Adding the linked contributions of Triples and Quadruples to a size-consistent Singles and Doubles CI

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Summary. A convenient procedure has been proposed recently to insure the size-consistence of Singles and Doubles CI; the method goes through a self-consistent dressing of the energies of the excited determinants which incorporates the unlinked effects of the Triples and Quadruples. Two strategies are proposed here to add the *linked* contributions of the Triples and Quadruples, either by an perturbative MP-type calculation of these effects, or by a redefinition of the dressing of the SD–CI matrix. Test calculations on Be_2, FH, NH_3 and F_2 molecules show that both methods efficiently approach the Full CI results (error $\sim 1 \, kcal \, mol^{-1}$). The second one satisfactorily treats the single-bonds breaking. It is finally shown that the effect of the T–Q linked effects may be efficiently approximated by truncating the MO basis set to the most occupied virtual quasi-natural MOs.

Key words: Size-consistence – CI – Singles/Doubles

1 Introduction

The low convergence of the *l*-expansion for the calculation of the dynamical correlation energy [1] is a major problem. The recent progresses proposed by Kutzelnigg [2–7] to combine the explicit introduction of the r_{12} factor with classical expansions of the wavefunction in terms of configurations in a basis of Molecular Orbitals, appears as a promising answer. Nevertheless, the obtaining of efficient, cheap, universal and well-conditioned techniques to approximate the Full Configuration Interaction (FCI) in a given basis remains an important task.

The most elegant solution consists in the Coupled Cluster formulation [8], which insures the requirements of size-consistence, separability and invariance under unitary transformation of the MOs. However, the extension of that formulation to multireference zeroth-order descriptions is necessary to treat correctly bond dissociations and has not yet received fully satisfactory solutions [9]. The most largely used level of that method restricts the excitation operator acting on ϕ_0 to

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the Single and Double excitations (CCSD). Inclusion of the effect of the Triple excitations is frequently done perturbatively at the fourth-order Möller–Plesset (MP4) level and appears in the literature as the CCSD + T(CCSD) approximation [10]. The non-perturbative inclusion of the triple excitations (CCSDT) is much more costly.

A cheaper method was proposed by Kelly [11] and later developed by Meyer [12], Alrichs, Kutzelnigg and coworkers [13], under the name of Coupled Electron Pair approximations. This method is size extensive and some formulations insure the invariance under the rotations of the MOs, but they do not insure the separability even into closed-shell fragments. The method does not incorporate the effect of the Triple excitations. Size extensivity is also obtained in the Coupled Pair Functional (CFP) [14] through a modification of the norm in the Singles and Doubles CI (SDCI).

A recent proposal, derived from the intermediate Hamiltonian formalism [15], has shown that the SDCI ground-state solution may be made size extensive (and even strictly separable when localized MOs are used), provided that the SDCI matrix receives appropriate self-consistent dressings [16]. These dressings consist in modifications of the matrix elements. They may concern either the $\langle \phi_0 | H | \phi_i \rangle$ column of the matrix (ϕ_0 = HF determinant, ϕ_i = singly or doubly excited determinant), or the elements $\langle \phi_i | H | \phi_j \rangle$, or – more conveniently – the diagonal elements $\langle \phi_i | H | \phi_i \rangle$. The justification of the method, its practical implementation and its efficiency have been reported in detail elsewhere [17]. The method – hereafter called – Self-Consistent Size-Consistent SDCI ((SC)^{2}SDCI) suppresses all the unlinked contributions of the Triples and Quadruples and incorporates all the Exclusion Principle Violating diagrams of various orders of the type:
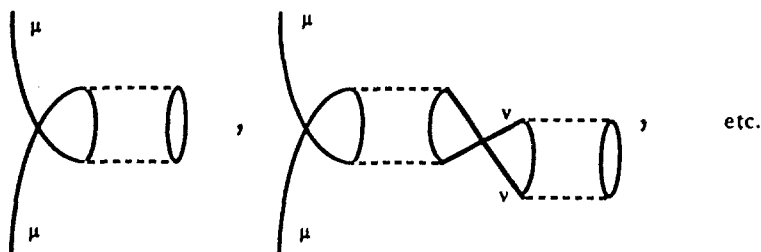
where the labels μ, v run over either holes or particles. The method may be considered as an "exact-CEPA" version since it correctly treats the EPV contributions which are either neglected (CEPA-O) or partially incorporated (through the holes only in the other CEPA versions). If one thinks in terms of Many Body Perturbation Theory, its main defect is the omission of the linked 4th-order diagrams going through the Triples and Quadruples.

There are several ways to go besides this approximation. Ref. [17] has proposed a universal solution to make size-extensive (and separable if localized MOs are used) any CI, for instance any Multireference (and in particular Complete Active Space) Singles and Doubles CI (MR-SDCI). It works as well on rationally selected CI's, or on arbitrarily truncated CI's. The size-consistence is again obtained through a self-consistent dressing of the CI matrix. One may find in Ref. [18] a set of test calculations illustrating the power and accuracy of these size-consistent dressed CIs, the dressing being introduced in Direct Selected CIs algorithms [19].

This general strategy is certainly the most attractive for the future, but we examine here another possibility, namely the addition of the *linked* contributions arising from the Triples and Quadruples to the $(SC)^2SDCI$ energy. This addition may be performed along two different schemes, namely

i) the simple addition of the Möller–Plesset 4th-order linked contributions of Triples and Quadruples, as done in CCSD + T(CCSD). The method is MP4-like; since the coefficients of the Doubles are determined from a non-perturbative method it might be labelled $(SC)^2SDCI(TQ)_L$, the parentheses indicating that the corresponding *linked* effect is treated perturbatively.
ii) a revision of the dressing of the SD-CI matrix to incorporate the linked effects of T and Q.

These two schemes have been implemented in an efficient algorithm proposed recently by Maynau and Heully [20] and will be explicited in the next Section, which also discusses the physical effects incorporated, in comparison with other methods. They are tested on a series of calculations for which FCI results are available (FH at three interatomic distances, NH_3 at equilibrium geometry, Be_2 potential energy curve) and on the F_2 potential energy (a rather difficult problem), in order to compare with the most sophisticated treatments. The results are reported and discussed in Sect. 3. Finally Sect. 4 discusses the possibility to restrict the summation over the Triples and Quadruples by freezing the less occupied approximated natural MOs as calculated at the $(SC)^2SDCI$ level.

2 Method

2.1 The $(SC)^2SDCI$

The starting point may be described as the best CEPA approximation (treating *all* EPV terms). It has been obtained as a special application of a universal procedure based on the intermediate effective Hamiltonian Theory, but it might be obtained from the CEPA approach or from CC-SD as well. Purvis and Bartlett had suggested such a strategy in an early paper [21].
    The method consists in diagonalizing a matrix built on ϕ_0 (the Hartree–Fock single determinant) and the Singles and Doubles ϕ_i. If P is the projector on the corresponding space:

$$P = |\phi_0\rangle\langle\phi_0| + \sum_{i \in S,D} |\phi_i\rangle\langle\phi_i|$$

one diagonalizes a matrix:

$$\tilde{H} = P(H + \tilde{V})P$$

where the $\tilde{V}$ matrix is purely diagonal:

$$\langle\phi_i| \tilde{V} |\phi_j\rangle = 0 \quad \text{if} \quad i \neq j$$

The eigenvector of $\tilde{H}$:

$$\tilde{H}\tilde{\psi} = \tilde{E}\tilde{\psi}$$

is $\tilde{\psi}$, which in the intermediate normalization is written:

$$\tilde{\psi} = \phi_0 + \sum_{i \in S,D} \tilde{C}_i \phi_i$$

and the dressing of each diagonal term associated with ϕ_i is a function of $\tilde{\psi}$:

$$\langle \phi_i | \tilde{V} | \phi_i \rangle = \sum_{\substack{j \\ D_j^+ \phi_i \neq 0}} \tilde{C}_j \langle \phi_0 | H | \phi_j \rangle \qquad (1)$$

where D_j^+ represents the double excitation operator creating ϕ_j from ϕ_0:

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

In other words the energy of a determinant ϕ_i is shifted by the effect of the double excitations which remain possible on it. Actually it is clear that:

$$\tilde{E} = \sum_i \tilde{C}_i \langle \phi_0 | H | \phi_i \rangle$$

So that the dressing may be rewritten:

$$\langle \phi_i | \tilde{V} | \phi_i \rangle = \tilde{E} - \sum_{\substack{j \\ D_j^+ \phi_i = 0}} \tilde{C}_j \langle \phi_0 | H | \phi_j \rangle \qquad (2)$$

The two formulations (Eqs (1) and (2)) make evident the fact that the dressing incorporates:

i) the unlinked effects of the Triples on the Singles and of the Quadruples on the Doubles, which cancels the unlinked terms brought by the truncation of the CI space to the Doubles.

ii) the EPV terms, which give the last summation of Eq. (2). One incorporates therefore 3rd-order diagrams of the type:
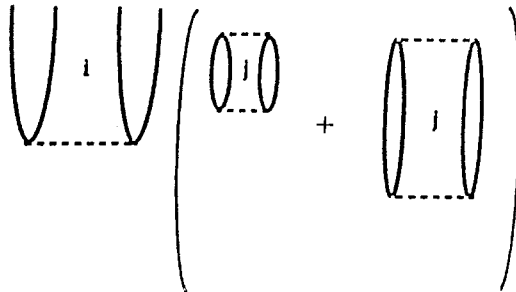
which will disappear when diagonalizing $H + \tilde{V}$ and the EPV ones:
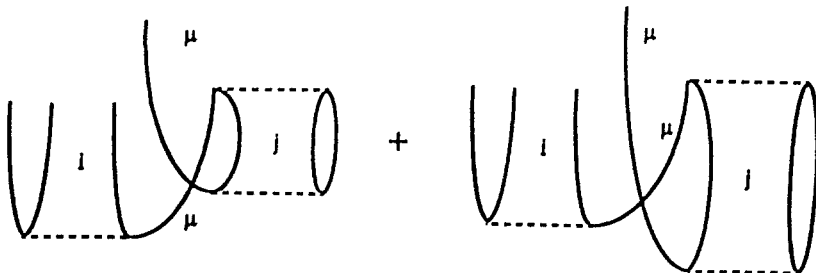
which stand.

The Self-consistent character of the dressing insures that higher orders are included, which are obtained by adding additional interaction lines on the left and/or right parts of the above diagrams.

Ref. [17] had discussed the practical implementation of the method, which may cost the same price as a SDCI diagonalization, since the dressing may be incorporated within the Davidson's diagonalization [22] itself. The rapid computation of the dressing goes through a storage of one-, two-, and three-indexes arrays making partial summations of the increments $\tilde{C}_j \langle \phi_0 | H | \phi_j \rangle$. One should mention that the $(SC)^2$SDCI method does not diverge when studying a single bond breaking but that it is not invariant under the rotation of the MOs.

2.2 Addition of MP4-linked contributions

To go besides that approximation the lacking MP4 terms should be added. The MP4 diagrams going through intermediate Singles and Doubles are already incorportated in $\tilde{E}$. The lacking contributions are those which go through Triples and Quadruples. One might add them by taking their effect from a full MP4 program, using of course the high quality variationally calculated coefficients $\tilde{C}_i$ of the Singles and Doubles. Within the algorithm proposed by Maynau and Heully [20], one calculates:

$$E_Q = \sum_{Q_\alpha} \frac{|\langle \tilde{\psi} | H | Q_\alpha \rangle|^2}{\Delta Q_\alpha}$$

where $\Delta Q_\alpha = E_0^{MP} - E_{Q_\alpha}^{MP}$ is the difference between the monoelectronic energies of the holes and particles defining the Quadruple configuration Q_α and similarly:

$$E_T = \sum_{T_\alpha} \frac{|\langle \tilde{\psi} | H | T_\alpha \rangle|^2}{\Delta T_\alpha}$$

However, these quantities include the unlinked effects of the Quadruples on the Doubles and of the Triples on the Singles.

The unlinked effects of the Triples and Quadruples, E_T^{UL} and E_Q^{UL}, are then subtracted according to a procedure detailed in Appendix 1. Then:

$$E_Q^L = \sum_{Q_\alpha} \frac{|\langle \tilde{\psi} | H | Q_\alpha \rangle|^2}{\Delta Q_\alpha} - E_Q^{UL} \tag{3}$$

and

$$E_T^L = \sum_{T_\alpha} \frac{|\langle \tilde{\psi} | H | T_\alpha \rangle|^2}{\Delta T_\alpha} - E_{T_\alpha}^{UL} \tag{4}$$

The final expression of the energy is:

$$E_{(SC)^2 SD (TQ)_L} = \tilde{E} + E_T^L + E_Q^L \tag{5}$$

The acronym follows the well-accepted labelling of the CCSD(T) approximation, and the subscript L stands for *Linked*.

If one thinks in terms of MP expansion, the socalculated energy $\tilde{E} + E_Q^L + E_T^L$ incorporates all the 4th-order energy corrections of the MP expansion, plus infinite summations of diagrams obtained by introduction of additional interaction lines between the first and the second and/or the third and the fourth interaction lines

of the basic 4th-order diagrams. For instance, for a quadruple excitation $D_i^+ D_j^+ = D_k^+ D_l^+$:
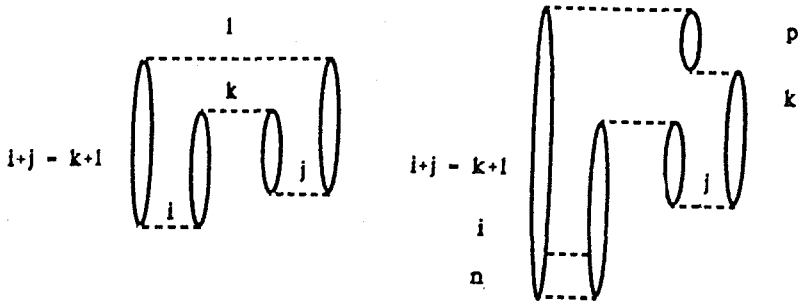
the effective coefficients $\tilde{C}_i$ and $\tilde{C}_k$ incorporate the effect of interactions with other double excitations D_n^+, D_p^+, while one does not consider any interaction between the Quadruples.

Of course, the coefficients of the Doubles are bound, they never exceed unity:

$$|\tilde{C}_i| \leqslant 1$$

whatever the $\langle \phi_0 | H | \phi_i \rangle / \Delta_i$ ratio. One may thus expect that the energy $E_Q^L + E_T^L$ will never diverge when a single bond is broken, i.e. will never tend to infinity since the energy denominator ΔT_α and ΔQ_α are always different from zero. However, one may fear that $E_Q^L + E_T^L$ becomes exceedingly large when a near-degeneracy occurs. Actually the addition of EPV diagrams where the violation takes place on the Quadruple intermediate configuration should strongly balance the main term. The effect of the interaction between Quadruples would certainly go in the same direction, as occurs for the interaction between the Doubles.

2.3 Improvement of the dressing of the SD-CI matrix

In that second strategy, one wants to include the linked and unlinked effects of the Triples and Quadruples on the Singles and Doubles through an improved dressing of the energies of the Singles and Doubles. Let be ϕ_α a Triple or Quadruple determinant, and let us suppose that it interacts with a configuration ϕ_i belonging to the SD-model space ($\langle \phi_i | H | \phi_\alpha \rangle \neq 0$). Its effect on the coefficients $\tilde{C}_i$ of ϕ_i appears at the 3rd order:

$$\delta \tilde{C}_i^{(3)} = \langle \phi_i | H | \phi_\alpha \rangle C_\alpha^{(2)} / \Delta_i$$

where $C_\alpha^{(2)}$ is the coefficient of ϕ_α in the 2nd-order perturbed wavefunction $\psi^{(2)}$. More precisely

$$C_\alpha^{(2)} = \langle \phi_\alpha | H | \psi^{(1)} \rangle] / \Delta_\alpha \tag{6}$$

which may be replaced, including higher order contributions by:

$$C_\alpha' = \langle \phi_\alpha | H | \tilde{\psi} \rangle / \Delta_\alpha$$

where the prime in C' indicates that we are working in the intermediate normalization.

This may be rewritten:

$$\delta \tilde{C}_i = \langle \phi_i | H | \phi_\alpha \rangle C'_\alpha / \Delta_i \tag{7}$$

by including higher-order contributions through C'_α. This effect of ϕ_α on ϕ_i may be obtained by a proper dressing $\langle \phi_i | \tilde{V}'_\alpha | \phi_i \rangle$ of the diagonal energy of ϕ_i:

$$\langle \phi_i | \tilde{V}'_\alpha | \phi_i \rangle = \langle \phi_i | H | \phi_\alpha \rangle \frac{C'_\alpha}{\tilde{C}_i} \tag{8}$$

since the increment $\delta \tilde{C}_i$ is given in the perturbative development of $H + \tilde{V}'_\alpha$ by:

$$\delta \tilde{C}_i = \frac{\langle \phi_i | \tilde{V}'_\alpha | \phi_i \rangle}{\Delta_i} \left[\frac{\langle \phi_i | H | \phi_0 \rangle}{\Delta_i} + \text{higher orders} \right]$$

$$= \frac{\langle \phi_i | \tilde{V}'_\alpha | \phi_i \rangle}{\Delta_i} \tilde{C}_i$$

This is equivalent to Eq. (7) if one replaces $\langle \phi_i | \tilde{V}'_\alpha | \phi_i \rangle$ by Eq. (8). Then, the whole dressing of any determinant ϕ_i by the outer space is:

$$\langle \phi_i | \tilde{V}' | \phi_i \rangle = \sum_\alpha \langle \phi_i | \tilde{V}'_\alpha | \phi_i \rangle$$

$$= \left(\sum_\alpha \langle \phi_i | H | \phi_\alpha \rangle C'_\alpha \right) \Big/ \tilde{C}_i \tag{9}$$

The most accurate treatment would consist in diagonalizing the dressed matrix $P(H + \tilde{V}')P$, instead of $P(H + \tilde{V})P$, in the basis of the determinants:

$$P(H + \tilde{V}')P | \tilde{\psi}' \rangle = \tilde{E}' | \tilde{\psi}' \rangle$$

Instead of performing this full treatment, which will be the subject of a further work, we have used here a convenient approximation. We can consider that $\| \tilde{V}' - \tilde{V} \|$ is much smaller than $\| \tilde{V} \|$, as evident from the fact that while $\langle i | \tilde{V} | i \rangle$ is almost equal to $\tilde{E}$ (i.e. proportional to the number of electrons) $\| \tilde{V}' - \tilde{V} \|$ simply brings the linked effects of the Triples and Quadruples, which is much smaller. Therefore one may except that $\| \tilde{\psi} - \tilde{\psi}' \|$ is small, i.e. that the coefficients $\tilde{C}_i$ and $\tilde{C}'_i$ are very similar. Then instead of diagonalizing $P(H + \tilde{V}')P$ one may simply calculate $\tilde{E}' - \tilde{E}$ as a first-order correction:

$$\tilde{E}' = \langle \tilde{\psi} | H + \tilde{V}' | \tilde{\psi} \rangle$$

$$= \tilde{E} + \langle \tilde{\psi} | \tilde{V}' | \tilde{\psi} \rangle - \langle \tilde{\psi} | \tilde{V} | \tilde{\psi} \rangle \tag{10}$$

where $\tilde{\psi}$ is the normalized vector $\tilde{\psi}$:

$$\tilde{\psi} = \tilde{\psi} \times C_0$$

(C_0 being the coefficient of ϕ_0 in the normalized function $\tilde{\psi}$).

The energies have been calculated according to Eqs. (9) and (10) using different evaluations of the coefficients C'_α of the Triples and Quadruples. For the Triples the coefficients have always been estimated perturbatively according to Eq. (6), using Epstein–Nesbet type denominators.

Approximation td-1 (where td stands for "total dressing") uses the same perturbative evaluation of the coefficients of the quadruples Eq. (6). Some practical details about the implementation of this approximation are given in Appendix 2, which also discusses the interest of considering Epstein–Nesbet denominators.

Better approximations may be derived by considering non-perturbative evaluations of the coefficients of the Quadruples. *Approximation td-2′* uses the expression of the coefficients C'_{Q_α} assumed by the CCSD expansion:

$$C'_{Q_\alpha} = \sum_{\substack{(i,j) \\ D^+_i D^+_j \phi_i = Q_\alpha}} \tilde{C}_i \tilde{C}_j \tag{11}$$

where (i, j) stands for a *couple* $((i, j) = (j, i))$.

In a slightly different *approximation td-2*, one may use an improved evaluation [16], which does not require the energy denominator additivity, and write:

$$C^0_{Q_\alpha} = \sum_{\substack{(i,j) \\ D^+_i D^+_j \phi_0 = Q_\alpha}} \tilde{C}_i \tilde{C}_j \frac{\Delta_i + \Delta_j}{\Delta Q_\alpha} \tag{12}$$

where Δ_i, Δ_j and ΔQ_α are the Epstein–Nesbet energy denominators relative to the Doubles ϕ_i and ϕ_j and to the Quadruples Q_α.

Both $E_{\text{td-2}}$, and $E_{\text{td-2}}$ incorporate some of the interactions between the Quadruples, i.e. add an infinite number of interaction lines between the 2nd and the 3rd interaction lines in the following diagram, inside the rectangular windows, but not between the windows.
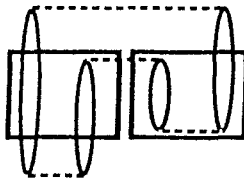
These effects were not incorporated in $E_{\text{td-1}}$.

The last approximation $E_{\text{td-2}}$ incorporates some "diagonal" 5th- and higher-order diagrams which link 4th-order unlinked diagrams without changing the labels of the propagation lines.
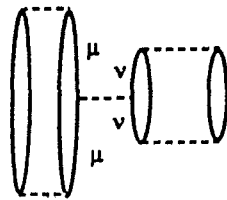
2.4 Comparison with other methods

It may be worth comparing our proposals to the existing methods. As already said, the starting point $(SC^2)SDCI$ can be considered as a CEPA-with *all* EPV contributions. The coefficients of the Doubles and Singles are free from unlinked contributions but their determination does not take into account the linked effects of the Quadruples, which play a role in the determination of the amplitude in CCSD. Thus they are less accurate than those of CCSD, but obtained at a much lower price and are qualitatively correct.

The main point is to avoid the unlinked contributions in the amplitudes of the Doubles (which make the coefficients of SDCI qualitatively wrong) and the linked effects of the Quadruples may be added *a posteriori*. This is the strategy followed in the present paper. Once the amplitudes of the Singles and Doubles are qualitatively correct, one may deviate from the full CCSD treatment by treating more approximately some linked contributions and this was the freedom exploited by the so-called Quadratic CI [23], although this method remains very close to the CC-SD method. Here the distance to CCSD is larger. The inclusion of the linked effects of the Quadruple (and of course of the Triples) is purely perturbative in our $(TQ)_L$ approximation, while a Coupled-Cluster expression for the coefficients of the Quadruple is accepted in the td-2' approximation. As remarked by a referee, if the dressing td-2' by the Quadruples only was fully treated, through the building and diagonalization of the newly dressed matrix and iterated to self-consistence, the method should converge to the solution of the CCSD equations and might be seen as a practical procedure to find this solution. But there is no reason to forget the linked effect of the Triples which apparently is more important than the linked effect of the Quadruples in many molecular problems.

In the td-2 approximation, the energy of the Quadruples appears explicitly and permits the inclusion of some T4 corrections (i.e. deviations of the coefficients of the Quadruples from the products of the coefficients of the Double). On the contrary the present approximations do not consider the 3rd-order connected contributions on the coefficients of the Triples and Quadruples (of the types below which are incorporated in the CCSD(TQ*) [24] and, of course, in the CCSDTQ [25] and reflect the interaction between Triples and Quadruples.
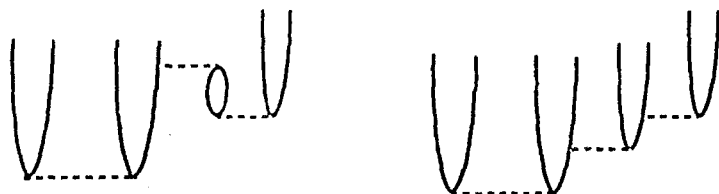
3 Results

We selected 3 molecules for which Full CI results are available; namely i) HF at three interatomic distances in a DZP basis set [26], ii) Be_2 at four interatomic distances in a $7s$, $3p$, $1d$ basis set [27], iii) NH_3 at its equilibrium distance in a DZP basis set [28].

In all cases the energies have been calculated with four approximations, namely those which have been called $(SC)^2SD(TQ)_L$, E_{td-1}, E_{td-2}, and E_{td-2}. In most cases the two last methods give very close results so that we shall only give the E_{td-2} values except when the difference become significant.

For HF, the results appear in Table 1. The comparison with FCI and with other estimates is only possible for r_e, 1.5 r_e and 2.0 r_e and are detailed in Table 2. Using canonical MOs the error of the $(SC)^2SDCI$ is 1.2 to 1.8 times larger than the error of the CCSD. One expects that the inclusion of the linked effects of the Triples and Quadruples should lead close to the CCSD(T) values, if not of these of the CCDST method. The errors of the CCSD(T) are .000099, .000149 and .0019 Hartree at $r = 1$, 1.5 and 2 r_e, respectively, and those of CCSDT are more regular (.000266,

Table 1. Calculated potential energy curve of the HF molecule (DZP basis set). ($r_e = 1.733$ bohr) (origin of the energy $= -99$ Hartree)

Interat. distance r/r_e	SCF	$(SC)^2$ SD	$(SC)^2SD(TQ)_L$	E_{td-1}	E_{td-2}	FCI
.65	− 0.760176	− 0.943915	− 0.947749	− 0.948341	− 0.947756	
.75	− 0.942939	− 1.131271	− 1.135453	− 1.136130	− 1.135438	
.9	− 1.038652	− 1.233164	− 1.237903	− 1.238739	− 1.237849	
1.0	− 1.047087	− 1.245386	− 1.250526	− 1.251444	− 1.250414	− 1.250969
1.1	− 1.035486	− 1.237507	− 1.243062	− 1.244044	− 1.242868	
1.5	− 0.933229	− 1.152184	− 1.159786	− 1.160876	− 1.159076	− 1.160393
2.0	− 0.817572	− 1.068377	− 1.080749	− 1.081085	− 1.078438	− 1.081108
3.0	− 0.686299	− 1.020537	− 1.051007	− 1.040793	− 1.037671	
4.0	− 0.630972	− 1.015339	− 1.057698	− 1.039687	− 1.036640	
5.0	− 0.607955	− 1.014428	− 1.060592	− 1.040436	− 1.037465	

Table 2. Calculated correlation energies for the HF molecule Full CI = exact correlation energies (Hartree) in the $(4s, 2p, 1d)$ basis set; the other numbers are the absolute errors in mH ($r_e = 1.733$ bohr)

	r_e	$1.5\ r_e$	$2.0\ r_e$
Full CI[a]	− .203882	− 0.227164	− 0.263536
CCSDTQ[b]	0.018	0.041	0.062
CCSDT[c]	0.266	0.646	1.125
CCSD(T)[d]	0.099	0.149	− 1.90
CCSD[e]	3.01	5.10	10.18
This work canon. MOs			
$(SC)^2$ SD	5.58	8.21	12.7
$(SC)^2$ SD(TQ)$_L$	0.443	0.607	0.359
td-1	− 0.475	− 0.483	0.023
td-2′	0.327	0.774	1.65
td-2	0.555	1.32	2.67
This work quasi natural MOs			
$(SC)^2$ SD	5.76	8.423	13.1
$(SC)^2$ SD (TQ)$_L$	0.523	0.741	0.644
td-1	− 0.760	− 0.986	− 0.362
td-2′	0.408	.997	2.06
td-2	0.482	1.14	2.40

[a] Ref. [26]
[b] Ref. [25]
[c] Ref. [30]
[d] Ref. [29]

.000646 and .001125 Hartree). Our worse results are those of the E_{td-2} approximation (despite its more elaborate character) and the errors are about twice those of CCSDT. The comparison with CCSDT is a bit better for E_{td-2}, (see Table 2). Surprisingly the two other approximations give lower errors (in absolute value),

Table 3. Spectroscopic properties (in cm^{-1}; R_e in Å) and dissociation energies (in eV) of HF

Type of calculation	R_e	D_e	ω_e	$X_e\omega_e$	B_e	α_e
Experiment[a]	0.9168	6.128[b]	4138.32	89.88	20.9557	0.798
This work[c]						
$(SC)^2SD$	0.917		4234.8	88.48	20.943	0.746
$(SC)^2SD(TQ)_L$	0.919	5.17[d]	4199.9	90.09	20.862	0.761
td-1	0.919	5.74[d]	4201.1	90.49	20.852	0.761
td-2	0.919	5.79[d]	4211.9	90.05	20.881	0.757
td-2	0.919	5.75[d]	4208.0	90.35	20.875	0.760

[a] Ref. [33]
[b] $D_0^0 = 5.869$ eV from Ref. [33]
[c] From fitting using Hutson method (Ref. [34]). Numerical integrations between 0.65 r_e and 4 r_e; ($r_e = 1.733$ bohr)
[d] From the values of energy at $(R = 5 \, r_e) - (R = r_e)$

especially at long interatomic distances. The major deviation (for $E_{td\text{-}2}$ at $2r_e$) is 1.7 kcal mol^{-1}.

As mentioned elsewhere, the method is not invariant under unitary transformations of the MOs. Table 2 gives the results when using quasi-natural MOs obtained from the Möller–Plesset 1st-order coefficients [31]. The variation of the energies is very small, and the percentage of the correlation energy in the td-2 approximation (99.80%, 99.53% and 99.10% at r_e, 1.5 r_e and $2r_e$ respectively) parallels those of CCSDT [32] (99.87, 99.7 and 99.36%). Whatever the choice of the MOs, our treatments of the linked effects of Triples and Quadruples reduces the error of the $(SC)^2SDCI$ by one order of magnitude.

The $(SC)^2SDCI$ converges at large interatomic distance but give a significantly overestimated dissociation energy $(E(5r_e) - E(r_e)) = 6.28$ eV as discussed below. We have not found the exact energy of F· in that basis so that the Full CI dissocation energy is not known. Table 3 gives the dissociation energy calculated as $E(5r_e) - E(r_e)$. The perturbative evaluation of $(SC)^2 SDCI (TQ)_L$ is too small (5.17 eV), while those of the total dressing are reasonable in view of the smallness of the basis set (5.74 and 5.79 eV), to be compared with the experimental value (6.13 eV) [33]. As expected, the $(SC)^2SDCI (TQ)_L$ method does not diverge but does not behave properly at large interatomic distances since the potential curve decreases by 5.6 kcal mol^{-1} between $3 \, r_e$ and $5 \, r_e$. The energies after total dressing exhibit a slight reminder of that anomaly since they present a very small barrier (.47 kcal mol^{-1} for $E_{td\text{-}1}$ and .51 kcal mol^{-1} for $E_{td\text{-}2}$) at $4r_e$.

Regarding spectroscopic properties, for which we have no FCI values, the $(SC)^2SDCI$ estimates fortunately compare very well with the experimental values (cf. Table 3) and the three procedures to include the linked TQ effects are consistent and remain in good agreement with experiment.

For Be_2, the Full CI energies are known for the potential well ($r = 4.5, 4.75, 5.0$ and 5.25 bohr) [27]. These values correspond to a slightly different basis set ($5d$) leading to an energy of about $+ .04$ mH [35]. For that molecule the role of the Triples is known to be dramatic since it is responsible for the very small potential well. The results appear in Tables 4 and 5. The $(SC)^2SDCI$ potential energy curve is purely repulsive and 2 to 4 mH above the CCSD potential curve (using localized MOs the agreement between $(SC)^2SDCI$ and CCSD was much better [17]).

Table 4. Calculated potential energy curve of Be$_2$ molecule ($7s$, $3p$, $1d$ basis set) in Hartree. (In parentheses, errors with respect to Full CI [27], in mH). Origin of the energy = -29 Hartree

r (bohr)	SCF	(SC)^{2}SD	(SC)^{2}SD(TQ)$_L$	E$_{td-1}$	E$_{td-2'}$	E$_{td-2}$	E$_{FCI}$
4.5	$-.131664$	$-.230396$	$-.235262$ (1.68)	$-.236810$ (0.13)	$-.236472$ (0.47)	$-.236588$ (0.35)	$-.236940$
4.75	$-.134977$	$-.231470$	$-.236018$ (1.73)	$-.237565$ (0.18)	$-.237257$ (0.49)	$-.237397$ (0.35)	$-.237747$
5.0	$-.137287$	$-.231862$	$-.236127$ (1.77)	$-.237667$ (0.24)	$-.237389$ (0.51)	$-.237561$ (0.34)	$-.237903$
5.25	$-.138980$	$-.231964$	$-.235983$ (1.81)	$-.237510$ (0.29)	$-.237262$ (0.53)	$-.237473$ (0.32)	$-.237797$
5.5	$-.140281$	$-.231985$	$-.235792$	$-.237301$	$-.237080$	$-.237335$	
6.5	$-.143453$	$-.232272$	$-.235492$	$-.236894$	$-.236746$	$-.237197$	
8.0	$-.145291$	$-.232687$	$-.235500$	$-.236789$	$-.236670$	$-.237375$	
8.5	$-.145526$	$-.232714$	$-.235463$	$-.236706$	$-.236618$	$-.237391$	
9.5	$-.145752$	$-.232693$	$-.235370$	$-.236608$	$-.236507$	$-.237388$	
11.0	$-.145843$	$-.232626$	$-.235258$	$-.236453$	$-.236384$	$-.237374$	

Table 5. Calculated correlation energy for the Be_2 molecule. Full CI = exact correlation energies (Hartree); the other numbers are the absolute errors in mH

r (bohr)	4.5	4.75	5.0	5.25
Full CI[a]	− .1052	− .1027	− .1006	− .0988
CCSDT[b]	0.3	0.2	0.2	0.2
CC-SD(T)[b]	1.0	0.9	0.9	0.8
CC-SD[c]	4.8	4.2	3.6	3.1
This work				
$(SC)^2SD$	6.5	6.2	6.0	5.8
$(SC)^2SD(TQ)_L$	1.7	1.7	1.8	1.8
td-1	− 0.1	0.2	0.2	0.3
td-2'	0.5	0.5	0.5	0.5
td-2	0.4	0.4	0.3	0.3

[a] Ref. [27]
[b] Ref. [35]
[c] Ref. [36]

Regarding the difference with full CI in the potential well region, the largest error concerns the perturbative estimate $(SC)^2SDCI(TQ)_L$; it varies from 1.68 to 1.81 mH between 4.5 and 5.0 bohr. The proximity with the Full CI is better for the total-dressing, the errors being of the order of 0.5 mH and the parallelism of the $E_{td-2'}$ and E_{td-2} values with the Full CI ones is surprising. These results compare better than those of CCSD(T) and are very close to those of CCSDT.

At larger interatomic distances, the FCI results are not reported, except as a curve in Ref. [27], up to 11 bohr. The potential curve is not regular and exhibits a shoulder at 6.5 bohr. The behaviour of the $(SC)^2SD(TQ)_L$ and td-1 and td-2' approximations are satisfactory, while the curve given by the td-2 approximation is more similar to that of CCSD(T) at large distances, as appears in Fig. 1 and Table 1 of Ref. [35].

The calculation of NH_3 in a DZP basis set has been the largest Full CI calculation [28] for a while, concerning in principle more than 2×10^8 determinants but actually limited to the 8×10^5 determinants of largest amplitude. The results are reported in Table 6, concerning both the canonical MOs and approximate Natural MOs (obtained from the 1st-order MP wavefunction). The results are similar for the two MO sets and for the various approximations, and the main result is the significant improvement brought by the inclusion of the linked effects of Triples and Quadruples, which reduces the error by about one order of magnitude with respect to $(SC)^2SDCI$. The largest error is 1.1 kcal mol^{-1}. In that case the total dressings lead to overestimated correlation energies. One must mention, however, that our $(SC)^2$ Selected CI led us to revise [18] the estimate of the correlation energy of Ref. [28] to larger absolute value.

The electronic correlation – and especially the dynamical correlations – plays a crucial role in the construction of the bond in the F_2 molecule. We have chosen a moderate size basis set $(4s, 3p, 1d)$ which has been used in several previous works [37]. Full CI was not performed on that problem, but the best estimates of the dissociation energy in that basis are about 1.2 eV instead of the 1.66 eV experimental value. The total energies are reported in Table 7 and Fig. 1, together with CCSD, CCSD(T), CCSDT-1 (approximation to CCSDT) and Multireference
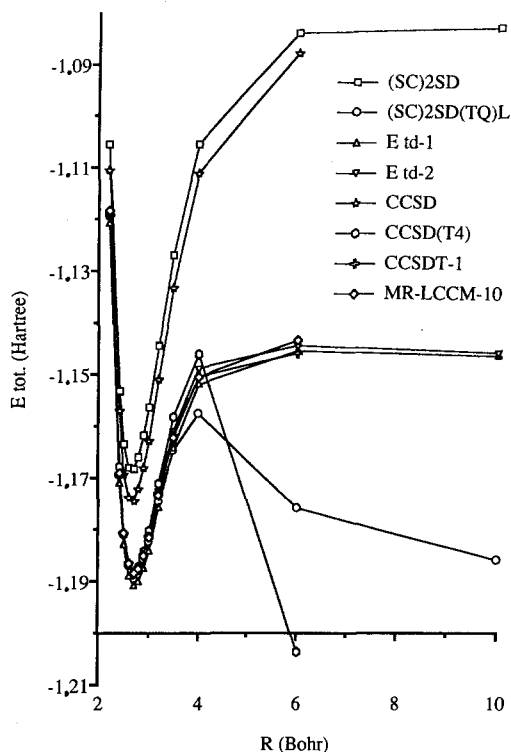
Fig. 1. Potential energy curves of F_2

Table 6. Correlation energy of the NH_3 molecule in a DZP basis set in Hartree (and error in mH with respect to the Full CI estimate $= -.2098 \pm 0.0001$)[a]

	Canonical MOs	Approximate natural MOs
$(SC)^2 SD$	$-.203288\ (6.5)$	$-.202913\ (6.9)$
$(SC)^2 SD\,(TQ)$	$-.209624\ (0.2)$	$-.209751\ (0.1)$
td-1	$-.210867\ (-1.1)$	$-.211581\ (-1.8)$
td-2	$-.209965\ (-0.2)$	$-.210323\ (-0.5)$

[a] Ref. [28] gives the total energy as -56.4236 ± 0.0001 Hartree. In the same basis set, the SCF energy is -56.213741 Hartree. Other calculations (Ref. [18]) suggests that the correlation energy is slightly larger (in absolute value)

Linear Coupled Cluster (MRLCCM-10) based on a 10-configuration MCSCF wavefunction, all taken from Ref. [37]. The results deserve the following comments:

i) the $(SC)^2$ SDCI energy is about 0.6 mH above the CCSD value (as mentioned elsewhere [17]), and they both give an overestimated dissociation energy: 2.36 eV (this work, from 10 bohr $-$ 2.7 bohr), 2.33 eV in CCSD (6.0 bohr $-$ 2.7 bohr),
ii) all methods including the Triples and linked effects of the Quadruples agree to locate the minimum of the curve at $r_e \sim 2.7$ bohr and an energy of 199.188 Hartree $\pm$ 1 mH, (except the td-1 approximation which gives 199.191,

Table 7. Calculated potential energy curve of the F_2 molecule ($4s$, $3p$, $1d$ basis set). Origin of the energy = -198 Hartree. CC calculations taken from Ref. [37]

Distances (bohr)	SCF	(SC)²SD	(SC)²SD(TQ)$_L$	E$_{td-1}$	E$_{td-2}$	CCSD	CCSD(T4)	CCSDT-1	MR-LCCM-1
2.0	− 0.597306	− 0.996160	− 1.008043	− 1.009311	− 1.008044	− 1.00067	− 1.00825	− 1.00809	− 1.00589
2.2	− 0.696599	− 1.105427	− 1.119269	− 1.120777	− 1.119188	− 1.11043	− 1.11946	− 1.11925	− 1.11832
2.4	− 0.733109	− 1.153071	− 1.169318	− 1.171131	− 1.169140	− 1.15681	− 1.16761	− 1.16919	− 1.16887
2.5	− 0.737428	− 1.163348	− 1.180932	− 1.182870	− 1.180668	− 1.16912	− 1.18089	− 1.18071	− 1.18056
2.6	− 0.735725	− 1.167813	− 1.186838	− 1.188869	− 1.186460	− 1.17379	− 1.18660	− 1.18651	− 1.18646
2.7	− 0.729734	− 1.168209	− 1.188761	− 1.190841	− 1.188233	− 1.17433	− 1.18824	− 1.18829	− 1.18832
2.8	− 0.720780	− 1.165812	− 1.188018	− 1.190094	− 1.187303	− 1.17206	− 1.18712	− 1.18739	− 1.18746
2.9	− 0.709852	− 1.161617	− 1.185596	− 1.187604	− 1.184652	− 1.16794	− 1.18421	− 1.18478	− 1.18490
3.0	− 0.697670	− 1.156334	− 1.182228	− 1.184094	− 1.181004	− 1.16271	− 1.18024	− 1.18118	− 1.18137
3.2	− 0.671451	− 1.144403	− 1.174564	− 1.175868	− 1.172587	− 1.15077	− 1.17103	− 1.17293	− 1.17326
3.5	− 0.631568	− 1.126978	− 1.164605	− 1.164197	− 1.160852	− 1.13313	− 1.15809	− 1.16162	− 1.16210
4.0	− 0.571845	− 1.105329	− 1.157498	− 1.151814	− 1.148826	− 1.11099	− 1.14603	− 1.15036	− 1.15034
6.0	− 0.443279	− 1.083716	− 1.175875	− 1.145484	− 1.144358	− 1.08772	− 1.20354	− 1.14580	− 1.14338
10.0	− 0.390441	− 1.082728	− 1.185867	− 1.146521	− 1.145870				

Table 8. Spectroscopic properties (in cm^{-1}; R_e in Å) and dissociation energies (in eV) for F_2

Type of calculation	R_e	D_e	ω_e	$X_e\omega_e$	B_e	α_e
Experiment[a]	1.412	1.66	917	11.2	0.8902	0.0141
CCSD[b]	1.410	2.36[c]	945	12.6	0.892	0.0127
CCSD(T4)[b]	1.430	–[d]	870	19.1	0.868	0.0149
CCSDT-1[b]	1.434	1.13[c]	844	14.8	0.863	0.0159
MR-LCCM-10[b]	1.435	1.22[c]	842	15.3	0.862	0.0157
This work[f]						
(SC)^2 SD	1.407	2.33[g]	923	8.98	0.897	0.0131
(SC)^2 SD(TQ)$_L$	1.437	–[h]	830	17.1	0.865	0.0197
td-1	1.437	1.23[c]	834	14.3	0.862	0.0172
td-2	1.433	1.19[c]	848	14.9	0.867	0.0173

[a] Ref. [38]

[b] Ref. [37]

[c] From the values of energy at ($R = 6.0$ bohr) and ($R = 2.7$ bohr)

[d] Divergent behaviour of the potential curve at long-range distances. D_e from $E(R = 4.0$ bohr$) - E(R = 2.7$ bohr$) = 1.15$ eV

[e] See c): ($R = 100.0$ bohr) $-$ ($R = 2.7$ bohr)

[f] From fitting using Hutson method (Ref. [34]); numerical integrations between $R = 2.0$ bohr and $R = 6.0$ bohr

[g] See c): ($R = 10.0$ bohr) $-$ ($R = 2.7$ bohr)

[h] Non-divergent unsatisfactory energy decrease besides 4.0 bohr. D_e from $E(R = 4.0$ bohr$) - E(R = 2.7$ bohr$) = 0.85$ eV

iii) the perturbative addition of the Triples in Ref. [37] leads to a divergence besides 4 bohr, certainly because of perturbative evaluation for the coefficients of the Doubles. Our perturbative estimate of the linked effects of the Triples and Quadruples (SC)^{2}SD(TQ)$_L$ suffers a pathological (although non-divergent) energy decrease at large interatomic distances, as occurred in FH,

iv) the approximate results of the total dressing (td-1 and td-2) are very close to the CCSDT-1 and MR-LCCM results. They present a slight barrier (smaller than 1 kcal mol^{-1}) at 6 bohr, a spurious behaviour also exhibited by these elaborate CC methods.

The ground-state spectroscopic properties and the evaluation of D_e appear in Table 8. The results show the strong agreement between the results of our total-dressing procedure and those of CCSDT-1 or MR-LCCM.

4 Possible truncations of the Triples and Quadruples

The present proposals for including the linked effects of Triples and Quadruples require approximately the same computation time, which increases roughly as $n_0^4 \times n_v^4$ where n_0 and n_v are the number of occupied and virtual MOs respectively. For large basis sets and/or large number of electrons the calculation of these effects is significantly larger than the preliminary (SC)^2 SDCI, which behaves as a normal SDCI. It may thus be interesting to see whether one could not truncate the set of Triples and Quadruples to reduce the computational time of the lengthy step.

The easiest way to perform this truncation in a systematic manner consists in freezing some virtual MOs in the generation of the Triples and Quadruples. This

Table 9. Efficiency of the trunction of virtual MOs in the calculation of the linked effects of Triples and Quadruples in NH_3 with quasi-natural MOs

Number of virtual MOs	% of occupation	% of energy			% of computation time
		$(SC)^2SD(Td)_L$	td-1	td-2	
6	78	42	45	39	0.38
9	92	53	55	50	7.5
14	97	79	81	78	12
18	99	92	93	92	32
24	100	100	100	100	100

is only meaningful if one uses quasi-natural MOs as obtained, e.g. after the $(SC)^2SDCI$ step or from the MP 1st-order wavefunction, and if one considers the occupation number as a selection criterion. The efficiency of such a selection has been tested on the NH_3 problem with MP1 approximate natural MOs [31].

We have selected successively the 6, 9, 14 and 18 most occupied virtual quasi-natural MOs over a total of 24. The fraction of the total energy lowering brought by the linked effects of the Triples and Quadruples is given in Table 9, together with the fraction of computation time with respect to the full one. Although the convergence of the energetic effect does not follow the rate of occupation in the virtual space, the efficiency in terms of computation time is dramatic. One can obtain 50% of the linked contributions of Triples and Quadruples with 10% only of the computation time, and with a computational effort divided by a factor 3, one only misses 8% of the desired energy correction.

5 Discussion

The present work has proposed two efficient procedures to add the linked contributions of Triples and Quadruples to a size-consistent self-consistently dressed Singles and Doubles CI. The first procedure consists in a perturbative calculation of these effects. It proves to be very accurate in the potential well region, but, although it does not diverge under bond breaking, it becomes much less reliable in these regions. The second procedure consists in an improvement of the dressing of the SD–CI matrix to incorporate these linked effects. The three here-proposed approximations (td-1, td-2′, td-2) go through a recalculation of the mean value of the dressing operator in an unchanged SD wavefunction. Among the three dressings, td-2 is in principle the most sophisticated one; however, going from td-2′ to td-2 (i.e. in corporating the diagonal T4 diagram through Eq. (12)) does not bring any significant improvement of the results and since the calculation of td-2′ is much shorter, we would recommend that version. Anyway the three approximations give very similar results, which compare very well with either CCSD(T) or CCSDT results. For all the available Full CI benchmarks the error is within 1 kcal mol^{-1}, even when a single bond is being broken. The error is one order of magnitude smaller than for the $(SC)^2SDCI$ which compared with CCSD. The treatments satisfactorily give the following features:

i) the major change of the HF potential curve toward the FCI one, with a significant reduction of D_e
ii) appearance of the potential well of Be_2

iii) a decrease of the dissociation energy of F_2 by a factor 2, the potential curve lying very near of the best available MRCC calculations.

The method is very easy to implement, and it does not require any extra intermediate arrays to be stored in the computer memory (while the efficient CC algorithms require such intermediate arrays). As a result of that simplicity the computation time is surprisingly low, despite the $n_0^4 n_v^4$ dependence, since in the NH_3 molecule for instance, the 2.3×10^6 Quadruples and Triples are considered in less than 10' on a HP750 work station.

One may wonder whether the method may be improved. Of course one might rediagonalize the SDCI matrix after the total dressing rather than using the unchanged wavefunction. This will be explored in further works. The main improvement should be the generalization to a valence CAS reference, replacing the HF single determinant. The generalization of the $(SC)^2 SDCI$ to a $(SC)^2 MRSDCI$ is already available [17, 18], and the extension of the here-proposed treatment of Triples and Quadruples to the MR space is under work. One may expect that such an improvement would suppress the small irregularities (< 1 kcal mol^{-1}) exhibited at long interatomic distances in the HF and F_2 potential curves. For molecular systems where the number of TQ determinants would be too large, it has been shown that using approximate natural MOs and restricting the TQ space to the most occupied natural MOs may save a lot of computation time while bringing most of the searched correction to the correlation energy. Finally, for very large systems we are currently considering a three-class algorithm treating the small double excitations in a perturbative manner, the other ones being treated size-consistently through the $(SC)^2 SDCI$ treatment and the most important Triples and Quadruples by the procedure presented in that work.

Appendix 1. Substraction of the unlinked effects of Triples and Quadruples in the $(SC)^2$ SDCT $(TQ)_L$ version
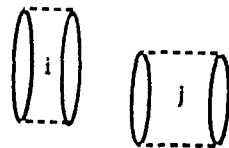
If a Quadruple determinant Q_α may be written:

$$Q_\alpha = D_i^+ D_j^+ \phi_0$$

where D_i^+ and D_j^+ are disjoined (no hole nor particle in common), the unlinked 4th-order interactions which, in a diagrammatic picture close on ϕ_0 coming from ϕ_i, are:

$$\frac{\langle \phi_0 | H | \phi_i \rangle \langle \phi_i | H | Q_\alpha \rangle \langle Q_\alpha | H | \phi_j \rangle \langle \phi_j | H | \phi_0 \rangle}{\Delta_i \Delta Q_\alpha \Delta_j}$$
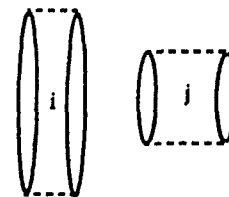
$$= C_i^{(1)} C_j^{(1)} \frac{\langle \phi_0 | H | \phi_j \rangle \langle \phi_i | H | \phi_0 \rangle}{\Delta Q_\alpha}$$

and

$$\frac{\langle \phi_0 | H | \phi_i \rangle \langle \phi_i | H | Q_\alpha \rangle \langle Q_\alpha | H | \phi_i \rangle \langle \phi_i | H | \phi_0 \rangle}{\Delta_i \Delta Q_\alpha \Delta_i}$$

$$= C_i^{(1)} C_i^{(1)} \frac{\langle \phi_0 | H | \phi_j \rangle \langle \phi_j | H | \phi_0 \rangle}{\Delta Q_\alpha}$$

where $C_i^{(1)}$ is the coefficient of ϕ_i in the 1st-order wave function $\psi^{(1)}$.

Due to the Möller–Plesset energy denominator additivity:

$$\Delta Q_\alpha = \Delta_i + \Delta_j$$

it is possible to write the sum of the two effects as:

$$(C_i^{(1)})^2 \frac{\langle\phi_0|H|\phi_j\rangle\langle\phi_j|H|\phi_0\rangle}{\Delta_j}$$

$$= (C_i^{(1)})^2\langle\phi_0|H|\phi_j\rangle C_j^{(1)}$$

One recognizes here the lowest-order approximation of the terms $\tilde{C}_i^2\langle\phi_i|\tilde{V}|\phi_i\rangle$ where $\langle\phi_i|\tilde{V}|\phi_i\rangle$ is given by Eq. (1) and which already belongs to $\tilde{E}$.

$$\tilde{E} = \langle\tilde\psi|H|\tilde\psi\rangle + \langle\tilde\psi|\tilde{V}|\tilde\psi\rangle$$

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

This is true for each decomposition of Q_α into double excitations and one must compute for each Q_α:

$$E_{Q_\alpha}^{UL} = \sum_{\substack{(i,j)\\D_i^+ D_j^+ \phi_0 = Q_\alpha}} \left(\frac{\langle\phi_0|H|\phi_i\rangle\tilde{C}_j + \langle\phi_0|H|\phi_j\rangle\tilde{C}_i}{\Delta Q_\alpha}\right)^2$$

where the summation runs over the *couples* of complementary double excitations contained in Q_α.
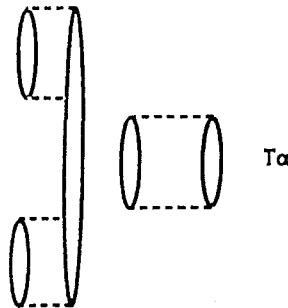
For the Triples, one must consider all the decompositions:

$$T_\alpha = D_i^+ M_j^+ \phi_0$$

where M^+ is a single excitation, and one must compute:

$$E_{T_\alpha}^{UL} = \sum_{\substack{(i,j)\\D_i^+ D_j^+ \phi_0 = T_\alpha}} \tilde{C}_j^2 \left(\frac{\langle\phi_0|H|\phi_i\rangle}{\Delta T_\alpha}\right)^2$$

where D_i^+ is a double excitation contained in T_α and M_j^+ is the complementary single excitation. One may remark that if ϕ_0 is self-consistent, the unlinked contributions in E_T are of sixth order only.

T_α

Appendix 2. Practical implementation of the total dressing (Approximation td-1)

Regarding the *Triples*, the coefficients of which are taken from Eq. (6), one should remember that the dressing of the Singles incorporates the effect of three types of unlinked diagrams when the Brillouin theorem is satisfied, namely:
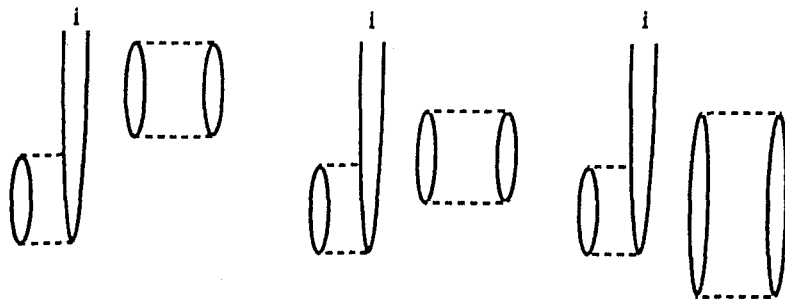
and the dressing $\langle \phi_i | \tilde{V}' | \phi_i \rangle$ of the Single ϕ_i only incorporates the first effect while the three of them were considered in the dressing $\langle \phi_i | \tilde{V} | \phi_i \rangle$. Hence the effect of a Triple excitation T_α becomes:

$$\delta T_\alpha = \frac{|\langle \tilde{\psi} | H | T_\alpha \rangle|^2}{\varDelta T_\alpha} - \sum_{\substack{(i,j) \\ \phi_\alpha = D_j^+ M_i^+ \phi_0}} \frac{C_i^2 |\langle \phi_0 | H | \phi_j \rangle|^2}{\varDelta T_\alpha}$$

which keeps the effect of the two last diagrams which were brought by $\tilde{V}$ and simply avoids a reductant inclusion of the first one.

Regarding the *Quadruples*, one may simply use Eq. (6) and one obtains an analogous expression:

$$\delta Q_\alpha = \left(\langle \tilde{\psi} | H | Q_\alpha \rangle|^2 - \sum_{\substack{(i,j) \\ D_i^+ D_j^+ \phi_0 = \phi_\alpha}} (C_i \langle \phi_0 | H | \phi_j \rangle + C_j \langle \phi_0 | H | \phi_i \rangle)^2 \right) \bigg/ \varDelta Q_\alpha$$

In this expression the coefficients C_i are those of the normalized function $\tilde{\psi}$ and the second term represents the unlinked contributions of the Quadruple Q_α, already incoporated in $\tilde{E}$. Finally, the expression of the energy in this approximation (Approx. 1) is given by:

$$E_{\text{td-1}} = \tilde{E} + \sum_{\alpha \text{ triples}} \delta T_\alpha + \sum_{\alpha \text{ quadruples}} \delta Q_\alpha$$

where td stands for total dressing.

In the calculations, the energy denominators are differences between the mean energies of the reference determinant ϕ_0 and of the Triple or Quadruple determinant. The use of these Epstein–Nesbet denominators incorporates 5th- and higher-order corrections which were not considered in the previous MP approximation. However, the present approximation cannot be regarded as an Epstein–Nesbet version of Eqs. (3, 4) since it now goes through a redefinition of the dressing, as is clear from the appearance of the normalized coefficients. In fact, this approximation should have a more satisfactory behaviour when the correlation becomes strong (e.g. under bond breaking).

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