proposed generalization of effective Hamiltonians [4]. We shall not follow the heuristic steps which have led us to the proposals of that Letter. A full-length derivation of one of these dressings is given in ref. [5] together with a generalization to energy-selected CI and with numerical illustrations. The present Letter schematically gives the logic of the dressings, discusses their relationship and differences, and demonstrates that they satisfy the exact separability for localized MOs and therefore size-consistency.

## 2. Expression of four self-consistent dressings of the CISD matrix

The lack of size-consistency of CISD is easily traced back to the absence of the triples and quadruples (at least to the fourth-order of perturbation) which does not balance the normalization of the wavefunction. The crucial point is to take into account the unlinked diagrams going through the triples and quadruples. If we concentrate on the quadruples, which play a much larger role than the triples when one starts from an HF determinant, these unlinked processes are of two types: if a quadruply excited determinant may

*Correspondence to:* J.-L. Heully, IRSAMC, Laboratoire de Physique Quantique, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France.

be read as the product of two disjoint double excitations on the ground state determinant  $\Phi_0$ ,

$$\Phi_{i+j} = D_i^\dagger D_j^\dagger \Phi_0,$$

this determinant is involved in four different unlinked fourth-order processes,

$$\Phi_0 \leftarrow \Phi_i \leftarrow \Phi_{i+j} \leftarrow \Phi_i \leftarrow \Phi_0, \quad (a)$$

$$\Phi_0 \leftarrow \Phi_i \leftarrow \Phi_{i+j} \leftarrow \Phi_j \leftarrow \Phi_0, \quad (b)$$

$$\Phi_0 \leftarrow \Phi_j \leftarrow \Phi_{i+j} \leftarrow \Phi_i \leftarrow \Phi_0, \quad (a')$$

$$\Phi_0 \leftarrow \Phi_j \leftarrow \Phi_{i+j} \leftarrow \Phi_j \leftarrow \Phi_0. \quad (b')$$

They respectively give

$$a = \langle \Phi_0 | H | \Phi_i \rangle \langle \Phi_i | H | \Phi_{i+j} \rangle \\ \times \langle \Phi_{i+j} | H | \Phi_i \rangle \langle \Phi_i | H | \Phi_0 \rangle \\ \times [(E_0 - E_i)(E_0 - E_i)(E_0 - E_{i+j})]^{-1}$$

and

$$b = \langle \Phi_0 | H | \Phi_i \rangle \langle \Phi_i | H | \Phi_{i+j} \rangle \\ \times \langle \Phi_{i+j} | H | \Phi_j \rangle \langle \Phi_j | H | \Phi_0 \rangle \\ \times [(E_0 - E_i)(E_0 - E_j)(E_0 - E_{i+j})]^{-1}$$

with  $a'$  which permutes  $i$  and  $j$  and  $b'$  equals  $b$ .

The quantities in the denominator are the eigenvalues of an as yet unspecified zeroth-order Hamiltonian:

$$H_0 \Phi_i = E_i \Phi_i.$$

For compactness, the notation

$$\langle \Phi_0 | H | \Phi_i \rangle = h_{0i}, \quad \langle \Phi_i | H | \Phi_0 \rangle = h_{i0},$$

$$E_0 - E_i = \Delta_i, \quad E_0 - E_{i+j} = \Delta_{i+j}$$

will be used.

Two zeroth-order Hamiltonians will be considered. The first one is the Møller-Plesset [6] one-electron Hamiltonian (in terms of orbital energies)

$$H_0 = \sum_p e_p a_p^\dagger a_p,$$

which insures transition energy additivity:

$$\Delta_{i+j} = \Delta_i + \Delta_j.$$

The corresponding dressing operators will be  $W_n$ . The second one may be the Epstein-Nesbet Hamiltonian [7]

$$H_0 \Phi_i = \langle \Phi_i | H | \Phi_i \rangle \Phi_i,$$

which does not assume that additivity and the corresponding dressing will be written  $W_n$ . The perturbative dressing will be denoted  $\tilde{V}$  (or  $\tilde{W}$ ) and the self-consistent ones with a tilde  $\tilde{V}$  (or  $\tilde{W}$ ).

Then, noting that

$$\langle \Phi_i | H | \Phi_{i+j} \rangle = \langle \Phi_0 | H | \Phi_j \rangle,$$

$$a = \frac{h_{0i} h_{0j} h_{j0} h_{i0}}{\Delta_i^2 \Delta_{i+j}},$$

$$b = \frac{h_{0i} h_{0j} h_{j0} h_{i0}}{\Delta_i \Delta_{i+j} \Delta_j}.$$

The general idea is to add terms in the CISD matrix (this is what we call dressing) in such a way that the diagonalization of the dressed matrix produces the unlinked terms  $a$ ,  $b$ ,  $a'$  and  $b'$ . This is a perturbative dressing. The self-consistent versions are such that the lowest root of the new matrix satisfies strict additivity for non-interacting subsystems and become exact when they reduce to electron pairs. Such a new CISD should be an efficient approximate method for interacting systems as well. We also want the eigenvector to be correct (i.e. to be the projection of the exact eigenvector on the SD space for non-interacting electron pairs).

These conditions only impose  $n$  conditions (one energy,  $n-1$  coefficients) for an  $n \times n$  matrix. This underdetermination is typical of the intermediate effective Hamiltonians [4] (and absent in the usual effective Hamiltonians), and explains the non-uniqueness of the dressing.

### 2.1. Non-Hermitian first-column dressing

If we add the extra terms

$$\langle \Phi_i | \tilde{W}_1 | \Phi_0 \rangle = \frac{h_{0j} h_{j0} h_{i0}}{\Delta_{i+j}} \left( \frac{1}{\Delta_i} + \frac{1}{\Delta_j} \right) \\ = \frac{h_{0j} h_{j0}}{\Delta_j} \frac{h_{0i}}{\Delta_i} \left( \frac{\Delta_i + \Delta_j}{\Delta_{i+j}} \right)$$

to the CISD Hamiltonian matrix, the diagonalization of  $H + \tilde{W}$  will produce a second-order correction

$$\frac{\langle \Phi_0 | H | \Phi_i \rangle \langle \Phi_i | \tilde{W}_1 | \Phi_0 \rangle}{\Delta_i} = a + b,$$

the sum of the two previously lacking corrections  $a$  and  $b$  ( $a'$  and  $b'$  would be incorporated through  $\langle \Phi_j | \bar{W}_1 | \Phi_0 \rangle$ ). Hence a proposal: defining  $D_i$  as the set of double excitations  $D_j^+$  which are such that

$$D_j^+ \Phi_i \neq 0$$

i.e. which have neither particle nor hole in common with those defining  $\Phi_i$ . One may define a column dressing of the matrix

$$\langle \Phi_i | \bar{W}_1 | \Phi_0 \rangle = \frac{h_{0i}}{\Delta_i} \sum_{j \in D_i} \frac{h_{0j} h_{j0}}{\Delta_j} \frac{\Delta_i + \Delta_j}{\Delta_{i+j}},$$

or, assuming additivity of transition energies,

$$\langle \Phi_i | \bar{V}_1 | \Phi_0 \rangle = \frac{h_{0i}}{\Delta_i} \sum_{j \in D_i} \frac{h_{0j} h_{j0}}{\Delta_j}.$$

Then the diagonalization of  $H + \bar{V}$  or  $H + \bar{W}$  will produce all unlinked fourth-order diagrams required to cancel the fourth-order effect of the CI truncation to the doubles. Let us now propose an improvement which will make the dressing size-consistent. Noticing that in the intermediate normalization

$$\Psi = \Phi_0 + \sum_i \tilde{c}_i D_i^+ \Phi_0,$$

and that

$$\tilde{c}_i = \frac{h_{i0}}{\Delta_i} + \text{higher-order terms},$$

we may rewrite the dressing as

$$\langle \Phi_i | \bar{W}_1 | \Phi_0 \rangle = \tilde{c}_i \sum_{j \in D_i} \tilde{c}_j h_{0j} \left( \frac{\Delta_i + \Delta_j}{\Delta_{i+j}} \right)$$

or

$$\langle \Phi_i | \bar{V}_1 | \Phi_0 \rangle = \tilde{c}_i \sum_{j \in D_i} \tilde{c}_j h_{0j}.$$

This transformation will include higher-order terms and, in fact, for non-interacting systems and localized MOs will give the exact additivity (and even the exact result, when the system is composed of non-interacting electron pairs).

## 2.2. Hermitian full-dressing

One may as well incorporate the effects  $a$  and  $b$  through two different dressings. The term  $a$  may be

taken into account by defining a diagonal matrix element correction

$$\langle \Phi_i | \bar{W}_2 | \Phi_i \rangle = \frac{h_{0i} h_{i0}}{\Delta_{i+j}},$$

since the third-order correction in the diagonalization of  $H + \bar{W}_2$  gives the term  $a$

$$\begin{aligned} \frac{\langle \Phi_i | H | \Phi_i \rangle \langle \Phi_i | \bar{W}_2 | \Phi_i \rangle \langle \Phi_i | V | \Phi_i \rangle}{\Delta_i \Delta_i} \\ = \frac{|h_{0i}|^2 |h_{i0}|^2}{\Delta_i \Delta_i \Delta_{i+j}}. \end{aligned}$$

The term  $b$  may be included through the definition of an extradiagonal term of the operator  $\bar{W}_2$ ,

$$\langle \Phi_i | \bar{W}_2 | \Phi_j \rangle = \frac{h_{0i} h_{j0}}{\Delta_{i+j}},$$

since the diagonalization of the  $H + \bar{W}_2$  leads to

$$\begin{aligned} \frac{\langle \Phi_i | H | \Phi_i \rangle \langle \Phi_i | \bar{W}_2 | \Phi_j \rangle \langle \Phi_j | V | \Phi_0 \rangle}{\Delta_i \Delta_j} \\ = \frac{|h_{0i}|^2 |h_{0j}|^2}{\Delta_i \Delta_j \Delta_{i+j}} = b. \end{aligned}$$

In full generality

$$\langle \Phi_i | \bar{W}_2 | \Phi_i \rangle = \sum_{j \in D_i} \frac{h_{0i} h_{j0}}{\Delta_{i+j}} = \sum_{j \in D_i} \frac{|\langle \Phi_0 | H | \Phi_j \rangle|^2}{(E_0 - E_{i+j})},$$

while

$$\langle \Phi_i | \bar{W}_2 | \Phi_j \rangle = \frac{h_{0i} h_{j0}}{\Delta_{i+j}}, \quad \text{if } j \in D_i.$$

Notice that if  $j \in D_i$ , then  $i \in D_j$  so that the dressing is Hermitian for real Hamiltonian matrix elements:

$$\langle \Phi_i | \bar{W}_2 | \Phi_j \rangle = \langle \Phi_j | \bar{W}_2 | \Phi_i \rangle.$$

Instead of a perturbative dressing, one may propose a self-consistent Hermitian dressing

$$\begin{aligned} \langle \Phi_i | \bar{W}_2 | \Phi_i \rangle &= \sum_{j \in D_i} \tilde{c}_j h_{0j} \frac{\Delta_j}{\Delta_{i+j}}, \\ \langle \Phi_i | \bar{W}_2 | \Phi_j \rangle &= \tilde{c}_i h_{0j} \frac{\Delta_i}{\Delta_{i+j}}, \quad \text{if } j \in D_i. \end{aligned}$$

The versions  $V_2$  and  $\bar{V}_2$  simply consist in replacing  $\Delta_{i+j}$  by  $\Delta_i + \Delta_j$  in the denominators.

### 2.3. Diagonal dressing

Terms  $a$  and  $b$  may be incorporated by defining a purely diagonal dressing (of course Hermitian)

$$\langle \phi_i | \bar{W} | \phi_i \rangle = \frac{h_{0j} h_{j0}}{A_j} \frac{A_i + A_j}{A_{i+j}},$$

since the third-order correction in the diagonalization of  $H + \bar{W}$  will give  $a + b$ . In a general manner:

$$\langle \phi_i | \bar{W} | \phi_i \rangle = \sum_{j \in D_i} \frac{h_{0j} h_{j0}}{A_j} \frac{A_i + A_j}{A_{i+j}},$$

$$\langle \phi_i | \bar{V} | \phi_i \rangle = \sum_{j \in D_i} \frac{h_{0j} h_{j0}}{A_j}.$$

The corresponding self-consistent expressions are immediately written

$$\langle \Phi_i | \tilde{W} | \Phi_i \rangle = \sum_{j \in D_i} \tilde{c}_j h_{0j} \frac{A_i + A_j}{A_{i+j}},$$

$$\langle \Phi_i | \tilde{V} | \Phi_i \rangle = \sum_{j \in D_i} \tilde{c}_j h_{0j}.$$

This last version, both Hermitian and compact, has been exploited in ref. [5] (hence the absence of subscript).

### 2.4. Non-Hermitian first-column-diagonal dressing

One might as well incorporate the term  $a$  through the definition of a diagonal correction

$$\langle \Phi_i | \bar{W}_3 | \Phi_i \rangle = \sum_{j \in D_i} \frac{h_{0j} h_{j0}}{A_{i+j}},$$

which produces  $a$  as a third-order contribution in the diagonalization of  $H + \bar{W}_3$ . The term  $b$  may be produced as a second-order correction in the diagonalization of  $H + \bar{W}_3$ ,

$$\langle \Phi_i | \bar{W}_3 | \Phi_j \rangle = h_{i0} \sum_{j \in D_i} \frac{h_{0j} h_{j0}}{A_{i+j} A_j}.$$

The corresponding self-consistent version would be expressed as

$$\langle \Phi_i | \tilde{W}_3 | \Phi_0 \rangle = \tilde{c}_i A_i \sum_{j \in D_i} \tilde{c}_j \frac{h_{0j}}{A_{i+j}},$$

$$\langle \Phi_i | \tilde{W}_3 | \Phi_i \rangle = \sum_{j \in D_i} \tilde{c}_j h_{0j} \frac{A_j}{A_{i+j}}.$$

The dressing operator  $V_3$  is given from  $W_3$  by considering

$$A_{i+j} = A_i + A_j.$$

### 3. Equivalence of the four self-consistent dressings for the ground state

We demonstrate here that these four dressings  $\tilde{W}_n$  (resp.  $\tilde{W}_n$ ) lead to the same ground-state solution when self-consistency is achieved.

Actually the eigenequation

$$(H + \tilde{W}_n - \tilde{E})\tilde{c} = 0$$

may be written for the line associated with  $\Phi_i = D_i^+ \Phi_0$ .

(i) For  $\tilde{W}_1$ ,

$$h_{i0} + \tilde{c}_i \sum_{j \in D_i} \tilde{c}_j h_{0j} \frac{A_j + A_i}{A_{i+j}} + \sum_e h_{ie} \tilde{c}_e + (h_{ii} - \tilde{E})\tilde{c}_i = 0.$$

(ii) For  $\tilde{W}_2$ ,

$$h_{i0} + \sum_{j \in D_i} \tilde{c}_j h_{0j} \frac{A_i}{A_{i+j}} + \sum_e h_{ie} \tilde{c}_e + \left( h_{ii} + \sum_{j \in D_i} \tilde{c}_j h_{0j} \frac{A_j}{A_{i+j}} - \tilde{E} \right) \tilde{c}_i = 0,$$

which, adding the two summations over  $j \in D_i$ , reduces to the preceding equation.

(iii) For  $\tilde{W}$ ,

$$h_{i0} + \sum_e h_{ie} \tilde{c}_e + \left( h_{ii} + \sum_{j \in D_i} \tilde{c}_j h_{0j} \frac{A_i + A_j}{A_{i+j}} - \tilde{E} \right) \tilde{c}_i = 0$$

is the same.

(iv) For  $\tilde{W}_3$ ,

$$h_{i0} + \tilde{c}_i \sum_{j \in D_i} \tilde{c}_j h_{0j} \frac{A_i}{A_{i+j}} + \sum_e h_{ie} \tilde{c}_e + \left( h_{ii} + \sum_{j \in D_i} \tilde{c}_j h_{0j} \frac{A_j}{A_{i+j}} - \tilde{E} \right) \tilde{c}_i = 0.$$

The identity of the solutions for the four dressings  $\tilde{W}_n$  is evident from the equations. Therefore the self-

consistent ground-state solution of  $H + \tilde{V}_n$  (respectively  $H + \tilde{W}_n$ ) is a self-consistent solution of  $H + \tilde{V}_m$  (respectively  $H + \tilde{W}_m$ ). The four dressings lead to a unique ground-state eigenvector and energy. However the four self-consistently dressed matrices are all different. They only have *one* root and *one* eigenvector in common. For instance it is evident that the dressing  $V_1$  increases the amplitude of the off-diagonal elements

$$\langle \Phi_i | H + \tilde{V}_1 | \Phi_0 \rangle,$$

since

$$c_i c_j h_{0j} \approx \frac{h_{0i} h_{0j}^2}{\Delta_i \Delta_j} \quad \text{and } \Delta_i \Delta_j > 0,$$

and thus broadens the spectrum (with respect to the undressed matrix), while  $V$  essentially shifts down all the diagonal energies of the matrix and lowers the whole spectrum.

#### 4. Demonstration of the strict separability of the self-consistent dressings

Since the ground-state energy and eigenvector are identical for the four dressings, it is sufficient to demonstrate the separability for one dressing, say  $\tilde{V}_1$  or  $\tilde{W}_1$  (for a demonstration concerning  $\tilde{V}$ , see ref. [5]). Let us consider a system made of two non-interacting (infinitely remote) subsystems A and B, and let us assume that all MOs are *localized* on either A or B. The only non-zero coefficients are those of single and double excitations involving two or four MOs on the same subsystem.

In the following the primed quantities  $c'$  and  $E'$  will refer to the supersystem problem, the unprimed quantities  $c$  and  $E$  refer to the isolated subsystems problem treated with the same procedure. Notice that

$$\Phi'_0 = \Phi_{0A} \Phi_{0B},$$

then the double excitation  $D_i^+$  gives

$$\Phi_{iA} = D_{iA}^+ \Phi_0, \quad \text{of coefficient } c_{iA},$$

$$\Phi'_{iA} = D_{iA}^+ \Phi'_0 = \Phi_{iA} \Phi_{0B}, \quad \text{of coefficient } c'_{iA},$$

$$\langle \Phi'_0 | H | \Phi'_{iA} \rangle = \langle \Phi_{0A} | H | \Phi_{iA} \rangle,$$

$$\langle \Phi'_{iA} | H | \Phi'_{jA} \rangle = \langle \Phi_{iA} | H | \Phi_{jA} \rangle.$$

Also notice that since  $\Phi_{iA}$  and  $\Phi_{jB}$  differ by four MOs

$$\langle \Phi'_{iA} | H | \Phi'_{jB} \rangle = 0, \quad \forall i_A, j_B.$$

For the subsystem A and the line  $i_A$  the eigenequation is written

$$h_{iA0} + \tilde{c}_{iA} \sum_{j \in D_{iA}} \tilde{c}_{jA} h_{0jA} \frac{\Delta_{iA} + \Delta_{jA}}{\Delta_{iA+jA}} + \sum_{eA} h_{iAeA} \tilde{c}_{eA} + (h_{iAiA} - \tilde{E}) \tilde{c}_{iA} = 0,$$

while for the same excitation in the supersystem the eigenequation becomes

$$h_{iA0} + \tilde{c}'_{iA} \left( \sum_{j \in D_{iA}} \tilde{c}'_{jA} h_{0jA} \frac{\Delta_{iA} + \Delta_{jA}}{\Delta_{iA+jA}} + \sum_{jB \in D_{iB}} \tilde{c}'_{jB} h_{0jB} \frac{\Delta_{iA} + \Delta_{jB}}{\Delta_{iA+jB}} \right) + \sum_{eA} h_{iAeA} \tilde{c}'_{eA} + (h'_{iAiA} - \tilde{E}') \tilde{c}'_{iA} = 0.$$

In that equation the sum over  $j_B$  is without restriction since any  $j_B$  belongs to  $D_{iA}$ . Now we may notice that, due to the separation of the subsystems,

$$\Delta_{iA+jB} = \Delta_{iA} + \Delta_{jB}$$

One may also write

$$\tilde{E}' = \tilde{E}_{0A} + \tilde{E}_{0B} + \tilde{E}'_A + \tilde{E}'_B,$$

with

$$\sum_{jB} \tilde{c}'_{jB} h_{0jB} = \tilde{E}'_B - E_{0B}.$$

Since, also due to the separation,

$$h'_{iAiA} = h_{iAiA} + E_{0B},$$

$$\sum_{jB} \tilde{c}'_{jB} h_{0jB} \frac{\Delta_{iA} + \Delta_{jB}}{\Delta_{iA+jB}} + h'_{iAiA} - \tilde{E}' = h_{iAiA} - \tilde{E}'_A.$$

Hence the eigenequation for the supersystem is satisfied when

$$\tilde{E}'_A = \tilde{E}_A \quad \text{and the same for B,}$$

$$\tilde{c}'_{jA} = \tilde{c}_{jA}, \quad \forall j_A.$$

#### 5. Discussion

These self-consistently dressed CISD matrices being strictly separable when localized MOs are used, are necessarily *size extensive* (even when using non-localized MOs). The main approximation is the ne-

glect of connected fourth-order diagrams involving triples and quadruples, the latter being considered, for instance, in SD-coupled-cluster methods.

The various dressings are equivalent for the ground state and their relative merits for approximate descriptions of the excited states should be analyzed in the future. From a practical point of view versions  $\tilde{V}_2$  and  $\tilde{W}_2$  are memory consuming since nearly all elements become non-zero. The matrix loses its sparsity. The original formulation of intermediate Hamiltonians led to such a dressing (of perturbative character) of the full matrix.  $\tilde{V}_3$  and  $\tilde{W}_3$  are less simple than the most elegant dressings  $\tilde{V}_1$  and  $\tilde{V}$ . One advantage of versions  $\tilde{V}_1$  and  $\tilde{V}$  over all others concerns the computation time. These two versions involve summations of the type

$$\sum_{j \in D_i} f(j), \quad \text{instead of summations } \sum_{j \in D_i} f(i, j)$$

for the others versions (all  $\tilde{W}_n$ ,  $\tilde{V}_2$  and  $\tilde{V}_3$ ). Then one may notice that the sum over  $j$  requires a quadruple summation (two holes, two particles), but

$$\sum_{j \in D_i} f(j) = \sum_{j \text{ all}} f(j) - \sum_{j \notin D_i} f(j),$$

and the first summation is made once and for all while the second is much shorter since at least a hole or a particle of  $D_j^+$  belongs to  $D_i^+$ .

A practical trick, first proposed in a perturbative summation of EPV diagrams [8], has been used in ref. [8] to calculate the diagonal dressing  $\tilde{V}$  without any summation through the storage of one-, two- and triple-index partial summations. The resulting computational time reduces to the CISD computation time. The same trick might be used for the first-column dressing  $\tilde{V}_1$ . Despite their non-Hermitian character column dressings are specially interesting if one wants to generalize the process to the research of several eigenstates.

The advantage of the dressing  $\tilde{W}_n$  over the dressing  $\tilde{V}_n$  is that they do not assume the transition energy additivity, and that they may incorporate a certain number of Møller-Plesset fifth-order effects, or of  $T_4$  operator in the coupled-cluster expansion language. But so far their practical implementation seems difficult and the numerical results of  $\tilde{V}$  are so convincing that one may be tempted to exploit that version which is most convenient.

We would like to comment on the fact that our self-consistent intermediate Hamiltonians, although energy-dependent, are not the effective Hamiltonians produced by the partitioning technique [9]

$$\tilde{H}_{aa} = H_{aa} + H_{ab}(E - H_{bb})^{-1}H_{ba},$$

since we never used the whole  $H_{bb}$  matrix, nor its limitation to the triples and quadruples (which again would not be size-consistent).

One may establish a direct connexion between the proposed diagonal dressing and the well known CEPA techniques [2] since they also proceed through an energy shift of the diagonal energies of the determinants. As discussed in ref. [5] the various CEPA versions differ by a neglect of partial considerations of the exclusion principle violating (EPV) contributions. The  $\tilde{V}$  dressing correctly treating all EPV terms may be seen as the most accurate CEPA algorithm.

We would finally like to point out that all the above dressings may be generalized to any selected CI space  $S$  by simply changing the definition of  $D_i$ :

$D_i$  = sum of all diexcitations  $D_j^+$  such that

$$D_j^+ \Phi_i \neq 0 \text{ and } D_j^+ \Phi_i \notin S.$$

## Acknowledgement

The laboratoire de Physique Quantique is Unité Associée (No. 505) du CNRS.

## References

- [1] K.A. Brueckner, Phys. Rev. 97 (1955) 1353.
- [2] W. Kutzelnigg, in: Modern theoretical chemistry, Vol. 3, ed. H.F. Schaefer III (Plenum Press, New York, 1977).
- [3] S.R. Langhoff and E.R. Davidson, Intern. J. Quantum Chem. 8 (1974) 61.
- [4] J.P. Malrieu, Ph. Durand and J.P. Daudey, J. Phys. A 18 (1985) 809.
- [5] J.P. Daudey, J.L. Heully and J.P. Malrieu, submitted for publication.
- [6] C. Møller and M.S. Plesset, Phys. Rev. 46 (1934) 618.
- [7] P.S. Epstein, Phys. Rev. 28 (1926) 695.
- [8] M.B. Lepetit and J.P. Malrieu, J. Chem. Phys. 87 (1987) 5937.
- [9] P.-O. Löwdin, J. Math. Phys. 3 (1958) 969.