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Size-consistent single-reference methods for electronic correlation: a unified formulation through intermediate hamiltonian theory

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Abstract. Using the intermediate hamiltonian theory as a unique conceptual frame and the technique of CI matrix dressing, a wide series of single-reference methods for the treatment of the ground state correlation are reviewed, compared, and sometimes improved. These methods range from independent excitation approximation (the very next step beyond MP2) to coupled cluster, going through the so-called electron pair approximations and the $(SC)^2CI$ formalism. A hierarchy of these methods can be established according to two criteria:

1. The physical effects incorporated in the model space, the choice of which is flexible.
2. The quality of the evaluation of the coefficients of the external space determinants. This evaluation, which remains based on a single reference expansion of the wave function, may simply ensure the size consistency or incorporate the linked contributions from the outer space.

These formulations in terms of diagonalizations of dressed CI matrices avoid convergence problems, but their main advantage is their flexibility, since they apply to multi-reference SDCI spaces as well as to SDCI spaces. The use of a common frame allows one to propose consistent combinations of methods of various costs for the treatment of various parts of the correlation energy.

Key words: Dressed CI – Intermediate hamiltonians – Many body perturbation theory – Coupled pair approximations – Coupled cluster

1 Introduction

In the study of molecular electronic energy of the ground state, ab initio calculations usually start from a Hartree–Fock (HF) SCF calculation [1–4] that provides the one-electron space of MO's adapted to an optimized single-reference configuration ϕ_0. In spite of its approximate nature, which is related to the average Fock's electron potential [4], the SCF wavefunction and energies show a number of formal properties that make them notably useful for their application in a variety of situations of chemical and physical interest. We can point out here the correct dependence of the energy on the number N of electrons that is ensured by the strict avoidance of unlinked contributions in the energy (extensivity), independence of the energy and wavefunction of a molecular fragment from the other fragments when they are at infinite distance, e.g., after breaking of a chemical or a van der Waals bond (size-consistency or separability) as well as invariance on the rotation of occupied MO's. Besides this, the variational nature of the HF equations provides additional interest to the calculations as far as absolute energies are concerned because it provides a secure and comfortable guide for systematic improvements of the theoretical approach.

In the search for less approximated or post-HF methods, the whole set of formal good properties is found again in the (exact for a given basis set) Full CI solution, which is impractical but for small systems and reduced basis [5–10].

So, considerable efforts have been devoted to the development of methods for dealing with electronic correlation adhering to three conditions:

1. having reasonable cost in terms of computational resources,
2. recovering of the most significant correlation contributions, and
3. keeping the validity of the above-mentioned formal properties.

By cost we mean not only the required resources but also the practicability of the method, i.e., the numerical stability and reliability of computational algorithms in different physical situations. Consider, e.g., that some methods may be well adapted to calculations in equilibrium conformations but numerically unstable far from equilibrium conformations.

By most significant correlation contributions we mean not only the major effects (e.g., the dominant role of double excitations in equilibrium closed shell states) but also the ability to incorporate other effects that could become important along dissociation curves (e.g., the relevant role of triply excited configurations as wavefunctions become more and more correlated).

Among the formal properties, extensivity and size-consistency have deserved special attention. Only size-extensive methods can be reliable when applied to larger and larger systems that become accessible to calculation by the increasing power of computing facilities. Only reasonably separable methods are promising as far as bond breaking is involved in chemical problems.

Many body perturbation theory (MBPT) appears to be the logical guide [11, 12] in the understanding of correlation effects and of the relative importance of different configurations. MBPT provides the linked-cluster theorem [11], a powerful tool for correlation analysis. In particular, it provides the key rationale that size-consistency can be achieved only by methods that either do include only linked diagrams (among which the so-called exclusion principle violating diagrams, EPV) or include all linked and unlinked terms to ensure the cancellation of the unlinked ones at each (considered) order of perturbation. Even if they are very popular and useful near equilibrium geometry of most closed shell molecules, MBPT methods suffer serious convergence problems out of this limited domain.

There exists an impressing panoply of non-perturbative methods for the study of the correlated ground state. In the present study we shall only consider single-reference methods, which attribute a special role to a single determinant ϕ_0, usually the HF solution. Among the most popular, one may quote

- The truncated CI's which are variational but not size-extensive, a defect sometimes approximately corrected through Davidson's type corrections [13] or through more elaborated coupled pair functional (CPF) treatments [14];

- The coupled electron pair approximation (CEPA) [15–17];
- The coupled cluster (CC) method [18–23],

each level presenting several variants. Recently, our groups have contributed to this panoply by new methods, which refer to the concept of dressing techniques of various levels of complexity [24–26].

The aim of the present work is to fight this increasing entropy (to which we contributed) and to provide a *unifying frame* into which the various methods find a logical position. We intend to clarify the connections between the different methods and to show in a systematic way the physical effects treated by each of them.

Our main tool in this presentation will be the theory of intermediate hamiltonians [25, 27–31] for the special case of a single state search, since it provides a very flexible conceptual frame. The principles of this theory will be recalled briefly in Sect. 2, which will introduce the idea of CI matrix dressing. Section 3 will present a series of methods which ensure size consistency through a minimal dressing. This idea applies to various types of model spaces and provides dressed independent electron approximation [32], an improved independent electron pair approximation [33, 34], an improved CEPA version which is identical to the $(SC)^2$SDCI technique [35], and the $(SC)^2$CI method in its full generality [24].

Section 4 will consider more elaborate dressing methods adding linked effects of the outer space determinants. The perturbative evaluation of their effect leads to the shifted-B_k approximation [36–38] and to an improved version of it [25] while a factorized evaluation of the external space coefficients results in a rewriting [26, 39] of CC methods as dressed CI techniques, opening the way to a very flexible and reciprocal mapping between CI and CC formalisms [40].

Section 5 takes benefit of the common conceptual frame to show how to combine in a consistent way methods of different degrees of complexity and cost.

2 Intermediate effective hamiltonian theory

2.1 General presentation

2.1.1 The correlation energy

The FCI wavefunction for the state Ψ_0, which satisfies the exact wave equation in the basis set

$$H\Psi_0 = \varepsilon_0 \Psi_0 \tag{1}$$

may be seen as resulting from the action of some wave operator Ω on the reference space of configurations. If nothing else is indicated, we deal in the following with single-reference cases, so that

$$\Psi_0 = \Omega\phi_0 \tag{2}$$

and, in intermediate normalization

$$\Psi_0 = \phi_0 + \sum_i^S c_i^S \phi_i + \sum_j^D c_j^D \phi_j + \sum_\alpha^T c_\alpha^T \phi_\alpha + \sum_\beta^Q c_\beta^Q \phi_\beta + \cdots , \tag{3}$$

where i runs over single excited configurations (S), j over double excited ones (D), α over Triples (T) and so on.

It is well known that the singles and doubles play a special role since the exact energy is obtained by projecting the eigenequation on the left by ϕ_0

$$\varepsilon_0 = \langle \phi_0 | H | \phi_0 \rangle + \sum_i^S \langle \phi_0 | H | \phi_i \rangle c_i^S + \sum_j^D \langle \phi_0 | H | \phi_j \rangle c_j^D . \tag{4}$$

The correlation energy, $E_{\text{corr}} = \varepsilon_0 - \langle \phi_0 | H | \phi_0 \rangle$, is then obtained simply as

$$E_{\text{corr}} = \sum_j^D \langle \phi_0 | H | \phi_j \rangle c_j^D \tag{5}$$

provided that Brillouin's theorem holds.

The goal of any not-full CI method is, in general, to achieve an estimate, as accurate as possible, of a subset of the exact coefficients c_k (at least $\{c_j^D\}$) and of the exact energy ε_0. So, as an example, a truncated CI limited to S and D will provide an estimate of ε_0 (other states are not relevant in the present discussion) and a set $\{c_k\}$ of coefficients of the singles (c_i^S) and the doubles (c_j^D). Any selection or truncation of a CI subspace implicitly defines a model space, since it treats at a higher level of accuracy the interactions staying in this space. Of course, the reliability of a model space depends on the way one decouples the model and the outer space. From this point of view, intermediate effective Hamiltonians are a tool of choice if a unified description of different methods is expected since they work on a selected model space, $\mathscr{S}_{\text{M}}$, of dimension n lesser than the FCI space, and are devised to look for a subset of exact roots and projected wavefunctions. This subset can be limited to just one root and just one state, of course, and this is the case we deal with in the present work. Note that the term *model space* is taken in the present work in the usual sense of the effective Hamiltonian theory. It has to be distinguished from the reference space of MR-CI calculations which may receive a dressing, as discussed in Sects. 3.4 and 4.3.

2.1.2 The dressing operator

Let $\mathscr{S}$ be the full space of configurations ϕ_i so that

$$\Psi_0 = \sum_{i \in \mathscr{S}} c_i \phi_i . \tag{6}$$

For a given Hamiltonian H, the exact energy is

$$\varepsilon_0 = \langle \Psi_0 | H | \Psi_0 \rangle . \tag{7}$$

We can divide the whole space $\mathscr{S}$ into two subspaces, $\mathscr{S}_{\text{M}}$ (model space of dimension n) and $\mathscr{S}_{\text{E}}$ (external space or outer space), as it is usual in effective Hamiltonian theories [27, 28]. Instead of looking for the n roots that can be got from the model space, intermediate Hamiltonians look for a number $n_0 < \dim\{\mathscr{S}_{\text{M}}\}$ of exact roots. This can be achieved through a further partition of the model space into a *principal* or *main* space $\mathscr{S}_{\text{P}}$ and an *intermediate* space $\mathscr{S}_{\text{I}}$ (see scheme 1). Such a partition has shown to be very convenient to avoid the undesirable effects of the so-called intruder states, i.e., those states that being mainly described by configurations belonging to $\mathscr{S}_{\text{E}}$ are quasi-degenerate in energy with the higher states described from $\mathcal{S}_{\mathrm{M}}$ so that perturbational treatments introduce dramatic numerical instabilities.

$$\overbrace{\overbrace{\overbrace{\phi_0}^{\mathcal{S}_P}\ \overbrace{--\{\phi_i\}--}^{\mathcal{S}_I}}^{\mathcal{S}_M}\ \ \overbrace{----\{\phi_\alpha\}----}^{\mathcal{S}_E}}^{\mathcal{S}}$$

In the present paper we consider only the cases where $\mathcal{S}_{\mathrm{P}}$ is just made of one reference, ϕ_0, this ϕ_0 being the determinant of the largest coefficient in Ψ_0. The projecting operator P_{M} corresponding to the model space $\mathcal{S}_{\mathrm{M}}$ can be written as

$$P = |\phi_0\rangle\langle\phi_0| + \sum_{i\in\mathcal{S}_I} |\phi_i\rangle\langle\phi_i|, \tag{8}$$

where the subscript M has been dropped from P_{M} for simplicity. We look then for intermediate Hamiltonians $\bar{H}$ that satisfy the following conditions:

$$\bar{H} = P\bar{H}P, \tag{9}$$

i.e., $\bar{H}$ is defined on the space $\mathcal{S}_{\mathrm{M}}$, and

$$\bar{H}\bar{\Psi}_0 = \varepsilon_0\bar{\Psi}_0, \tag{10}$$

where

$$\bar{\Psi}_0 = P\Psi_0. \tag{11}$$

In the above equations, Ψ_0 and ε_0 are the exact wavefunctions and energy as defined in Eq. (1) or Eqs. (6) and (7).

We can think of $\bar{H}$ as being a projection of a *dressed* H operator, so that

$$\bar{H} = P(H + \Delta)P \tag{12}$$

and call Δ a *dressing* operator, so that we can write

$$P(H + \Delta)P\Psi_0 = \varepsilon_0 P\Psi_0. \tag{13}$$

It is easy to understand the role played by the operator Δ by starting from Eqs. (1) and (10). After having defined the subspaces $\mathcal{S}_{\mathrm{M}} = \mathcal{S}_{\mathrm{P}} \cup \mathcal{S}_{\mathrm{I}}$ and $\mathcal{S}_{\mathrm{E}}$, we can write

$$\Psi_0 = \phi_0 + \sum_{i\in\mathcal{S}_{\mathrm{I}}} c_i\phi_i + \sum_{\alpha\notin\mathcal{S}_{\mathrm{M}}} c_\alpha\phi_\alpha. \tag{14}$$

We close now Eqs. (1) and (10) from the left by $\phi_i \in \mathcal{S}_{\mathrm{M}}$ so that

$$H_{io} + \sum_{j\neq 0,i,\ j\in\mathcal{S}_{\mathrm{M}}} c_j H_{ij} + c_i(H_{ii} - \varepsilon_0) + \sum_{\alpha,\ \alpha\notin\mathcal{S}_{\mathrm{E}}} c_\alpha H_{i\alpha} = 0. \tag{15}$$

Equation (15) is to be compared to

$$H_{io} + \sum_{j\neq 0,i,\ j\in\mathcal{S}_{\mathrm{M}}} c_j H_{ij} + c_i(H_{ii} - \varepsilon_0) + \sum_{j\in\mathcal{S}_{\mathrm{M}}} c_j \Delta_{ij} = 0. \tag{16}$$

Hence, the matrix elements of Δ must satisfy

$$\sum_{j \in \mathscr{S}_M} c_j \Delta_{ij} = \sum_{\alpha,\, \alpha \in \mathscr{S}_E} c_\alpha H_{i\alpha}. \tag{17}$$

It is important to note here that we have only n unknowns, n being the dimension of $\mathscr{S}_M$, i.e., $n = \dim\{\mathscr{S}_M\}$. The unknowns are ε_0 and $n-1$ coefficients c_i, so that Eq. (17) can be used to have different, but obviously related, definitions of Δ_{ij}. If we choose to take $\Delta_{ij} = 0$ whenever $i \neq j$, we will have a *diagonal dressing operator* defined as

$$\Delta_{ii} = c_i^{-1} \sum_{\alpha,\, \alpha \in \mathscr{S}_E} c_\alpha H_{i\alpha}. \tag{18}$$

Instead, if we choose to have $\Delta_{ij} = 0$ whenever $j \neq 0$, we will have a *first column dressing operator*

$$\Delta_{i0} = \sum_{\alpha,\, \alpha \in \mathscr{S}_E} c_\alpha H_{i\alpha}. \tag{19}$$

The equivalence between different forms for the dressing operator Δ and their properties has been discussed and shown elsewhere [25, 26, 35]. We will say here only that if $|c_0| > |c_i|$ for every c_i, the first-column dressing is that which ensures the minimal norm dressing and that some versions of the diagonal dressing have proved to be very efficient for the calculation of excited roots in correlation problems [41].

2.2 *Matrix formulation*

It is worthwhile to consider the dressing operator from the point of view of its operator matrix $\boldsymbol{\Delta}$ in order to show how intermediate Hamiltonian equations can be written, under a very general condition, as eigenvalue equations.

For the column vector $\boldsymbol{c}$, the exact Eq. (1) reads

$$\boldsymbol{Hc} = \varepsilon_0 \mathbf{1}\, \boldsymbol{c}. \tag{20}$$

If we define the projection operator $\boldsymbol{Q}$ as the complementary of $\boldsymbol{P}$, i.e.,

$$\boldsymbol{Q} = 1 - \boldsymbol{P}, \tag{21}$$

we can write for the rows associated to the model space $\mathscr{S}_M$,

$$\boldsymbol{PHPc} + \boldsymbol{PHQc} - \varepsilon_0 \boldsymbol{P1Pc} = 0. \tag{22}$$

The $\boldsymbol{PHQc}$ term is a column vector $\boldsymbol{V}$ so that its ith element is

$$V_i = \sum_{\alpha,\, \alpha \in \mathscr{S}_E} c_\alpha H_{i\alpha}. \tag{23}$$

Equation (22) is a matrix equation that can be reduced to an eigenvalue equation if a square matrix $\boldsymbol{\Delta} = \boldsymbol{P\Delta P}$ is defined so that the following condition is satisfied:

$$\boldsymbol{\Delta c} = \boldsymbol{V}, \tag{24}$$

where the $\boldsymbol{P}$ operator has been dropped for simplicity.

Equation (24) represents a matrix formulation of Eq. (17) and it allows to write Eq. (22) as

$$[\boldsymbol{P}(\boldsymbol{H}+\boldsymbol{\Delta}-\varepsilon_0\,\mathbf{1})\boldsymbol{P}]\,\boldsymbol{c}=0 \tag{25}$$

which is an eigenvalue problem for the operator $H+\Delta$ limited to the model space $\mathscr{S}_M$.

Note that FCI represents the trivial case where $\mathscr{S}_M=\mathscr{S}$ and for which the dressing vanishes, $\Delta=\mathbf{0}$.

2.3 *Application conditions*

No matter what definition we choose for nonzero Δ_{ij} elements, the key information relies in the quantities V_i introduced in Eq. (23), which depend on the c_α coefficients.

The following choices must then be made in order to develop practical applications of the intermediate hamiltonian theory (IHT).

(I) *Choice of the principal model space* $\mathscr{S}_\mathrm{P}$. In the present work $\mathscr{S}_\mathrm{P}$ will always be equal to the single-reference ϕ_0 having the largest coefficient in the state Ψ_0 of interest. The following remark may be added: we do not impose the condition that the c_0 coefficient corresponding to ϕ_0 in ordinary normalization should be nearly unity. The unique condition is that other configurations ϕ_i must have $c_i \lesssim c_0$ in Ψ_0.

(II) *Choice of the intermediate model space* $\mathscr{S}_\mathrm{I}$. The whole model space $\mathscr{S}_\mathrm{M}$ is then defined by means of $\mathscr{S}_\mathrm{P}$ and $\mathscr{S}_\mathrm{I}$.

(III) *Choice of the external space* $\mathscr{S}_\mathrm{E}$. All the complementary space of $\mathscr{S}_\mathrm{M}$ should be considered in principle. However, due to the bielectronic nature of H, only single and double excitations on the determinants belonging to $\mathscr{S}_\mathrm{M}$ need to be considered. In some cases, further restrictions may be introduced.

(IV) *Estimation of c_α from the set of model space coefficients c_i.* All the equations above are exact but for a possible truncation of the external space $\mathscr{S}_\mathrm{E}$. However, practical implementation requires to have estimates of c_α, which are unknown, to built the dressing operator Δ. Note that the most natural choice is to determine each c_α from the set of c_i coefficients, and, whatever be the procedure followed to achieve this determination, it represents a way of decoupling the set of FCI equations (which can be written in the form of Eq. (15) for *all* ϕ_i's). Such a decoupling is achieved in different manners in many ab initio correlation methods [42, 43].

(V) *Iterative self-consistent process.* If the c_α's are estimated from the c_i's, an iterative process can be conceived which can lead to self-consistency. Each iteration step has the structure

$$\{c_i^{(\mathrm{Step}\,n-1)}\}\to\Delta_{ij}^{(\mathrm{Step}\,n)}=f(\{c_i^{(\mathrm{Step}\,n-1)}\})\to\text{Diagonalize }\{\boldsymbol{P}\,(\boldsymbol{H}+\Delta)\boldsymbol{P}\}^{(\mathrm{Step}\,n)}$$

and yields an improved estimate of ε_0 and of the c_i coefficients corresponding to $\phi_i\in\mathscr{S}_\mathrm{M}$. Note that only linear equation system matrix operations are involved in each step. Of course, the whole diagonalization is not required at each step as far as we are concerned in a root or a few ones.

This paper aims to show that an adequate selection of choices II, III, and IV allows to formulate a great variety of known correlation methods. The noteworthy among them are the following:

1. The so-called electron pair methods (e.g. CEPA-*n* ... [15, 44, 45]);

2. Perturbation–variation methods (e.g. Davidson's Shifted-B_k [36–38]);
3. Coupled cluster methods (e.g. CCD, CCSD, CCSDT-1*a*, …, [46, 47]).

As it is shown below, the dressing operator Δ can be chosen just to ensure extensivity and size-consistency, i.e., just to ensure that diagonalizing $\boldsymbol{H}+\Delta$ cancels all the non-linked diagrams' contributions and shows proper asymptotic behaviour of both the energy and the wavefunction for separate systems. In this case, a number of methods result following choices II and III above (and the possible further imposition of the condition that the methods became exact for two electron systems), and they are presented under the heading *minimal size-consistent dressing* in Sect. 3. On the other hand, Δ can be thought to include additional effects, and particularly, additional linked-diagrams' effects. We present the resulting methods under the heading *total dressing methods* in Sect. 4.

3 Minimal size-consistent dressing methods

3.1 Implications of the separability requirement

Consider a composite system made of two subsystems A and B, and suppose that these two subsystems no longer interact. Also assume that the orbitals are localized on either A or B. Let us call ϕ_{0_A} and ϕ_{0_B} the two single-reference determinants for the separate subsystems and Ψ_A and Ψ_B the exact wavefunctions

$$\Psi_A = \phi_{0_A} + \sum_i c_{i_A} \phi_{i_A}, \tag{26}$$

$$\Psi_B = \phi_{0_B} + \sum_j c_{j_B} \phi_{j_B}. \tag{27}$$

The wave equation for the supersystem is the product of Ψ_A and Ψ_B

$$\Psi_{AB} = \Psi_A \Psi_B \tag{28}$$

so that we have

$$\Psi_{AB} = \phi_{0_A}\phi_{0_B} + \sum_{i_A} c_{i_A}\phi_{i_A}\phi_{0_B} + \sum_{j_B} c_{j_B}\phi_{j_B}\phi_{0_A} + \sum_{i_A}\sum_{j_B} c_{i_A} c_{j_B}\phi_{i_A}\phi_{j_B}. \tag{29}$$

The last term in this equation includes the composite excitations on the supersystem which appear with coefficients which are products of the coefficients of the combined local excitations on the subsystems.

Let us concentrate on the double excitations on system B that we represent with the double excitation operator $D^+_{j_B}$. Any multiple excitation $D^+_{j_B}\,\phi_{i_A}$, resulting from a double excitation $D^+_{j_B}$ on ϕ_{i_A}, has a coefficient

$$c_{D^+_{j_B}\phi_{i_A}} = c_{i_A}\, c_{D^+_{j_B}\phi_{0_B}}. \tag{30}$$

This asymptotic requirement is the key point of both separability and size-consistency. So, for a quadruple excitation $D^+_{i_A} D^+_{j_B}$, its coefficient is

$$c_{i_A j_B} = c_{i_A}\, c_{j_B}, \tag{31}$$

where $c_{i_A} = c_{D^+_{i_A}\phi_0}$ and $c_{j_B} = c_{D^+_{j_B}\phi_0}$. This means that remote double excitations are independent, a physically fundamental requirement. Notice that a quadruple excitation of that type involves two holes and two particles on system A, as well as two holes and two particles on system B

$$\phi_{i_A j_B} = D^{+r_A s_A}_{a_A b_A} D^{+t_B u_B}_{c_B d_B} \phi_0 . \tag{32}$$

The mixed excitations, such as $D^{+r_A t_B}_{a_A b_A}$, involving charge transfer have zero coefficients at infinite distances. If the subsystems get closer, these charge transfer excitations begin to have nonzero coefficients and one may write

$$c_{i_A j_B} = c_{i_A} c_{j_B} + \text{remainder}. \tag{33}$$

One may generalize this remark and say that if one can apply a double excitation D_j^+ on a determinant ϕ_i, one can write

$$c_{D_j^+ \phi_i} = c_{D_j^+ \phi_0} c_i + \text{remainder}. \tag{34}$$

The following set of *approximations* presented in Sect. 3 are based on the *omission of the remainder*, so that

$$c_{D_j^+ \phi_i} \approx c_{D_j^+ \phi_0} c_i \tag{35}$$

and especially for the quadruples $\phi_\alpha = D_j^+ \phi_i$ we will take simply

$$c_\alpha \approx c_j c_i . \tag{36}$$

In summary, if a double excitation D_j^+ can be performed on a determinant ϕ_i, whatever the degree of excitation of ϕ_i, and leads to determinant ϕ_α, the coefficient c_α will be taken as the product of the coefficient c_i of the original determinant ϕ_i times the coefficient c_j of the determinant $\phi_j = D_j^+ \phi_0$. Note that the estimate of c_α provided by Eq. (36) depends on the determinant ϕ_i we are dealing with, as a consequence of omitting the remainder as indicated above. It is this fact which makes the main difference between the approaches discussed in Sect. 3 and those discussed in Sect. 4. The methods presented in Sect. 4 no longer apply this simplification.

3.2 An elementary modification of the MP2 method: the dressed independent excitation approximation

As mentioned in Eq. (5) above, the knowledge of the coefficients of the doubles is sufficient to calculate the correlation energy. The simplest evaluation of these coefficients comes in the first order perturbation

$$c_i^{(1)} = \frac{H_{i0}}{E_0^0 - E_i^0}, \tag{37}$$

where the denominator depends on the choice of the zeroth order hamiltonian (e.g., Møller–Plesset or Epstein–Nesbet denominators). This perturbative evaluation can be seen as an approximation of a two-dimensional CI matrix spanned by ϕ_0 and ϕ_i. Actually, diagonalizing such matrices provides a non-perturbative evaluation of the coefficients of each doubly excited determinant, and represents an independent excitation approximation [32,48]. The advantage of this procedure over MP2 is twofold:

1. it includes higher order contributions through infinite partial summation of diagrams; and
2. it never diverges even when some $|c_i|$ tend to unity.

From the effective Hamiltonian point of view one may consider that ϕ_0 and ϕ_i define a 2×2 model space $\mathcal{S}_M = \{\phi_0, \phi_i\}$ and one may be tempted to apply our basic procedure of dressing. The reference determinant ϕ_0 interacts with all other doubly excited determinants $\phi_j \neq \phi_i$ which belong to the outer space, so that Eq. (18) gives

$$\Delta_{00}^{i} = \sum_{j \neq i} c_j H_{0j} \tag{38}$$

which, taking into account Eq. (5), is equivalent to

$$\Delta_{00}^{i} = E_{\mathrm{corr}} - c_i H_{0i}. \tag{39}$$

The determinant ϕ_i interacts, in principle, with some singles, doubles, triples and quadruples. We shall restrict the outer space to the quadruples in order to take into account the effect of the double excitations which already dressed ϕ_0. Those which interact with ϕ_i are obtained from it by double-excitations $\phi_\alpha = D_j^+ \phi_i$. If we accept Eq. (36) and noticing that

$$\langle \phi_i | H | \phi_\alpha \rangle = H_{0j}, \tag{40}$$

one obtains

$$\Delta_{ii}^{i} = \sum_{j,\ D_j^+ \phi_i \neq 0} c_j H_{0j}. \tag{41}$$

Eq. (41) may be presented differently (and more conveniently from a computational point of view) as

$$\Delta_{ii}^{i} = \sum_{j,\ \phi_j = D_j^+ \phi_0} c_j H_{0j} - \sum_{j,\ D_j^+ \phi_i = 0} c_j H_{0j} \tag{42}$$

or, in other words,

$$\Delta_{ii}^{i} = E_{\mathrm{corr}} - E_i^{\mathrm{EPV}}, \tag{43}$$

where E_i^{EPV} represents the energetic contribution of all double excitations *which cannot be applied on i*, because they involve at least one hole or a particle of ϕ_i.

In practice, the dressed-IEA method proceeds through successive diagonalization of 2×2 dressed matrices, until the coefficients convergence. In fact, the EPV contribution may be calculated without any additional loop and the cost of the process remains similar to that of an MP2 calculation. Despite the neglect of all H_{ij} interactions the EPV's term introduces some interdependence between the excited amplitudes. This 2×2 CI matrix method incorporates some third and higher order perturbation effects as well as EPV diagrams of all orders acting through ϕ_i as it has been discussed elsewhere [32]. Some few tests have exhibited a surprising numerical efficiency [32].

3.3 The dressed independent electron pair approximation (dressed IEPA)

One may consider as model space ϕ_0 and the set of *all doubles which have the same holes a and b*. Let us call $\mathscr{S}_{ab}$ this model space. One may apply the same logics as above in dressing the CI matrix. If one calls

$$e_{cd} = \sum_{j,\,\phi_j \in \mathscr{S}_{cd}} c_j H_{0j} \tag{44}$$

then

$$E_{\text{corr}} = \sum_{c<d} e_{cd} \tag{45}$$

and the dressing matrix elements will be for the $\mathscr{S}_{ab}$ CI matrix

$$\Delta_{00}^{ab} = E_{\text{corr}} - e_{ab} \tag{46}$$

and

$$\Delta_{ii}^{ab} = E_{\text{corr}} - \sum_{j,\ D_j^+\phi_i = 0} c_j H_{0j}. \tag{47}$$

Note that, as in the IEA case, E_{corr} may be eliminated for the determination of the coefficients since the final correlation energy is calculated from the coefficients of the doubles (see Eq. (45)). If one dresses by

$$\Delta_{00}^{ab} = -e_{ab} \tag{48}$$

and

$$\Delta_{ii}^{ab} = -\sum_{j,\ D_j^+\phi_i = 0} c_j H_{0j} = -E_i^{\text{EPV}}, \tag{49}$$

one obtains a *dressed* IEPA approximation, taking into account all EPV's. Historically, IEPA has been proposed as the independent diagonalization of undressed CI matrices for each $\mathscr{S}_{ab}$ space. We maintain the term *independent*, despite some interdependence through EPV's, since the H_{ij} interactions for ϕ_i and ϕ_j having different hole pairs are omitted. This method is presented here for the first time and has never been used.

3.4 Size-consistent SDCI and beyond

3.4.1 Singles and doubles model space: improving CEPA

The next approximations above MP2 are those which incorporate the interaction between the doubles such as MP3 and SDCI. Let us take the model space as the SDCI space. The dressing of ϕ_0 is zero since it does not interact with outer space determinants (i.e., triples or higher). The singles interact with triples and the doubles interact with triples and quadruples. We shall neglect at this stage the interaction between the doubles and the triples and only consider the effect of double excitations D_j^+ on the singles and the doubles.

In each case we shall assume that Eq. (35) holds and we obtain, from Eq. (18),

$$\Delta_{ii} = c_i^{-1} \sum_{j,\, D_j^{+}\phi_i \neq 0} \langle \phi_i | H | D_j^{+} \phi_i \rangle \, c_j c_i = \sum_{j,\, D_j^{+}\phi_i \neq 0} H_{0j} c_j \tag{50}$$

which, as discussed above, can be written as

$$\Delta_{ii} = E_{\text{corr}} - E_i^{\text{EPV}}. \tag{51}$$

This equation is identical to Eq. (43) but it works now in a SD model space. This is the leading equation defining the diagonal dressing of an SDCI matrix which makes it size-consistent and exact for two electron systems, provided that the procedure has been iterated to convergence. Hence, the resulting method has been labeled (SC)^{2}SDCI which stands for *self-consistent size-consistent singles and doubles* CI [24]. The CI acronym is kept in the label although the procedure is not variational to indicate that it proceeds through matrix diagonalizations and handles only c_i coefficients. It has been shown [24] that the dressing defined in Eq. (51) ensures the strict separability of an $A \cdots B$ problem into noninteracting A and B subsystems provided that the MOs are localized. The defect of the method is that it is not invariant under rotation of occupied or virtual orbitals. From a practical point of view, the method is very easily implemented and the extra cost over a traditional SDCI calculation is made very small by an efficient computation of the EPV corrections through storage of partial summations [49]. As it will be seen in the next section, the method is easily generalized to any CI space.

It is enlightening to compare the (SC)^{2}SDCI method to the variants of the well known CEPA method. We consider, for instance, the most elaborated version CEPA-3 [17, 44, 50] in terms of spin orbitals [42]. In CEPA-3, the row i corresponding to the doubly excited configuration $\phi_i = |\phi_{ab}^{rs}\rangle$ can be written as

$$H_{i0} + \sum_{j,\ \phi_j = D_j^{+}\phi_0} \langle \phi_i | H - E_0 | \phi_j \rangle \, c_j - c_i \left[\sum_{k_{(i)}} c_{k_{(i)}} H_{0k_{(i)}} \right] = 0, \tag{52}$$

where index $k_{(i)}$ runs over diexcited configurations *which have the same holes a, b as* ϕ_i and $E_0 = H_{00}$.

The dressing formulation is now easy if one compares with Eq. (16) written for the diagonal dressing case Δ_{ii}

$$H_{i0} + \sum_{j \neq 0, i,\ j \in \mathcal{S}_M} c_j H_{ij} + c_i (H_{ii} - \varepsilon_0) + c_i \Delta_{ii} = 0. \tag{53}$$

Taking $\mathcal{S}_{\text{M}}$ as the whole set of double-excitations $\{\phi_j\}$ and remembering that $E_{\text{corr}} = \varepsilon_0 - E_0$, it is immediately seen that

$$\Delta_{ii}^{\text{CEPA}} = E_{\text{corr}} - \sum_{k_{(i)}} c_{k_{(i)}} H_{0k_{(i)}}, \tag{54}$$

where the meaning of index $k_{(i)}$ has been indicated above.

Of course, Eqs. (53) and (54) are nothing but another way of writing CEPA equations, and are included here only for the purpose of unifying the presentation of different methods. Note, however, that CEPA incorporates only a part of the EPV corrections. CEPA-0 [15, 16, 42] neglects all of them, while CEPA-3 [44, 50] only considers the EPVs which violate the exclusion principle through the holes and omits the violations through the particles. Hence, an $(SC)^2$DCI method can be considered as a *full* CEPA method. From this analysis, which symmetrizes the role of holes and particles, the reference to electron pairs in the CEPA acronym is a purely historical remainder.

Notice that $(SC)^2$SDCI incorporates the effect of singles and this opens the way to further generalizations.

3.4.2 $(SC)^2$CI for a general CI space

It has been shown elsewhere [24] that the $(SC)^2$ procedure is easily generalized to an $\mathscr{S}_{\mathrm{M}}$ space made of any selected CI including all the doubles as well as a selection of singles, triples, etc. Then one shall again restrict the effect of the outer space to the effect of the double excitations on each determinant ϕ_i belonging to the model space. Assuming once more Eq. (35) to be valid whatever the degree of excitation of ϕ_i, one obtains the general expression for the dressing

$$\Delta_{ii} = \sum_{j,\ D_j^+\phi_i \neq 0,\ \notin \mathscr{S}_{\mathrm{M}}} H_{0j}\, c_j \tag{55}$$

or, equivalently

$$\Delta_{ii} = E_{\mathrm{corr}} - E_i^{\mathrm{EPV}} - R_i, \tag{56}$$

where the new contribution R_i is given by

$$R_i = \sum_{j,\ D_j^+\phi_i \neq 0,\ \in \mathscr{S}_{\mathrm{M}}} H_{0j} c_j \tag{57}$$

and has been introduced to avoid any redundancy that would result from dressing the configuration $\phi_i \in \mathscr{S}_{\mathrm{M}}$ by a double excitation D_j^+ which acting on ϕ_i would send to a determinant already belonging to $\mathscr{S}_{\mathrm{M}}$.

This method applies for instance to MR-SDCI spaces (e.g., CAS-SDCI). In this case, the dressing will never affect the diagonal energies of the reference configurations that do not interact with the outer space determinants $\phi_\alpha \in \mathscr{S}_{\mathrm{E}}$. Note that the method is also applicable to selected CI spaces which do not include all doubles.

A *crucial remark* must be formulated at this stage. Despite the multireference character of the model space, the $(SC)^2$CI method remains a single-reference dressing, since the principal model space $\mathscr{S}_{\mathrm{P}}$ introduced in Sect. 2.1 above remains reduced to ϕ_0. One should distinguish between the type of model space treated and the dressing technique. The first one may be multireference, while the second one is single-referential *all along this work*. An $(SC)^2$MR-SDCI is a special case of an $(SC)^2$ selected CI. It should not be confused with a MR$(SC)^2$CI [51, 52] where the dressing would be performed from a multideterminantal principal model space and would be multireferential in nature. This last problem is out of the scope of the present paper.

Table 1 shows schematically the set of methods which have been collected under the heading of minimal size-consistent dressing methods.

Table 1. Hierarchy of minimal size – consistent dressing methods. The main model space is always equal to ϕ_0

Method	Intermediate model space $\mathscr{S}_1$	Useful external space $\mathscr{S}_{\mathrm{E}}$	Diagonal dressing Δ_{ii}	Comments
Dressed IEA	only one $\phi_i \in \{D\}$	$\phi_j \in \{D\}, \phi_j \neq \phi_i$ $\phi_\alpha \in \{D_j^+ \phi_i\}$	$\begin{cases} \Delta_{00} = (E_{\mathrm{corr}}) - c_i H_{0i} \\ \Delta_{ii} = (E_{\mathrm{corr}}) - \sum_{j, D_j^+ \phi_i = 0} c_i H_{0j} \end{cases}$	Requires N 2×2 diagonalizations for N = number of doubles
Dressed IEPA	$\phi_i \in \mathscr{S}_{ab}$ $\mathscr{S}_{ab} = \begin{Bmatrix} D \\ \text{having same} \\ \text{holes } a \text{ and } b \end{Bmatrix}$	$\phi_j \in \mathscr{S}_{ab}$ $\phi_\alpha \in \{D_j^+ \phi_k\}_{\phi_k \in \mathscr{S}_{ab}}$	$\begin{cases} \Delta_{00} = (E_{\mathrm{corr}}) - \sum_{j \in \mathscr{S}_{ab}} c_j H_{0j} \\ \Delta_{ii} = (E_{\mathrm{corr}}) - \sum_{j, D_j^+ \phi_i = 0} c_j H_{0j} \end{cases}$	Requires $\sim n_{\mathrm{oc}}^2$ diagonalizations of dimension $\sim n_{\mathrm{virt}}^2$ + iteration
CEPA	$\phi_i \in \{D\}$	$\phi_\alpha \in \{Q\}$	$\begin{cases} \Delta_{00} = 0 \\ \Delta_{ii} = E_{\mathrm{corr}} - \sum_{\substack{k \\ \phi_k \text{ has same holes as } \phi_i}} c_k H_{0k} \end{cases}$	Diagonalization + iteration EPV's through holes only
(SC)^{2}SDCI	$\phi_i \in \{S, D\}$	$\phi_\alpha \in \{T, Q\}$	$\begin{cases} \Delta_{00} = 0 \\ \Delta_{ii} = E_{\mathrm{corr}} - \sum_{k, D_k^+ \phi_i = 0} c_k H_{0k} \end{cases}$	Full CEPA, all EPV's considered
(SC)^2 selected CI on space $\mathscr{S}$ (e.g. MRSDCI)	$\phi_i \in \mathscr{S}, \phi_i = \phi_0$	$\phi_\alpha \in \{T, Q\}$/MReferences	$\begin{cases} \Delta_{00} = 0 \\ \Delta_{ii} = E_{\mathrm{corr}} - \sum_{k, D_k^+ \phi_i = 0 \text{ or } \in \mathscr{S}} c_k H_{0k} \end{cases}$	Diagonalization + iteration

4 Total dressing methods

We move back to the problem of how to obtain the c_α coefficients for $\phi_\alpha \in \mathscr{S}_E$ in terms of the c_i ones ($\phi_i \in \mathscr{S}_M$), but now we want to include, besides the nonlinked effects that ensure size-extensivity, additional linked-diagrams effects. This will remove, moreover, the inconsistency of using different estimates for a given c_α depending on which ϕ_i one is dealing with.

Two ways for estimating c_α have been tried. The first one uses purely perturbative-like expressions for c_α, and leads to perturbation–diagonalization methods. The second one involves products of c_i coefficients and, alone or combined with perturbative contributions to c_α, leads to coupled cluster methods.

A great variety of methods can then be conceived and some systematic notation is needed. We will denote thereafter each method according to the following pattern:

$$\text{Model space [external space]}_x$$

where the subindex incorporates additional information, e.g. if a perturbative (denoted as subindex p) or a factorization (denoted as subindex f) approach has been used. Model and external spaces will be described in the conventional way, namely, S for singles, D for doubles, etc. [53].

4.1 Perturbative total dressing or simplified shifted-B_k

We can consider the following zeroth order Hamiltonian

$$H_0 = \sum_{j \in \mathscr{S}_M} E_j^0 |\phi_j\rangle \langle\phi_j| + \sum_{\alpha \in \mathscr{S}_E} E_\alpha^0 |\phi_\alpha\rangle \langle\phi_\alpha|. \tag{58}$$

At second order, c_α is given by

$$c_\alpha^{(2)} = \left(\sum_{j \in \mathscr{S}_M} c_j^{(1)} H_{j\alpha} \right) (E_0^0 - E_\alpha^0)^{-1}. \tag{59}$$

Taking the same expression for c_α but replacing c_j for $c_j^{(1)}$, and from Eq. (19), we have for the dressing

$$\Delta_{i0}^p = \sum_{\alpha \notin \mathscr{S}_M} \left(\sum_{j \in \mathscr{S}_M} c_j H_{j\alpha} \right) H_{i\alpha} (E_0^0 - E_\alpha^0)^{-1}. \tag{60}$$

We have now all the flexibility in the selection of $\mathscr{S}_M$ as well as in the choice of denominators (i.e., of H_0), that is characteristic of MBPT [54–58].

A noniterative intermediate Hamiltonian formulation had been previously proposed [25, 27] which leads to the so-called shifted-B_k approximation. Shifted-B_k was proposed by Davidson [36–38] in relation with a previous work by Shavitt [59] and it requires, in the usual IHT formulation, a full matrix dressing operator built to second order so that

$$\Delta_{ij}^{B_k} = \sum_{\alpha \notin \mathscr{S}_M} H_{i\alpha} H_{\alpha j} (E_0^0 - E_\alpha^0)^{-1}. \tag{61}$$

The equivalence of our Δ_{i0} dressing given at Eq. (60) and the shifted-B_k dressing of Eq. (61) is shown by comparing the row relative to $\phi_i \in \mathscr{S}_{\mathrm{M}}$ in the equations

$$P\,(H + \Delta^{B_k})\,P\,\Psi_0 = \varepsilon_0\,\Psi_0 \tag{62}$$

and

$$P\,(H + \Delta^{P})\,P\,\Psi_0 = \varepsilon_0\,\Psi_0\,. \tag{63}$$

This equivalence, as well as the interest of our formulation, have been discussed in a previous work [25] and will not be repeated here. We prefer, instead, to remark an important characteristic of total perturbative dressing procedures, notably, its ability to incorporate EPV diagrams' effects by means of a denominator shift.

The argument leading to this improvement is very simple in the context of this paper. Suppose that we let a ϕ_α belonging to $\mathscr{S}_{\mathrm{E}}$ to be included in $\mathscr{S}_{\mathrm{M}}$. The row corresponding to ϕ_α in $\boldsymbol{P(H + \Delta)\,P}\,\Psi_0 = \varepsilon_0\Psi_0$ is now

$$\sum_{j \in S_{\mathrm{M}},\, j \neq \alpha} c_j\,H_{j\alpha} + c_\alpha\,(H_{\alpha\alpha} + \Delta_{\alpha\alpha} - \varepsilon_0) = 0, \tag{64}$$

where $\Delta_{\alpha\alpha}$ is taken as the only non zero $\Delta_{\alpha j}$ element (i.e., as a diagonal dressing). Isolating c_α we have

$$c_\alpha = \frac{\sum\limits_{j \in S_{\mathrm{M}},\, j \neq \alpha} c_j H_{j\alpha}}{\varepsilon_0 - [H_{\alpha\alpha} + \Delta_{\alpha\alpha}]}\,. \tag{65}$$

We have now different options for $\Delta_{\alpha\alpha}$.

1. We can take $\Delta_{\alpha\alpha} = \varepsilon_0 - E_0^0 = E_{\mathrm{corr}}$. In this case, we have the nonimproved perturbative dressing of Eq. (60), i.e., we have shifted-B_k.

2. If we take $\Delta_{\alpha\alpha}$ as a *size-consistent dressing* as it was discussed above (see Sect. 3 of this paper), we have

$$\Delta_{\alpha\alpha} = E_{\mathrm{corr}} - \sum_{i,\; D_i^{+}\phi_\alpha = 0} c_i\,H_{0i} = E_{\mathrm{corr}} + E_\alpha^{\mathrm{EPV}} \tag{66}$$

and

$$c_\alpha = \frac{\sum\limits_{j \in S_{\mathrm{M}},\, j \neq \alpha} c_j H_{j\alpha}}{E_0^0 - [H_{\alpha\alpha} + E_\alpha^{\mathrm{EPV}}]}\,. \tag{67}$$

This correction has shown to be very efficient to improve the behavior of the perturbative total dressing model for the treatment of single bond breaking [25].

If $\mathscr{S}_{\mathrm{M}}$ is made of S and D we should label, according to our above conventions, SDCI$[TQ]_p$ the method that is equivalent to shifted-B_k and SDCI$[TQ]_{p+\mathrm{EPV}}$ the improved method.

As a restrictive comment on this approach one should mention the fact that the perturbative evaluation of the outer space coefficients destroys the strict separability for intermolecular problems although it remains numerically accurate [25].

4.2 Factorized total dressing or coupled cluster theory

Let us assume that $\mathscr{S}_{\mathrm{M}}$ is reduced to ϕ_0 and the doubles, $\mathscr{S}_{\mathrm{M}} = \{\phi_0, \phi_i = D_i^+ \phi_0\}$, and that we restrict the outer space $\mathscr{S}_{\mathrm{E}}$ to the quadruples. It is well known from perturbation theory that the second order coefficient of a quadruple can be written as

$$c_\alpha^{(2)} = \sum_{(k,l),\ \phi_\alpha = D_k^+ D_l^+ \phi_0} c_k^{(1)} c_l^{(1)}, \tag{68}$$

where the running indexes (k, l) are *enclosed in parentheses* to indicate that the summations run on *all different pairs of complementary double excitations k and l into which ϕ_α can be decomposed,* i.e., such that $\phi_\alpha = D_k^+ D_l^+ \phi_0$. Of course, a proper account of the signs of the coefficients of the doubles according to the diverse permutations of the labels of holes and particles is implicitly defined in the conditions appearing under the summations and will be assumed in the following.

Adding higher order effects one may write

$$c_\alpha = \sum_{(k,l),\ \phi_\alpha = D_k^+ D_l^+ \phi_0} c_k c_l . \tag{69}$$

The dressing of the DCI matrix by the effect of the quadruples can now become nonperturbative by writing

$$\Delta_{i0} = \sum_{\alpha,\, \alpha \in \mathscr{S}_{\mathrm{E}} = \{Q\}} c_\alpha H_{i\alpha} = \sum_{j,\, D_j^+ \phi_i \neq 0} \left(\sum_{(k,\ l),\, D_k^+ D_l^+ = D_i^+ D_j^+} c_k^D c_l^D \right) H_{0j}, \tag{70}$$

where $H_{i\alpha}$ has been replaced by H_{0j}. The above equation provides a dressing formulation for the CCD method, as it has been recently tested [26, 39], even though the possibility of calculating a CCD wavefunction by iterative solutions of a secular equation is well known [60].

We can describe briefly the way in which CC problems can be formulated as iterative series of eigenvalue-like equations by means of dressing matrix techniques.

Coming again to Eqs. (2) and (3) and equalling the FCI and the CC ansatz [20, 22] expansions of Ψ_0, we have

$$\Psi_0 = \Omega \phi_0 = (1 + C_1 + C_2 + C_3 + C_4 + \cdots) \phi_0 = \exp(T_1 + T_2 + T_3 + \cdots) \phi_0, \tag{71}$$

where the C_n and T_n operators have the same formal structure, namely,

$$C_n = \sum_{ab \ldots n,\, rs \ldots z} c_{ab \ldots n}^{rs \ldots z} \hat{X}_{ab \ldots n}^{rs \ldots z} \tag{72}$$

with $t_{ab \ldots n}^{rs \ldots z}$ amplitudes instead of c coefficients for T_n, and where the $\hat{X}$ are excitation operators in the normal form [58]

$$\hat{X}_{ab \ldots}^{rs \ldots} = a_r^+ a_s^+ \cdots a_b a_a . \tag{73}$$

Equation (71) leads easily to the well known hierarchy of equations relating C_n and T_n operators [61–64].

As an example, for the CCSD approach, we have

$$C_1 = T_1, \tag{74}$$

$$C_2 = T_2 + \tfrac{1}{2} T_1^2, \tag{75}$$

$$C_3 = T_1 T_2 + \tfrac{1}{6} T_1^3, \tag{76}$$

$$C_4 = \tfrac{1}{2} T_2^2 + \tfrac{1}{24} T_1^4 + \tfrac{1}{2} T_1^2 T_2. \tag{77}$$

The CCSD equations can be conveniently written as

$$\langle \phi_0 | H | (C_2)\, \phi_0 \rangle = E_{\text{corr}}, \tag{78}$$

$$\langle \phi_i^S | \bar{H} | (C_1 + C_2)\, \phi_0 \rangle + \langle \phi_i^S | \Delta | \phi_0 \rangle = c_i^S E_{\text{corr}}, \tag{79}$$

$$\langle \phi_j^D | \bar{H} | (1 + C_1 + C_2)\, \phi_0 \rangle + \langle \phi_j^D | \Delta | \phi_0 \rangle = c_j^D E_{\text{corr}}, \tag{80}$$

where the terms which are not linear in the c_i^S or c_j^D coefficients, i.e. the terms dealing with T_n products or powers which cannot be included into a complete C_n operator, have been grouped into the dressing terms and $\bar{H} = H - E_0$. The equivalence in the role of these dressing terms and those defined in Eqs. (18) and (19) is made clearer if we write Ψ_0 in the following way

$$\begin{aligned}\Psi_0 &= \phi_0 + (T_1 + T_2 + \tfrac{1}{2} T_1^2)\, \phi_0 + (T_1 T_2 + \tfrac{1}{6} T_1^3 + \tfrac{1}{2} T_1^2 T_2 + \tfrac{1}{2} T_2^2 + \tfrac{1}{24} T_1^4) \phi_0 \\ &= \phi_0 + (C_1 + C_2)\phi_0 + (C_3 + C_4)\phi_0 .\end{aligned} \tag{81}$$

One immediately sees that the role of dressing in Eqs. (79) and (80) is just to take account of triply and quadruply excited configurations, so that the natural partition of spaces for having CCSD is to take $\mathcal{S}_{\text{M}} = \{\phi_0, S, D\}$ and $\mathcal{S}_{\text{E}} = \{T, Q\}$.

The effect of the external space is introduced in the usual way, as defined in Eq. (19), but now the form of calculating c_α is derived from the set of Eqs. (74)–(77), from which it is easily deduced that

$$C_3 = C_1 C_2 - \tfrac{1}{3} C_1^3 , \tag{82}$$

$$C_4 = \tfrac{1}{2} C_2^2 - \tfrac{1}{12} C_1^4. \tag{83}$$

These expressions provide a guide on how the c_α coefficients of quadruples and triples can be obtained from appropriate combinations of products of coefficients of singles and doubles. Notably, if we take $\mathcal{S}_{\text{M}} = \{\phi_0, D\}$ and $\mathcal{S}_{\text{E}} = \{Q\}$, we can use Eq. (83) to take

$$c_\alpha = \sum_{(i,j)} c_i^D c_j^D \tag{84}$$

as it was deduced above in Eq. (69) from perturbation theory arguments. Hence, the dressing can be written as in Eq. (70). We then have a method which in the systematic notation introduced above would be called DCI$[Q]_f$ and which is identical to CCD [26, 39].

If one wants to take account of singles and the disconnected contributions of triples on them, one simply has to include $\{S\}$ in $\mathcal{S}_{\text{M}}$ and to take (see Eq. (82))

$$c_\alpha^{T_{dc}} \approx \sum_{(i,j)} c_i^S c_j^D, \tag{85}$$

where (i, j) enclosed in parentheses has the same meaning as before, but now $\phi_\alpha = M_i^+ D_j^+ \phi_0$ where M_i^+ is the single-excitation operator which generates the single ϕ_i from ϕ_0. The resulting method, SDCI$[TQ]_f$ only differs from CCSD in the neglecting of third and fourth powers of c_i^S in Eqs. (82) and (83). These powers of coefficients of singles can be included if an unusually high weight of singles contributions occurs.

Another correlation technique called QCI or QCISD, first proposed by Pople et al. [65], is somehow related to CCSD [43]. It can be expressed by a set of non-linear equations similar to those of CCSD but only a few cluster product terms are retained, namely $T_1 T_2$ in the equations corresponding to single excitations and $\frac{1}{2}T_2^2$ in the equations of doubles. These terms are kept because they represent the minimal requirement to warrant size-consistency. A formulation in terms of IHT, very similar to that of CCSD discussed above, is then possible, but the removal of disconnected products corresponding to $\frac{1}{2}T_2^2$ from the c_j^D coefficients of doubles would be needed because these terms are actually present after diagonalization of $\mathscr{S}_{\mathrm{M}} = \{S, D\}$. Equations (84) and (85) would then be used to calculate c_α coefficients.

The leading effect lacking in CCSD or equivalent treatments is the connected contribution of triples [66–69]. It is in fact the only missing 4th order contribution to the energy. The simplest approach one can build including T_3 operators is to expand $\exp(T_1 + T_2 + T_3)$ but to neglect all cluster product terms which lead to excitations higher than quadruple excitations. The first C_n operator whose direct relation to T_n operators is then affected in Eqs. (74)–(77) is C_3 which becomes

$$C_3 = T_1 T_2 + \tfrac{1}{6} T_1^3 + T_3 . \tag{86}$$

Taking into account Eqs. (76) and (82), one can write

$$C_3 = C_1\, C_2 - \tfrac{1}{3} C_1^3 + C_3^L , \tag{87}$$

where $C_3^L \equiv T_3$ has been introduced to make clear that the t_3 amplitudes are to be taken directly as a term which contributes to the coefficients of triples, namely, the connected triples part. We can then resort to a perturbation-like estimate of these contributions, so that

$$c_\alpha^{T_c} = \left(\sum_{i,\, \phi_i \in S_{\mathrm{M}}} c_i \langle \phi_0 | H - F | \phi_i \rangle \right) (E_0^0 - E_\alpha^0)^{-1} , \tag{88}$$

where F is the Fock operator relative to ϕ_0. This expression should replace Eq. (22) of Ref. [26] the results of which have been obtained from the above Eq. (88).

In this way, the connected effects of triples are coupled with the configurations of $\mathscr{S}_{\mathrm{M}}$ through diagonalization of $\boldsymbol{P}(\boldsymbol{H} + \boldsymbol{\Delta})\boldsymbol{P}$, but there is no direct coupling between them. This procedure is more elaborate than CCSD(T) [66, 70, 71] (where all the connected effects of triples are treated at the MP4 level on the energy but have no effect on the calculation of c_i^S and c_j^D) but less accurate than CCSDT [72] (where all the effects of triples are completely coupled with all the space of S, D, T, and Q, the only limitation coming from the truncation of the cluster series to $T_1 + T_2 + T_3$). In fact, our procedure is equivalent to Bartlett's CCSDT-1a approach [47, 73], as it has been discussed in a previous work [26], provided that the same perturbative partition of H (namely, the Møller–Plesset partition) would be used. Note also that EPV corrections can be added in the denominators of Eq. (88) in the same way as was discussed in Sect. 4.1 above.

4.3 Generalization: coupled cluster type dressing of an arbitrary CI matrix

Consider a CI space $\mathscr{S}$, which can be for instance an MR- or a CAS-SDCI space. The eigenvector of $P_{\mathscr{S}}HP_{\mathscr{S}}$ which satisfies

$$P_{\mathscr{S}}HP_{\mathscr{S}}\Psi_0 = \varepsilon_0^{\mathscr{S}}\Psi_0^{\mathscr{S}} \tag{89}$$

is a linear combination of the determinants, with the largest coefficient on a single determinant ϕ_0, which we shall call the generator. In the intermediate normalization

$$\Psi_0^{\mathscr{S}} = \phi_0 + \sum_i c_i\phi_i \tag{90}$$

with $|c_i| \leqslant 1$.

It is important to remark again that despite the possible MR character of the CI space, one and only one determinant (which must be one of these references) plays a special role in the forthcoming development.

One may wonder whether the CI wavefunction might be written as the projection in the space $\mathscr{S}$ of a coupled cluster type wavefunction, which uses ϕ_0 as the CC single-reference $\Psi_0 = \exp(S)\,|\phi_0\rangle$, i.e., whether one may write

$$\Psi_0^{\mathscr{S}} = P_{\mathscr{S}}\exp(S)\,|\phi_0\rangle \tag{91}$$

or, equivalently,

$$c_i = \langle\phi_i|\exp(S)\,|\phi_0\rangle. \tag{92}$$

It is always possible to find an S satisfying both Eqs. (90) and (91), provided that one introduces a sufficiently complex form of S, i.e., as many operators as determinants

$$S = \sum_i t_i\hat{X}_i, \tag{93}$$

where

$$|\phi_i\rangle = \hat{X}_i|\phi_0\rangle. \tag{94}$$

The $\hat{X}_i$ are the multiple-excitation operators creating the various determinants from ϕ_0 as they were introduced in Eq. (73). It is necessary to consider all of them since the c_i coefficients of the CI wavefunction are, a priori, independent variables, not obtainable by products of lower rank amplitudes. The t_i amplitudes are easily obtained from the considered c_i's by using the cascade of Eqs. (74)–(77) discussed in the previous section. Hence, for single excitations,

$$t_i = c_i \tag{95}$$

while for double-excitations

$$t_i = \tfrac{1}{2}\sum_{(k,l),\ T_kT_l = T_i} t_k t_l - c_i, \tag{96}$$

etc.

The CI wavefunction may always be shaped in an exponential expansion from ϕ_0. Once S is so defined, it is easy to calculate the outer space coefficients

$$c_\alpha = \langle\phi_\alpha|\exp(S)|\phi_0\rangle \tag{97}$$

especially those which interact with the ϕ_i's and are therefore triples and quadruples with respect to the references if $\mathcal{S}$ is an MR-SDCI space. One should remark that some outer space determinants may not appear in $\exp(S)\,|\phi_0\rangle$ (Eq. (97) giving $c_\alpha = 0$) as already occurs for singles, triples, pentuples, ... in CCD. One may also remark that the evaluation of c_α from Eq. (97) may be poor, as is already true for the triples in CCSD which misses the dominant second-order component of their coefficient.

For the coefficient c_α determined by Eq. (97) one may easily define

$$V_i = \sum_\alpha H_{i\alpha}\, c_\alpha \tag{98}$$

and define a diagonal or a column dressing Δ by means of Eqs. (18) and (19). Then one may diagonalize the dressed MR-SDCI matrix

$$P_{\mathcal{S}}(H + \Delta)P_{\mathcal{S}}\,|\underline{\Psi}_0\rangle = \underline{\varepsilon}_0\,|\underline{\Psi}_0\rangle \tag{99}$$

repeating the process to self-consistency between Δ and Ψ. This procedure, recently proposed by Adamowicz and one of us [40], represents a mapping of an arbitrary CI into a CC logics for the research of a single state accepting one determinant as generator (i.e., the determinant of largest coefficient). Note that this very general method might in principle be applied as well to excited states dominated by a single determinant. Anyway, it illustrates the fantastic flexibility offered by the dressing technique, and its heuristic strength. One also sees in this proposal the use of a general logics which consists in a back and forth movement between CI and CC. From the CI wave function we guess amplitudes of an exponential wave operator, then we calculate the coefficients of the useful outer space determinants, redefine a dressed CI matrix, and repeat the procedure to self-consistency.

Table 2 summarizes the different methods which result from the choices of $\mathcal{S}_{\mathrm{M}}$, $\mathcal{S}_{\mathrm{E}}$ and the way of calculating c_α when a total dressing is used.

5 Combination of dressings of different accuracies

Since we have formulated a hierarchy of methods, ranging from independent excitation approximation, IEA, (i.e., 2 × 2 CI dressed matrices) to a general CC, in a *unique frame offered by the concept of intermediate hamiltonians*, it is possible to combine these various levels of treatment in a consistent manner. The present section is intended to present some of these possibilities without aiming exhaustion.

5.1 Combinations of (SC)^2 and CC dressing techniques

1. A first combination has been already explored and it consists of two separate steps:

(a) An (SC)^2 calculation, which fixes a set of size-consistent coefficients for the singles and doubles, i.e., a well behaving $\tilde{\Psi}_0$ function, followed by

(b) the calculation of the linked effects of triples and quadruples, as a first-order perturbative correction taken on the $\tilde{\Psi}_0$ function.

Table 2. Hierarchy of total dressing methods. The main model space is equal to ϕ_0. The solution proceeds through dressed CI diagonalization + iteration

Method	Equivalent to	Intermediate model space $\mathscr{S}_\mathrm{I}$	Useful external space $\mathscr{S}_\mathrm{E}$	c_α evaluation	Comments
SDCI [TQ] $_\mathrm{p}$	Shifted B_k	$\phi_i \in \{S, D\}$	$\phi_\alpha \in \{T, Q\}$	$\dfrac{\sum\limits_i c_i H_{\alpha i}}{E_0^0 - E_\alpha^0}$	Epstein–Nesbet H_0
SDCI $[\mathrm{TQ}]_{\mathrm{p+EPV}}$		$\phi_i \in \{S, D\}$	$\phi_\alpha \in \{T, Q\}$	$\dfrac{\sum\limits_i c_i H_{\alpha i}}{E_0^0 - E_\alpha^0 - \mathrm{EPV}_\alpha}$	
DCI $[\mathrm{Q}]_f$	CCD	$\phi_i \in \{D\}$	$\phi_\alpha \in \{Q\}$	$\sum\limits_{\substack{(k,l) \\ D_k^+ D_l^+ \phi_0 = \phi_\alpha}} c_k c_l$	Easier convergence than CCD for near degeneracies
SDCI $[\mathrm{T_{dc}Q}]_f$	≅ CCSD	$\phi_i \in \{S, D\}$	$\phi_\alpha \in \{T, Q\}$	$\sum\limits_{\substack{(k,l) \\ D_k^+ D_l^+ \phi_0 = \phi_\alpha^0 \text{ or} \\ D_k^+ S_l^+ \phi_0 = \phi_\alpha^\mathrm{T}}} c_k c_l$	Differs from CCSD by C_1^3 and C_1^4
SDCI $[\mathrm{TQ}]_\mathrm{f}$	≅ CCSDT-1a if Moller–Plesset denominators	$\phi_i \in \{S, D\}$	$\phi_\alpha \in \{T, Q\}$	$c_\alpha^\Omega = \sum\limits_{\substack{(k,l) \\ D_k^+ D_l^+ \phi_0 = \phi_\alpha^0}} c_k c_l$ $c_\alpha^\mathrm{T} = \sum\limits_{\substack{(k,l) \\ D_k^+ S_l^+ \phi_0 = \phi_\alpha^\mathrm{T}}} c_k c_l + \dfrac{\sum\limits_i (H_{\alpha i} - F_{\alpha i}) C_i}{E_0^0 - E_\alpha^0}$	EPV's can be added in denominators of c_α^T
MRSDCI $[\mathrm{TQ}]_\mathrm{f}$		$\phi_i \in$ MRSDCI	$\phi_\alpha \in \{T, Q\}$/MReferences	$c_\alpha = \langle \phi_\alpha \| \exp(S) \| \phi_0 \rangle$	S is determined by exponentialization of the MRSDCI wavefunction

In other words, we can calculate the expected value of $\tilde{\Psi}_0$ after having incorporated the linked effects of the external space $\mathcal{S}_E$ as a dressing of the Hamiltonian operator, $P(H + \Delta)P$. Hence, we write

$$\langle\tilde{\Psi}_0|P(H+\Delta)P|\tilde{\Psi}_0\rangle = \langle\tilde{\Psi}_0|PHP|\tilde{\Psi}_0\rangle + \langle\tilde{\Psi}_0|P\Delta P|\tilde{\Psi}_0\rangle. \tag{100}$$

Such a calculation can provide a good approach to the exact energy ε_0 and represents a moderate-cost high-quality approach because only a non-iterative second step is required. Other well behaving $\tilde{\Psi}_0$ functions can be easily obtained also at a moderate cost, e.g., CCSD. However, in actual calculations, care must be taken to ensure that the dressing Δ in Eq. (100) includes *only those effects which were not yet taken into account in* $\tilde{\Psi}_0$. Otherwise, a further *partial undressing* process would be required.

An example of this procedure is provided by the method that we call mean value total dressing, MVTD, which was first published as *total dressing*-2′ [74] and labeled *td*-2′ and has been recently used for a detailed study of the correlation contributions along some single bond breakings [69].

2. One may do better than a CCSDT-1a calculation without going to the complexity of a general MR–CI–CC mapping presented above in Sect. 4.3. One may perfectly consider a CI space consisting of ϕ_0, all singles and doubles and selected triples, quadruples, ... for instance, those which belong to an MR- or CAS–SDCI space. Then one may dress the triples, quadruples, etc. in a simple $(SC)^2$ mode according to Eq. (56), and dress the singles and doubles totally by the linked and unlinked effects of the triples and quadruples which do not belong to the CI space. This procedure is better than CCSDT-1a since it considers the interactions between the selected triples, quadruples, etc. It is much less expensive than the MR–CI–CC mapping since it only retains singles and doubles excitation operators in the CC expansion and only applies it to the external triples and quadruples. The computational time should remain close to that of the CCSDT-1a procedure since the $(SC)^2$ dressing is straightforward.

3. One may propose combinations of $(SC)^2$ and CC which *cost less* than the full CCSDT-1a approximation. One suggestion consists in defining two sets of MOs. From a $(SC)^2$ preliminary calculation, or from another low cost approximation (MP2, IEA ...) one may calculate the approximate natural orbitals, diagonalizing an approximate correlated density matrix. Then one may partition the set of MOs by selecting the MOs having the occupation numbers closer to unity (closer to 1/2 for spin-orbitals) and define them as class-1 orbitals. The single and double excitations can then be divided into those which only involve class-1 holes and particles, and the others. Let us call the first ones class-1 excitations. The triples and quadruples may be partitioned accordingly, and one may consider a full dressing of the SDCI matrix by the class-1 triples and quadruples only, the effect of the other triples and quadruples being treated at the $(SC)^2$ level only.

The advantage of this procedure is that it reduces the bottleneck loop in actual calculations to the N_1 orbitals of the class-1 ($(N_1)^7$ step for the triples of class-1). In the canonical CCSDT-1a method one might also freeze the orbitals to class-1 but then the effect of the class-2 double excitations, which is important, would be omitted. The use of a unique dressing frame, calculated at various levels of accuracy, offers rational and consistent combinations of approaches.

5.2 *Combination of $(SC)^2$ and IEA*

For very large molecules and/or basis sets, the SDCI space may be already too large for performing the dressed SDCI diagonalization even with direct techniques. In that case it is worth to combine the low-cost IEA technique with $(SC)^2$ approximations. From a full IEA or an MP2 preliminary calculation one may select a subset of important doubles, e.g., those with a coefficient greater than a given threshold. The doubles of lower coefficient will be treated at the IEA level only. Of course, they will be by far the most numerous. Then one may dress the selected CI matrix according to $(SC)^2$ methods discussed above. The EPV's contributions are calculated exhaustively by considering the double excitations which are impossible to apply to the considered determinant ϕ_i, whatever its level of treatment, IEA or $(SC)^2$. This is easily taken into account through the use of unique arrays of partial summations, as it has been discussed in detail in Refs. [24, 49]. This method has been already tested [52] with convincing results not only for cases where the CI space was composed of selected singles and doubles, but also for cases where it involved selected higher excitations.

5.3 *Combination of CC, $(SC)^2$ and IEA techniques*

In principle one may perfectly combine our three levels of treatment in a consistent manner. For instance one may divide the approximate natural orbitals (or the original MOs) into three groups according to their occupation number (i.e., according to their contribution to the correlation energy). Let us call class-1, -2 and -3 the three classes of increasing values of the quantities $|n_i - 1|$, i.e., by decreasing importance in the correlation phenomenon. We may take a model space built of the singly and doubly excited configurations involving only the MOs of classes 1 and 2. The other double excitations (i.e., those which involve at least one MO of the 3rd class) will be treated at the cheapest level (IEA). Then the dressing of the SDCI matrix will be performed as follows:

- The triples and quadruples which only involve holes and particles of class-1 will bring their linked and unlinked effects to the dressing. They will be treated at the CCSDT-1a level.
- The other triples and quadruples are treated in an $(SC)^2$ model by the straightforward dressing of Eq. (56).

Thus one would obtain a method applying various intensities to different subsets of excitations, rationally selected. A convenient application should balance the computational effort in the three levels.

6 Conclusions

We have shown in this work how a great variety of common methods for the treatment of electron correlation can be understood from the unique point of view of intermediate hamiltonians theory. Hence IHT provides a common reference framework allowing to classify and establish a hierarchy of all single-reference methods ranging from simplest dressing of 2 × 2 CI matrices to the most elaborated CC methods. This does not mean, of course, that IHT is necessary or even the easiest way, in most cases, for formulating these methods, but it just provides a way of thinking that can be fruitful and is very flexible.

The three degrees of freedom in the IHT formulation which have been exploited to generate the panoply of methods collected in Tables 1 and 2 are the following:

1. *choice of the model space* which may range from a minimal dimension of 2 (ϕ_0 plus each ϕ_i independently) to MR-SDCI.
2. *choice of the external space* determinants which are considered in the dressing process. In general one would consider all single and double excitations on the model space determinants but some of them may be neglected without destroying size extensivity.
3. *mode of evaluation of the external space coefficients.* Two aspects have to be considered here, namely, (i) the task demanded to the dressing, simple achievement of size consistency (Sect. 3) or incorporation of the linked effects of the outer space (Sect. 4), and (ii) the way of evaluating these coefficients, in a perturbative manner or as a product of coefficients of the model space determinants (or as combinations of these two techniques).

As by-products of this effort of synthesis, some new levels of approximation have been mentioned here (e.g., an improved or dressed IEPA), but the main practical benefit of this systematization consists (cf. Sect. 5) in the proposition of consistent combinations of methods of various costs and accuracies to treat different parts of the correlation energy. These combinations may imply very simple IEA evaluations of the smallest CI coefficients up to CCSDT-1 evaluations of the most important ones.

Finally, we would like to stress the fact that the dressing techniques reviewed here are single-reference dressings since for their evaluation a determinant plays a special role, but they may be perfectly applied to multireference CI model spaces, as already shown for the (SC)^2 CI approximation. The conception of multireference dressing techniques, in which several determinants will play an equal role in the evaluation of the dressing operator is the subject of a work under progress [51, 52, 75].

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