

Valence bond corrected single reference coupled cluster approach

I. General formalism

J. Paldus*, **J. Planelles****

Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario,
N2L 3G1 Canada. Fax: (519) 746-4319

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Summary. An extension of the single reference coupled cluster method truncated to 1- and 2-body cluster components (CCSD) to quasidegenerate systems, where 3- and 4-body connected cluster components play an important role, is proposed. The basic idea is to extract the information concerning the 3- and 4-body clusters from some independent source, similarly as was implicitly done in the so-called ACPQ or ACC(S)D methods, and correct accordingly the absolute term in the CCSD equations. As a source of these approximate 3- and 4-body clusters, simple valence bond (VB) type wave functions are employed, since they are capable of describing electronic structure of various molecular systems for a wide range of nuclear conformations including their dissociation. The cluster analysis of these VB wave functions, that provides the desired information concerning the connected 3- and 4-body cluster components, is outlined and the explicit form of required correction terms to the CCSD equations is given.

Key words: Coupled cluster method – CCSD – Quasidegeneracy effects – Valence bond (VB) wave functions – VB corrected CCSD method – 3- and 4-body connected cluster amplitudes

1 Introduction

Various single reference (SR) coupled cluster (CC) approaches to the many-electron correlation problem [1–5] are nowadays routinely employed in investigating the electronic structure of small and medium size molecular systems. The principal advantages of these approaches – stemming from the CC exponential Ansatz for the wave function – are (i) their size extensivity and (ii) the fact that higher than triexcited effects arise primarily from disconnected clusters that manifest

* Also at the Department of Chemistry and Guelph-Waterloo Center for Graduate Work in Chemistry, Waterloo Campus, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

** *Permanent address:* Departament de Ciències Experimentals, Campus de la Carretera de Borriol, Universitat Jaume I, Apartat 224, 12080 Castelló de la Plana, Spain

themselves through appropriate non-linear terms in CC equations rather than through higher dimensionality. Thus, in standard CCSD approaches that explicitly consider connected one- and two-body cluster components, the dimensionality of the resulting problem is the same as in the corresponding configuration interaction (CI) method limited to singly- and doubly-excited configurations (CISD), even though the CCSD approach accounts also for the bulk of quadruple excitation effects (through the non-linear terms arising from the interaction of pair clusters) and is thus approximately equivalent to the CISDQ approximation (CISD including quadruples) rather than to the CISD method [2].

In their study of the performance of various SR CC methods, Kucharski et al. [6] distinguish between standard and nonstandard CC methods. The former ones result from truncation of the full SR CC chain of equations at the appropriate level, namely by restricting the connected cluster components to pair clusters (CCD), one- and two-body clusters (CCSD), up to and including three- and four-body clusters (CCSDT and CCSDTQ, respectively), etc. Methods which neglect terms that are *a priori* known to be negligible under given circumstances (e.g., cubic and quartic one-body terms when the Hartree–Fock (HF) wave function represents a good approximation, non-linear terms involving 3-body clusters [2], etc.) may also be regarded as standard or quasi-standard. On the other hand, methods using perturbative estimates for certain cluster contributions, including certain terms in a non-iterative fashion or using approximate estimates or cancellations of various terms are referred to as nonstandard CC approaches.

By now it has been well established [3–5] that for most non-degenerate closed-shell ground states, the standard (either full or quadratic) CCSD method yields very accurate results, since in these cases the contribution from connected 4-body clusters is negligible. Usually small 3-body cluster effects (that arise primarily from connected 3-body components in contrast to 4-body effects) can be, in most cases, well accounted for perturbatively, using one of the following approximation schemes (cf. [7]): CCSD+T(CCSD) [8], CCD+ST(CCD) [9] or CCSDT-1 [8, 10a]. Unfortunately, the significance of connected 3- and 4-body clusters dramatically increases once the ground state becomes quasidegenerate with other low lying states. This is almost invariably the case when considering molecules (even closed shell ones) away from their equilibrium geometries, or when applying the SRCC approaches to open-shell systems (as long as nondynamical correlation effects do not arise and a SR zero-order description is at all possible). Of course, the multi-reference (MR) generalization of CC theory appears to be the most natural answer in such cases. We must keep in mind, however, that both theoretical and computational problems brought about by such generalizations are formidable [4, 11]. Even though the conceptual problems associated with MR CC approaches were, to a large extent, resolved during the past decade (see, for example, [12]) and two viable formalisms, referred to as Fock and Hilbert space (or valence and state universal, respectively) open shell CC methods, are available, their practical implementation is rather demanding and often leads to serious problems (intruder state problems, incomplete model space problem, spin-adaptation problems, multiplicity of solutions problem, etc.) that have not yet been fully resolved in spite of a very remarkable progress that is being made in this direction (see, for example, [4b, c; 11–18]).

A brute force account of 3- and 4-body connected clusters within the framework of standard SR CC approaches, represented by the full CCSDT and CCSDTQ methods, can provide very useful and highly accurate results, but is limited to small systems and small basis sets. It can thus hardly be considered as the

answer to the above outlined problems in general. Not only does the dimensionality of the problem drastically increase with the electron number and basis set size, so that the above-mentioned advantage of CCSD vs CISDQ is lost, but the CC equations must again be similarly truncated as in the CCSD case, only at a higher excitation level. In highly degenerate situations, however, when 4-body components become as significant as 2-body components, there is no *a priori* guarantee of the validity of such a truncation. These limitations seem to be avoided in the recently introduced state-specific or state-selective MRCC approaches [18], which basically represent a suitably truncated SR-CCSDTQ method, and which can very effectively limit the number of higher order than pair clusters that must be considered.

An interesting attempt to approximately account for the connected 4-body clusters in the SR CCSD method resulted in the so-called ACPQ (approximate coupled-pairs with quadruples) [19] or closely related ACC(S)D (also referred to as ACP or ACP-D45) method [20, 21] (see also [7]). The essence of this approach is to estimate the unknown connected 4-body (i.e. T_4) components from some independent source and to use this information in CCSD equations. Since the direct perturbation theoretical estimate of these components is computationally demanding¹ [19a], our attention was turned to the broken symmetry wave functions of the unrestricted Hartree–Fock (UHF) type or, rather, to their spin projected variants such as the projected HF (PHF), extended HF (EHF) or alternant molecular orbital (AMO) methods.

We wish to emphasize, at this point, that the ACPQ or ACCD approaches are very different from the often exploited CCSD method employing a UHF wave function as reference. Although the latter approach can provide very useful results for many open-shell systems with relatively little effort (in fact, most generally available *ab initio* program packages employ the same spin orbital based code even for the RHF reference, thus unnecessarily more than doubling the number of pair amplitudes), it has severe inherent limitations and shortcomings. It is well known that the UHF reduces to the standard RHF whenever the latter is triplet (doublet, etc.) stable [22]. This transition usually occurs somewhere between the equilibrium geometry and stretched geometry, whose energy is close to that of the dissociated system. It is known [22, 23] that at this triplet instability point, the resulting potential energy surface (or curve) will show non-analytic behavior (although the energy as a function of geometry parameters will be continuous, the derivatives will show discontinuity). Moreover, in both open and closed shell situations, the UHF based wave function is no longer an eigenfunction of the total spin operator \hat{S}^2 and thus cannot be used for the description of different multiplets characterized by the same orbital occupancies.

In contrast to the UHF based CCSD methods, the approximate CC approaches leading to the ACPQ-type methods use the UHF or one of its projected versions to provide an estimate of the connected 4-body clusters that are then employed to achieve a more precise decoupling of the CCSD equations from the general CC chain. In fact, it turns out that by assuming the UHF wave function to provide the exact T_4 clusters, their account leads to a cancellation of certain $\frac{1}{2}T_2^2$ contributions (namely those arising from the first two Hugenholtz diagrams,

¹ In fact, even the CC based perturbative estimates of T_4 clusters, such as the CCSDTQ-1 [10b], CCSD+TQ*(CCSD) [10c] or CCSDT+Q(CCSDT) [10b] methods, are computationally very demanding.

see e.g. Fig. 5 of [19a]) and to a modification of a spin-adaptation factor associated with pair cluster interaction terms that result by projection onto biexcited configurations with triplet intermediate coupling of hole and particle pairs [19a]. The latter factor is not modified in the original ACP or ACCD approach [20, 21].

The ACPQ approach performs remarkably well in highly quasidegenerate situations, such as those encountered when handling correlation effects in quasi-one-dimensional systems. Considering, for example, the PPP model of cyclic polyenes C_NH_N with nondegenerate ground state ($N=4v+2$; $v=1, 2, \dots$), one finds [19b] that already for $N=14$ the CCD (equivalent in this case to CCSD) method breaks down altogether when we approach the highly correlated limit (namely, when the resonance integral $\beta = \beta_{\text{crit}}^{\text{CCD}} = -1.75$ eV). For larger cyclic polyenes, this breakdown already occurs in the physical region of the coupling constant (e.g., for $N=26$, $\beta_{\text{crit}}^{\text{CCD}} = -2.55$ eV) [18b]. This breakdown is linked with an increasing role of T_4 clusters as N increases (or $|\beta|$ decreases), and for $|\beta| < |\beta_{\text{crit}}^{\text{CCD}}|$ no real solution of CCD equations exists. Remarkably enough, the ACPQ solution exists in the whole range of the coupling constant providing an excellent approximation to the energy. For intermediate values of the coupling constant, the performance of this approach can be further enhanced by simultaneously considering the effect of T_3 clusters (ACPTQ method) [7b]. Another type of the perturbative estimate of T_3 contributions within the ACPQ scheme, referred to as the ACPQ+ST(ACPQ) method, improves the ACPQ results in the entire region of the coupling constant [7c].

Although in all known cases the ACPQ energies are closer to the exact ones than the CCSD energies, the simultaneous account of T_3 clusters may lead to an overestimate of the exact energies (and to a larger absolute error than that obtained with the ACPQ method), or even to a breakdown of the ACPTQ method, as the examples of cyclic polyenes in a strongly correlated limit [7b] and the H_4 model [6] indicate. Moreover, the UHF type wave-functions only contain even-number-of-times-excited cluster components, since all odd-number-of-times-excited contributions are annihilated when projecting out a singlet component. Consequently, a similar procedure cannot be used to obtain estimates of 3-body cluster (even though in deriving the ACPQ equations we only exploit “effective” UHF T_4 clusters and never actually evaluate them).

In this series of papers we explore another possibility of obtaining approximate connected 3- and 4-body clusters by exploiting valence bond (VB) wave functions involving a small number of covalent (and ionic, if necessary) structures that are capable of describing the desired dissociation process. In fact, this is the first time that the 3- and 4-body cluster components are *first* determined using an independent, non-CC and non-perturbative procedure and *subsequently* used to improve the decoupling of the CCSD equations. In the following we develop these basic ideas and derive the required formalism, which is tested in subsequent papers using simple semiempirical PPP model systems. The advantages of employing simple model Hamiltonians for such a study are not only the simplicity, easier insight and the facility with which the exact solutions may be obtained [using the existing full CI (FCI) or full VB (FVB) programs], but also the possibility of examining the performance of the proposed procedure for a whole range of coupling constants and varying degrees of reference state quasidegeneracy, as well as the ease in obtaining VB solutions at various levels of accuracy using our recently developed CAUGA based PPP-VB formalism [24]. In the future, we hope to test this procedure at the ab initio level using both generalized valence bond (GVB) [25] and spin-coupled VB [26] wave functions.

2 Basic assumptions and notation

In order to introduce the necessary notation and concepts that will enable us to formulate basic ideas of our approach and to derive the required formulas, we first briefly outline the CC(S)D formalism.

We consider the closed shell ground state of an $N=2n$ electron system that is described by a spin-independent Hamiltonian involving at most 2-body scalar potentials. Employing the second quantization formalism based on a given independent particle model (IPM) reference state $|\Phi_0\rangle$ (in all applications we shall in fact employ the RHF wave function as a reference), regarded as a Fermi vacuum, we can express our Hamiltonian in the following normal product form [4, 27]

$$H_N \equiv H - \langle \Phi_0 | H | \Phi_0 \rangle = F_N + V_N, \quad (1)$$

$$F_N = \sum_{i,k} \langle i | \hat{f} | k \rangle \sum_{\sigma} n [X_{i\sigma}^{\dagger} X_{k\sigma}], \quad (2)$$

$$V_N = \frac{1}{2} \sum_{i,j,k,l} \langle ij | \hat{v} | kl \rangle \sum_{\sigma,\tau} n [X_{i\sigma}^{\dagger} X_{j\tau}^{\dagger} X_{l\tau} X_{k\sigma}], \quad (3)$$

where

$$\langle i | \hat{f} | k \rangle = \langle i | \hat{z} | k \rangle + \sum_a (2 \langle ia | \hat{v} | ka \rangle - \langle ia | \hat{v} | ak \rangle). \quad (4)$$

Clearly, $X_{i\sigma}$ ($X_{i\sigma}^{\dagger}$) designates the annihilation (creation) operator associated with the IPM spin orbital $|i\rangle|\sigma\rangle \equiv |I\rangle$, while $\langle i | \hat{z} | k \rangle$ and $\langle ij | \hat{v} | kl \rangle$ designate one- and two-electron integrals in the IPM orbital basis. The generic, occupied (hole) and unoccupied (particle) orbitals are labeled by the lower case letters from the middle (i, j, k, l, \dots), beginning (a, b, c, d, \dots) and the end (r, s, t, u, \dots) of the Latin alphabet, respectively, while the spin orbitals are labeled by corresponding capitals or by a pair consisting of an orbital and a spin label, the latter designated by a Greek lower case letter.

Using the standard SR CC Ansatz, we express the exact wave function $|\Psi\rangle$ in the form

$$|\Psi\rangle = \exp(T) |\Phi_0\rangle, \quad (5)$$

where the cluster operator T is given as a sum of its i -body components T_i ,

$$T = \sum_{i=1}^N T_i. \quad (6)$$

The i -body (or i -times excited) cluster operator is then expressed as a linear combination of a suitable set of excitation operators $G_{J_i}^{(i)}$ producing a complete and normalized (but not necessarily orthogonal) N -electron basis (configurations) for the i -times excited component of the N -electron Hilbert space (given by the N th rank tensor power of the IMP spin-orbital space employed). Thus, we can write generally,

$$T_i = \sum_{J_i} t_{J_i}^{(i)} G_{J_i}^{(i)}, \quad (7)$$

with $G_{J_i}^{(i)}$ representing the i -body excitation operator and $t_{J_i}^{(i)}$ designating the corresponding cluster amplitude. Using the simplest spin-orbital (i.e., spin non-adapted) formalism, the excitation operators producing i -times excited configurations have the form

$$G_{J_i}^{(i)} = X_{R_1}^{\dagger} X_{R_2}^{\dagger} \cdots X_{R_i}^{\dagger} X_{A_1} \cdots X_{A_{i-1}} X_{A_i}, \quad (8)$$

so that

$$|\Phi_{J_i}^{(i)}\rangle \equiv \left| \begin{matrix} R_1 R_2 \cdots R_i \\ A_1 A_2 \cdots A_i \end{matrix} \right\rangle = G_{J_i}^{(i)} |\Phi_0\rangle, \quad (9)$$

J_i designating here the set of hole and particle spin-orbital labels, $J_i \equiv \{A_1, A_2, \dots, A_i; R_1, R_2, \dots, R_i\}$. In this case, the cluster amplitudes are also designated explicitly as

$$t_{J_i}^{(i)} = \langle R_1 R_2 \cdots R_i | \hat{t}_i | A_1 A_2 \cdots A_i \rangle_{\mathcal{A}} = \sum_{P \in S_i} (-1)^P \langle R_1 \cdots R_i | \hat{t}_i | A_{P_1} \cdots A_{P_i} \rangle, \quad (10)$$

the subscript \mathcal{A} indicating the antisymmetry property of these quantities, $P \in S_i$ designating a general permutation $P: j \mapsto P_j (j=1, \dots, i)$ of the symmetric group S_i and $(-1)^P$ the parity of P . We thus have that

$$\begin{aligned} T_i |\Phi_0\rangle &= \sum_{\substack{R_1 < R_2 < \cdots < R_i \\ A_1 < A_2 < \cdots < A_i}} \langle R_1 \cdots R_i | \hat{t}_i | A_1 \cdots A_i \rangle_{\mathcal{A}} \left| \begin{matrix} R_1 \cdots R_i \\ A_1 \cdots A_i \end{matrix} \right\rangle \\ &= (i!)^{-2} \sum_{\substack{R_1, R_2, \dots, R_i \\ A_1, A_2, \dots, A_i}} \langle R_1 \cdots R_i | \hat{t}_i | A_1 \cdots A_i \rangle_{\mathcal{A}} X_{R_1}^\dagger \cdots X_{R_i}^\dagger X_{A_1} \cdots X_{A_i} |\Phi_0\rangle, \end{aligned} \quad (11)$$

the first sum extending over ordered configurations only.

When considering a spin independent Hamiltonian, Eq. (1), it is often convenient to employ spin-adapted [1, 4, 27], or even orthogonally spin-adapted [28, 29] CC formalism. In the latter case, it is best to choose the particle-particle-hole-hole (pp - hh) coupling scheme. Clearly, in spin-adapted cases, the subscript J_i in Eq. (7) designates both orbital and intermediate spin-coupling labels. Let us illustrate this on the most important biexcited case. To simplify our notation we indicate the down spin by an overbar. Using this notation, the two singlet pp - hh orthogonally spin-adapted configurations take the form [28, 30, 31]

$$|\Phi_{(rs,ab;0,0)}^{(2)}\rangle = \frac{1}{2} N (G_3 + G_4 - G_5 - G_6), \quad (12a)$$

$$|\Phi_{(rs,ab;1,1)}^{(2)}\rangle = \frac{1}{2\sqrt{3}} (2G_1 + 2G_2 + G_3 + G_4 + G_5 + G_6), \quad (12b)$$

where

$$G_1 = \left| \begin{matrix} r\bar{s} \\ a\bar{b} \end{matrix} \right\rangle, \quad G_2 = \left| \begin{matrix} rs \\ ab \end{matrix} \right\rangle, \quad G_3 = \left| \begin{matrix} r\bar{s} \\ a\bar{b} \end{matrix} \right\rangle, \quad (13)$$

$$G_4 = \left| \begin{matrix} r\bar{s} \\ a\bar{b} \end{matrix} \right\rangle, \quad G_5 = \left| \begin{matrix} r\bar{s} \\ ab \end{matrix} \right\rangle, \quad G_6 = \left| \begin{matrix} r\bar{s} \\ a\bar{b} \end{matrix} \right\rangle,$$

and the normalization factor N is given by

$$N = [(1 + \langle r|s\rangle)(1 + \langle a|b\rangle)]^{-1/2}. \quad (14)$$

Thus, when $r=s$ and/or $a=b$, the triplet-triplet coupled second configuration (12b) vanishes. Writing

$$\left| \begin{matrix} rs \\ ab \end{matrix} \right\rangle_{S_i} = |\Phi_{(rs,ab;S_i,S_i)}^{(2)}\rangle, \quad (15)$$

we find the following simple symmetry properties of pp - hh coupled spin-adapted configurations

$$\left| \begin{matrix} rs \\ ab \end{matrix} \right\rangle_{S_i} = (-1)^{S_i} \left| \begin{matrix} rs \\ ba \end{matrix} \right\rangle_{S_i} = \left| \begin{matrix} sr \\ ba \end{matrix} \right\rangle_{S_i}. \quad (16)$$

The corresponding spin-adapted cluster amplitudes $\langle rs|\hat{t}_2|ab\rangle_{S_i}$, that are associated with configurations (15) or (16), are given by the same transformation

$$\begin{aligned} \langle rs|\hat{t}_2|ab\rangle_0 &= \frac{1}{2} N (\langle \bar{r}s|\hat{t}_2|\bar{a}b\rangle_{\mathcal{A}} + \langle r\bar{s}|\hat{t}_2|a\bar{b}\rangle_{\mathcal{A}} - \langle \bar{r}s|\hat{t}_2|a\bar{b}\rangle_{\mathcal{A}} - \langle r\bar{s}|\hat{t}_2|\bar{a}b\rangle_{\mathcal{A}}) \\ &= N (\langle rs|\hat{t}_2|ab\rangle + \langle rs|\hat{t}_2|ba\rangle), \end{aligned} \quad (17a)$$

and

$$\langle rs|t_2|ab\rangle_1 = \sqrt{3} (\langle rs|t_2|ab\rangle - \langle rs|t_2|ba\rangle), \quad (17b)$$

where we used the fact that

$$\langle RS|\hat{t}_2|AB\rangle_{\mathcal{A}} = \langle RS|\hat{t}_2|AB\rangle - \langle RS|\hat{t}_2|BA\rangle \quad (10')$$

and

$$\langle RS|\hat{t}_2|AB\rangle \equiv \langle r\rho s\sigma|t_2|a\eta b\tau\rangle = \langle rs|\hat{t}_2|ab\rangle \langle \rho|\eta\rangle \langle \sigma|\tau\rangle. \quad (18)$$

Again, these amplitudes possess the same symmetry properties as the corresponding configurations (or excitation operators), namely

$$\langle rs|\hat{t}_2|ab\rangle_{S_i} = (-1)^{S_i} \langle rs|t_2|ba\rangle_{S_i} = \langle sr|t_2|ba\rangle_{S_i}, \quad (19)$$

so that again the triplet-coupled ($S_i = 1$) component vanishes unless $r \neq s$ and $a \neq b$. The spin-adaptation of one-body clusters is, of course, straightforward, since $\langle R|\hat{t}_1|A\rangle_{\mathcal{A}} = \langle R|\hat{t}_1|A\rangle$. In order to distinguish spin-adapted and spin-orbital components, we attach the subscript 0 to the former ones, i.e.

$$\langle r|\hat{t}_1|a\rangle_0 = (1/\sqrt{2}) [\langle \bar{r}|\hat{t}_1|\bar{a}\rangle + \langle r|\hat{t}_1|a\rangle] = \sqrt{2} \langle r|\hat{t}_1|a\rangle. \quad (20)$$

As is well known (see, e.g. [1, 2, 4, 28, 29]) the energy is completely determined by one- and two-body cluster components, namely

$$\begin{aligned} \Delta E &= E - \langle \Phi_0|H|\Phi_0\rangle = E - E_0 = \sum_{R,A} \langle A|\hat{f}|R\rangle \langle R|\hat{t}_1|A\rangle \\ &\quad + \frac{1}{2} \sum_{R,S,A,B} \langle AB|\hat{v}|RS\rangle_{\mathcal{A}} (\langle R|\hat{t}_1|A\rangle \langle S|\hat{t}_1|B\rangle) + \frac{1}{2} \langle RS|\hat{t}_2|AB\rangle_{\mathcal{A}} \\ &= \sqrt{2} \sum_{r,a} \langle a|\hat{f}_2|r\rangle \langle r|\hat{t}_1|a\rangle_0 + \frac{1}{2} \sum_{r,s,a,b} \langle ab|\hat{v}|rs\rangle (2\langle r|\hat{t}_1|a\rangle_0 \langle s|\hat{t}_1|b\rangle_0 \\ &\quad - \langle r|\hat{t}_1|b\rangle_0 \langle s|\hat{t}_1|a\rangle_0 + N^{-1} \langle rs|\hat{t}_2|ab\rangle_0 + \sqrt{3} \langle rs|\hat{t}_2|ab\rangle_1), \end{aligned}$$

with N defined by Eq. (14). In turn, the cluster amplitudes are found by solving the appropriate energy independent CC equations. In the standard CCSD approach, only T_1 and T_2 cluster components are retained. Since the CCSD equations are well known (see, e.g., [1, 2, 4, 28, 29]), we only briefly indicate their general form and their origin in the full CC chain. Thus, substituting the cluster Ansatz (5) into the time-independent Schrödinger equation, premultiplying with the inverse of the

wave operator $W = \exp(T)$ and projecting onto the appropriate set of excited configurations we obtain, generally,

$$\langle \Phi_{J_k}^{(k)} | \exp(-T) H_N \exp(T) | \Phi_0 \rangle = 0, \quad (k = 1, 2, \dots, N). \quad (22)$$

Considering the first two classes of CC equations in the full CC chain of equations (22), namely those associated with singly and doubly excited configurations ($k = 1$ and 2 , respectively), we have that

$$\langle \Phi_{J_1}^{(1)} | H_N + H_N(T_1 + T_2 + T_3) + \frac{1}{2} H_N(T_1^2 + 2T_1T_2) + \frac{1}{6} H_N T_1^3 | \Phi_0 \rangle_C = 0, \quad (23a)$$

$$\begin{aligned} \langle \Phi_{J_2}^{(2)} | H_N + H_N(T_1 + T_2 + T_3 + T_4) + \frac{1}{2} H_N(T_1^2 + T_2^2 + 2T_1T_2 + 2T_1T_3) \\ + \frac{1}{6} H_N(T_1^3 + 3T_1^2T_2) + \frac{1}{24} H_N T_1^4 | \Phi_0 \rangle_C = 0, \end{aligned} \quad (23b)$$

where the subscript C indicates the connected component. In order to decouple these equations from the rest of the CC chain (22), one normally neglects all higher than biexcited cluster components

$$T_3 = T_4 = 0, \quad (24)$$

obtaining the well known CCSD equations (for spin orbital form, see e.g. [4b, 32], for spin-adapted form, see e.g. [1, 2], and for orthogonally spin-adapted form, see e.g. [29]).

From the non-truncated form of the CCSD equations (23a, b) we see immediately that having available T_3 and T_4 amplitudes from an independent source, we could evaluate the appropriate terms and include them in the absolute term of the CCSD equations. Clearly, using exact T_3 and T_4 amplitudes, the exact T_1 and T_2 amplitudes would result and thus the exact energy. Of course, we do not have the exact T_3 and T_4 amplitudes to our disposal, unless we possess the exact (i.e. FCI or FVB) solution, but we can obtain their approximate estimate using some approximate wave function. Obviously, we wish to use for this purpose a wave function that accounts for the possible quasidegeneracy of our reference state. In the ACPQ-type approaches discussed earlier, this was the projected UHF wave function that served us as a guideline, although no explicit estimates of the T_4 clusters were actually computed in this case. If we also wish to account for 3-body components, an approximate VB wave function seems to be an excellent candidate, since it can easily describe the breaking or forming of various bonds, while employing only a few VB structures. Of course, any appropriate yet simple MC-type wave function can be used for this purpose.

For this reason we first rewrite Eqs. (23) in the form

$$\sum_{k=0}^{i+2} A^{(k)}(\mathbf{J}_i) + \sum_{k=1}^i \Theta^{(k)}(\mathbf{J}_i) = 0, \quad i = 1, 2, \quad (25)$$

where

$$A^{(0)}(\mathbf{J}_i) = \langle \Phi_{J_i}^{(i)} | H_N | \Phi_0 \rangle, \quad i = 1, 2, \quad (26a)$$

$$A^{(1)}(\mathbf{J}_i) = \langle \Phi_{J_i}^{(i)} | H_N(T_1 + T_2) | \Phi_0 \rangle, \quad i = 1, 2, \quad (26b)$$

$$A^{(2)}(\mathbf{J}_i) = \frac{1}{2} \langle \Phi_{J_i}^{(i)} | H_N(T_1^2 + 2T_1T_2 + \delta_{i2}T_2^2) | \Phi_0 \rangle_C, \quad i = 1, 2, \quad (26c)$$

$$A^{(3)}(\mathbf{J}_i) = \frac{1}{6} \langle \Phi_{J_i}^{(i)} | H_N(T_1^3 + 3\delta_{i2}T_1^2T_2) | \Phi_0 \rangle_C, \quad i = 1, 2, \quad (26d)$$

$$A^{(4)}(\mathbf{J}_2) = \frac{1}{24} \langle \Phi_{J_2}^{(2)} | H_N T_1^4 | \Phi_0 \rangle_C, \quad (26e)$$

and

$$\Theta^{(1)}(\mathbf{J}_i) = \langle \Phi_{\mathbf{J}_i}^{(i)} | H_N(T_3 + \delta_{i2}T_4) | \Phi_0 \rangle, \quad i=1,2, \quad (27a)$$

$$\Theta^{(2)}(\mathbf{J}_2) = \langle \Phi_{\mathbf{J}_2}^{(2)} | H_N T_1 T_3 | \Phi_0 \rangle_C. \quad (27b)$$

Thus, A -terms involve only T_1 and T_2 clusters while the Θ -terms involve also T_3 and T_4 clusters. Clearly, the order of each term is indicated by the superscript (k), and δ_{ij} designates the Kronecker symbol. Neglecting T_3 and T_4 clusters by setting $\Theta^{(k)}(\mathbf{J}_i) = 0$ we recover the standard CCSD equations

$$\sum_{k=0}^{i+2} A^{(k)}(\mathbf{J}_i) = 0, \quad i=1,2. \quad (28)$$

Assuming, next, that we have available T_3 and T_4 cluster components, we evaluate Θ -terms (27) and correct the absolute term $A^{(0)}(\mathbf{J}_i)$ in CCSD equations (28). We thus define

$$\tilde{A}^{(0)}(\mathbf{J}_i) = A^{(0)}(\mathbf{J}_i) + \Theta^{(1)}(\mathbf{J}_i) + \delta_{i2} \Theta^{(2)}(\mathbf{J}_i), \quad i=1,2, \quad (29a)$$

$$\tilde{A}^{(k)}(\mathbf{J}_i) = A^{(k)}(\mathbf{J}_i), \quad k \neq 0, \quad i=1,2, \quad (29b)$$

and consider the corrected CCSD equations

$$\sum_{k=0}^{i+2} \tilde{A}^{(k)}(\mathbf{J}_i) = 0, \quad i=1,2, \quad (30)$$

which we designate as CCSD(T_3), CCSD(T_4), CCSD($T_3 + T_4$), CCSD($T_1 T_3$) or CCSD(F) when we include as correcting terms those arising from T_3 , T_4 , T_3 and T_4 , $T_1 T_3$ or all the terms in (29a), respectively. In the following sections we first discuss the cluster analysis of VB-type wave functions that will provide us with approximate (or exact if FVB is used) T_3 and T_4 components, while in the last section we give explicit expressions for Θ correction terms (27).

3 Cluster analysis of VB wave functions

Although we could attempt a direct determination of the required corrections using a given VB-type wave function, we prefer to carry out first its cluster analysis and compare the resulting cluster structure with that obtained by cluster analysis of the FCI or FVB wave functions, at least for small model systems. In this way we shall be able to gain an insight into the cluster structure of the VB-type wave functions and thus assess, at least qualitatively, the ability of approximate VB wave functions to provide higher excited cluster components.

We first recall the well known relationship between the CC and CI expansions. A general CI-type wave function has the form

$$|\Psi\rangle = C |\Psi_0\rangle, \quad (31)$$

where

$$C = \sum_{i=0}^N C_i, \quad (32)$$

with C_i representing the operator of the i -fold excitation, analogously as T_i (cf. Eq. (7)), so that

$$C_i = \sum_{J_i} c_{J_i}^{(i)} G_{J_i}^{(i)}, \quad i = 1, 2, \dots, N, \quad (33)$$

with C_0 being a scalar operator $C_0 = c\hat{1}$. Assuming the intermediate normalization, we thus have that $C_0 = \hat{1}$ (the identity operator), while the genuine excitation operators are related with corresponding cluster operators as follows [4, 33]

$$C_i = T_i + Q_i, \quad (34)$$

with

$$Q_i = \sum_{\mathcal{P}_i} \prod_{j=0}^{i-1} (r_j!)^{-1} T_j^{r_j}, \quad (35)$$

representing the disconnected i th order cluster component of C_i , so that

$$\sum_{j=1}^{i-1} j r_j = i, \quad 0 \leq r_j \leq i; \quad T_j^0 = \hat{1}. \quad (36)$$

This relationship may be easily inverted so that for the first four connected cluster components we find

$$T_1 = C_1, \quad (37a)$$

$$T_2 = C_2 - \frac{1}{2} C_1^2, \quad (37b)$$

$$T_3 = C_3 - C_1 C_2 + \frac{1}{3} C_1^3, \quad (37c)$$

$$T_4 = C_4 - C_1 C_3 + C_1^2 C_2 - \frac{1}{2} C_2^2 - \frac{1}{4} C_1^4. \quad (37d)$$

Considering now the VB-type wave function, we assume that it is expressed as a linear combination of various valence bond structures $|\mathcal{E}_A\rangle$ (or bonded tableaux), namely

$$|\Psi_{\text{VB}}\rangle = \sum_A \alpha_A |\mathcal{E}_A\rangle. \quad (38)$$

Each VB structure $|\mathcal{E}_A\rangle$ involves n_b bonds between AO's λ_i and μ_i , $i = 1, \dots, n_b$ and n_p isolated electron pairs (or lone pairs) ($\kappa_i \bar{\kappa}_i$) in addition to $n_u = 2S$ unpaired AOs ν_k when total spin quantum number $S \neq 0$, and may be uniquely characterized by a two-column bonded tableau [34] or a corresponding Young diagram [$2^a 1^b$], $a = n_p + n_b$, $b = n_u$,

$$|\mathcal{E}_A\rangle = \begin{vmatrix} \kappa_i & \kappa_i \\ \lambda_j & \mu_j \\ \vdots & \vdots \\ \nu_k & \\ \vdots & \end{vmatrix}, \quad (i = 1, \dots, n_p; j = 1, \dots, n_b, k = 1, \dots, n_u). \quad (39)$$

To simplify conceptually our task, we first expand each bonded tableau in terms of CAUGA symmetrized states [35], or Waller–Hartree functions [36], or Slater determinants. For example, considering a simple closed shell case when $n_p = 0$, $n_b = 2$ and $S = 0$, we have symbolically

$$\mathcal{E}_{\{1234\}} = \begin{vmatrix} 1 & 2 \\ 3 & 4 \end{vmatrix} = \omega \left(\begin{vmatrix} 1 & 2 \\ 3 & 4 \end{vmatrix} + \begin{vmatrix} 2 & 1 \\ 3 & 4 \end{vmatrix} \right), \quad (40a)$$

where on the right-hand side appear symmetrized CAUGA tableaux (indicated by a comma separating both columns) [35, 37], which we could also label by the CAUGA two-box tableaux, and ω designates an appropriate normalization factor. Equivalently, each symmetrized CAUGA state can be represented by a pair of Waller–Hartree two-determinantal functions, i.e.

$$\mathcal{E}'_{\{1234\}} = |13| \otimes |\bar{24}| + |24| \otimes |\bar{13}| + |23| \otimes |\bar{14}| + |14| \otimes |\bar{23}|, \quad (40b)$$

where we ignored the normalization factor ω for simplicity. Likewise, we can represent $\mathcal{E}_{\{1234\}}$ in terms of Slater determinants, obtaining

$$\mathcal{E}''_{\{1234\}} = |\bar{1234}| + |\bar{123\bar{4}}| - |\bar{12\bar{3}4}| - |\bar{12\bar{3}\bar{4}}|. \quad (40c)$$

Clearly, in the $S=0$ case, only half of the terms need be explicitly considered [38].

The AOs involved are, of course, the so-called overlap enhanced AOs (OEAOs) [39] that are essential for a successful application of VB theory [24, 26, 39, 40]. For the PPP-type Hamiltonians, it is often sufficient to employ a single parameter OEAOs of the form [24]

$$\tilde{\chi}_i = \chi_i + \varepsilon \sum_{j(\sim i)} \chi_j, \quad (41)$$

where the sum extends over the nearest neighbors i of j (designated as $j \sim i$). Moreover, when considering standard π -electron systems in their equilibrium geometries, we can choose $\varepsilon = 0.31$ [24a] assuming that $\beta_0 = -2.4$ eV.

In order to obtain MO based cluster components, we first rewrite our VB wave function, Eq. (38), in terms of configurations (represented as Slater determinants, Waller–Hartree functions, etc.) built from a chosen set of orthonormal molecular (spin) orbitals $\{\phi_k\}$, i.e.

$$|\Psi_{\text{VB}}\rangle = \sum_{\mathbf{K}} c_{\mathbf{K}} |\Phi_{\mathbf{K}}\rangle, \quad (42)$$

with \mathbf{K} designating the spin orbital set involved. Thus, the general structure of the expansion (42) is the same as for a CI wave function, except that the coefficients $c_{\mathbf{K}}$ corresponds to a given VB wave function (38). In other words, Eq. (42) represents a CI expansion for a VB wave function (38) with the coefficients $c_{\mathbf{K}}$ given by the overlaps

$$c_{\mathbf{K}} = \langle \Psi_{\text{VB}} | \Phi_{\mathbf{K}} \rangle = \sum_{\mathbf{A}} \alpha_{\mathbf{A}} \langle \mathcal{E}_{\mathbf{A}} | \Phi_{\mathbf{K}} \rangle. \quad (43)$$

Recalling that $|\mathcal{E}_{\mathbf{A}}\rangle$ are expressible in terms of CAUGA (or Waller–Hartree) states,

$$|\mathcal{E}_{\mathbf{A}}\rangle = \sum_{\{i,j\}} \lambda_{\{i,j\}}^{\mathbf{A}} |\tilde{\chi}_i \tilde{\chi}_{i_2} \cdots| \otimes |\tilde{\chi}_{j_1} \tilde{\chi}_{j_2} \cdots|, \quad (44)$$

with $\lambda_{\{i,j\}}^{\mathbf{A}}$ designating corresponding normalization factors, we get finally that

$$c_{\mathbf{K}} = \sum_{\mathbf{A}} \alpha_{\mathbf{A}} \sum_{\{i,j\}} \lambda_{\{i,j\}}^{\mathbf{A}} \langle \{\tilde{\chi}_i \tilde{\chi}_{i_2} \cdots\} | \{\phi_{k_1} \phi_{k_2} \cdots\} \rangle \langle \{\tilde{\chi}_{j_1} \tilde{\chi}_{j_2} \cdots\} | \{\phi_{l_1} \phi_{l_2} \cdots\} \rangle, \quad (45)$$

where we expressed $|\Phi_{\mathbf{K}}\rangle$ as follows

$$|\Phi_{\mathbf{K}}\rangle = |\{\phi_{k_1} \phi_{k_2} \cdots\}\rangle \otimes |\{\phi_{l_1} \phi_{l_2} \cdots\}\rangle,$$

the braces indicating the antisymmetry property [4b]. Thus, finally

$$c_{\mathbf{K}} = \sum_A \alpha_A \sum_{\{i,j\}} \lambda_{\{i,j\}}^A |\mathbf{D}\{i,k\}| \cdot |\mathbf{D}\{j,l\}|, \quad (46)$$

where \mathbf{D} are the overlap matrices between the OEAOs and MOs with entries given by $\langle \tilde{\chi}_i | \phi_k \rangle$ and $\langle \tilde{\chi}_j | \phi_l \rangle$, respectively.

Once we possess the CI-type coefficients $c_{\mathbf{K}}$, associated with a chosen MO-type basis set, we can carry out a standard cluster analysis, obtaining the desired connected cluster amplitudes. For this purpose it is convenient to relabel the coefficients $c_{\mathbf{K}}$, Eqs. (42) and (46), with molecular spin-orbital labels relative to a chosen IPM reference configuration $|\Phi_0\rangle$. We thus obtain monoexcited (c_A^R , c_B^S , etc.), biexcited (c_{AB}^{RS} , c_{CD}^{TU} , etc.), triexcited (c_{ABC}^{RST} , etc.), etc., coefficients characterizing the CI expansion of a given VB function (38). We then simply rely on Eqs. (37) to obtain the desired cluster components. Thus, for example,

$$t_{AB}^{RS} = c_{AB}^{RS} - \frac{1}{2} \{C_1^2\}_{AB}^{RS}, \quad (47a)$$

$$t_{ABC}^{RST} = c_{ABC}^{RST} - \{C_1 C_2\}_{ABC}^{RST} + \frac{1}{3} \{C_1^3\}_{ABC}^{RST}, \text{ etc.}, \quad (47b)$$

where

$$\{C_1^2\}_{AB}^{RS} = 2!(c_A^R c_B^S - c_B^R c_A^S), \quad (48a)$$

$$\begin{aligned} \{C_1 C_2\}_{ABC}^{RST} = & c_A^R c_{BC}^{ST} + c_B^R c_{CA}^{ST} + c_C^R c_{AB}^{ST} \\ & + c_A^S c_{BC}^{TR} + c_B^S c_{CA}^{TR} + c_C^S c_{AB}^{TR} \\ & + c_A^T c_{BC}^{RS} + c_B^T c_{CA}^{RS} + c_C^T c_{AB}^{RS}, \end{aligned} \quad (48b)$$

$$\begin{aligned} \{C_1^3\}_{ABC}^{RST} = & 3!(c_A^R c_B^S c_C^T + c_B^R c_C^S c_A^T + c_C^R c_A^S c_B^T \\ & - c_B^R c_A^S c_C^T - c_C^R c_B^S c_A^T - c_A^R c_C^S c_B^T), \end{aligned} \quad (48c)$$

and similarly for the four-body clusters.

In closing this section, we note that for simplicity's sake no spin adaptation was assumed at the MO level. Moreover, the 3- and 4-body cluster components need not be stored (unless we wish to use them for other purposes) but can be immediately used to compute corresponding corrections to the CCSD equations using the expressions given in the next section.

4 VB corrections to CCSD equations

Having determined 3- and 4-body cluster components, issuing from a chosen VB wave function, we now proceed to the determination of corresponding corrections, as outlined in Section 2. We again employ the simple spin orbital form and give the explicit expressions for the correcting terms $\Theta^{(k)}(J_i)$, Eqs. (27). Even when we employ the orthogonally spin-adapted CCSD formalism, the resulting spin-orbital corrections are easily transformed to their spin-adapted form relying on Eqs. (17) and (20). Clearly, only the required spin-orbital cluster components need be evaluated, since there will be a considerable repetition of equivalent terms differing only by their spin components. It should also be noted that the expressions given below are formally identical with those generated by the corresponding terms in the CCSDT and/or CCSDTQ equations. In the present case, however, these terms

are evaluated only once, using the 3- and 4-body cluster components derived from a chosen VB function, and are then employed to correct the absolute term in the CCSD equations as explained in Sect. 2. We now present explicit form for these corrections employing standard diagrammatic formalism [4b].

4.1 T_3 corrections

4.1.1 Mono-excited subset. There is only one Hugenholtz skeleton (Fig. 1a) that contributes to $\Theta^{(1)}(\mathbf{J}_1)$ term, Eq. (27a). Its topological weight factor is $w = \frac{1}{4}$, so that using a Brandow diagram of Fig. 1(b), we find immediately that the correction

$$\theta_a^r \equiv \langle r | \hat{\theta}_1^{(3)} | a \rangle \equiv \Theta^{(1)}(\{r\sigma; a\sigma\}) = \theta(t_3)_{a\sigma}^{r\sigma} =: \theta_A^R \quad (49)$$

is given by the expression

$$\theta_A^R = \sum_{S < T} \sum_{B < C} \langle BC | \hat{v} | ST \rangle_{\mathcal{A}} \langle RST | \hat{t}_3 | ABC \rangle_{\mathcal{A}}. \quad (50)$$

Corresponding spin adapted correction is then

$$\langle r | \hat{\theta}^{(3)} | a \rangle_0 = \sqrt{2} \theta_a^r. \quad (51)$$

4.1.2. Biexcited subset. In this case, both one- and two-body parts of the Hamiltonian (1) may contribute. The contribution involving one-electron component (assuming that other than RHF reference is employed) is characterized by the Hugenholtz skeleton shown in Fig. 2(a) with weight $w = 1$. Employing the corresponding Brandow diagram shown in Fig. 2(b) we get immediately the following contribution

$$\theta_1(t_3)_{ab}^{rs} \equiv \langle rs | \theta_1^{(3)} | ab \rangle = \theta_1(t_3)_{(a\sigma)(b\tau)}^{(r\sigma)(s\tau)} = \theta_1(t_3)_{AB}^{RS} = \sum_C \sum_T \langle C | \hat{f} | T \rangle \langle ABC | \hat{t}_3 | RST \rangle_{\mathcal{A}}. \quad (52)$$

The 2-electron contribution to $\Theta^{(1)}(\mathbf{J}_2)$ is given by $\langle \Phi_{J_2}^{(2)} | V_N T_3 | \Phi_0 \rangle \equiv \left\langle \begin{matrix} RS \\ AB \end{matrix} \middle| V_N T_3 \middle| \Phi_0 \right\rangle$, and is characterized by two Hugenholtz skeletons shown in Figs. 3(a) and (b). Drawing corresponding Brandow diagrams (Figs. 3(c) and (d)) and realizing that for both diagrams the weight factor equals to $\frac{1}{2}$, we find

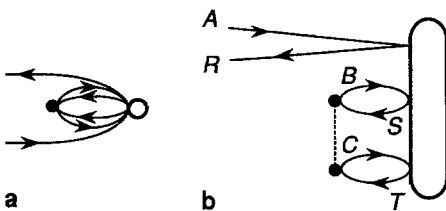


Fig. 1. The Hugenholtz skeleton (a) and the corresponding Brandow diagram (b) for the T_3 correction to the monoexcited CCSD subset of equations, represented by the term $\langle \Phi_{J_1}^{(1)} | H_N T_3 | \Phi_0 \rangle = \langle \Phi_{J_1}^{(1)} | V_N T_3 | \Phi_0 \rangle$

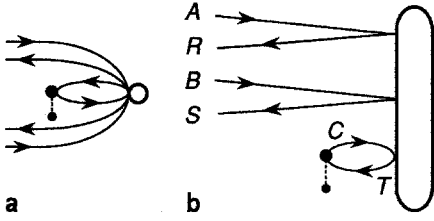


Fig. 2. Same as Fig. 1 for the biexcited subset and the one-particle component of the Hamiltonian, i.e. for the term $\langle \Phi_{J_2}^{(2)} | F_N T_3 | \Phi_0 \rangle$

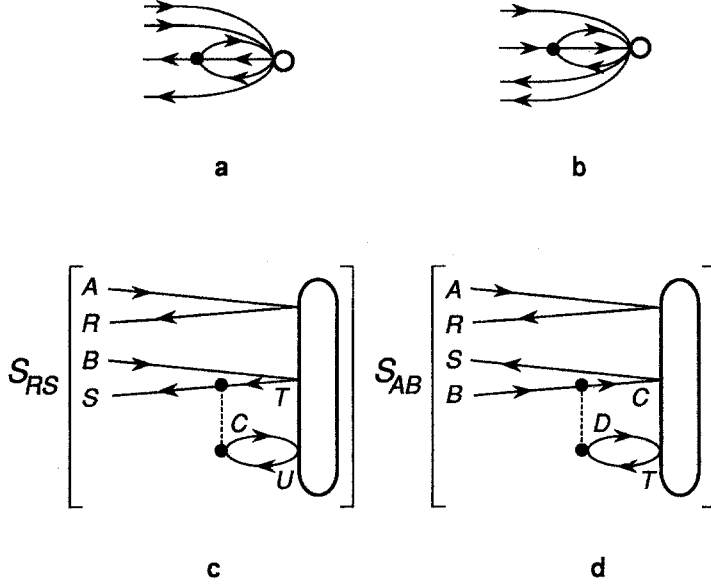


Fig. 3. The Hugenholtz skeletons (a, b) and the corresponding Brandow diagrams (c, d) for the T_3 correction to the biexcited CCSD subset of equations and the two-particle component of the Hamiltonian, represented by the term $\langle \Phi_{J_2}^{(2)} | V_N T_3 | \Phi_0 \rangle$. The operator S_{IJ} implies the symmetrization in I and J labels

immediately that

$$\begin{aligned}
 \theta_2(t_3)_{ab}^{rs} &\equiv \langle rs | \hat{\theta}_2^{(3)} | ab \rangle = \theta_2(t_3)_{(a\sigma)(b\tau)}^{(r\sigma)(s\tau)} = \theta_2(t_3)_{AB}^{RS} \\
 &= \sum_C \sum_{T < U} (\langle SC | \hat{v} | TU \rangle_{\mathcal{A}} \langle RTU | \hat{t}_3 | ABC \rangle_{\mathcal{A}} \\
 &\quad - \langle RC | \hat{v} | TU \rangle_{\mathcal{A}} \langle STU | \hat{t}_3 | ABC \rangle_{\mathcal{A}}) \\
 &\quad + \sum_T \sum_{C < D} (-\langle CD | \hat{v} | BT \rangle_{\mathcal{A}} \langle RST | \hat{t}_3 | ACD \rangle_{\mathcal{A}} \\
 &\quad + \langle CD | \hat{v} | AT \rangle_{\mathcal{A}} \langle RST | \hat{t}_3 | BCD \rangle_{\mathcal{A}}). \tag{53}
 \end{aligned}$$

The corresponding orthogonally spin-adapted components are then given by

$$\langle rs | \hat{\theta}_2^{(3)} | ab \rangle_0 = N(\theta_{ab}^{rs} + \theta_{ba}^{rs}) \tag{54a}$$

$$\langle rs | \hat{\theta}_2^{(3)} | ab \rangle_1 = \sqrt{3}(\theta_{ab}^{rs} - \theta_{ba}^{rs}), \tag{54b}$$

with N defined as in Section 2 and

$$\theta_{ab}^{rs} = \theta_1(t_3)_{ab}^{rs} + \theta_2(t_3)_{ab}^{rs}. \quad (55)$$

4.2 T_4 corrections

Four-body clusters can only contribute to the biexcited subset of CCSD equations as implied by Eq. (27a). Their contribution is characterized by a single Hugenholtz diagram shown in Fig. 4(a). Its weight being 1/4, we find immediately from one of the corresponding Bradow diagrams (Fig. 4(b)) that

$$\begin{aligned} \theta_2(t_4)_{ab}^{rs} &\equiv \langle rs | \hat{\theta}^{(4)} | ab \rangle = \theta(t_4)_{(ar)(br)}^{(rs)} =: \theta(t_4)_{AB}^{RS} \\ &= \sum_{C < D} \sum_{T < U} \langle CD | \hat{v} | TU \rangle_{\mathcal{A}} \langle ABCD | \hat{t}_4 | RSTU \rangle_{\mathcal{A}}. \end{aligned} \quad (56)$$

4.3 T_1T_3 corrections

Again, this correction only contributes to the biexcited subset of CCSD equations, Eq. (27b). The relevant Hugenholtz and Bradow diagrams are shown in Figs. 5(a)–(c) and 5(d)–(f), respectively, yielding immediately

$$\begin{aligned} \theta(t_1t_3)_{ab}^{rs} &\equiv \theta(t_1t_3)_{(ar)(br)}^{(rs)} =: \theta_{AB}^{RS} = \frac{1}{2} \sum_{C,D} \sum_{T,U} \langle CD | \hat{v} | TU \rangle_{\mathcal{A}} (2 \langle T | \hat{t}_1 | C \rangle \langle RSU | \hat{t}_3 | ABD \rangle_{\mathcal{A}} \\ &\quad + \langle T | \hat{t}_1 | A \rangle \langle RSU | \hat{t}_3 | BCD \rangle_{\mathcal{A}} - \langle T | \hat{t}_1 | B \rangle \langle RSU | \hat{t}_3 | ACD \rangle_{\mathcal{A}} \\ &\quad + \langle R | \hat{t}_1 | C \rangle \langle STU | \hat{t}_3 | ABD \rangle_{\mathcal{A}} - \langle S | \hat{t}_1 | C \rangle \langle RTU | \hat{t}_3 | ABD \rangle_{\mathcal{A}}). \end{aligned} \quad (57)$$

The corresponding orthogonally spin adapted components are again given by Eqs. (54).

Obviously, in this last case, it would also be possible to consider t_3 -corrections to the linear terms, involving the t_1 -cluster components that arise in the biexcited subset of the CCSD equations, rather than correcting the absolute term in this same subset using Eq. (57). This would, in fact, be more appropriate, since we consider the t_1 -clusters as unknowns in the CCSD or VB-corrected CCSD method. However, since we expect the effect of these terms to be very small, being quadratic in the 1- and 3-body cluster components (particularly when using RHF orbitals), and since we have to determine approximate t_1 -clusters anyway when cluster

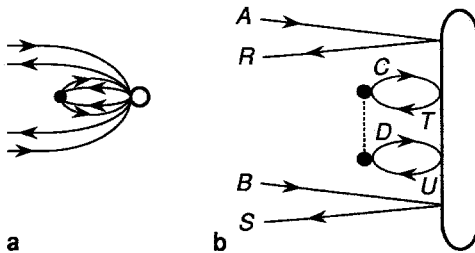


Fig. 4. Same as Fig. 1 for the T_4 correcting term $\langle \Phi_{J_2}^{(2)} | H_N T_4 | \Phi_0 \rangle = \langle \Phi_{J_2}^{(2)} | V_N T_4 | \Phi_0 \rangle$

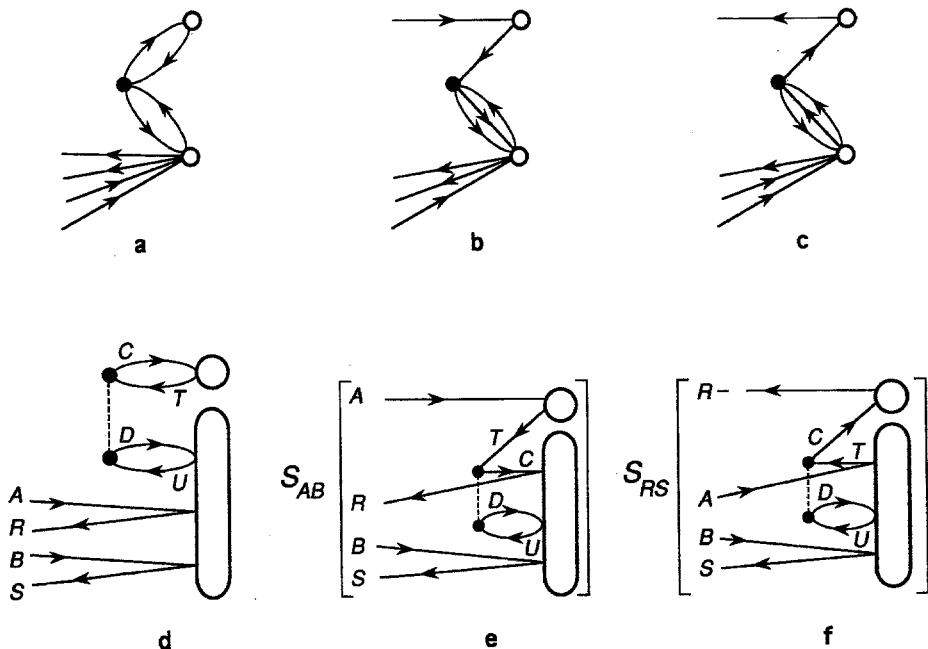


Fig. 5. The Hugenholtz skeletons (a–c) and the corresponding Brandom diagrams (d–f) for the T_1T_3 correcting term $\Theta^{(2)}(J_2) = \langle \Phi_{J_2}^{(2)} | H_N T_1 T_3 | \Phi_0 \rangle = \langle \Phi_{J_2}^{(2)} | V_N T_1 T_3 | \Phi_0 \rangle$. The operator S_{IJ} implies the symmetrization in I and J labels

analyzing our VB wave functions, we have decided, at least at this stage, to treat these terms in the same way as those arising solely from the connected 3- and 4-body clusters. The required linear term corrections when treating the T_1T_3 contribution as a quasi-linear rather than an absolute term follow easily from Eq. (57). However, while the last two terms (corresponding to diagrams (b), (c) or (e), (f) of Fig. 5) will be represented as effective two-body operators, the first term (corresponding to Fig. 5(a) or 5(d)) gives rise to an effective three-body potential. Nonetheless, the latter term can be effectively handled by precalculating an effective p - h one-body potential \hat{g} ,

$$\langle c | \hat{g} | t \rangle_{(rs)(st)}^{(ra)(sv)} = \langle c | \hat{g} | t \rangle_{AB}^{RS} = \sum_{D,U} \langle CD | \hat{v} | TU \rangle_{\mathcal{A}} \langle RSU | \hat{t}_3 | ABD \rangle_{\mathcal{A}}, \quad (58)$$

for each equation in the biexcited subset labeled by $(rs; ab)$.

5 Conclusions

This paper continues an attempt to obtain an independent yet reliable source of higher order connected cluster components that become important when a single reference coupled cluster Ansatz is employed in quasidegenerate situations and thus to achieve a physically meaningful decoupling of the CC chain of equations at the pair-cluster level. In this way the SR CCSD approach, which provides excellent results for nondegenerate ground states, could be extended to degenerate or quasidegenerate situations that generally arise when other than equilibrium

geometries are considered or, in other words, when chemical bonds are being formed or broken. Since these situations can be well characterized by the VB approach, often involving only a few covalent-type structures, it is worth investigating if a suitable approximate VB wave function could provide the missing information concerning the 3- and 4-body connected clusters, thus making the SR CCSD approach operative even in situations where the standard CCSD approach is either very inaccurate or even breaks down.

We would like to emphasize that the proposed approach is not intended to replace in any way MR CC methods, which obviously represent the most appropriate avenue to the open shell or quasidegenerate closed shell problems. However, in view of the complexity and high computational demands presented by the MR approaches, or in fact SR CCSDT and CCSDTQ approaches, it is of interest to search for a workable extension of the well established and affordable CCSD method or its variants (e.g., so-called quadratic CISD method [41, 42]) that are capable of providing reasonably accurate and reliable correlated wave functions and energies over a wide range of nuclear framework geometries, including situations where the standard CCSD approach must be abandoned. Of course, the same procedure can be employed with the 4- and/or 3-body connected cluster components resulting from whichever source is available or appropriate (e.g., UHF wave functions for the 4-body components as discussed earlier [19–21])². In this series of papers we shall employ simple VB-type wave functions for this purpose, testing the method using simple semiempirical PPP-type Hamiltonians.

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² We were informed by one of the referees that a similar idea, suggesting the use of the CAS SCF CC amplitudes in a SR-CC scheme in order to account for non-dynamical correlation effects, was recently proposed by Stolarczyk [43], and we thank the referee for providing us with the preprint of this paper. Although no actual implementation of this suggestion has been carried out, nor the explicit formalism for its implementation presented [43], this suggestion is very akin to the recently published state-selective MRCC formalism by Piecuch et al. [18b] and should be easy to implement in their codes [18c] by determining the internal 3- and 4-body clusters by the cluster analysis of the corresponding CAS SCF wave function.

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