



# Multireference F12 coupled cluster theory: The Brillouin-Wigner approach with single and double excitations

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## ABSTRACT

This Letter reports development and implementation of the explicitly correlated multireference Brillouin Wigner (MR BW-CC) coupled cluster method with Slater type geminals. The performance of the new approach is tested on the H4 model system and the dissociation curve of the fluorine molecule. Like in single reference methods, results show a dramatically improved convergence of total energies towards complete basis set limit as compared to a conventional MR BW-CC approach. In comparison with previously reported calculations with a linear correlation factor, there is a better performance for calculations in smaller basis sets.

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## 1. Introduction

Traditional methods based on the configuration interaction type expansion of the wave function describe the Coulomb cusp very poorly. As a result, conventional methods converge as slowly as  $\propto (L+1)^{-3}$  with respect to the measure of the basis set saturation. Here,  $L$  is the highest angular momentum function included in the basis.

To overcome the aforementioned shortcoming, it is highly beneficial to include the inter-electronic interaction explicitly in the wave function. This is effectively accomplished by the R12 ansatz suggested by Kutzelnigg a quarter of century ago [1]. Due to the improved description of the dynamical electron correlation within the latter approach, the convergence is accelerated to  $\propto (L+1)^{-7}$ .

Let  $(\Phi)$  be a reference function based on the one-particle approximation. The application of the R12 ansatz to the coupled cluster (CC) theory leads to the wave function in the general form [2–4]

$$|\Psi\rangle = e^{(\hat{T}+\hat{R})} |\Phi\rangle, \quad (1)$$

where, beside the global excitation operator  $\hat{T}$ , the operator  $\hat{R}$  is related to the correlation factor which contains explicitly the inter-electronic coordinate.

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The original R12 approach used a linear correlation factor  $r_{12}$ , which provides a correct description of the short range interaction (when  $r_{12} \rightarrow 0$ ), while the infinite value in the long range limit is only compensated by the zero value of the wave function expansion in the conventional basis. This is certainly not an ideal solution for the long range part, and it can cause undesired numerical problems, especially when the conventional one-particle basis is not enough saturated. Lack of the higher powers of the  $r_{12}$  also implies that the Coulomb hole is not correctly described in the broader vicinity of  $r_{12} \rightarrow 0$ . This failure can again be corrected via an expansion in the computational basis, if the latter is saturated enough. Practical approaches that aim at using less saturated smaller basis sets are focused on an alternative correlation factor. The Slater-type geminal function (STG) [5] provides a correct asymptotical behavior in both the short and long range limits and numerous studies during the last five years have confirmed STG as the optimal choice. Approaches using this correlation factor either directly [5–7] or through expansions in a set of GAUSSIAN type geminals [8–12] nowadays dominate and have adopted a notation ‘F12’ instead of the original ‘R12’.

Despite the success of the explicitly correlated CC methods in the treatment of the dynamical correlation, an accurate description the static correlation plays a crucial role in many systems of chemical interest. Therefore, a multireference generalization of the CC-R12/F12 method is highly desirable. As in the case of a conventional CC treatment, the latter generalization is by no means unique. Possible approaches are offered by following the basic ideas behind the numerous conventional MR CC concepts.

Combination of the linear ( $r_{12}$ ) correlation factor with the MR configuration interaction (MR-CI) and MR averaged coupled pair

functional (MR-ACPF) was implemented more than a decade ago by Gdanitz [13]. His implementation followed the principles of standard approximation (SA) [14] and was limited to very small systems using extensive basis sets [15,16]. More practical use of MR treatment in combination with F12 approach has been reported within the SP *ansatz* with fixed cusp conditions in the MR second order perturbation theory [17–19] and very recently also within the MR CI [20]. Such treatment corresponds to the use of internally contracted geminal basis.

Genuine multireference coupled cluster approaches can be divided into several groups: the Fock space methods which use a common cluster excitation operator for all the references [21–23]; and Hilbert space methods where each reference is related with a distinct cluster operator [24–32]. The Hilbert space approaches can be further divided to state universal and state specific methods, depending on the number of states studied at a time. In state universal approaches, all states are obtained simultaneously, however, these methods were found to suffer from the so called intruder state problem giving rise to serious convergence problems. In state specific approaches, only one state is studied at a time and the intruder state problem can thus be avoided.

Historically the first of these methods, the Brillouin Wigner (BW) variant [27,28,33–37] is resistant to the intruder state problem thanks to the denominator shift. At the same time the cluster equations are relatively simple, closely following the single reference problem. Major drawback of the BW variant is the lack of the size-extensivity and hence, for large systems, a need for *a posteriori* corrections [35,36]. Nonetheless, the method has been successfully applied to study of several biatomic to mid-size molecules, see e.g. [38,39].

Due to the simple structure of the cluster equations and smooth convergence, the Brillouin-Wigner method is well suited as a starting point for the development of explicitly correlated MR CC approaches. Recently, we have outlined this way with preliminary results using the linear  $r_{12}$  correlation factor [40].

In the present Letter, we report an implementation of the multireference BW-CC-F12 method with STG correlation factor. However, it should be stressed that this is only the first step, and that we plan to move to size-extensive methods, for example the state-specific MR CC method by Mukherjee et al. [30,31] which presently seems to be the most promising from the Hilbert-space MR CC methods [41–43].

## 2. Theory

The theory section is divided into two parts. In the first part, the basic framework of the MR BW-CC theory is presented. In the second part, the explicit form of the cluster equations is derived.

Throughout the text, we use  $p, q, r$  as indices corresponding to general spinorbitals,  $i, j, k \dots$  for occupied spinorbitals,  $a, b, c \dots$  for virtual spinorbitals, and  $\alpha, \beta, \gamma \dots$  for spinorbitals from the complementary space which is the orthogonal complement to the computational basis set. Einstein summation convention is used for indices corresponding to spinorbitals.

### 2.1. MR BW-CC-F12 method

Let a model space be spanned by  $M$  reference configurations  $\Phi_\mu$ . As a general function within the model space, the reference state can be written as a linear combination of these reference configurations as

$$|\Psi_\omega^p\rangle = \sum_{\mu=1}^M C_\mu^\omega |\Phi_\mu\rangle, \quad (2)$$

where the index  $\omega$  denotes the chosen state.  $\hat{P}$  is the projector onto the model space and  $\hat{Q} = 1 - \hat{P}$  is its orthogonal complement. The exact wave function can be expressed by the means of the wave operator  $\hat{\Omega}_\omega$ .

$$|\Psi_\omega\rangle = \hat{\Omega}_\omega |\Psi_\omega^p\rangle \quad (3)$$

Here, we assume the wave operator in the form of the augmented Jezierski Monkhorst *ansatz*

$$\hat{\Omega}_\omega = \sum_{\mu=1}^M e^{\hat{S}(\mu)} |\Phi_\mu\rangle \langle \Phi_\mu|, \quad (4)$$

where  $S(\mu)$  is a global excitation operator defined with respect to the  $\mu$ -th reference determinant. For simplicity, we have omitted the  $\omega$  index for the  $S(\mu)$ , as well as the cluster amplitudes. For a proper description of the Coulomb cusp in the many-electron wave function, we include into the  $S(\mu)$ , apart from the conventional cluster operator  $\hat{T}(\mu)$ , also the F12 part  $\hat{\mathcal{R}}(\mu)$

$$\hat{S}(\mu) = \hat{T}(\mu) + \hat{\mathcal{R}}(\mu). \quad (5)$$

Analogously to  $\hat{\mathcal{R}}$  in the single reference theory, the operator  $\hat{\mathcal{R}}(\mu)$  for the  $\mu$ -th reference in the most general form reads:

$$\begin{aligned} \hat{\mathcal{R}}(\mu) &= \hat{\mathcal{R}}_1(\mu) + \hat{\mathcal{R}}_2(\mu) \\ &= c_k^i(\mu) \tilde{\mathcal{R}}_i^k(\mu) + \frac{1}{4} c_{kl}^{ij}(\mu) \tilde{\mathcal{R}}_{ij}^{kl}(\mu); \end{aligned} \quad (6)$$

$$\tilde{\mathcal{R}}_i^k(\mu) = \tilde{F}_{ij}^{kj}(\mu) \tilde{a}_i^\alpha(\mu) \equiv F_\alpha^k(\mu) \tilde{a}_i^\alpha(\mu), \quad (7)$$

$$\tilde{\mathcal{R}}_{ij}^{kl}(\mu) = \frac{1}{2} \tilde{F}_{\alpha\beta}^{kl}(\mu) \tilde{a}_{ij}^{\alpha\beta}(\mu) + \tilde{F}_{ab}^{kl}(\mu) \tilde{a}_{ij}^{ab}(\mu). \quad (8)$$

Here,  $c_{\dots}^{\dots}$  are parameters to be determined,  $\tilde{a}$  are normal ordered replacement operators with respect to the pertinent references, and the matrix elements

$$F_{\alpha\beta}^{kl}(\mu) = \langle kl | f_{12}(r_{12}) | \alpha\beta \rangle \quad (9)$$

correspond to integrals over the correlation factor,  $f_{12}(r_{12})$ .

As shown above, the  $\hat{\mathcal{R}}(\mu)$  operator involves occupied orbitals related to the  $\mu$ -th reference as well as orbitals from the complement to the computational basis. This complement is the same for all references  $\Phi_\mu$ , since all the references use a common set of molecular orbitals.

The exact energy can be obtained as an eigenvalue of the effective Hamiltonian. The eigenvalue equation can be written in the matrix representation

$$\sum_{\nu} H_{\mu\nu}^{\text{eff}} C_\nu^\omega = E^\omega C_\mu^\omega, \quad (10)$$

where the eigenvector coefficients are the same as in Eq. (2).

In the case of a complete model space, cluster amplitudes corresponding to excitations within the model space are set to zero, in order to maintain the intermediate normalization. The remaining cluster amplitudes are obtained by solving cluster equations

$$\begin{aligned} (\mathcal{E}_\omega - H_{\mu\mu}^{\text{eff}}) \langle \Phi_\mu^{(\mu)} | e^{\hat{S}(\mu)} | \Phi_\mu \rangle &= \langle \Phi_\mu^{(\mu)} | [\hat{H}_N(\mu) e^{\hat{S}(\mu)}]_C | \Phi_\mu \rangle \\ &+ \langle \Phi_\mu^{(\mu)} | [\hat{H}_N(\mu) e^{\hat{S}(\mu)}]_{\text{DC,L}} | \Phi_\mu \rangle, \end{aligned} \quad (11)$$

where C indicates the connected part of the expression and DC,L the disconnected linked part.

The projection manifold  $\langle \Phi_\mu |$  consists of the conventional part  $\langle \Phi_\mu | \tilde{a}_{\dots}^{\dots}$  and the F12 specific part  $\langle \Phi_\mu | [\tilde{\mathcal{R}}_{\dots}^{\dots}(\mu)]^\dagger$ . As in the conventional MR BW-CC approach, after solving Eqs. (11), *a posteriori* correction for the size-extensivity error can be applied in a single iteration [36].

The matrix elements of the effective Hamiltonian,  $H_{\mu\nu}^{\text{eff}}$ , are given as

$$H_{\mu\nu}^{\text{eff}} = \langle \Phi_\mu | \hat{H} | \Phi_\mu \rangle \delta_{\mu\nu} + \langle \Phi_\mu | [\hat{H}_N(v)e^{S(v)}]_C | \Phi_\nu \rangle. \quad (12)$$

The diagonal elements have the same formal structure as the correlation energy in the single reference coupled cluster theory. The off-diagonal terms are obtained as the residuals corresponding to the internal excitation transforming  $\Phi_\nu$  to  $\Phi_\mu$ .

## 2.2. Working equations

In this subsection, explicit formulas for the cluster equations are presented with a particular emphasis on the new terms in MR BW-CCSD-F12 which have to be included in addition to terms emerging either in the conventional MR BW-CCSD or the single reference CCSD-F12 theory. The equations are presented for a general case. However, the present implementation was restricted to SA [14], employing the variant C for evaluation of the matrix elements [44].

In order to do that, we introduce the following partitioning of the normal ordered Hamiltonian  $H_N(\mu)$  [45]

$$\hat{H}_N(\mu) = \hat{H} - \langle \Phi_\mu | \hat{H} | \Phi_\mu \rangle = \hat{H}_N^{\text{ao}}(\mu) + \hat{H}_N^{\text{comp}}(\mu) \quad (13)$$

$$\hat{H}_N^{\text{ao}}(\mu) = f_p^q(\mu) \tilde{a}_q^p(\mu) + \frac{1}{4} \bar{g}_{pq}^{rs} \tilde{a}_{rs}^{pq}(\mu), \quad (14)$$

$$\begin{aligned} \hat{H}_N^{\text{comp}}(\mu) = & f_p^\alpha(\mu) \tilde{a}_\alpha^p(\mu) + f_\alpha^p(\mu) \tilde{a}_p^\alpha(\mu) + f_\beta^\alpha(\mu) \tilde{a}_\alpha^\beta(\mu) \\ & + \frac{1}{2} \left[ \bar{g}_{\alpha q}^{rs} \tilde{a}_{rs}^{\alpha q}(\mu) + \bar{g}_{pq}^{\alpha s} \tilde{a}_{\alpha s}^{pq}(\mu) + \bar{g}_{\alpha\beta}^{\gamma s} \tilde{a}_{\gamma s}^{\alpha\beta}(\mu) + \bar{g}_{\alpha q}^{\gamma\delta} \tilde{a}_{\gamma\delta}^{\alpha q}(\mu) \right] \\ & + \bar{g}_{\alpha q}^{\gamma s} \tilde{a}_{\gamma s}^{\alpha q}(\mu) + \frac{1}{4} \left[ \bar{g}_{\alpha\beta}^{rs} \tilde{a}_{rs}^{\alpha\beta}(\mu) + \bar{g}_{pq}^{\gamma\delta} \tilde{a}_{\gamma\delta}^{pq}(\mu) + \bar{g}_{\alpha\beta}^{\gamma\delta} \tilde{a}_{\gamma\delta}^{\alpha\beta}(\mu) \right]. \end{aligned} \quad (15)$$

where  $\hat{H}_N^{\text{ao}}(\mu)$  is the part of the Hamiltonian describable in the conventional basis,  $\hat{H}_N^{\text{comp}}(\mu)$  contains the remaining terms involving indices from the complementary space.  $f_p^q(\mu)$  are matrix elements of the Fock matrices and  $\bar{g}_{pq}^{rs} = \langle pq | \frac{1}{r_12} | rs \rangle$ .

In the following text we use

$$\begin{aligned} \langle \Phi_{i\dots}^{a\dots}(\mu) | e^{\tilde{R}}(\mu) | \Phi_\mu \rangle &= 0 \\ \Rightarrow \langle \Phi_{i\dots}^{a\dots}(\mu) | e^{\tilde{S}(\mu)} | \Phi_\mu \rangle &= \langle \Phi_{i\dots}^{a\dots}(\mu) | e^{\tilde{T}(\mu)} | \Phi_\mu \rangle \end{aligned} \quad (16)$$

$$\begin{aligned} \langle \Phi_\mu | \hat{\mathcal{R}}^\dagger(\mu) e^{\tilde{T}(\mu)} | \Phi_\mu \rangle &= 0 \\ \Rightarrow \langle \Phi_\mu | \hat{\mathcal{R}}^\dagger(\mu) e^{\tilde{S}(\mu)} | \Phi_\mu \rangle &= \langle \Phi_\mu | \hat{\mathcal{R}}^\dagger(\mu) e^{\tilde{R}(\mu)} | \Phi_\mu \rangle \end{aligned} \quad (17)$$

Projection of Eq. (11) onto the single excitations gives rise to:

$$\begin{aligned} (\mathcal{E}_\omega - H_{\mu\mu}^{\text{eff}}) \langle \Phi_\mu | \tilde{a}_a^i(\mu) e^{\tilde{T}(\mu)} | \Phi_\mu \rangle &= \langle \Phi_\mu | \tilde{a}_a^i(\mu) [\hat{H}_N^{\text{ao}}(\mu) e^{\tilde{T}(\mu)}]_C | \Phi_\mu \rangle \\ &+ \langle \Phi_\mu | \tilde{a}_a^i(\mu) [\hat{H}_N^{\text{comp}}(\mu) e^{\tilde{S}(\mu)}]_C | \Phi_\mu \rangle, \end{aligned} \quad (18)$$

where the term on the l.h.s. of this equation is identical to the l.h.s. of the singles equation of the conventional MR BW-CCSD method. The first term on the r.h.s. is also present in the conventional MR BW-CCSD, whereas the second term has a counterpart in the single reference CCSD-F12.

Eq. (11) projected onto conventional double excitations provides:

$$\begin{aligned} (\mathcal{E}_\omega - H_{\mu\mu}^{\text{eff}}) \langle \Phi_\mu | \tilde{a}_{ab}^{ij}(\mu) e^{\tilde{T}(\mu)} | \Phi_\mu \rangle &= \langle \Phi_\mu | \tilde{a}_{ab}^{ij}(\mu) [\hat{H}_N^{\text{ao}}(\mu) e^{\tilde{T}(\mu)}]_C | \Phi_\mu \rangle \\ &+ \langle \Phi_\mu | \tilde{a}_{ab}^{ij}(\mu) [\hat{H}_N^{\text{comp}}(\mu) e^{\tilde{S}(\mu)}]_{\text{DC.L}} | \Phi_\mu \rangle \\ &+ \langle \Phi_\mu | \tilde{a}_{ab}^{ij}(\mu) [\hat{H}_N^{\text{comp}}(\mu) e^{\tilde{S}(\mu)}]_C | \Phi_\mu \rangle \\ &+ \langle \Phi_\mu | \tilde{a}_{ab}^{ij}(\mu) [\hat{H}_N^{\text{comp}}(\mu) e^{\tilde{S}(\mu)}]_{\text{DC.L}} | \Phi_\mu \rangle. \end{aligned} \quad (19)$$

The term on the l.h.s., as well as the first two terms on the r.h.s. are again the same as in the conventional MR BW-CCSD, while the third term on the r.h.s. is the analogous as the corresponding term in the

single reference CCSD-F12. The last term on the r.h.s. can be factorized as

$$\begin{aligned} \langle \Phi_\mu | \tilde{a}_{ab}^{ij}(\mu) [\hat{H}_N^{\text{comp}}(\mu) e^{\tilde{S}(\mu)}]_{\text{DC.L}} | \Phi_\mu \rangle \\ = \bar{\delta}_{kl}^{ij} \bar{\delta}_{cd}^{ab} \langle \Phi_\mu | \tilde{a}_c^k(\mu) [\hat{H}_N^{\text{comp}}(\mu) e^{\tilde{S}(\mu)}]_C | \Phi_\mu \rangle t_d^l(\mu), \end{aligned} \quad (20)$$

where we have introduced

$$\bar{\delta}_{pt}^{rs} = \delta_p^r \delta_t^s - \delta_p^s \delta_t^r. \quad (21)$$

The term  $\langle \Phi_\mu | \tilde{a}_a^i(\mu) [\hat{H}_N^{\text{comp}}(\mu) e^{\tilde{S}(\mu)}]_C | \Phi_\mu \rangle$  is already known from Eq. (18).

Projection of Eq. (11) onto the unconventional space created by  $\tilde{\mathcal{R}}_1$  reduces to

$$\begin{aligned} (\mathcal{E}_\omega - H_{\mu\mu}^{\text{eff}}) \langle \Phi_\mu | [\tilde{\mathcal{R}}_i^k(\mu)]^\dagger e^{\tilde{R}(\mu)} | \Phi_\mu \rangle \\ = \langle \Phi_\mu | [\tilde{\mathcal{R}}_i^k(\mu)]^\dagger [\hat{H}_N^{\text{comp}}(\mu) e^{\tilde{S}(\mu)}]_C | \Phi_\mu \rangle, \end{aligned} \quad (22)$$

where the analog of r.h.s. is present in the single reference theory. The new l.h.s. term

$$\langle \Phi_\mu | [\tilde{\mathcal{R}}_i^k(\mu)]^\dagger e^{\tilde{R}(\mu)} | \Phi_\mu \rangle = F_i^\alpha(\mu) F_\alpha^m(\mu) c_m^k(\mu), \quad (23)$$

can be expressed by replacing the (complete) complementary basis by a complementary auxiliary basis set (CABS) [46], as long as the merger of CABS with the main computational basis is close to the Hartree-Fock limit basis.

Finally, in the equations obtained by projection of (11) onto the space created by  $\tilde{\mathcal{R}}_2$ ,

$$\begin{aligned} (\mathcal{E}_\omega - H_{\mu\mu}^{\text{eff}}) \langle \Phi_\mu | [\tilde{\mathcal{R}}_{ij}^{kl}(\mu)]^\dagger e^{\tilde{S}(\mu)} | \Phi_\mu \rangle \\ = \langle \Phi_\mu | [\tilde{\mathcal{R}}_{ij}^{kl}(\mu)]^\dagger [\hat{H}_N^{\text{comp}}(\mu) e^{\tilde{S}(\mu)}]_C | \Phi_\mu \rangle \\ + \langle \Phi_\mu | [\tilde{\mathcal{R}}_{ij}^{kl}(\mu)]^\dagger [\hat{H}_N(\mu) e^{\tilde{S}(\mu)}]_{\text{DC.L}} | \Phi_\mu \rangle, \end{aligned} \quad (24)$$

the l.h.s. can be evaluated using

$$\begin{aligned} \langle \Phi_\mu | [\tilde{\mathcal{R}}_{ij}^{kl}(\mu)]^\dagger e^{\tilde{S}(\mu)} | \Phi_\mu \rangle \\ = \frac{1}{2} \left[ \frac{1}{2} \bar{F}_{ij}^{\alpha\beta}(\mu) \bar{F}_{\alpha\beta}^{mn}(\mu) + \bar{F}_{ij}^{\alpha\beta}(\mu) \bar{F}_{\alpha\beta}^{mn}(\mu) \right] c_{mn}^{kl}(\mu) \\ + \frac{1}{2} \bar{F}_{ij}^{\alpha\beta}(\mu) F_\alpha^m(\mu) F_\beta^n(\mu) c_m^k(\mu) c_n^l(\mu) \\ - \bar{F}_{ij}^{\alpha\beta}(\mu) t_a^k(\mu) F_\beta^n(\mu) c_n^l(\mu) \\ = \frac{1}{2} \mathcal{X}_{ij}^{mn}(\mu) c_{mn}^{kl}(\mu) + \frac{1}{2} \mathcal{W}_{ij}^{mn}(\mu) c_m^k(\mu) c_n^l(\mu) \\ - \lambda_{ij}^{an}(\mu) t_a^k(\mu) c_n^l(\mu). \end{aligned} \quad (25)$$

All the matrix elements involving the complementary basis are calculated following Ref. [44]. The intermediates  $\mathcal{X}$  and  $\mathcal{W}$  in Eq. (25) are evaluated identically to those from Ref. [7], however, now they must be evaluated for each reference configuration. The first term on the r.h.s. of Eq. (24) is analogous to the single reference CCSD-F12. The last r.h.s. term can be more explicitly rewritten as:

$$\begin{aligned} \langle \Phi_\mu | [\tilde{\mathcal{R}}_{ij}^{kl}(\mu)]^\dagger [\hat{H}_N(\mu) e^{\tilde{S}(\mu)}]_{\text{DC.L}} | \Phi_\mu \rangle \\ = \bar{\delta}_{ij}^{mn} \left\{ \frac{1}{2} \bar{F}_{kl}^{\alpha\beta}(\mu) F_\alpha^o(\mu) c_o^m(\mu) \langle \Phi_\mu | \tilde{a}_\beta^n [\hat{H}_N^{\text{comp}}(\mu) e^{\tilde{S}(\mu)}]_C | \Phi_\mu \rangle \right. \\ + \bar{F}_{kl}^{\alpha\beta}(\mu) F_\alpha^o(\mu) c_o^m(\mu) \langle \Phi_\mu | \tilde{a}_\beta^n [\hat{H}_N(\mu) e^{\tilde{S}(\mu)}]_C | \Phi_\mu \rangle \\ \left. + \bar{F}_{kl}^{\alpha\beta}(\mu) \langle \Phi_\mu | \tilde{a}_\alpha^m [\hat{H}_N^{\text{comp}}(\mu) e^{\tilde{S}(\mu)}]_C | \Phi_\mu \rangle t_b^n \right\}. \end{aligned} \quad (26)$$

This term as a whole clearly vanishes within the SA when the one-particle resolution of identity is approximated by the projector onto the computational basis, i. e. saturation at one-particle level is

assumed. If this is not satisfied, the summations over  $\alpha$  or  $\beta$  have to be replaced by summations over CABS. Matrix elements within  $\langle \rangle$  are analogous to those in Eq. (18).

### 3. Computational

#### 3.1. H<sub>4</sub> model

The MR BW-CCSD-F12 method was tested on the H<sub>4</sub> model system first suggested by Jankowski and Paldus [47]. Here, four hydrogens are placed into the four vertices of the isosceles trapezoid, with the fixed distance of 2 a.u. between the neighboring atoms. The geometrical configurations can be characterized by the angle between the height and side of the trapezoid, varying from 0 for the square structure to  $\pi/2$  for the linear geometry. While the linear structure is well described at single reference level, the (nearly) square structure has a multireference character due to the (quasi) degeneracy of the HOMO and LUMO orbitals.

Throughout the calculations, the model space consisting of two references HOMO<sup>2</sup>LUMO<sup>0</sup> (I) and HOMO<sup>0</sup>LUMO<sup>2</sup> (II) was employed, as constructed from the Hartree Fock orbitals. The calculations used four basis sets: the R12 optimized 9s6p4d3f basis [48], as well as its 9s, 9s6p, and 9s6p4d subsets. These basis sets are saturated enough to be used within the SA [14]. The correlation factor was taken both as the linear  $r_{12}$  and the Slater type geminal,  $e^{-\gamma r_{12}}$ , with a fixed value of  $\gamma = 1.0$ .

#### 3.2. Fluorine molecule

Dissociation curve of the fluorine molecule was calculated for a set of 15 intermolecular distances in the range between 2.0 and 5.6 Bohr. The model space was formed from 3  $\sigma_g^2$  and 3  $\sigma_u^2$  orbitals that become degenerate for large interatomic distances. Within this model space, the references  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_g^4 1\pi_u^4 3\sigma_g^2$  and  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_g^4 1\pi_u^4 3\sigma_u^2$  were used, while the monoexcited references were omitted because of symmetry considerations. Calculations were performed using SA and employing the R12 suited 19s14p8d6f4g3h basis [49] together with its subsets 19s14p8d6f and 19s14p8d6f4g. The calculations were performed without a *a posteriori* size-extensivity correction.

### 4. Results and discussion

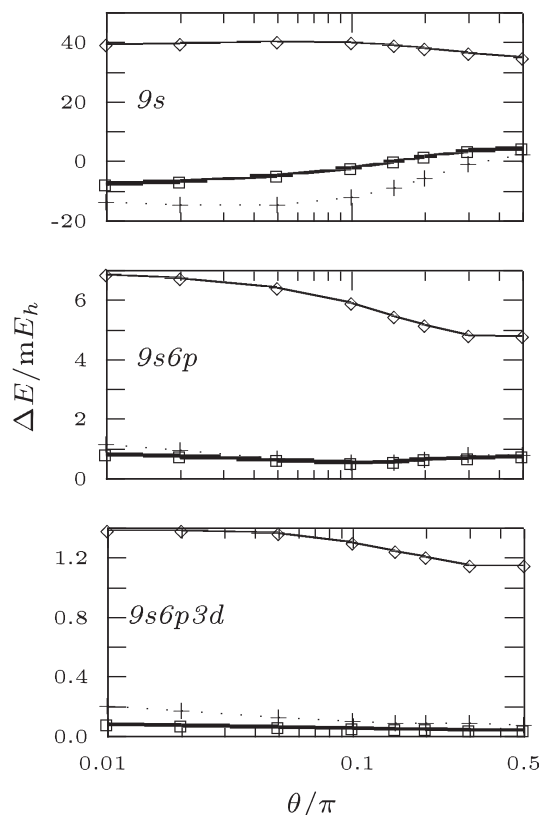
#### 4.1. H<sub>4</sub> model

The resulting energies of the H<sub>4</sub> system are listed in Table 1. In Figure 1, we present deviations from the reference energy, taken as

**Table 1**

Geometry and the basis set dependence of the total MR BW-CCSD energies for the H<sub>4</sub> model. Energies are in  $E_h$ . For geometry and the basis set specification see the text.

| $\theta/\pi$          | 9s        | 9s6p      | 9s6p4d    | 9s6p4d3f  |
|-----------------------|-----------|-----------|-----------|-----------|
| <i>MR BW-CCSD</i>     |           |           |           |           |
| 0.00                  | -2.060940 | -2.093642 | -2.099197 | -2.099945 |
| 0.02                  | -2.075590 | -2.108671 | -2.114027 | -2.114768 |
| 0.10                  | -2.150466 | -2.184585 | -2.189177 | -2.189832 |
| 0.50                  | -2.223060 | -2.253237 | -2.256894 | -2.257451 |
| <i>MR BW-CCSD-R12</i> |           |           |           |           |
| 0.00                  | -2.126476 | -2.101485 | -2.100409 | -2.100515 |
| 0.02                  | -2.144353 | -2.116592 | -2.115355 | -2.115386 |
| 0.10                  | -2.213502 | -2.191568 | -2.190495 | -2.190480 |
| 0.50                  | -2.259192 | -2.257913 | -2.258016 | -2.258039 |
| <i>MR BW-CCSD-F12</i> |           |           |           |           |
| 0.00                  | -2.108423 | -2.099702 | -2.100499 | -2.100590 |
| 0.02                  | -2.122113 | -2.114649 | -2.115338 | -2.115417 |
| 0.10                  | -2.192521 | -2.189945 | -2.190427 | -2.190483 |
| 0.50                  | -2.253317 | -2.257292 | -2.258005 | -2.258047 |



**Figure 1.** Energy errors ( $\Delta E$ ) for the MR BW-CCSD, ( $\diamond$ ) MR BW-CCSD-R12 ( $+$ ) and MR BW-CCSD-F12 ( $\square$ ) methods in  $mE_h$  with respect to the *spdf* MR BW-CCSD-F12 values as functions of the basis sets and the geometry of the H<sub>4</sub> model.

the MR BW-CCSD-F12 results with STG using the 9s6p4d3f basis set. Conventional MR BW-CC methods yield maximum deviations from the reference 40, 6.4, 1.4, and 0.7  $mE_h$  in *s*, *sp*, *spd*, and *spdf* basis sets, respectively. At the R12 level, we observe significant improvement of the basis set convergence, where the maximum deviations are  $-28.9$ , 1.2, and 0.1  $mE_h$  in the *s*, *sp*, and *spd* basis sets, respectively. The energies calculated in the *sp* set thus lie between results of conventional MR BW-CC method in *spd* and *spdf* bases. The performance in the *s* basis set is relatively poor, due to unsatisfactory saturation of the basis set that in this case does not truly meet the conditions for the SA. Nevertheless, with the STG correlation factor the maximum deviation with *s* set is reduced to  $-8 mE_h$ , while improvement is also noticeable with the *sp* basis (0.9  $mE_h$ ). Also, unlike with the linear correlation factor, the error curves are monotonous. With the *spd* and *spdf* sets the R12 and F12 results are practically indistinguishable. These observations underline our recent finding related to single reference CCSD-R12/F12 theories [7].

In order to complete the picture on the R12/F12 impact, we have also investigated the changes of the weights of the two reference configurations along the curve, as shown in Table 2. These weights are expected to be almost independent from the dynamical correlation introduced via R12/F12. Yet, little impact is seen. At the level of MR BW-CCSD, the weights change very little with the extension of the basis set. When MR BW-CCSD-R12 is compared with MR BW-CCSD in the multireference region, we see a significant change of the weights in 9s basis set. These differences rapidly decrease with the size of the basis set. In contrast, with the STG correlation factor, no such trend is observed and the weights lie close to each other in all the four basis sets, as should be expected. This is another evidence of the superior performance of MR BW-CC-F12 approach.

**Table 2**

Comparison of the reference determinants weights for the H4 model at selected geometries using conventional and explicitly correlated MR BW-CCSD.

| $\theta/\pi$ | Reference configuration |        |        |        |        |        |
|--------------|-------------------------|--------|--------|--------|--------|--------|
|              | I                       |        | II     |        | II     |        |
|              | conv.                   | R12    | F12    | F12    | F12    | F12    |
| 9s           |                         |        |        |        |        |        |
| 0.00         | 0.5695                  | 0.4304 | 0.6443 | 0.3556 | 0.5655 | 0.4345 |
| 0.02         | 0.8424                  | 0.1575 | 0.8841 | 0.1158 | 0.8514 | 0.1486 |
| 0.10         | 0.9859                  | 0.0140 | 0.9891 | 0.0108 | 0.9878 | 0.0122 |
| 0.50         | 0.9986                  | 0.0013 | 0.9988 | 0.0011 | 0.9988 | 0.0012 |
| 9s6p         |                         |        |        |        |        |        |
| 0.00         | 0.5752                  | 0.4247 | 0.5859 | 0.4140 | 0.5764 | 0.4236 |
| 0.02         | 0.8781                  | 0.1218 | 0.8836 | 0.1163 | 0.8794 | 0.1206 |
| 0.10         | 0.9918                  | 0.0081 | 0.9921 | 0.0078 | 0.9920 | 0.0080 |
| 0.50         | 0.9992                  | 0.0007 | 0.9992 | 0.0007 | 0.9992 | 0.0008 |
| 9s6p4d       |                         |        |        |        |        |        |
| 0.00         | 0.5766                  | 0.4233 | 0.5799 | 0.4200 | 0.5771 | 0.4229 |
| 0.02         | 0.8792                  | 0.1207 | 0.8808 | 0.1191 | 0.8797 | 0.1203 |
| 0.10         | 0.9931                  | 0.0068 | 0.9931 | 0.0068 | 0.9932 | 0.0068 |
| 0.50         | 0.9996                  | 0.0003 | 0.9996 | 0.0003 | 0.9996 | 0.0004 |
| 9s6p4d3f     |                         |        |        |        |        |        |
| 0.00         | 0.5767                  | 0.4232 | 0.5784 | 0.4215 | 0.5770 | 0.4230 |
| 0.02         | 0.8793                  | 0.1206 | 0.8802 | 0.1197 | 0.8797 | 0.1203 |
| 0.10         | 0.9932                  | 0.0067 | 0.9932 | 0.0067 | 0.9933 | 0.0067 |
| 0.50         | 0.9996                  | 0.0003 | 0.9996 | 0.0003 | 0.9996 | 0.0004 |

**Table 3**

Convergence of the total energies towards the basis set limit for the F<sub>2</sub> molecule at selected interatomic distances (R) using conventional and explicitly correlated MR BW-CCSD approaches. Energies are in E<sub>h</sub>.

| R                     | 19s14p8d6f  | 19s14p8d6f4g | 19s14p8d6f4g3h |
|-----------------------|-------------|--------------|----------------|
| <i>MR BW-CCSD</i>     |             |              |                |
| 2.0                   | −199.179416 | −199.198648  | −199.204059    |
| 2.6                   | −199.342271 | −199.360243  | −199.365217    |
| 3.2                   | −199.318380 | −199.335420  | −199.340152    |
| 3.8                   | −199.289414 | −199.305958  | −199.310515    |
| 5.2                   | −199.271889 | −199.288157  | −199.292634    |
| <i>MR BW-CCSD-F12</i> |             |              |                |
| 2.0                   | −199.215346 | −199.215126  | −199.214825    |
| 2.6                   | −199.375208 | −199.375361  | −199.375367    |
| 3.2                   | −199.349697 | −199.350002  | −199.349982    |
| 3.8                   | −199.319656 | −199.320148  | −199.320182    |
| 5.2                   | −199.301628 | −199.302200  | −199.302241    |

**Table 4**

Selected spectroscopic parameters for F<sub>2</sub> molecule calculated from conventional and explicitly correlated MR BW-CCSD energies.

| Basis set           | R <sub>e</sub> /Å | E <sub>min</sub> /E <sub>h</sub> | w <sub>e</sub> /cm <sup>−1</sup> | w <sub>e</sub> x <sub>e</sub> /cm <sup>−1</sup> |
|---------------------|-------------------|----------------------------------|----------------------------------|---|
| <i>Conventional</i> |                   |                                  |                                  |   |
| 19s14p8d6f          | 1.4001            | −199.342761                      | 936.7                            | 11.10   |
| 19s14p8d6f4g        | 1.3963            | −199.360837                      | 951.5                            | 11.07   |
| 19s14p8d6f4g3h      | 1.3952            | −199.365966                      | 958.2                            | 11.06   |
| <i>F12</i>          |                   |                                  |                                  |   |
| 19s14p8d6f          | 1.3949            | −199.375676                      | 953.5                            | 10.70   |
| 19s14p8d6f4g        | 1.3950            | −199.375903                      | 954.4                            | 10.70   |
| 19s14p8d6f4g3h      | 1.3950            | −199.375850                      | 954.0                            | 10.70   |

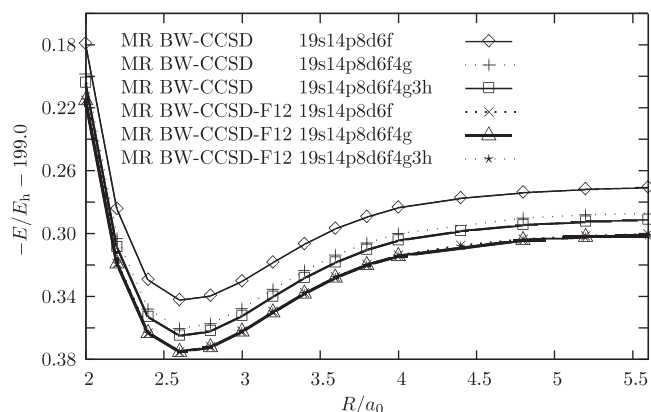
These have been obtained from the Morse potential fitted around the minimum in the range 2.2–3.4 Bohr. For us, most important is the fact that introducing F12 with the MR approach did not cause numerical imbalance, and one can really achieve the basis set limit similarly as with the SR approach. It is irrelevant to compare with experiment because the MR CCSD is still far from the full CI limit. For example, mere introduction of triple excitations changes (lowers) the harmonic frequencies by about 10% [50].

As far as convergence of cluster equations concerned, no serious problems were encountered and the MR BW-CC-F12 performance was on a par with its conventional counterpart. In all cases, no more than 26 iterations were required to converge the amplitudes to 10<sup>−7</sup>.

The *a posteriori* size-extensivity correction did not yield smooth enough potential energy curves due to the inherent intruder state problems, which are particularly strong due to use of highly saturated basis sets. We admit that MR BW-CC results without size-extensivity correction are of limited relevance; however, the aim of this study was the verification of the basis set convergence within MR CC framework and the MR BW-CC F12 should serve here as the first step in the development of MkCC F12.

## 5. Conclusions

Explicitly correlated MR BW-CCSD-F12 method with the correlation factor based on the Slater type geminals has been developed and implemented. The performance of the method was tested on the H4 model and dissociation curve of the fluorine molecule. As expected for both systems, the absolute energies converge much faster to the basis set limit values than using the conventional approach. It was also found that the use of STG's significantly improves the performance in 9s basis set in H4 system, compared with calculations with linear correlation factor. Furthermore, the

**Figure 2.** Potential energy curves for F<sub>2</sub> molecule.

## 4.2. Fluorine molecule

The calculated dissociation curves are presented in Figure 2 and for selected geometries also in Table 3. Since our aim in this Letter is to introduce the explicit correlation into the MR approaches, we shall focus merely on these effects. Other aspects of the MR BW-CC approach in comparison to alternative MR CC theories have been discussed elsewhere [31,42].

As expected, our conventional results show a very strong basis set dependence of the total energies. Energies calculated in the *spdf* basis set are 16–19 mE<sub>h</sub> above their *spdfg* counterparts, whereas the extension of the basis set to *spdfg* and *spdfgh* lowers the energies by additional 4.5–5 mE<sub>h</sub>.

In contrast, the basis set convergence is dramatically improved when MR BW-CCSD-F12 method is used. Energies calculated in the three basis sets fall within an interval of 1 mE<sub>h</sub> for all points along the dissociation curve. The difference between the *spdf* and *spdfg* energies range from −450 to 650 μE<sub>h</sub>, whereas the differences between *spdfg* and *spdfgh* energies are between −30 and 40 μE<sub>h</sub>.

Improvement in the basis set convergence of the absolute energies is reflected in Table 4, where we display the calculated equilibrium distances, harmonic frequencies and the anharmonicities.

MR BW-CC-F12 approach is numerically stable for fluorine at large intermolecular distance. The most important message is that introducing the electron correlation explicitly via the F12 approach into the multireference CC wave function when the F12 treatment is applied separately to each of the references did not cause numerical imbalance and can be effectively used in order to achieve the basis set limit values.

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