

# Size-consistent multireference CI method through the dressing of the norm of determinants.

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## Abstract

A new determinant specific, effective change ('dressing') of the norm of the Multireference Configuration Interaction (MRCI) wavefunction is proposed in order to achieve the size-consistency of the MRCI method. The new approach provides a unifying framework for analysis of size-consistent extensions of the MRCI method that are based on the Coupled Pair Functional (CPF) strategy and lead to simplified computations of the analytical gradients. Using the new framework, a generalized Multireference Full Coupled Pair Functional (MR-FCPF) method is introduced. The MR-FCPF method may be viewed as a functional counterpart of the recently proposed generalized ('full') Coupled Electron Pair Approximation (CEPA), referred to as the Size-consistent Self-consistent CI ((SC)<sup>2</sup>CI) method. A straightforward extension of the MR-FCPF method leads to a pseudo-functional form of the Coupled Cluster (CC) type formalisms. Therefore, the new approach may be used to introduce a simple alternative to existing CC-type gradient techniques. The new procedure is formally derived

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and compared with similar methods from the literature. Model systems calculations ( $\text{H}_2\text{O}$ ,  $\text{LiF}$ ,  $\text{CH}_2^+$ ) are further used to demonstrate the effect of various approximations and to elucidate the hierarchy of functional MR-CEPA schemes.

# 1 Introduction

The non-dynamical (or valence) correlation effects, manifesting in large contributions of a number of configurations to the electronic wavefunctions, have to be first taken into account when dealing with the chemical reactivity, dissociation processes, excited states, some open shell systems etc. The above observation has led to an impressive development of multiconfigurational *ab initio* approaches to the electron correlation problem, most notably the Multi-Reference Configuration Interaction (MRCI) approaches.

The MRCI method had been the most popular tool in molecular spectroscopy during a long time, due to its conceptual simplicity and robustness guaranteed by the variational principle [1]. On the other hand, however, the CI method is slowly convergent in terms of the length of its linear expansion. Truncation of the full CI expansion leads, in turn, to physically incorrect scaling with the number of particles in the system. Throughout this paper we shall adopt the Pople's definition of size-consistency in terms of proper separability [24], leaving the term size-extensivity as denoting the lack of unlinked diagrams in MBPT theories. Truncated CI is neither size-extensive nor size-consistent, which makes it inadequate for description of extended systems.

The alternative Coupled Cluster (CC) approach is in principle superior to CI. The exponential form of the CC wavefunction insures that although the method is not variational, it is highly accurate and extensive when truncated at a given level of excitations [2]. However, the MRCC generalizations are rather complex and numerically expensive [3] [4].

Having this in mind, various simplified schemes of the multireference Coupled Electron Pair Approximation (CEPA) type, which are less expensive computationally and effectively extensive, may be regarded as a pragmatic choice [5]. Reliability of such procedures for the description of conformational changes and excited states has been demonstrated in a number of studies (for a recent review see ref. [6]). When formulated in terms of the configuration space rather than in the many body,

integral based language, they may be seen as size-extensive modifications of the MRCI method.

However, many such developments aim primarily at the computation of the wavefunctions and the corresponding energies. Due to additional complexity, the corresponding energy gradient methods lag somewhat behind, although their significance can hardly be overestimated. Many important molecular properties are related to the derivatives (changes) of the energy with respect to some external perturbation, for example external electric field in case of polarizabilities or the change of the nuclei geometry in case of the geometry optimization. With the growing demand for reliable structural predictions, the latter case is of special importance.

The analytical energy gradients may be expressed and evaluated in a relatively simple form when the wavefunction is obtained as a result of energy functional minimization. In such a case, the derivatives with respect to the wavefunction parameters to be optimized are, by definition, equal to zero. The importance of a functional form was raised in the pioneering work of Pulay [12].

The analytical gradients are routinely available for MRCI [7] [8] and for single reference CC methods [9] [10]. Recently, analytical CC gradient methods became also available for the excited states, within the closely related Equation of Motion (EOM) CC and Symmetry Adapted Cluster (SAC) CI schemes [11]. To the best of our knowledge, there are no other practical examples of analytical gradient procedures for non-functional multireference schemes.

In the CI method, the energy functional is usually optimized only with respect to the configuration coefficients, but not with respect to the LCAO coefficients. Therefore, the Coupled Perturbed Hartree–Fock (CPHF) equations have to be solved, in order to evaluate the changes in molecular orbitals caused by the perturbation (e.g. change in the nuclei position) [8]. Fortunately, the so-called *Z*-matrix technique due to Handy and Schaefer [13] allows one to avoid the repeated solving of CPHF equations and significantly reduces the numerical cost.

The situation is more complicated in the case of non-variational methods that

do not have a functional form, such as CC method, because the number of non-variational parameters dramatically increases. Although using the Z-matrix technique again proves a powerful tool, the functional methods are nevertheless more efficient in this regard [8]. An interesting formal solution, which enables to reformulate various types of the CC method in a functional form, have been proposed by Szalay [14]. Unfortunately, this procedure seems to be quite expensive numerically.

Functional generalization of simplified single reference CEPA methods were considered already by Pulay [15]. They were based on an effective change of the norm of the wavefunction in the CI functional, cancelling to a large extent its unlinked terms. The Coupled Pair Functional (CPF) of Alrichs et. al. [16] and its multireference generalization - the Averaged Coupled Pair Functional (ACPF) of Gdanitz and Alrichs [17] followed the same strategy. The more recent Average Quadratic Coupled Cluster (AQCC) functional of Szalay and Bartlett [18] attempts to remove some drawbacks of its predecessors. In this work we present the hierarchy of approximate MR-CEPA type functionals using the new framework of the CI overlap matrix dressing.

As demonstrated recently, one may reformulate various CEPA type approximations and the CC method itself in terms of a modified ('dressed') CI problem [19]. In this approach, the non-linear terms are taken into account through an iterative dressing of the corresponding CI matrix. The new perspective proved to be very fruitful, giving rise to a number of new promising alternatives to the existing MR-CEPA and MRCC methods. The (SC)<sup>2</sup>CI method, which in the single reference case may be regarded as an exact (or full) CEPA method [20], new state specific and state universal MRCC [21] procedures have been proposed.

The above algorithms are based on an effective change of the CI Hamiltonian matrix. Equivalently, the norm of the determinants i.e. the CI overlap matrix can be modified. If the actual form of the dressing contains the unlinked non-linear terms only, it leads to a size-consistent modification of the CI method. The advantage of the new approach is that, in analogy with CPF-like computational schemes, one may define an approximate, functional form of the method in order to facilitate com-

putation of the analytical gradients and properties. In particular, the present paper introduces functional counterparts of the (SC)<sup>2</sup>CI method and its multireference generalization MR(SC)<sup>2</sup>CI [22], which will be referred to as Multireference Full Coupled Pair Functional (MR-FCPF).

The paper is organized as follows. In the next section the new method is formally introduced. Then its content is discussed and compared to other functional size-consistent methods. The CPF, ACPF and AQCC functionals are shown to be approximations with respect to the new MR-FCPF method. It is also suggested that through a dressing of the norms one can achieve an approximate functional form for the CC method, provided that the linked effects are also included in the dressing procedure. This enables one to formulate a simple alternative to existing CC gradient schemes, applicable to multireference, ground and excited states approaches. In the last section, numerical results for well understood model systems are used to gain further insights into the relationships between different MR-CEPA type functionals.

## 2 Theory

In the following we shall consider a MRCI expansion defined in the configuration space chosen as the union  $S \oplus s$  (with the associated projector  $\hat{P}_{S \oplus s}$ ), where  $S$  stands for a reference space spanned by reference determinants  $I$  and  $s$  for a space of excited determinants *i* e.g. single and double substitutions with respect to reference determinants.

### A) Size-consistent dressing of the CI overlap matrix

We shall first briefly recall the concept of self-consistent state-specific Intermediate Hamiltonian, which has been recently used to introduce the (SC)<sup>2</sup>CI method (and similar dressed CI schemes). The reader is referred to reference [23] for a more detailed presentation.

The Schrödinger equation reads:

$$\hat{H}|\Psi_m\rangle = E_m|\Psi_m\rangle, \quad (1)$$

where  $|\Psi_m\rangle$  and  $E_m$  are the exact eigenstates and eigenvalues. Using decomposition of the full space into orthogonal subspaces, we may write for a given state  $|\Psi_m\rangle$  (ground or excited state) its exact expansion in terms of orthonormalized  $N$ -electron basis  $\{|I\rangle, |i\rangle, |\alpha\rangle\}_{I \in S, i \in s, \alpha \notin S \oplus s}$ :

$$|\Psi_m\rangle = |\Psi_m^{S \oplus s}\rangle + |\Psi_m^\alpha\rangle. \quad (2)$$

The projections onto the MRCI space and outer space are defined as follows:

$$|\Psi_m^{S \oplus s}\rangle = \hat{P}_{S \oplus s}|\Psi_m\rangle = \sum_{I \in S} C_I^m |I\rangle + \sum_{i \in s} c_i^m |i\rangle, \quad (3)$$

$$|\Psi_m^\alpha\rangle = (1 - \hat{P}_{S \oplus s})|\Psi_m\rangle = \sum_{\alpha \notin S \oplus s} c_\alpha^m |\alpha\rangle. \quad (4)$$

Now, identifying the MRCI configuration space with the model space in the sense of effective Hamiltonian theory, we would like to define an *intermediate* effective Hamiltonian  $\hat{P}_{S \oplus s}(\hat{H} + \hat{\Delta}^m)\hat{P}_{S \oplus s}$ , where  $\hat{\Delta}^m$  is a dressing operator, such that

$$\hat{P}_{S \oplus s}(\hat{H} + \hat{\Delta}^m)\hat{P}_{S \oplus s}|\Psi_m\rangle = E_m\hat{P}_{S \oplus s}|\Psi_m\rangle. \quad (5)$$

As usually for effective Hamiltonians, we require the exact energy when acting on the projection of the exact eigenvector onto the model space. However, contrary to the effective Hamiltonians that are required to reproduce all the roots in the model space, the state-specific intermediate Hamiltonians are only required to give one exact root (one-dimensional main model space) [23].

In order to satisfy eq. (5) the outer space summation has to be transformed into a proper matrix element of a dressing operator in the model space. This may be easily verified by writing down explicitly the algebraic form of the exact equation (1) for the  $c_i^m$  amplitude. A diagonal dressing [23]:

$$\Delta_{ij}^m = \left( \sum_{\alpha \notin S \oplus s} H_{i\alpha} c_\alpha^m \right) (c_i^m)^{-1} \delta_{ij} \quad (6)$$

is one of the possible forms of introducing an effective Hamiltonian that satisfies eq. (5) exactly. The concept of such defined dressing scheme opens a way for systematic modifications of the original CI problem [23], as described in the next paragraph.

The MRCI configuration space is  $S \oplus s$ . We do not know the outer space determinants coefficients  $c_\alpha^m$  and we approximate them using cluster theorem, as products of the lower excitations coefficients (see for example eq. (14)), following the CC strategy. This leads to an iterative, self-consistent scheme of solving pseudo-eigenvalue problem. In the first iteration, properly decomposed CI coefficients provide the starting guess of the CC amplitudes, from which one may calculate the non-linear contributions (dressing) to be added to the CI matrix. Next diagonalization (or iteration of a diagonalization algorithm) provides new estimates and the iterations are continued until self-consistency is achieved. As a result one may restore the size-consistency of CI (when dressing by unlinked effects only) or reproduce CC solutions (when the linked terms are also included).

We have been assuming so far that the dressing concerns the Hamiltonian matrix. Introducing a generalized eigenvalue problem one may, however, redefine the problem in terms of a dressing of the overlap matrix. While the idea of a dressing procedure as an actual realization of the intermediate Hamiltonian theory [25] may not apply anymore, the general strategy of taking into account some outer space contributions remains the same. As discussed in the remaining parts of the paper, adding the non-linear terms to the overlap matrix, which is equivalent to an effective change of the norm of the MRCI wavefunctions, opens new possibilities from both: formal and practical point of view.

Let us consider a generalized pseudo-eigenvalue problem:

$$\mathbf{H}\mathbf{c} = E\mathbf{S}_m^{\text{eff}}\mathbf{c}, \quad (7)$$

where  $\mathbf{S}_m^{\text{eff}}$  is an effective state-specific, diagonal overlap matrix:

$$S_{m,ii}^{\text{eff}} = 1 - \left( \sum_{\alpha \notin S \oplus s} H_{i\alpha} c_\alpha^m \right) / (E_m c_i^m). \quad (8)$$



One may easily verify that the above definition reproduces the  $m$ th exact (full CI) solution. Indeed, the explicit equation for the  $c_i^m$  coefficient ( $i$ th row in eq. (7) reads:

$$\sum_{I \in S} H_{iI} C_I^m + \sum_{\substack{j \in s \\ j \neq i}} H_{ij} c_j^m + (H_{ii} - E_m S_{m,ii}^{\text{eff}}) c_i^m = 0. \quad (9)$$

Since the outer space summation is completely taken into account via  $\mathbf{S}_m^{\text{eff}}$ , the above equation is equivalent to that of the exact eigenproblem (1). Certainly, in analogy to the state-specific intermediate Hamiltonians, all the other roots of eq. (7) are formally not correct, though they may still be useful (see discussion in the next section).

Notice, that using the definition of the diagonal dressing  $\Delta_{ii}^m$ , one is led to the following, energy and outer space determinants coefficients dependent form of a determinant specific dressing of the wavefunction norm:

$$S_{m,ii}^{\text{eff}} = 1 - \Delta_{ii}^m / E_m. \quad (10)$$

So far the dressing  $\Delta_{ii}^m$  remains unspecified and may take different forms, for example, single or multireference, CEPA or CC type. The iterative character of a procedure based on the above expression is clear again. However, a ratio of two quantities changing with the iterations in a correlated way appears in eq. (10), as opposed to eq. (6).

It is also worth remarking that one may reformulate the general eigenvalue problem of eq. (7) in the form of an expectation value expression. In order to establish a link with functional methods considered in the subsequent sections of the paper we define a state-specific operator:

$$\hat{G}^m = \sum_{I \in S} g_I^m |I\rangle\langle I| + \sum_{i \in s} g_i^m |i\rangle\langle i|. \quad (11)$$

Acting on the left hand side of the exact eigenequation (1) with  $\langle \Psi_m^{S \oplus s} |$  one gets after trivial manipulation that:

$$E_m = \frac{\langle \Psi_m^{S \oplus s} | \hat{H} | \Psi_m^{S \oplus s} \rangle}{\langle \Psi_m^{S \oplus s} | \Psi_m^{S \oplus s} \rangle - (1/E_m) \langle \Psi_m^{S \oplus s} | \hat{H} | \Psi_m^\alpha \rangle}. \quad (12)$$

The contributions due to a given determinant  $i$  in the denominator of the last equation are  $(c_i^m)^2$  and  $-c_i^m \sum_\alpha c_\alpha^m H_{i\alpha} / E_m$ . Defining the  $g_i^m$  quantities of  $\hat{G}^m$  as  $g_i^m = S_{m,ii}^{\text{eff}}$  and grouping together contributions due to a given determinant one may write:

$$E_m = \frac{\langle \Psi_m^{S\oplus s} | \hat{H} | \Psi_m^{S\oplus s} \rangle}{\langle \Psi_m^{S\oplus s} | \hat{G}^m | \Psi_m^{S\oplus s} \rangle}. \quad (13)$$

If the references are not dressed, then the  $g_I^m$  coefficients will be equal to one. Otherwise, one may define them in a similar way as  $g_I^m = S_{m,II}^{\text{eff}}$ . The above reformulation allows one to introduce for a specific form of the dressing its functional counterpart that offers an important advantage, namely the simplicity of analytical gradient calculations. In that regard, the present approach is an extension of the closely related CPF strategy.

Finally, we would like to reiterate that even though the scheme considered here is not restricted to the ground state only, it remains a one-state formalism i.e. for each state the whole procedure has to be in principle applied separately. Unfortunately generalizations to many states formalisms are not straightforward. However, an approximate reformulation of multistate dressings of the Hamiltonian matrix [21] in terms of the overlap matrix dressing may be achieved, for example, by averaging the energy over all the states considered in the dressing (in analogy to MCSCF procedure for an average of the reference states).

## B) The (SC)<sup>2</sup>CI and MR(SC)<sup>2</sup>CI methods revisited

The new MR-FCPF method may be seen as a functional reformulation of the self-consistent size-consistent dressing of the MRCI matrix employed in the (SC)<sup>2</sup>CI method [20]. Therefore, the latter method is briefly described below. Strictly speaking, the (SC)<sup>2</sup>CI is a single reference method, as one of the reference determinants plays a distinguished role. Nevertheless, it may in fact work in an arbitrary multireference space (e.g. numerically selected), leading to a ground state dressing of the MRCI matrix. Here, for simplicity, we shall explicitly consider (SC)<sup>2</sup>CI method in the MRCISD space.

Let the reference space  $S$  consists of the HF determinant  $|0\rangle$  and some other relevant determinants that are used to generate the  $s$  space of all the single and double excitations from references. The relevant outer space determinants  $|\alpha\rangle$  are triplets and quadruples with respect to the references. The outer space determinants are subsequently redefined in terms of excitations from the HF determinant only and are decomposed as products of lower ( $s$ -space) excitations with respect to  $|0\rangle$ . The state-specific dressing concerns the ground state only and in the following the state index  $m$  will be omitted.

The intermediate normalization is employed and the outer space determinants coefficients are approximated by the products of the coefficients of determinants belonging to  $s$ . Thus, for  $|\alpha\rangle = \hat{e}_j \hat{e}_i |0\rangle$  where  $\hat{e}_j$  and  $\hat{e}_i$  are defined by  $|j\rangle = \hat{e}_j |0\rangle$  and  $|i\rangle = \hat{e}_i |0\rangle$  respectively, for some determinants  $i, j \in s$ , we postulate that:

$$c_\alpha = c_i c_j. \quad (14)$$

Inserting (14) into (6) and using the fact that the determinant basis is used (implying that  $H_{i\alpha} = H_{0j}$ ), one gets the following form of the diagonal dressing:

$$\Delta_{ii} = E_{corr} + EPV_i + R_i. \quad (15)$$

In the above equation,  $E_{corr} = \sum_j H_{0j} c_j$  is the correlation energy and  $EPV_i$  denotes sum over contributions from the conjoint or Exclusion Principle Violating (EPV) terms:

$$EPV_i = - \sum_{j; \hat{e}_j \hat{e}_i = 0} H_{0j} c_j. \quad (16)$$

The term  $R_i$  takes care of possible redundancy effects. For example, a quadruple with respect to one reference may nevertheless belong to the  $s$  space as a double from another reference and should not be approximated in terms of the decompositions into  $s$  space determinants. Therefore,

$$R_i = - \sum_{j; \hat{e}_j \hat{e}_i |0\rangle \in S \oplus s} H_{0j} c_j. \quad (17)$$

The dressing takes into account *all* EPV effects and therefore the (SC)<sup>2</sup>CI method may be regarded as an exact (full) CEPA method, when restricted to doubles only.

Of course,  $\hat{\Delta}$  is dependent on the coefficients and the method is iterative. From the practical point of view it is sufficient to calculate efficiently the EPV contributions. Since this can be done easily, using a trick proposed for the infinite summation of EPV diagrams [26], the method is simple modification of the original CI problem.

Numerical results support the claim that the (SC)<sup>2</sup>CI method ensures sufficient quality of the ground state PES [20]. Perhaps surprisingly, the (SC)<sup>2</sup>CI was also successfully applied to the description of many excited states, even though the ground state dressing is used [27] (see discussion in the next section). There are however many cases, such as strong quasi-degeneracy and certain excited states, that require a truly multireference description. The Multireference Self-consistent Size-consistent Configuration Interaction method [22] is a generalization of the (SC)<sup>2</sup>CI method, and it aims at such difficult cases. In MR(SC)<sup>2</sup>CI all the reference determinants contribute to the dressing in a way that reflects their total contribution to the correlation energy. The diagonal, state-specific dressing of the MR(SC)<sup>2</sup>CI method, as introduced in ref. [22], reads:

$$\Delta_{ii}^m = \sum_I (h_I^m + EPV(i, I)^m + R(i, I)^m) \rho_{iI}^m. \quad (18)$$

The  $h_I^m$  denote here the effective energy shifts of the references:

$$h_I^m = \left( \sum_{i \in s} c_i^m H_{Ii} \right) C_I^{m-1}, \quad (19)$$

whereas the terms  $EPV(i, I)^m$  and  $R(i, I)^m$  take care of all exclusion and redundancy effects, with respect to a reference  $|I\rangle$  [22]. The weighting factor (parentage ratio) is given by  $\rho_{iI}^m = H_{iI} C_I^m / \sum_J H_{iJ} C_J^m$ .

As pointed out before, MR(SC)<sup>2</sup>CI and (SC)<sup>2</sup>CI methods are non-functional. In the next subsection we propose a simple solution to this problem.

### C) Multireference Full Coupled Pair Functional

The CI wavefunctions are obtained as solutions of the secular equation, which arises when making the CI energy functional  $F_{ci}[\Phi] = \langle \Phi | \hat{H} | \Phi \rangle / \langle \Phi | \Phi \rangle$  stationary with respect to the variations of the CI expansion coefficients  $c_k$ ,  $|\Phi\rangle = \sum_k c_k |\Phi_k\rangle$ . Suppose

that the functions  $|\Phi_k\rangle$  are normalized and orthogonal  $\langle\Phi_k|\Phi_l\rangle = \delta_{kl}$  and consider a modified functional:

$$F_G[\Phi] = \langle\Phi|\hat{H}|\Phi\rangle/\langle\Phi|\hat{G}|\Phi\rangle, \quad (20)$$

where  $\hat{G} = \sum_k g_k |\Phi_k\rangle\langle\Phi_k|$  and  $g_k$  are some real numbers,  $g_k \in (0, 1]$ . Following the standard variational procedure one gets from such defined functional a generalized eigenvalue problem (7), with a diagonal overlap matrix  $\mathbf{S}^{\text{eff}} \equiv \mathbf{G}$ . The quantity  $E$ , which is the minimal value of  $F_G$ , is no longer bound from below by the real energy (except for the case when all the diagonal elements of the overlap matrix  $g_k$  are equal to one as in the original CI functional). One may, however, verify that  $E$  is bound from below by a number  $M = E^{ci}/\min_k\{g_k\}$ , where  $E^{ci}$  is in turn bounded from below by the real energy.

Any truncated CI functional is an approximation with respect to the full CI functional,  $F_{\text{fci}}[\Psi] = \langle\Psi|\hat{H}|\Psi\rangle/\langle\Psi|\Psi\rangle$ , leading to solutions that are not size-consistent. One may ask, however, whether it is possible to define the quantities  $g_k$  such that the modified (truncated) functional  $F_G$ , although not having the variational upper bound property, would preserve size-consistency and provide better approximations to the FCI solutions. Recalling now our previous considerations regarding the dressing of the CI overlap matrix we may easily find the desired form of  $\hat{G}$ .

As previously, we only consider one-state formalisms, assuming that  $|\Phi_m\rangle$  is the  $m$ th MRCI eigenstate in the space  $S \oplus s$ . Putting now together (7) and (13) on one hand and (20) on another, one finds that the  $m$ th exact (full CI) eigenvalue is reproduced by the truncated functional  $F_G$ , if the  $g_k$  quantities are identified with the corresponding state-specific dressing of the overlap matrix,  $S_{m,kk}^{\text{eff}} = 1 - \Delta_{kk}^m/E_m$ . For a specific form of the dressing,  $\Delta_{kk}^m$ , there is a corresponding functional scheme. Before we introduce the Multireference Full Coupled Pair Functional (MR-FCPF), which employs the MRCEPA type dressing, we shall modify slightly our definitions and notation in order to keep consistency with other works devoted to similar functionals.

From now on, the reference space  $S$  will be further divided into two orthogonal

subspaces, taking a zeroth order approximation to the  $m$ th state  $|\Phi_m^0\rangle = \sum_{I \in S} \tilde{C}_I^m |I\rangle$  as spanning one subspace and the remaining linear combinations of reference determinants spanning its orthogonal complement  $S_{Q_0}$ . Assuming the intermediate normalization,  $\langle \Phi_m^0 | \Phi_m \rangle = 1$ , we may write:

$$|\Phi_m\rangle = |\Phi_m^0\rangle + |\Phi_m^c\rangle = |\Phi_m^0\rangle + |\Phi_m^a\rangle + |\Phi_m^e\rangle, \quad (21)$$

where  $|\Phi_m^a\rangle$  includes  $S_{Q_0}$ -space functions and  $|\Phi_m^e\rangle$  denotes now  $s$ -space functions, respectively and  $|\Phi_m^c\rangle = |\Phi_m^a\rangle + |\Phi_m^e\rangle$ . The general expression for the expectation value of the energy in the state  $|\Phi_m\rangle$  may be rewritten in the form of the correlation energy expectation value:

$$E_{corr}^m = \frac{\langle \Phi_m^0 + \Phi_m^c | \hat{H} - E_m^0 | \Phi_m^0 + \Phi_m^c \rangle}{1 + \langle \Phi_m^a | \Phi_m^a \rangle + \langle \Phi_m^e | \Phi_m^e \rangle}, \quad (22)$$

with the zero of the energy taken as  $E_m^0 = \langle \Phi_m^0 | \hat{H} | \Phi_m^0 \rangle$  and obtained by the diagonalization in the reference space  $S$ .

The new MR-FCPF functional may be defined now. It reads:

$$F_{\text{fcpf}}^m[\Phi^c] = \frac{\langle \Phi_m^0 + \Phi^c | \hat{H} - E_m^0 | \Phi_m^0 + \Phi^c \rangle}{1 + \langle \Phi^a | \hat{G}_a^m | \Phi^a \rangle + \langle \Phi^e | \hat{G}_e^m | \Phi^e \rangle}. \quad (23)$$

The state-specific dressing of the norm of determinants is defined as follows (with  $k$  index standing for  $n$  or  $i$ ):

$$\hat{G}_a^m = \sum_{n \neq m} g_n^m |\Phi_n^0\rangle \langle \Phi_n^0| \quad ; \quad \hat{G}_e^m = \sum_i g_i^m |i\rangle \langle i| \quad (24)$$

$$g_k^m = 1 - \Delta_{kk}^m / E_{corr}^m. \quad (25)$$

The actual form of the dressing  $\Delta_{kk}^m$  in (25) will be the MR-CEPA type dressing, either of the (SC)<sup>2</sup>CI or of the MR(SC)<sup>2</sup>CI method, as defined in the eq. (15) or eq. (18), respectively. In order to distinguish between these two versions we shall denote the one corresponding to the (SC)<sup>2</sup>CI method by MR-FCPF(g), with g standing for the ground state dressing.

It is important to realize that the quantities  $g_k$ 's are coefficient and energy (and thus also nuclear coordinates) dependent,  $g_k \equiv g_k(\mathbf{C}(\mathbf{R}), E(\mathbf{R}))$ . Reflecting a pseudo-

eigenvalue problem arising within the self-consistent intermediate Hamiltonian dressing scheme, the expression in the definition (23) of the MR-FCPF remains a *pseudo-functional*. In order to obtain a purely functional form that may be used for efficient gradient computations one has to get rid of these dependencies. We propose here a simple solution to that problem, namely fixing  $g_k$ 's as numbers at a conveniently chosen geometry,  $\mathbf{R}_0$ . Either converged (“dressed”) or partial solutions,  $\mathbf{C}(\mathbf{R}_0)$ , taken from a given dressing iteration or even from the pure CI eigenstate may be used to evaluate  $g_k$ 's. As discussed in the next section, such an approximation works well since the coefficients  $g_k$  are slowly changing ratios of two quantities.

The formal properties of  $F_{\text{fcf}}^m[\Phi^c]$  are the same as that of the general  $F_G$  functional. It is an approximation to the FCI functional without the variational upper bound property, although it is bound from below by a finite number. Variations with respect to the expansion coefficients in  $\Phi^c$  (subject to normalization constraints) give rise to a generalized eigenvalue problem, with the diagonal elements of the overlap matrix equal to the corresponding coefficients  $g_k$ , when they are fixed as numbers. As we demonstrate in the next section, other MR-CEPA type functionals, such as ACPF and AQCC are approximations with respect to MR-FCPF.

## D) Discussion and comparison with other methods

The CPF, ACPF and AQCC functionals are based on the observation that the effect of higher excitations (necessary to restore size-extensivity) manifests in a partial cancellation of the CI functional norm denominator or in other words that the outer space effect may be effectively taken into account by a proper change of the normalization [15] [16]. Clearly, the new MR-FCPF is closely related to CPF-like functional methods.

Let us first consider the MR-FCPF(g) variant, which employs the ground state dressing of the (SC)<sup>2</sup>CI method,  $\Delta_{ii} = E_{\text{corr}} + EPV_i + R_i$ . Now, the zeroth order approximation to the exact ground state is just the HF determinant  $|0\rangle$  and zero of the energy is taken as  $E_0 = \langle 0|H|0\rangle$ . The MR-FCPF(g) dressing of the norm of

determinants is given by:

$$g_i = S_{ii}^{\text{eff}} = -(EPV_i + R_i)/E_{\text{corr}}. \quad (26)$$

In the CPF method, on the other hand, one defines pair functions (in the usual CEPA sense) and then norm of each pair function is multiplied by a factor  $g_\mu$  chosen to satisfy certain limit conditions [16]. The ACPF employs an averaged, common factor  $g = 2/N$ , derived from a requirement of a correct description of a supersystem of  $n_p$  identical, non-interacting pair systems:

$$g_\mu = g = \frac{1}{n_p} = \frac{2}{N}, \quad (27)$$

where  $N$  is the number of electrons and  $2n_p = N$ . The single reference ACPF energy functional reads

$$F_{\text{acpf}}[\Psi_c] = \frac{\langle 0 + \Psi_c | \hat{H} - E_0 | 0 + \Psi_c \rangle}{1 + g \langle \Psi_c | \Psi_c \rangle}. \quad (28)$$

In the single reference case the difference between CPF and ACPF comes simply from the less refined statistical limit employed by the latter method. For heterogeneous electronic systems the  $g_i$  factors may significantly vary within a given pair since they may involve excitations to orbitals of very different nature. As demonstrated by the explicit computation of  $g_i$  quantities for some model systems they are indeed quite different. In light of this observation, the ACPF approximation appears to be weakly grounded.

However, the notion of the electron pair is no longer employed in ACPF and the method may be defined for the MRCISD functional with respect to a multireference zeroth order energy, for both - ground and excited states [17]. Such a generalization is rather heuristic, as discussed later. Nevertheless, the reported so far numerical results of the MR-ACPF method are very encouraging [6] and it is desirable to understand this fact better. The MR-AQCC method [18], which may be viewed as a functional generalization of the Meissner's size-extensivity correction for single reference CI [29], represents an improvement over MR-ACPF as it partially takes into account the EPV terms due to the particle indices. Recently, a further improvement of MR-AQCC has been proposed, which partially includes also redundancy effects [18].



The MR-FCPF(g) method is different from the original CPF by determinant-specific change of the norm. One also avoids restrictions to pair and single reference closed shell theories as in MR-ACPF. However, contrary to MR-ACPF or MR-AQCC, both the EPV and redundancy contributions are taken into account exactly, without any averaging.

In the limit of non-interacting pairs the determinant specific  $g_i$  factors of the FCPF(g) functional reduce to the common ACPF factor. Consider the (SC)<sup>2</sup>CID dressing for a system of  $n_p$  identical non-interacting, closed shell electron pairs (e.g. separated  $H_2$  molecules). In the single reference case,  $\Delta_{ii} = E_{corr} + EPV_i$ , since the redundancies are only relevant when one dresses the MRCI. Let the determinant  $|i\rangle \equiv |{}^{ab}_{mn}\rangle$  belong to a pair  $\mu \equiv mn$ . Certainly, all excitations  $\hat{e}_j, |j\rangle \equiv |{}^{cd}_{mn}\rangle \in \mu$ , are not possible on  $i$ , whereas charge transfer excitations involving indices of different pairs have vanishing matrix elements. Thus, we get that  $EPV_i = -\epsilon_\mu$ . The supersystem correlation energy is equal to the sum of localized pair energies and therefore:

$$g_i = \frac{-EPV_i}{E_{corr}} = \frac{\epsilon_\mu}{\sum_{\nu=1}^{n_p} \epsilon_\nu} = \frac{2}{N}. \quad (29)$$

Note, that putting all EPV's as zero one gets the functional form of CEPA(0) found already by Čížek [16] [2].

Regarding the practical implementation let us notice that the determinant dependent  $g_i$  factors may be evaluated at some geometry of interest or averaged over a range of nuclear frames. Furthermore, they may be obtained from pure CI coefficients i.e. effectively from the first iteration of dressing or after subsequent iterations. One has to diagonalize the CI matrix first (dressed or not) or provide another (e.g. perturbative) starting guess and then use such evaluated  $g_i$  in the MR-FCPF step. In this way one obtains a functional (and not only pseudo-functional) form of dressing, differing from the CPF one by the fact that all diagonal elements of the overlap matrix are different. It means that the density matrix and gradients may be evaluated analogously, as described in ref. [16], with the numerical cost essentially the same as that of CI gradient computation. The  $g_i$  coefficients should not strongly depend on the dressing steps since they are relative quantities. Fixing them from the pure

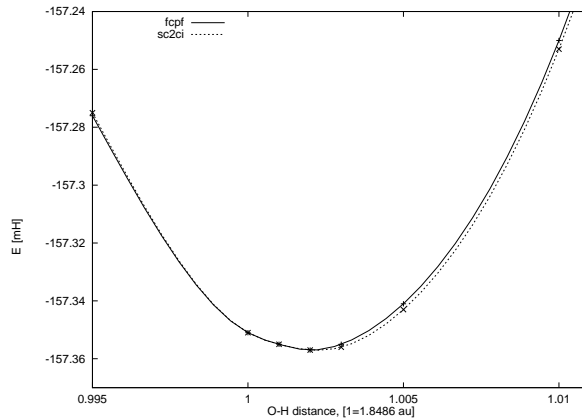


Figure 1: Symmetrical bond stretching in water. MR-FCPF( $g$ ) curve compared to that of its parent (SC)<sup>2</sup>CI method. DZ basis set and equilibrium geometry ( $R_{O-H} = 1$ ) from Saxe *et al* [33]. The CIPSI procedure used to select numerically the reference space of 21 determinants. Zero of the energy is set to 76.0 H.

CI coefficients (by simple evaluation of EPV contributions) brings about only small error as shown by preliminary numerical applications presented in the next section. Let us also note that the results of the MR-FCPF and its non-functional counterpart, (SC)<sup>2</sup>CI, will be only identical at a specific nuclear frame that was used to compute the  $g_i$  coefficients.

As already pointed out in the Introduction, even keeping the coefficient dependent factors  $g_i$ , one may define a functional, which furnishes the starting equations (of the CEPA or CC type) when making it stationary with respect to variations of the coefficients. Nevertheless, such a functional depends on additional parameters (Lagrangian multipliers) [14] and therefore the calculations of derivatives becomes expensive [6]. The simple alternative, which is presented here, provides an excellent approximation to the true functionals in the local neighborhood of the geometry to be optimized (see next section) and may be viewed as pragmatic solution applicable to various MRCC type formalism. Starting from the definition of eq. (6) one may add the linked CC type corrections as well, obtaining the CC type of dressing [19] [21] and then the corresponding functional approximation.

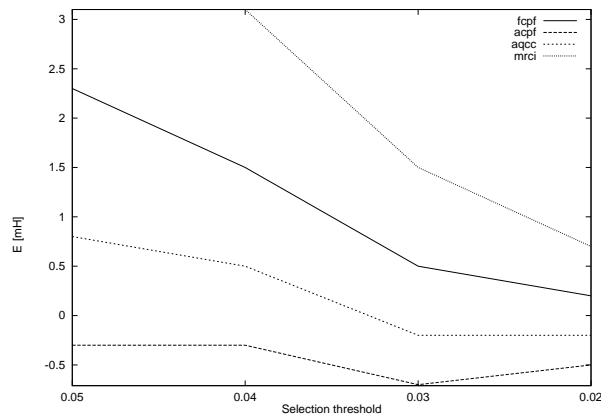


Figure 2: Convergence of MR-CEPA type functionals for water at equilibrium geometry. The MR-FCPF(g)/(SC)<sup>2</sup>CI results with the increasing size of the reference space are compared to that of other multireference functional methods. DZ basis set and equilibrium geometry from Saxe *et al* [33]. The CIPSI procedure used to select numerically the reference spaces which consist of 5, 8, 21 and 46 reference determinants with the selection threshold  $\eta = 0.05, 0.04, 0.03$  and  $0.02$ , respectively.

Let us finally comment that MR-FCPF(g), following its non-functional counterpart, is essentially a single reference formalism working in the multireference CI space. Thus, we assume that the outer space determinants coefficients are defined with respect to a single determinant,  $|0\rangle$ , and the remaining references play only the role of generators of the CI space, assuring that the non-dynamical correlation effects are taken into account. In MR-FCPF(g), similarly to MR-ACPF or MR-AQCC methods, one may obtain solutions for excited states as well. However, the dressing or the change of the norm remains the ground state only. It cancels to a great extent the ground state unlinked effects, but the quality of the description of the excited states is, in principle, difficult to estimate.

Thus, the MR-FCPF method should be advocated for the description of the excited states. On the other hand, in many situations it is sufficient to calculate first the ground state correlation effects and then to take into account modifications due to excited states. In other words, one may assume the transferability of the correlation

effects between the ground and excited states. In fact, many methods for excited states, such as SAC-CI [30], EOM CC [31] and the Green function method [32], are such single reference formalisms working in the multireference spaces.

### 3 Numerical examples

As shown in the previous sections, the state-specific dressing of the Hamiltonian matrix may be transformed into a corresponding overlap matrix dressing and consequently into a functional procedure. However, the reverse is also true i.e. one may obtain the results of a given functional in terms of a proper Hamiltonian matrix dressing. This fact was used to obtain preliminary results of the MR-FCPF method, as well as calculated for comparison results of MR-AQCC and MR-ACPF. The latter method for instance leads to the following simple diagonal dressing of the MRCI Hamiltonian matrix:

$$\Delta_{ii,\text{acpf}}^m = (1 - g^{\text{acpf}}) E_{\text{corr}}^m = \frac{N-2}{N} E_{\text{corr}}^m, \quad (30)$$

where the correlation energy is defined with respect to zeroth order energy obtained by the diagonalization in the reference space.

**H<sub>2</sub>O** Symmetrical bonds stretching in water molecule using the DZ basis set is a well known benchmark [33] that has been used to test and calibrate many methods. We first examine the MR-FCPF(g) variant of the method and compare it in detailed manner with MR-AQCC and MR-ACPF. The CIPSI procedure [34] was used to generate the MRCI spaces: in the first step threshold  $\eta$  is set to choose references and in the second step all singles and doubles are produced with zero threshold.

The potential curves of (SC)<sup>2</sup>CI and MR-FCPF(g) methods, corresponding to the symmetrical stretching of the O-H bonds, are presented in Fig. 1. The numerical selection of reference functions leads to a reference space of 21 determinants (threshold

Table 1: Symmetrical bond stretching in water. DZ basis set and the geometry from Saxe *et al* [33] are employed. Energy errors in millihartrees, with respect to the full CI energy given in the first row. CAS reference space as specified in ref. [35]. *SCF*, *FCI* - ref. [33], *CASSCF*, *MRCI*, *MRCI<sub>Q</sub>* - ref. [35] and this work; *MRACPF*, *MRAQCC* - ref. [6]; *MR(SC)<sup>2</sup>CI* - ref. [28] and this work.

<i>Method</i>	$R_e$	$1.5R_e$	$2R_e$
<i>FCI</i>	-76.15787	-76.01452	-75.90525
<i>SCF</i>	148.0	211.0	310.1
<i>CASSCF</i>	95.0	90.2	78.0
<i>MRCI</i>	2.1	2.3	2.0
<i>MRACPF</i>	0.0	0.2	0.5
<i>MRAQCC</i>	0.6	0.8	0.9
<i>MR(SC)<sup>2</sup>CI<sub>0</sub></i>	-0.6	-0.3	-0.2
<i>MR(SC)<sup>2</sup>CI</i>	1.7	1.9	1.5
<i>MRFCPF</i>	1.7	2.0	2.0

$\eta = 0.03$ ). Once selected, determinants were kept as references while changing the geometry. The  $g_i$  coefficients of the MR-FCPF(g) are fixed here at the equilibrium geometry of the ref. [33] (O-H distance equal to 1 in the figure), from the converged (SC)<sup>2</sup>CI dressing. Thus, both methods give identical results at this geometry and there are growing discrepancies when going to elongated or squeezed geometries.

These discrepancies, however, are very small in the region near the equilibrium geometry or, in other words, in the neighborhood of the geometry at which the effective change of the norm was fixed. When using the  $g_i$ 's fixed from the pure CI coefficients (and not from the converged dressing) a hardly distinguishable curve is obtained (results not shown). For example, at  $R_{\text{O-H}} = 1.05R_{eq}$  (point not shown in the figure) the MR-FCPF(g) energy is shifted with respect to the (SC)<sup>2</sup>CI energy (which is in turn 1.1 mH below the MRCI result) by only 15  $\mu\text{H}$ , if the  $g_i$ 's are fixed

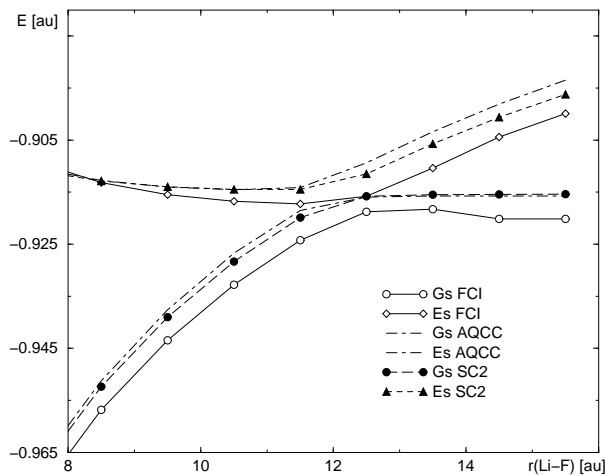


Figure 3: Weakly avoided crossing in LiF. The (SC)<sup>2</sup>CI (denoted by SC2) and AQCC potential energy curves of LiF are compared to FCI results. Ground (Gs) and excited (Es) states curves are presented. The basis set and reference spaces as described in Bauschlicher *et al* [37] and in the text. Note that location of the avoided crossing is not correct in AQCC case.

from the converged equilibrium geometry dressing, or by 24  $\mu$ H if the  $g_i$ 's are fixed from the equilibrium geometry CI coefficients.

Thus, one may conclude that the equilibrium geometry properties obtained using MR-FCPF(g) method should remain essentially the same as those of the (SC)<sup>2</sup>CI, even for a simple estimate of  $g_i$ 's in terms of the CI expansion coefficients. As we are interested in the relative errors, we may compare for example simple harmonic vibrational frequencies resulting from the curves presented in Fig. 1. They are different by 0.2  $\text{cm}^{-1}$ , with the absolute values of about 3472  $\text{cm}^{-1}$  (the experimental frequency of the symmetric stretching mode is equal to 3832  $\text{cm}^{-1}$ ). The differences between the equilibrium distances are also negligible - the change is smaller than 0.001 Angs.

Comparison of the MR-FCPF(g) results with those of MR-ACPF and MR-AQCC is also of interest. In Fig. 2 we show the convergence of the MR-FCPF(g),

MR-ACPF and MR-AQCC (the MR prefixes are skipped in the figure description) energies at the equilibrium geometry [33], with the growing size of the reference space. Again, the CIPSI procedure was used to generate the MRCI spaces and the number of reference determinants was equal to 5, 8, 21 and 46 with the selection threshold  $\eta = 0.05, 0.04, 0.03$  and  $0.02$  respectively.

For small reference spaces the MR-ACPF and MR-AQCC results (which were obtained using a simple modification of the CI problem based on the eq. (30)) seem to be favorable. One may notice however, that only the MR-FCPF(g) resembles the nice convergence of the variational MRCI, approaching smoothly the FCI result (zero of the energy in the figure) from above. We would like to stress that although the MR-ACPF and MR-AQCC methods may give in some cases better results due to a cancellation of different errors, namely the neglect of some EPV and redundancy contributions on one side and the contributions of triple excitations on the other, it is desirable to understand such coincidences using more accurate methods.

The explicit computation of the  $g_i$  quantities shows their inhomogeneous character. For the water molecule, a single ACPF factor of  $g^{\text{acpf}} = 0.2$  is used, in both - single and multireference case and for both - ground and excited states, while the correlation energy defining the final dressing of eq. (30) is state-specific. On the other hand, the actual (not averaged) values of the  $g_i$ 's are quite different. They may vary from 0.1 to 0.6 even within a given pair in the single reference FCPF(d) with doubles only. This simply reflects the fact that excitations to very different unoccupied orbitals are involved.

When the reference space becomes larger, inducing a more effective mixing of different categories of excitations and smaller size-inconsistency error already on the MRCI level, the corrections to be introduced by the change of the norm should be smaller. Indeed, the average value of the MR-FCPF(g)  $g_i$  factors for water at equilibrium geometry changes from 0.47 (which is much different from the 0.2 ACPF factor) in the single reference case to 0.74 with 21 reference determinants (the standard deviations are about 0.1 in both cases, showing quite wide distribution). MR-ACPF and

MR-AQCC methods account for this change using effectively smaller correlation energy, which is defined with respect to a multireference zeroth order function, whereas the correction factor is fixed and of single reference character. This strategy may fail when the reference space contribution to the total wavefunction and energy does not coincide with the decrease of the exact  $g_i$  factors. It is certainly more likely to occur in case of the less refined ACPF renormalization, explaining why AQCC seems to be less sensitive to the choice of the reference space [18].

On the other hand, the MR-FCPF( $g$ ) method, as its non-functional counterpart, must fail when strong quasi-degeneracy occurs. In such a case the truly multireference formalism of MR-FCPF, resulting from MR(SC)<sup>2</sup>CI method, should be used. In Table 1 we present results of the MR-FCPF method, in comparison with some other relevant methods. The CAS reference space of 20 determinants as specified in the ref. [35] is used. The  $g_i$  coefficients are fixed at the equilibrium geometry from the MR(SC)<sup>2</sup>CI solutions (alternatively, the simpler MR-CEPA(0) type approximation of MR(SC)<sup>2</sup>CI<sub>0</sub> method could be employed). The overall parallelism of the MR-FCPF and FCI results is quite nice, but simultaneously the deviation from the parent MR(SC)<sup>2</sup>CI method increases up to 0.5 mH at  $2R_e$ . Thus, fixing the effective change of the norm at one geometry works very well near this point, which is most essential from the point of view of geometry optimization, but does not necessarily insure sufficient accuracy in the whole range of the conformational changes. In such a case averaging the  $g_i$  coefficients over crucial geometries of interest may be used to improve the results.

**CH<sub>2</sub><sup>+</sup>** The five lowest states (1-5) <sup>2</sup>A<sub>1</sub> of CH<sub>2</sub><sup>+</sup>, for which the FCI results are known [36], were used as a test of ACPF method by Gdanitz and Ahlrichs [17]. It was also used to check the numerical efficiency of the MR(SC)<sup>2</sup>CI method [28]. This gives us the opportunity to reinterpret this test in terms of the functional counterpart of the MR(SC)<sup>2</sup>CI method. As these were single geometry calculations, the MR-FCPF results obtained from the converged MR(SC)<sup>2</sup>CI dressing are identical to the results



of MR(SC)<sup>2</sup>CI presented in detail in ref. [28]. We only summarize here that the MR-FCPF/MR(SC)<sup>2</sup>CI results are significantly better (except for the first root) than those of MR-ACPF method.

**LiF** For the sake of further comparison of the new MR-FCPF(g) method and its non-functional (SC)<sup>2</sup>CI counterpart, we calculated the potential energy curve of a strongly polar diatom. In such a molecule the dissociation breaks quite suddenly, through a weakly avoided crossing, the ionic  $Li^+F^-$  bond into a  $LiF$  pair of neutral free radicals. The change in the wavefunction occurs at rather long distance (ca 12 bohr) and its position is very sensitive to the precise inclusion of the dynamical correlation energy. The correlation energy lowers more the ionic forms than the neutral ones and thus moves the curve crossing towards larger interatomic distances. This curve crossing, involving the two lowest  $^1\Sigma^+$  states, has been the subject of several theoretical studies [37].

We shall adopt the same basis set and methodology as Bauschlicher *et al.* [37]. The active space consists of  $4\sigma$ ,  $5\sigma$ ,  $1\pi$  and  $2\pi$  orbitals, providing correct description in the dissociation limit. In contrast to Bauschlicher *et al.*, however, the orbitals  $1\sigma$ ,  $2\sigma$  and  $3\sigma$  were not frozen at the CASSCF level but only at the MRCI level. Thus, the molecular orbitals come from an average CASSCF(2220) calculations whereas the MRCISD is based on two electrons in two molecular orbitals CAS(2000) active space. We have also performed full CI calculations for both states involved in the dissociation.

As the electrons are localized, the number of interacting pairs varies with the distance. Indeed, below the critical interatomic distance the eight valence electrons are localized on  $F^-$  while in the neutral asymptote the valence electron on Li is not significantly correlated, at least not in the same proportions than in  $F^-$ . One may therefore expect that the AQCC correction, based upon a statistical calculation averaging the number of electrons pairs, will not yield the same error in the ionic region as in the neutral one. As a consequence the position of the avoided crossing

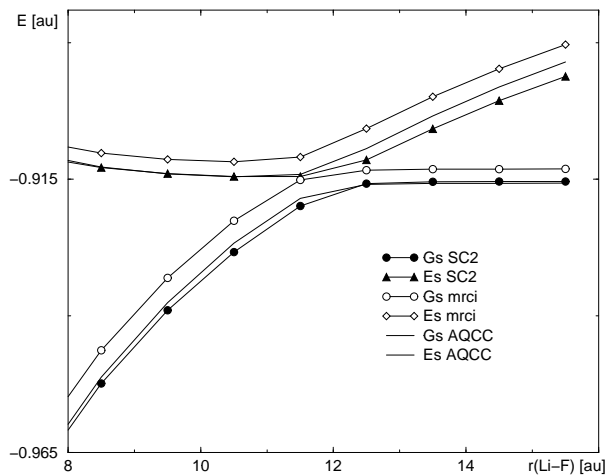


Figure 4: Weakly avoided crossing in LiF. Same as in Fig. 3, except that the (SC)<sup>2</sup>CI and AQCC potential energy curves of LiF are compared to MRCI results.

may be significantly shifted. In contrast, the (SC)<sup>2</sup>CI method, evaluating all specific EPV corrections, should give more reliable results.

Figure 3 presents the FCI, AQCC and (SC)<sup>2</sup>CI potential energy curves for the lowest states, whereas figure 4 reports the MRCISD results with their AQCC and (SC)<sup>2</sup>CI corrected counterparts. As can be seen, AQCC performs rather well, giving an error of ca  $10^{-3} au$ . However the error of (SC)<sup>2</sup>CI is always smaller for both states. Moreover, the AQCC error is larger for the ionic state, compared to the neutral one, and increases slightly with the interatomic distance. As a consequence the position of the curve crossing is shifted from 12.5 bohr (FCI result) to 11.8 bohr with the AQCC approximation. In contrast, the curve crossing position is correctly located with the (SC)<sup>2</sup>CI method.

This example demonstrates the limits of procedures that are based on statistical estimates of the EPV corrections. Using the proposed here generalized procedure, it is possible to obtain a good functional approximation to (SC)<sup>2</sup>CI in all parts of the potential energy curve, recalculating the  $g_i$  factors at some critical geometries of interest, such as the region of avoided crossing.

## 4 Conclusions

In this paper we formally develop a new size-consistent modification of the MRCI method, through an effective change of the norm of the MRCI wavefunction. Starting from a brief recall of the self-consistent, state-specific intermediate Hamiltonians theory [25], which was previously used to introduce various CEPA and CC type dressings of the MRCI Hamiltonian matrix, one derives an equivalent, general form of the dressing of the MRCI overlap matrix.

Its specific form in the case of the (SC)<sup>2</sup>CI and MR(SC)<sup>2</sup>CI methods is explicitly considered. The coefficient and energy dependent Hamiltonian matrix dressing of this method is transformed into effective change of the norm of determinants. Simple approximation is proposed, in order to obtain a functional form without dependence on the nuclei geometry. It is demonstrated that the determinant specific dressings change slowly with the change of geometry, as they are expressed in terms of ratios of two quantities that may change quickly, but in a correlated way. For this reason, one may evaluate an effective change of the norm at some geometry and use it also in its sufficiently large, for geometry optimization, proximity.

The above procedure was used to define the functional counterpart of (SC)<sup>2</sup>CI, referred to as the Multireference Full Coupled Pair Functional. The computation of analytical gradients within MR-FCPF follows the gradient procedures of approximate MR-ACPF and MR-AQCC functionals. The formal properties of ACPF and AQCC are revisited to understand better the way, in which cancellation of errors takes place, ensuring quite encouraging results of these simpler functionals. It is explained why ACPF and to a smaller extent AQCC are sensitive to the choice of the reference space, which may lead to their failure.

The discrepancies between strictly size-consistent treatment of (SC)<sup>2</sup>CI and only approximately size-consistent functional counterpart may become significant at geometries much distorted with respect to conformation used to define the effective norm. An apparently local character of MR-FCPF may be, however, circumvented. One may easily average the dressing over a few relevant geometries, if high accuracy

is required for a large geometrical region.

Another aspect of the new procedure may be of special interest. A determinant specific change of the norm is not restricted to the disconnected parts of the higher excitations. Taking into account linked terms of the CC method as well opens a way to introduce simple, approximate functional forms of various CC methods. In analogy with the MR-FCPF and MR-ACPF, the analytical gradient machinery developed for MRCI may be then utilized.

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## References

- [1] I. Shavitt, in *Methods of Electronic Structure Theory*, Ed. H.F. Schaefer III, Plenum Press 1977, p. 189
- [2] F. Coester, Nucl.Phys. **1**, 421 (1958); F. Coester and H. Kümmel, Nucl.Phys. **17**, 477 (1960); J. Čížek, J.Chem.Phys. **45**, 4256 (1966); Adv.Chem.Phys. **14**, 35 (1969); R.J. Bartlett, J.Chem.Phys. **93**, 1697 (1989)
- [3] J. Paldus, in *Relativistic and Electron Correlation Effects in Molecules and Solids*, Ed. G.L. Malli, Plenum Press 1994, p. 234; I. Lindgren and D. Mukherjee, Phys.Rep. **151**, 93 (1987); D. Mukhopadhyay Jr. and D. Mukherjee, Chem.Phys.Lett. **163**, 171 (1989); L. Meissner and R.J. Bartlett, J.Chem.Phys. **92**, 561 (1990)
- [4] R.J. Bartlett, Theor.Chim.Acta **80**, 71 (1991)
- [5] R.J. Gdanitz and R. Ahlrichs, Chem.Phys.Lett. **143**, 413 (1988); R. Fink and V. Staemmler, Theor.Chim.Acta **87**, 129 (1993); R.J. Cave and E.R. Davidson,

- J.Chem.Phys. **89**, 6978 (1988); P.J.A. Ruttink, J.H. van Lenthe, R. Zwaans and G.C. Groenenboom, J.Chem.Phys. **94**, 7212 (1991)
- [6] P.G. Szalay and R.J. Bartlett, J.Chem.Phys. **103**, 3600 (1995)
- [7] R. Shepard, H. Lischka, P.G. Szalay, T. Kovar and M. Ernzerhof, J.Chem.Phys. **96**, 6018 (1992)
- [8] Y. Yamaguchi, Y. Osamura, J.D. Goddard and H.F. Schaefer III, *A New Dimension to Quantum Chemistry: Analytic Derivative Methods in Ab Initio Molecular Electronic Structure Theory*, Oxford Univ. Press 1994; P. Pulay, in *Ab Initio Methods in Quantum Chemistry II*, Ed. K.P. Lawley, John Wiley & Sons 1987, p. 241
- [9] L. Adamowicz, W.D. Laidig and R.J. Bartlett, Int.J.Quantum Chem. : Quantum Chem. Symp. **18**, 245 (1984) J.D. Watts, J. Gauss and R.J. Bartlett, J.Chem.Phys. **98**, 8718 (1993);
- [10] J.A. Pople, M. Head-Gordon, D.J. Fox, K. Raghavachari and L.A. Curtiss, J.Chem.Phys. **90**, 5622 (1989)
- [11] J.F. Stanton, J.Chem.Phys. **99**, 8840 (1993); T. Nakajima and H. Nakatsuji, Chem.Phys.Lett. **280**, 79 (1997)
- [12] P. Pulay, Mol.Phys. **17**, 197 (1969)
- [13] N.C. Handy and H.F. Schaefer, J.Chem.Phys. **81**, 5032 (1984)
- [14] P. Szalay, Int.J.Quantum Chem. **55**, 151 (1995)
- [15] P. Pulay, Int.J.Quantum Chem. : Quantum Chem. Symp. **17**, 257 (1983)
- [16] R. Ahlrichs, P. Scharf and C. Ehrhardt, J.Chem.Phys. **82**, 890 (1984)
- [17] R.J. Gdanitz and R. Ahlrichs, Chem.Phys.Lett. **143**, 413 (1988)

- [18] P.G. Szalay and R.J. Bartlett, *Chem.Phys.Lett.* **214**, 481 (1993); L. Füst-Molnar and P.G. Szalay, *J.Chem.Phys.* **106**, 6288 (1996)
- [19] J. Sanchez-Marin, D. Maynau and J.P. Malrieu, *Theor.Chim.Acta* **87**, 107 (1993); I. Nebot-Gil, J. Sanchez-Marin, J.L. Heully, J.P. Malrieu and D. Maynau, *Chem.Phys.Lett.* **234**, 45 (1995), *J.Chem.Phys.* **103**, 2576 (1995)
- [20] J.P. Daudey, J.L. Heully and J.P. Malrieu, *J.Chem.Phys.* **99**, 1240 (1993); R. Caballol and J.P. Malrieu, *Chem.Phys.Lett.* **188** 126 (1992)
- [21] J. Meller, J.P. Malrieu and R. Caballol, *J.Chem.Phys.* **104**, 4068 (1996); L. Adamowicz, R. Caballol, J.P. Malrieu and J. Meller, *Chem.Phys.Lett.* **259**, 619 (1996)
- [22] J.P. Malrieu, J.P. Daudey and R. Caballol, *J.Chem.Phys.* **101**, 8908 (1994)
- [23] J.P. Malrieu, I. Nebot-Gil, J. Sanchez-Marin, and D. Maynau, *J.Chem.Phys.* **100**, 1441 (1994)
- [24] J.A. Pople, in: *Energy, structure and reactivity*. Eds. D.W. Smith, W.B. McRae (Wiley, N.Y. 1973), pp. 51-61;
- [25] J.P. Malrieu, Ph. Durand and J.P. Daudey, *J.Phys.A: Math.Gen.* **18**, 809 (1985)
- [26] M.B. Lepetit and J.P. Malrieu, *J.Chem.Phys.* **87**, 5937 (1987)
- [27] J.L. Heully and J.P. Malrieu, J I. Nebot-Gil, J. Sanchez-Marin, *Chem.Phys.Lett.* **256**, 589 (1996)
- [28] J. Meller, J.P. Malrieu and J.L. Heully, *Chem.Phys.Lett.* **244**, 440 (1995)
- [29] L. Meissner, *Chem.Phys.Lett.* **146**, 205 (1988)
- [30] H. Nakatsuji, *J.Chem.Phys.* **83**, 713 (1985); H. Nakatsuji, *J.Chem.Phys.* **95**, 4296 (1991)

- [31] D.J. Rowe, *Rev.Mod.Phys.* **40**, 153 (1968); J. Geertsen, M. Ritby and R.J. Bartlett, *Chem.Phys.Lett.* **164**, 57 (1989)
- [32] L.S. Cederbaum, *Mol.Phys.* **28**, 479 (1974)
- [33] P. Saxe, H.F. Schaefer III and N.C. Handy, *Chem.Phys.Lett.* **79**, 202 (1981); R.J. Harrison and N.C. Handy, *Chem.Phys.Lett.* **95**, 386 (1983)
- [34] S. Evangelisti, J.P. Daudey and J.P. Malrieu, *Chem.Phys.* **75**, 91 (1983)
- [35] W.D. Laidig and R.J. Bartlett, *Chem.Phys.Lett.* **104**, 424 (1984)
- [36] C.W. Bauschlicher and P.R. Taylor, *J.Chem.Phys.* **86**, 2844 (1987)
- [37] C.W. Bauschlicher and S.R. Langhoff, *J.Chem.Phys.* **89**, 4246 (1988); L.R.Kahn, P.J.Hay, and I. Shavitt, *J. Chem. Phys.* **61**, 3530 (1974); H.J. Werner and W. Meyer, *J. Chem. Phys.* **74**, 5802 (1981); H. Nakano, *J. Chem. Phys.* **99**, 7983 (1993)