Eur. Phys. J. D **20**, 61–69 (2002)
DOI: 10.1140/epjd/e2002-00103-6

THE EUROPEAN PHYSICAL JOURNAL D

A multi-reference exponential expansion for the electronic wave function

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Received 2 November 2000 / Received in final form 1st March 2002
Published online 28 June 2002

Abstract. The expansion structure of a CI vector as combination of excitations from a model-space reference determinant is investigated. It is shown that between the linear and the exponential expansions there is a relation which is similar to the single-reference case, if the internal excitations are adsorbed into the reference vector. Moreover, expansions with respect to different determinants are related by a set of linear equations. By using these two properties, a State-Specific Coupled-Cluster formalism is proposed.

PACS. 31.25.-v Electron correlation calculations for atoms and molecules –
31.15.Dv Coupled-cluster theory

1 Introduction

The Coupled Cluster (CC) is now a well established formalism, widely used in Quantum Chemistry [1–3]. In the Single-Reference (SR) version of this technique (SR-CC), the cluster expansion is usually truncated at the level of Single and Double (SD) excitations. The space in which the CC equations are projected is therefore the space of all SD excitations from a single determinant, which is called the reference function [4,5]. In the CC theory, as in Configuration Interaction (CI), if we wish to improve the approximation we have two possibilities. We can add the contribution of triple (or triple+quadruple, etc.) excitations, either in an approximate way [6–8] or within the full CC formalism [9–12]. Alternatively, we may consider a Multi-Reference (MR) reference function, *i.e.* a reference composed by a linear combination of many determinants, as is done in the Multi-Reference Configuration Interaction (MR-CI) approach. The experience of CI shows that the second possibility is by far the most effective in all cases where the wave-function has significant components over more than a single determinant, as in most bond-breaking cases. However, the generalization of the SR-CC approach to Multi-Reference Coupled Cluster (MR-CC) turned out to be far from trivial, and a number of different formalisms have been proposed. They can be divided into three broad classes [13,14]:

1. *valence-universal* or *Fock-space* theories (VU-CC) [14–21], where a family of model spaces is considered, characterised by a number of active electrons variable between 0 and the real value of the studied system. A cluster operator is then defined, that simultaneously transforms each model space into its corresponding exact target space;
2. *state-universal* or *Hilbert-space* theories (SU-CC) [22–28], where a single model space, characterised by the actual number of electrons of the system, is transformed by the cluster operator into the exact target space;
3. *one-state* or *state-selective* approaches (SS-CC) [30–46], where the cluster operator contains only the information about the actual state we want to study.

For review papers on this subject, see references [47–49].

From the point of view of the practical implementation, these approaches are of decreasing complexity, as the number of different exact states of the system that must be considered decreases going from 1 to 3. In particular, a state-selective formalism is very attractive, since we concentrate only on the specific state that is going to be studied and we do not need to consider a number of other, usually irrelevant, states. However, although very attractive from a computational point of view, most of the state-selective approaches presented so far suffer from serious drawbacks: these formalisms are usually incomplete (the Full-CI wave-function is not recovered if a complete expansion for the cluster operator is used) or redundant (the cluster operator contains amplitudes which cannot be uniquely determined within the formalism).

In this article, a Multi-Reference Cluster Expansion for the electronic wave function is proposed. The starting point of the formalism is the expansion of the exact

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wave function $|\Psi\rangle$ from an arbitrary Slater determinant belonging to the model space, $|\Phi_I\rangle$. The vector $|\Psi\rangle$ is expanded as a linear combination of excitation operators acting on $|\Phi_I\rangle$, that move electrons from occupied to virtual spin-orbitals (in $|\Phi_I\rangle$). This expansion is identical to the cluster expansion of SR-CC, hence the whole $|\Psi\rangle$ can be exactly recovered, provided all the possible excitations are considered. Each excitation operator can be expressed as a product of elementary (*i.e.*, one-electron) excitations: internal if going to an active spin-orbital, external otherwise.

As noted by several authors [38–40], the expansion operator from a given $|\Phi_I\rangle$ can be naturally partitioned into two terms: one containing purely internal excitations, and a remaining term with excitations containing at least one external elementary excitation. The internal part of the expansion operator, acting on $|\Phi_I\rangle$, produces the projection $|\bar{\Psi}\rangle$ of $|\Psi\rangle$ onto the model space, apart from a multiplicative constant. Therefore the exact wave function $|\Psi\rangle$ can be expressed in many equivalent ways as a non-internal excitation operator acting on $|\bar{\Psi}\rangle$, each operator being associated to a corresponding determinant $|\Phi_I\rangle$ of the model space. A set of relations connects the non-internal terms associated to different determinants $|\Phi_I\rangle$, and this permits to get rid of the redundancies often associated to State-Selective MR-CC. Finally, we assume that these equations, that are rigorously exact for the complete expansion of $|\Psi\rangle$, still hold if the expansion is truncated to a given level of excitation. In this way, a MR-CC scheme is obtained.

2 General formalism

We consider a system containing m electrons which can be variously distributed among n spin-orbitals. These are divided into:

1. *active spin-orbitals*, $|\phi_i\rangle$, which are the spin-orbitals that can be occupied in the reference function, and are indicated by the labels i, j, k, l, etc.;
2. *external spin-orbitals*, $|\phi_a\rangle$, which are always unoccupied in the reference, and are indicated by the labels a, b, c, d, etc.

The formalism can be easily generalized to the common three-class partition of the orbitals, where a third class of core orbitals, occupied in all the reference determinants, is also considered. For the sake of simplicity, we will consider here only the two-class partition. We will assume throughout that the multi-determinant reference wave-function is described as a combination of determinants generated from a complete active space (CAS). Although the restriction to a CAS reference might be seen as limiting, it leads to a much simpler theory.

We indicate with $\mathcal{L}$ the whole Hilbert space generated by all the Slater determinants having m electrons in n spin-orbitals. Slater determinants having electrons in internal spin-orbitals only are called *internal*, and indicated by $|\Phi_I\rangle$, $|\Phi_J\rangle$, etc., while determinants containing at least one external occupied spin-orbital are called *external*, and indicated by $|\Phi_A\rangle$, $|\Phi_B\rangle$, and so on.

We adopt the usual second-quantization formalism. The creation operators associated to an active (i) and external (a) spin-orbitals are indicated as a_i^+ and a_a^+, respectively, while the corresponding destruction operators as a_i and a_a. Since the number of electron is fixed, creation and destruction operators usually appear in pairs, and it is convenient to define the elementary excitation operators

$$\hat{E}_i^k \equiv a_k^+ a_i \tag{1}$$

and

$$\hat{E}_i^a \equiv a_a^+ a_i \tag{2}$$

that are the usual unitary-group generators. It is useful to have a short-hand notation for products of operators. We use the compact notations $\mathbf{i}_p$ and $\mathbf{a}_q$ to indicate the sets $i_1, ..., i_p$ and $a_1, ..., a_q$ respectively, where the indices are arranged in strictly ascending order: $i_1 < i_2 < ... < i_p$ and $a_1 < a_2 < ... < a_q$. Active spin-orbitals in $|\Phi_I\rangle$ can be either occupied or virtual, while external spin-orbitals are always virtual. An excitation operator, involving p internal and q external one-electron excitations is written as

$$\hat{E}^{\mathbf{k}_p\mathbf{a}_q}_{\mathbf{i}_{p+q}} = \hat{E}^{k_1}_{i_1} ... \hat{E}^{k_p}_{i_p} \hat{E}^{a_1}_{i_{p+1}} ... \hat{E}^{a_q}_{i_{p+q}}. \tag{3}$$

The short-hand notation $\hat{E}_\sigma$ instead of $\hat{E}^{\mathbf{k}_p\mathbf{a}_q}_{\mathbf{i}_{p+q}}$ will also be used.

The excitation $\hat{E}_\sigma$, acting on an internal determinant $|\Phi_I\rangle$, can produce either zero or an external determinant $|\Phi_A\rangle$ (purely internal excitations are not necessary and will not be considered in the present formalism). If the determinant $\hat{E}_\sigma|\Phi_I\rangle$ is not zero, the excitation $\hat{E}_\sigma$ is said *to belong* to $|\Phi_I\rangle$ (in short, $\hat{E}_\sigma \in |\Phi_I\rangle$). In this case, in equation (3) $\mathbf{i}$ runs over occupied spin-orbitals of $|\Phi_I\rangle$, while $\mathbf{k}$ and $\mathbf{a}$ run over virtual spin-orbitals of $|\Phi_I\rangle$ (active and external, respectively). The label (I) since the ranges of $\mathbf{i}$ and $\mathbf{k}$ depend on the reference index I, and the notation $\hat{E}_\sigma(I)$ is used to stress this fact.

An excitation operator $V(I)$, given by a linear combination of excitations $\hat{E}^{\mathbf{k}_p\mathbf{a}_q}_{\mathbf{i}_{p+q}}(I)$, can be decomposed as a sum of operators with given levels p and q of internal and external excitation, respectively:

$$V(I) = \sum_{p,q} V_{p,q}(I), \tag{4}$$

where we have defined

$$V_{p,q}(I) = \sum_{\mathbf{i}_{p+q}\,\mathbf{k}_p\,\mathbf{a}_q} \hat{E}^{\mathbf{k}_p\mathbf{a}_q}_{\mathbf{i}_{p+q}}(I) v^{\mathbf{k}_p\mathbf{a}_q}_{\mathbf{i}_{p+q}}(I) \qquad (p,\, q \text{ fixed}). \tag{5}$$

The two indices p and q in equation (4) run from zero to the total number of electrons, m. It is also useful to decompose $V(I)$ with respect to the level of external excitations only:

$$V(I) = \sum_q V_q(I), \tag{6}$$

with

$$V_q(I) = \sum_p V_{p,q}(I) \qquad (q \text{ fixed}). \tag{7}$$

A determinant $|\Phi\rangle$ belonging to $\mathcal{L}$ can be classified according to the number of external occupied spin-orbitals, and we write $|\Phi\rangle \in \mathcal{L}_q$ if it has exactly q external occupied spin-orbitals. We indicate by $\mathcal{L}_0$ the subspace spanned by the internal configurations, and by $\mathcal{L}^\perp$ its orthogonal complement. The subspace $\mathcal{L}_0$ is the Model Space, and let N be its dimension. We indicate by P_0 the orthogonal projector onto the model space:

$$P_0 = \sum_{I=1}^{N} |\Phi_I\rangle\langle\Phi_I|. \tag{8}$$

The $\mathcal{L}_q$ are mutually-orthogonal spaces, whose direct sum gives $\mathcal{L}$:

$$\mathcal{L} = \bigoplus_{q=0}^{m} \mathcal{L}_q. \tag{9}$$

We define also the subspace $\mathcal{L}_{p,q}(I)$ as the space spanned by all the possible determinants generated by p internal and q external excitations acting on the model-space determinant $|\Phi_I\rangle$. The $\mathcal{L}_{p,q}(I)$ are mutually-orthogonal spaces, whose direct sum over p gives $\mathcal{L}_q$:

$$\mathcal{L}_q = \bigoplus_{p=0}^{m} \mathcal{L}_{p,q}(I). \tag{10}$$

Note that $\mathcal{L}_{p,q} = \emptyset$ if $p + q > m$.

An eigenstate $|\Psi\rangle$ of the electronic Hamiltonian H satisfies the Schrödinger equation

$$H|\Psi\rangle = E|\Psi\rangle, \tag{11}$$

where E is the corresponding energy. A reasonable description of $|\Psi\rangle$ is by hypothesis given by the projection $|\bar{\Psi}\rangle$ of $|\Psi\rangle$ onto the model space,

$$|\bar{\Psi}\rangle = P_0|\Psi\rangle = \sum_I C_I|\Phi_I\rangle \cdot \tag{12}$$

It is convenient to adopt the so-called intermediate normalization, which consists in assuming that it is the projected solution $|\bar{\Psi}\rangle$, rather than the complete solution $|\Psi\rangle$, to be normalized:

$$\langle\bar{\Psi}|\bar{\Psi}\rangle = \sum_I C_I^2 = 1. \tag{13}$$

3 Cluster expansion

In this section the exponential expansion of a generic vector, from a Slater determinant $|\Phi_I\rangle$, will be obtained. The relations existing between the expansions from different determinants will also be discussed. We stress the fact that the relations obtained in the present section are valid for *any* vector belonging to $\mathcal{L}$, regardless its relationship with the Hamiltonian H. In the SR case, a vector $|\Psi\rangle$ can be obtained from a Slater determinant $|\Phi_0\rangle$ using a polynomial expansion,

$$|\Psi\rangle = (1 + R)|\Phi_0\rangle, \tag{14}$$

or an exponential expansion,

$$|\Psi\rangle = \mathrm{e}^T|\Phi_0\rangle \cdot \tag{15}$$

Equation (14) is at the basis of CI methods, while equation (15) is the starting point of CC methods.

To obtain the corresponding expansions in the MR case, let us consider all the possible excitations $\hat{E}_\sigma(I)$ that are not purely internal (*i.e.*, with $q \neq 0$). It is shown in the Appendix that, if $C_I \neq 0$, the vectors $|\hat{E}_\sigma(I)\bar{\Psi}\rangle$ (for a *fixed* value of I) are linearly independent and form a basis of $\mathcal{L}^\perp$. By taking advantage of this fact, we can express $|\Psi\rangle$ in this new basis and we obtain the expansion

$$|\Psi\rangle = (1 + R(I))|\bar{\Psi}\rangle \cdot \tag{16}$$

The excitation operator $R(I)$ has the structure defined by equations (4, 5):

$$R(I) = \sum_{p,q} R_{p,q}(I), \tag{17}$$

with

$$R_{p,q}(I) = \sum_{\mathbf{i}_{p+q}\,\mathbf{k}_p\,\mathbf{a}_q} \hat{E}^{\mathbf{k}_p\mathbf{a}_q}_{\mathbf{i}_{p+q}}(I) r^{\mathbf{k}_p\mathbf{a}_q}_{\mathbf{i}_{p+q}}(I). \tag{18}$$

Since $R(I)$ does not contain purely internal excitations, $R_0 = 0$, *i.e.* $R_{p,0} = 0$ for any p. In a similar way the exponential expansion equation (15) gives

$$|\Psi\rangle = \mathrm{e}^{T(I)}|\bar{\Psi}\rangle \cdot \tag{19}$$

(see, for instance, Refs. [38–40] for a detailed discussion of this point). By comparing the two expansions of $|\Psi\rangle$, equations (16, 19), one obtains

$$1 + R(I) = \mathrm{e}^{T(I)}. \tag{20}$$

By equating the terms corresponding to a fixed level of *external* excitations (internal levels are mixed, because the excitation operators act on the whole $|\bar{\Psi}\rangle$), we obtain

$$R_q(I) = \left[\mathrm{e}^{T(I)}\right]_q, \tag{21}$$

where the notation $[...]_q$ indicates that only terms with exactly q external excitations are kept. This chain of relations gives

$$\begin{aligned} R_1(I) &= T_1(I), \\ R_2(I) &= \frac{1}{2}T_1^2(I) + T_2(I), \quad ... \end{aligned} \tag{22}$$

with the obvious inverse relations

$$T_1(I) = R_1(I),$$
$$T_2(I) = \frac{1}{2}R_1^2(I) - R_2(I), \quad ... \tag{23}$$

These equations show that there is a very simple relation between $R(I)$ and $T(I)$, formally identical to the relation that holds in the single-reference case.

Different operators $R(I)$, relative to different determinants $|\Phi_I\rangle$, are not independent, but their amplitudes must satisfy a set of linear equations. To obtain these relations, we project equation (16) onto the linearly independent vectors $|\hat{E}_\sigma(I)\bar{\Psi}\rangle$:

$$\langle\hat{E}_\sigma\bar{\Psi}|\Psi\rangle = \langle\hat{E}_\sigma\bar{\Psi}|R(I)\bar{\Psi}\rangle \qquad \sigma \in I. \tag{24}$$

Note that, although the vectors $|\hat{E}_\sigma(I)\bar{\Psi}\rangle$ are not orthogonal, the projection onto these vectors is more convenient than the analogous projection onto the $|\hat{E}_\sigma(I)\Phi_I\rangle$. Indeed, the vectors $|\hat{E}_\sigma(I)\Phi_I\rangle$ depend explicitly on I, in the sense that the same excitation $\hat{E}_\sigma$ gives two different results when acting onto different determinants: $\hat{E}_\sigma|\Phi_I\rangle \neq \hat{E}_\sigma|\Phi_J\rangle$ if $I \neq J$. On the other hand, the vectors $|\hat{E}_\sigma(I)\bar{\Psi}\rangle$ do not depend on I, except for the requirement $\sigma \in I$, so can simply write $|\hat{E}_\sigma\bar{\Psi}\rangle$. Using the explicit expression for $R(I)$, equations (17, 18), we obtain

$$\langle\hat{E}_\sigma\bar{\Psi}|\Psi\rangle = \sum_{\tau\in I}\langle\hat{E}_\sigma\bar{\Psi}|\hat{E}_\tau\bar{\Psi}\rangle r^\tau(I) \qquad \sigma \in I, \tag{25}$$

where $r^\tau(I)$ is a short-hand notation to indicate a non-internal coefficient $r^{\mathbf{k}_p\mathbf{a}_q}_{\mathbf{i}_{p+q}}(I)$. This equation is of the form

$$r_\sigma(I) = \sum_{\tau\in I}\mathcal{C}_{\sigma\tau}(I)r^\tau(I) \qquad \sigma \in I, \tag{26}$$

where we have defined

$$r_\sigma(I) \equiv \langle\hat{E}_\sigma\bar{\Psi}|\Psi\rangle \qquad \sigma \in I, \tag{27}$$

and the metric matrix

$$\mathcal{C}_{\sigma\tau}(I) \equiv \langle\hat{E}_\sigma\bar{\Psi}|\hat{E}_\tau\bar{\Psi}\rangle \qquad \sigma,\tau \in I. \tag{28}$$

The coefficients $r_\sigma(I)$ and $r^\sigma(I)$ are the covariant and contravariant components, respectively, of $|\Psi\rangle$ in the $|\hat{E}_\sigma\bar{\Psi}\rangle$ basis. Note the asymmetry between the two sets: the $r^\sigma(I)$ depend explicitly on I, while the $r_\sigma(I)$ do not, $r_\sigma(I) = r_\sigma$. The relation between covariant and contravariant components is

$$\langle\Psi|\Psi\rangle = 1 + \sum_\sigma r^\sigma(I)r_\sigma \tag{29}$$

if the intermediate normalization is used for $|\Psi\rangle$.

Equation (26) can be inverted, since the metric $\mathcal{C}(I)$ is not singular, as shown in the Appendix. The matrix $\mathcal{C}(I)$ is a submatrix of the singular matrix $\mathcal{C}$, whose elements

$$\mathcal{C}_{\sigma\tau} \equiv \langle\hat{E}_\sigma\bar{\Psi}|\hat{E}_\tau\bar{\Psi}\rangle \tag{30}$$

do not depend on I. Therefore the metric $\mathcal{C}(I)$ depend on I only through the range of the indices σ and τ, that must belong to I. By inverting equation (26), we obtain

$$r^\sigma(I) = \sum_{\tau\in I}\mathcal{C}^{\sigma\tau}(I)\, r_\tau, \tag{31}$$

where $\mathcal{C}^{\sigma\tau}(I)$ are the elements of the inverse matrix of $\mathcal{C}(I)$:

$$\mathcal{C}^{\sigma\tau}(I) \equiv (\mathcal{C}^{-1})_{\sigma\tau}(I). \tag{32}$$

The coefficients of the matrix $\mathcal{C}^{-1}$ now depend explicitly on I. Equation (31) gives the desired relations that connect the coefficients $r^\sigma(I)$ to a unique set of amplitudes r_σ, so that the number of variables of the expansion is greatly reduced. The amplitudes r_σ are not completely arbitrary, since they are the components of the vector $|\Psi\rangle$ in the overcomplete basis $|\hat{E}_\sigma\bar{\Psi}\rangle$. The coefficients r_σ are therefore orthogonal to the null space of $\mathcal{C}$. A unique set of coefficients r_s can be obtained by working in the orthogonal complement of the null space.

From a computational aspect, it is noteworthy that the overlap matrix is block-diagonal, since the two functions $\hat{E}_\sigma|\bar{\Psi}\rangle$ and $\hat{E}_\tau|\bar{\Psi}\rangle$ are orthogonal if σ and τ differ in any external orbital [51,52]. This is a crucial point, since portions of the overlap matrix must be inverted in order to compute $\mathcal{C}^{\sigma\tau}(I)$. If the cluster operator is truncated at the level of double excitations, the dimension of largest blocks is given by the number of semi-internal excitations of the kind $a_p^+ a_i^+ a_j a_k|\bar{\Psi}\rangle$ with p fixed. Therefore, the dimension of each block is $N_{\rm act}^3$, well within the possibilities of modern computers for the values of $N_{\rm act}$ of the standard CAS-SCF calculations.

4 Coupled-cluster equations

The expansion obtained in the previous section is valid for any vector $|\Psi\rangle$. Let us suppose $|\Psi\rangle$ to be now an exact eigenvector of the Hamiltonian H. We expand $|\Psi\rangle$ in exponential form, $|\Psi\rangle = \mathrm{e}^{T(I)}|\bar{\Psi}\rangle$, and we impose $|\Psi\rangle$ to satisfy the Schrödinger equation:

$$H\mathrm{e}^{T(I)}|\bar{\Psi}\rangle = E\mathrm{e}^{T(I)}|\bar{\Psi}\rangle. \tag{33}$$

To obtain a MR-CC formalism, we proceed as in the standard SR-CC case, and we multiply on the left both members by $\mathrm{e}^{-T(I)}$:

$$\mathrm{e}^{-T(I)}H\mathrm{e}^{T(I)}|\bar{\Psi}\rangle = E|\bar{\Psi}\rangle. \tag{34}$$

If we take the scalar product with $\langle\hat{E}_\sigma\bar{\Psi}|$, we obtain

$$\langle\hat{E}_\sigma\bar{\Psi}|\mathrm{e}^{-T(I)}H\mathrm{e}^{T(I)}|\bar{\Psi}\rangle = 0 \qquad \sigma \in I \tag{35}$$

since the vectors $|\hat{E}_\sigma\bar{\Psi}\rangle$ are orthogonal to $|\bar{\Psi}\rangle$. If, on the other hand, we project equation (34) onto $\mathcal{L}_0$, we obtain

$$P_0\mathrm{e}^{-T(I)}H\mathrm{e}^{T(I)}|\bar{\Psi}\rangle = E|\bar{\Psi}\rangle. \tag{36}$$

To take the scalar product with the vectors $\langle \hat{E}_\sigma \bar{\Psi}|$ is crucial if the excitations are to be truncated at a given excitation level to obtain an approximate CC formalism, because the vectors $|\hat{E}_\sigma \bar{\Psi}\rangle$ span precisely the tangent space in $|\bar{\Psi}\rangle$ of the manifold described by the vectors $\mathrm{e}^{T(I)}|\bar{\Psi}\rangle$. This insures that there are exactly as many equations as coefficients.

Equations corresponding to different values of I must now be merged together, so that no determinant $|\Phi_I\rangle$ plays a special role, and we can take advantage of the relations (31). To this purpose, we multiply each equation (35), corresponding to a given value of I, by an arbitrary constant λ_I, and add together all the terms projected onto the same vector $\langle \hat{E}_\sigma \bar{\Psi}|$. There are many of such contributions, each one corresponding to a different I, *i.e.* each time we have $\sigma \in I$. Finally we get

$$\langle \hat{E}_\sigma \bar{\Psi}| \sum_{I \ni \sigma} \lambda_I \mathrm{e}^{-T(I)} H \mathrm{e}^{T(I)} |\bar{\Psi}\rangle = 0 \qquad \forall \sigma. \tag{37}$$

Note that the sum goes only on those I that admit σ as an excitation. These are the equations for the external excitations, one for each σ. There is a one-to-one correspondence between the equations and the coefficients r^σ that are needed to build up the excitation operator $T(I)$. In a similar way, if we project equation (36) onto $\mathcal{L}_0$, multiply by λ_I and add together all the contributions, we obtain

$$P_0 \sum_I \lambda_I \mathrm{e}^{-T(I)} H \mathrm{e}^{T(I)} |\bar{\Psi}\rangle = E \sum_I \lambda_I |\bar{\Psi}\rangle. \tag{38}$$

These are N equations, exactly the right number to obtain the energy E and the N coefficients C_I. In fact, since we adopted the intermediate normalization, the C_I are not all independent, but they must satisfy equation (13). Equations (37, 38) are coupled, and they must be solved simultaneously.

In mixing the equations corresponding to different values of I, some care must be put in the choice of the constant λ_I, that are completely arbitrary in the exact case. Because of the intermediate normalization, we can write

$$|\Psi\rangle = \sum_I C_I |\Psi_I\rangle \tag{39}$$

where we have defined

$$|\Psi_I\rangle \equiv C_I |\Psi\rangle. \tag{40}$$

Of course we have

$$|\bar{\Psi}_I\rangle \equiv P_0 |\Psi_I\rangle = C_I |\bar{\Psi}\rangle. \tag{41}$$

The $|\bar{\Psi}_I\rangle$ have a very simple geometrical interpretation: they are the projection onto the space generated by $|\Psi\rangle$ of the model-space determinants $|\Phi_I\rangle$. If we expand $|\Psi_I\rangle$ as

$$|\Psi_I\rangle = \mathrm{e}^{T(I)} |\bar{\Psi}_I\rangle, \tag{42}$$

we obtain

$$|\Psi\rangle = \sum_I C_I |\Psi_I\rangle = \sum_I C_I \mathrm{e}^{T(I)} |\bar{\Psi}_I\rangle = \sum_I C_I^2 \mathrm{e}^{T(I)} |\bar{\Psi}\rangle. \tag{43}$$

This suggests to choose $\lambda_I = C_I^2$. In this way the CC equations become

$$P_0 \sum_I C_I^2 \mathrm{e}^{-T(I)} H \mathrm{e}^{T(I)} |\bar{\Psi}\rangle = E |\bar{\Psi}\rangle \tag{44}$$

and

$$\langle \hat{E}_\sigma \bar{\Psi}| \sum_{I \ni \sigma} C_I^2 \mathrm{e}^{-T(I)} H \mathrm{e}^{T(I)} |\bar{\Psi}\rangle = 0. \tag{45}$$

Although the vectors $\langle \hat{E}_\sigma \bar{\Psi}|$ are in general linearly dependent, the projected equations (45) are not redundant, because of the limitation in the sum over I. For an example, see the following section.

Equations obtained up to this point are exact in the case of a complete expansion of the wave function. Their solution is equivalent to the solution of the Full-CI problem and therefore of no practical use. However, as common practice in the CC theory, they can be truncated at a given excitation level. In doing this, one assumes that the same relations that are true for the exact coefficients still hold for the approximated ones. At this point, some general consideration is appropriate. Firstly, it is important the fact that the one-to-one correspondence between equations (37) and the coefficients r_σ is always preserved, regardless the adopted truncation scheme. This insures that the right number of coefficients can always be determined, without need of further conditions. Moreover, the matrices $\mathcal{C}(I)$ are non-singular. Therefore it is possible to use equation (31) to go from the r_σ to the $r^\sigma(I)$, which are necessary to construct the operators $T(I)$. The formalism is both complete and not redundant.

The present approach is in some aspects similar to the formalism developed by Mukherjee and coworkers [42–44]. In both formalisms, a different cluster operator $T(I)$ is associated to each determinant $|\Phi_I\rangle$ of the model space. In the approach discussed in reference [44], a set of sufficient conditions for a unique determination of the coefficients $t^\sigma(I)$ is postulated, and the size extensivity of the resulting formalism is proved. In the present approach, on the other hand, the coefficients $t^\sigma(I)$ do not play the role of the fundamental variables, since they can be derived from a small number of independent quantities, *via* equations (31, 23). Therefore, while the number of independent amplitudes of the former approach is exactly the same as in SU-MRCC, in the present formalism this number is divided by a factor N (the size of the CAS).

Equation (44), on the other hand, is equivalent to diagonalizing an Effective Hamiltonian constructed with the current guess of internal CI coefficients C_I and external cluster amplitudes $T(I)$.

5 An illustrative example

In order to illustrate the structure of the proposed exponential ansatz, it is instructive to apply this scheme to a very simple case. The behaviour of approximated CC solutions with a three-dimensional Hamiltonian will be examinated. In this case, the CC equations become simple

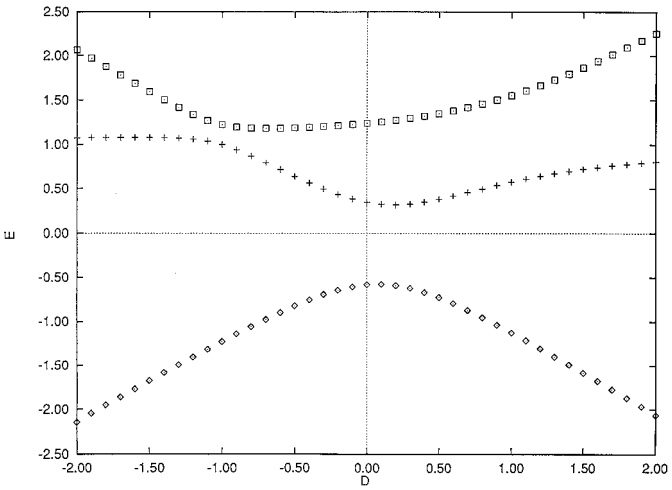

Fig. 1. Exact energies of the model Hamiltonian (Eq. (46)): ground-state energy E_0 ($\diamond$) and excited-state energies E_1 ($+$) and E_2 ($\square$).

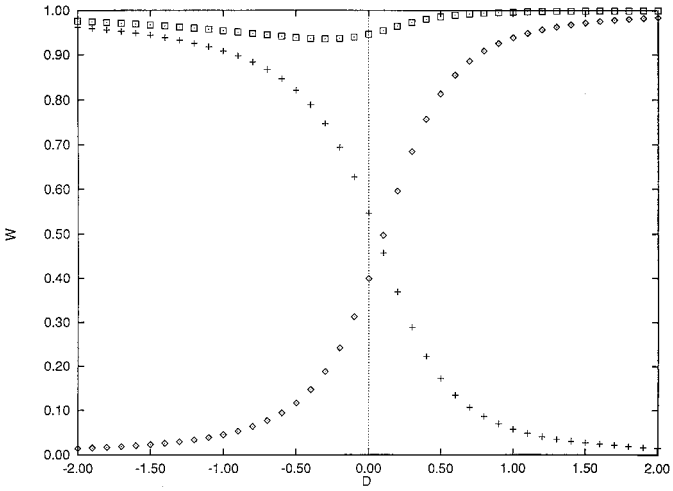

Fig. 2. Weights of the normalized ground-state wave function $|\Psi_0\rangle$ on the vectors $|\Phi_1\rangle$ ($\diamond$), $|\Phi_2\rangle$ ($+$), and on the whole CAS space, $|\Phi_1\rangle \oplus |\Phi_2\rangle$ ($\square$) (see text for the definition of the weight).

algebraic equations, and their solution is straightforward. Let us consider a system composed of one electron and three orbitals: two active (ϕ_i and ϕ_j) and one virtual (ϕ_a). The whole space is spanned by the three vectors

$$|\Phi_1\rangle \equiv a_i^+|0\rangle,$$
$$|\Phi_2\rangle \equiv a_j^+|0\rangle,$$
$$|\Phi_3\rangle \equiv a_a^+|0\rangle.$$

The first two form a basis for the model space, while the third one span the outer space. As Hamiltonian, let us choose the matrix

$$H = \begin{Vmatrix} -D & V & 0 \\ V & D & V \\ 0 & V & 1 \end{Vmatrix}. \tag{46}$$

The parameter D is chosen in the interval $[-2.0, +2.0]$. In the limit of weak coupling, we can predict the existence three avoided crossing between the states described by the basis vectors $|\Phi_1\rangle$, $|\Phi_2\rangle$ and $|\Phi_3\rangle$: in $D = 0$ (involving $|\Phi_1\rangle$ and $|\Phi_2\rangle$), $D = -1$ (involving $|\Phi_1\rangle$ and $|\Phi_3\rangle$), and $D = 1$ (involving $|\Phi_2\rangle$ and $|\Phi_3\rangle$). Two values of V are considered, corresponding to two different strengths of the coupling between model and outer space: weak ($V = 0.5$), and strong coupling ($V = 2.0$). Figure 1 shows the exact energies in the case $V = 0.5$. In Figure 2, for the same value of V, the weight of the normalized ground-state solution on $|\Phi_1\rangle$, $|\Phi_2\rangle$, and on the whole model space are reported. (The weight of a normalized vector $|\Psi\rangle$ onto a space spanned by basis orthogonal determinants $|\Phi_I\rangle$ is defined as $w = \sum_I |\langle\Psi|\Phi_I\rangle|^2$.) The exact solution changes its nature in correspondence of the avoided crossing ($D = 0$), but remains well described by the model space. Figure 3 reports, again for $V = 0.5$, the weight on the model space of the second and third solutions. It appears that there are two avoided crossings between these two solutions: a weakly-avoided one ($D = -1.0$), and a strongly avoided one ($D = 1.0$), as can also be seen from Figure 1.

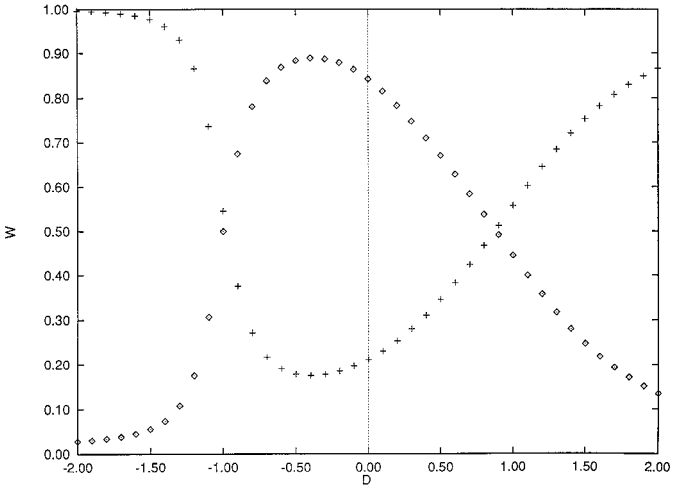

Fig. 3. Weights of the normalized excited-state wave functions $|\Psi_1\rangle$ ($\diamond$) and $|\Psi_2\rangle$ ($+$) on the CAS space.

For $|D| < 1$ the second solution is well described by the model space, while for $|D| > 1$ the situation changes, and it is the third solution that has a large weight on the model space. To describe the ground state we are forced to use a two-dimensional model space. It is clear that the ground state must belong to the target space. If we use a classical Jeziorski-Monkhorst formalism, that requires the same number of vectors in the model and in the target spaces, the choice of a second target state is problematic, since different states would be required for different values of d. As we will see, this problem is absent in the present formalism, since only one state belong to the target space.

With this simple Hamiltonian, the solution of CC equations (37, 38) restricted to single excitations is equivalent to the exact diagonalization of the Hamiltonian. However, an approximate solution can be obtained if the coefficients of the model-space determinants are constrained, and fixed to the values obtained from the diagonalization of H in the model space alone This approximation will

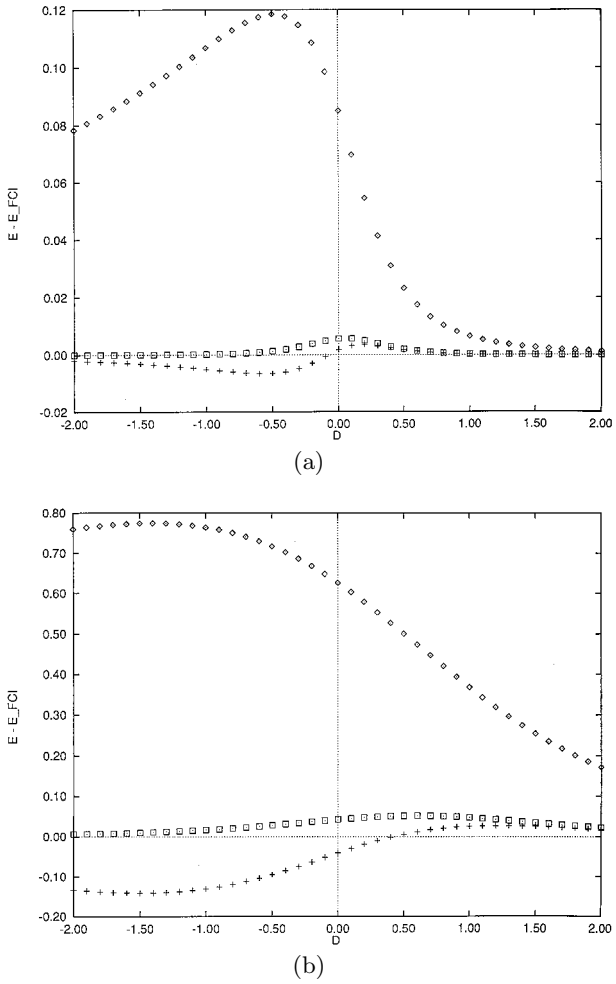

Fig. 4. Difference of the approximate energies from the exact ground-state energy E_0 for $V = 0.5$ (a) and $V = 2.0$ (b): CAS-CI ($\diamond$), LC-CC ($+$), and C-CC ($\Box$).

be indicated as C-CC, and corresponds to an unrelaxed formalism in the language of reference [44]. As a further approximation, the CC equations can be linearized, by neglecting all non-linear terms in equations (37, 38) (LC-CC). In Figures 4a and 4b the difference between the exact solution for the ground-state and the C-CC and LC-CC approximate solutions are reported for $V = 0.5$ and $V = 2.0$.

Also the energy error obtained by the diagonalization in the CAS space alone (CAS-CI) has been reported. The C-CC solution is very close to the exact solution in the whole interval. The LC-CC tends to overestimate the correction, a well-known behaviour of linearized CC methods [50]. It is worth noting that, although the two equations to be solved originate from the projection onto the same vector $|\Phi_3\rangle$, no redundancy occur, and no orthogonalization procedure is required.

6 Conclusions

The structure of a Multi-Reference exponential expansion of a vector $|\Psi\rangle$ from an arbitrary model-space determinant $|\Phi_I\rangle$ has been investigated. It has been shown that the expansion becomes particularly simple if the internal part of the cluster operator $T(I)$ is factorized out, by replacing the reference vector $|\Phi_I\rangle$ with the projection of $|\Psi\rangle$ onto the model space, $|\bar{\Psi}\rangle$. The principal results of the present work are represented by equations (20, 26). The first relates the non-internal part of $T(I)$ to the operator $R(I)$, which describes the linear expansion of $|\Psi\rangle$ onto the non-orthogonal basis set $\hat{E}_\sigma|\bar{\Psi}\rangle$ ($\sigma \in I$); the second the expansion coefficients of $R(I)$ (for any I) to a single set of coefficients r_σ, not depending on I. The r_σ are the scalar products of $|\Psi\rangle$ with the vectors $\hat{E}_\sigma|\bar{\Psi}\rangle$. This formalism describes the structure of the Multi-Reference cluster expansion for a generic vector $|\Psi\rangle$. If $|\Psi\rangle$ is an eigenvalue of the Hamiltonian of the system, it must satisfy the Schrödinger equation. By introducing $|\Psi\rangle$ into this equation, and after linear projection onto the vectors $\langle\hat{E}_\sigma\bar{\Psi}|$, a set of equations for the cluster amplitudes is obtained. These equations can be truncated at a given level of excitation, obtaining a Multi-Reference Coupled-Cluster structure.

A first check of the present formalism can be done at the level of the analysis of the wave function: starting from a Full-CI wave function $|\Psi\rangle$, it is possible to compute the coefficients r_σ, and from them the cluster operators $T(I)$. The results, obtained with a given truncation scheme of the expansion, must be compared with the exact solution. One can have, in this way, an idea of the cluster-ansatz quality. A much more ambitious program is the direct solution of the cluster equations, *i.e.* the implementation of a single-reference MR-CC formalism. However, several aspects of the present formalism should be deepened. In particular, the problem of the expansion weights from different determinants, and the precise structure of the truncated MR-CC equations, deserve further investigations. This will be crucial to estimate the possibility of practical application of the formalism.

Appendix A: Linear independence of the vectors $\mathsf{E}_\sigma|\bar{\Psi}\rangle$

Let $|\Phi_I\rangle$ be one of the determinants of the model space, and $|\bar{\Psi}\rangle$ a vector belonging to the model space. Consider the set of those excitations $\hat{E}_\sigma(I)$ such that $\sigma \in I$, (these are the excitations that, acting on $|\Phi_I\rangle$, give a non-zero result). It will be shown that the vectors $\hat{E}_\sigma(I)|\bar{\Psi}\rangle$ form a linearly independent system if $C \equiv \langle\Phi_I|\bar{\Psi}\rangle \neq 0$. First of all, we note that the vector $\hat{E}_\sigma(I)|\bar{\Psi}\rangle$, with $\sigma \in I$, is different from 0. In fact, $\sigma \in I$ implies $\hat{E}_\sigma|\Phi_I\rangle \neq 0$. Let us consider then a second determinant of the model space, $|\Phi_J\rangle$. The vector $\hat{E}_\sigma(I)|\Phi_J\rangle$ cannot coincide with $\hat{E}_\sigma(I)|\Phi_I\rangle$. Therefore $\langle\hat{E}_\sigma(I)\Phi_I|\hat{E}_\sigma(I)\bar{\Psi}\rangle = C$. Since C is non-null, $\hat{E}_\sigma(I)|\bar{\Psi}\rangle$ cannot be zero.

We have shown that the vectors

$$\text{set I:} \quad \{\hat{E}^{\mathbf{k}_p\mathbf{a}_q}_{\mathbf{i}_{p+q}}(I)|\bar{\Psi}\rangle \quad p=1,...,m\}$$

are non-zero. To prove that they are linearly independent, it is enough to show that they span the whole space $\mathcal{L}_q$. Indeed, in this case, let us consider the second set

$$\text{set II:} \quad \{\hat{E}^{\mathbf{k}_p\mathbf{a}_q}_{\mathbf{i}_{p+q}}(I)|\Phi_I\rangle \quad p=1,...,m\}.$$

Set (II) is also a linear independent vector system that span $\mathcal{L}_q$. Obviously, there is a one-to-one correspondence between the vectors of (I) and those of (II), which means that the two sets contain the same number of vectors. Therefore, since they both span $\mathcal{L}_q$, the linear independence of (II) implies the linear independence of (I).

Proof: We must show that set (I) spans $\mathcal{L}_q$. Let us consider an arbitrary vector $|\Psi_q\rangle \in \mathcal{L}_q$. We expand $|\Psi_q\rangle$ and $|\bar{\Psi}\rangle$ with respect to the determinant $|\Phi_I\rangle$:

$$|\bar{\Psi}\rangle = C(\sum_{p=0}^{m} S_{p,0})|\Phi_I\rangle = C(1+\sum_{p=1}^{m} S_{p,0})|\Phi_I\rangle \qquad (A.1)$$

and

$$|\Psi_q\rangle = C\sum_{p=0}^{m} S_{p,q}|\Phi_I\rangle. \qquad (A.2)$$

We must show that it is possible to obtain $|\Psi_q\rangle$ as a linear combination of the vectors $\hat{E}^{\mathbf{k}_p\mathbf{a}_q}_{\mathbf{i}_{p+q}}|\bar{\Psi}\rangle$, *i.e.* as

$$|\Psi_q\rangle = \sum_{p=0}^{m} R_{p,q}|\bar{\Psi}\rangle. \qquad (A.3)$$

By equating the two different expressions for $|\Psi_q\rangle$, we obtain

$$C\sum_{p=0}^{n} S_{p,q}|\Phi_I\rangle = C\sum_{p'=0}^{n} R_{p',q}\sum_{p''=1}^{n} S_{p'',0}|\Phi_I\rangle. \qquad (A.4)$$

The product $R_{p',q}S_{p'',0}$ has internal level of excitation equal to $p'+p''$. Since equation (A.4) must hold separately for each p, we obtain, after division by C on both sides,

$$S_{p,q}|\Phi_I\rangle = \sum_{j=0}^{p} R_{j,q}S_{p-j,0}|\Phi_I\rangle. \qquad (A.5)$$

This equation gives the chain of relations

$$R_{0,q} = S_{0,q} \qquad (A.6)$$

$$R_{p,q} = S_{p,q} - \sum_{j=1}^{p-1} R_{j,q}S_{p-j,0}, \qquad (A.7)$$

that is an explicit recursive way to build the desired operator R. This completes the proof.

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