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Explicitly correlated multireference configuration interaction: MRCI-F12

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An internally contracted multireference configuration interaction is developed which employs wave functions that explicitly depend on the electron–electron distance (MRCI-F12). This MRCI-F12 method has the same applicability as the MRCI method, while having much improved basis-set convergence with little extra computational cost. The F12b approximation is used to arrive at a computationally efficient implementation. The MRCI-F12 method is applied to the singlet–triplet separation of methylene, the dissociation energy of ozone, properties of diatomic molecules, and the reaction barrier and exothermicity of the $F + H_2$ reaction. These examples demonstrate that already with basis sets of moderate size the method provides near complete basis set MRCI accuracy, and hence quantitative agreement with the experimental data. As a side product, we have also implemented the explicitly correlated multireference averaged coupled pair functional method (MRACPF-F12).

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I. INTRODUCTION

The internally contracted multireference configuration interaction method^{1,2} (MRCI) is a powerful tool for highly accurate calculations of global potential energy surfaces, electronically excited states, and many other systems where near degeneracy situations occur and where single-reference electronic structure methods such as coupled-cluster (CC) theories are not applicable. However, the MRCI energies are slowly convergent with the orbital basis set size, a problem that is shared with all other conventional wave function methods. Thus, one needs to use very large basis set for predictive computations,³ and this can make accurate calculations very expensive.

The slow convergence of conventional correlation energy calculations is caused by deficiencies in the used N -electron basis sets: Linear combinations of Slater determinants are unable to properly represent the wave function cusp around the electron–electron coalescence $r_{ij} = 0$, where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between two electrons. In order to ameliorate this problem, in a seminal paper in 1985 Kutzelnigg proposed to augment the conventional wave function expansion by terms that are explicitly dependent on the electron–electron distances r_{ij} .⁴ Originally, only terms linear in r_{12} were included, since this is sufficient to describe the wave function cusp and its vicinity for small r_{12} (R12-methods). However, the linear r_{12} terms are unphysical for large r_{12} , and this leads to numerical problems and a loss of accuracy, in particular for larger molecules. This problem was first realized by Ten-no,⁵ who proposed to use a short-range Slater-type geminal function $F_{12}(r_{12}) = -\gamma^{-1}e^{-\gamma r_{12}}$. The use of this function in the so-called F12-methods leads to a dramatic improvement of the accuracy and numerical stability. Meanwhile, extensive benchmark calculations for numerous properties have shown that F12-methods yield results with near complete basis set (CBS) limit accuracy already with

triple- ζ basis sets.^{6–13} In order to achieve a comparable accuracy with conventional methods, at least quintuple- ζ basis sets are necessary. This means that F12-methods reduce the computational cost for calculations of similar quality typically by 2 orders of magnitude.

A fundamental problem of explicitly correlated wave function methods was that a straightforward derivation of the theory leads to three-electron and four-electron integrals. Since these integrals are extremely numerous and expensive, their exact calculation is only possible for very small molecules and basis sets. This has hampered the development and application of explicitly correlated methods for a long time. A solution was first proposed by Kutzelnigg and Klopper.^{14,15} By insertion of resolutions of the identity (RI), the many-electron integrals can be approximated by sums of products of two-electron integrals. Several important techniques were developed in the last decade that improved the accuracy and efficiency of these approximations. These include the use of auxiliary basis sets for the RI,¹⁶ the construction of a complementary auxiliary orbital basis (CABS) from the union of the orbital and auxiliary basis sets,¹⁷ and density fitting approximations for efficient F12 integral evaluations.^{18,19} The computation of the two-electron integrals over the F_{12} correlation factor can be done analytically,^{5,20,21} but in most current implementations the Slater geminal is fitted to a linear combination of Gaussian geminals in order to simplify the integral evaluation. For more details and references the reader is referred to the papers describing the various variants of MP2-F12 theory,^{16,22–25} or to recent reviews.^{26,27}

A lot of recent works have been focused on approximate explicitly correlated CC models, such as CCSD(T)-F12 x ($x = a, b$),^{9,28} CCSD(T)_{F12},^{29–31} and CCSD(T)(F12*).¹³ These approximations to the full CC-F12 method^{32–34} provide near CBS CCSD(T) accuracy with little additional computational cost as compared to conventional CCSD(T) calculations with the same basis set. The approximate models are vital for practical purposes since the full CC-F12 method suffers from numerical instabilities and high

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computational cost. There have also been extensions of the CC-F12 theory to local CC-F12 methods,^{35–37} higher order CC methods,^{38,39} response properties,^{40,41} and unconventional triples excitations.⁴² However, most of the work was restricted to single-reference correlation models.

The first explicitly correlated MRCI method has been developed by Gdanitz quite long time ago,^{43,44} using a linear R12 correlation factor. In his method R12 excitations were generated from uncontracted reference configurations. Only recently, the F12 theory has been further explored.^{45–48} Ten-no⁴⁵ has introduced an internally contracted geminal excitation operator (combined with uncontracted multireference Møller–Plesset perturbation theory⁴⁹). An *a posteriori* F12 approach for arbitrary correlation models using the reduced density matrices (RDM) of the underlying models has been subsequently proposed by Torheyden and Valeev.⁴⁶ There has been also an attempt to combine the F12 theory with complete active space self-consistent field (CASSCF) by Varganov and Martínez.⁴⁷

In a preceding Communication,⁴⁸ we have developed an efficient and accurate internally contracted explicitly correlated multireference perturbation method (CASPT2-F12). In this work, we extend this formalism to MRCI-F12 and multireference averaged coupled pair functional (MRACPF-F12).⁵⁰ We present preliminary applications for the singlet–triplet separation of methylene, the dissociation energy of ozone, the equilibrium distances, harmonic frequencies, and dissociation energies of diatomic molecules, and the reaction barrier and exothermicity of $F + H_2$ reaction. An extension to excited-state calculations will be reported elsewhere.

II. THEORY

This section is organized as follows: In Sec. II A we will briefly recapitulate the internally contracted MRCI method of Werner and Knowles,¹ on which the current work is based. In Sec. II B we will describe the ansatz for the explicitly correlated MRCI-F12 wave function. Based on this, the expressions for the energy expectation value and the resulting amplitude equations will be derived in Secs. II C and II D. Finally, in Secs. II E and II F approximations that significantly reduce the computational cost are introduced. These are similar to the (F12*) and F12b approximations in CC-F12 theory.

Explicitly correlated calculations require two Gaussian type (GTO) basis sets: (i) the orbital basis set (OBS), as used in any conventional calculation; and (ii) an auxiliary (RI) basis used to approximate the resolution of the identity. In the following, we will use several orthonormal orbital spaces: the orbitals that are occupied in any of the reference configurations are denoted occupied or internal. The remaining orbitals in the orbital basis are denoted external or virtual. Orbitals outside the OBS are denoted complementary (CO) orbitals. A finite subset of this infinite set is represented in the union of the OBS and the RI and is denoted complementary auxiliary orbital basis set (CABS). The index notation used for these spaces is summarized in Table I. Repeated indices which do not occur on the left hand side of the equations imply summation over them unless otherwise stated.

TABLE I. Orbital spaces and associated indices used in this work.

Space	Abbreviation	Indices
<i>Finite spaces:</i>		
Occupied orbitals (including core)		o
Correlated (valence) orbitals		i, j, k, l, m, n
External orbitals in the OBS		a, b, c, d
All orbitals in the OBS		r, s, t, u
Complementary auxiliary orbitals	CABS	x, y
<i>Complete (infinite) spaces:</i>		
Complementary orbitals	CO	x', y', z'
Any external orbitals		α, β
Any orbitals		$\kappa, \lambda, \mu, \nu$

A. Internally contracted MRCI

The (partially) contracted MRCI wave function used in this work is defined as

$$\begin{aligned}
 |\Psi_{\text{MRCI}}\rangle &= \sum_I t_I |I\rangle + \sum_S \sum_a t_a^S |S^a\rangle \\
 &+ \sum_{p=\pm 1} \sum_{i \geq j} \sum_{ab} T_{ab}^{ijp} |\Phi_{ijp}^{ab}\rangle \\
 &\equiv t_I |I\rangle + t_a^S |S^a\rangle + T_{ab}^{ijp} |\Phi_{ijp}^{ab}\rangle, \quad (1)
 \end{aligned}$$

where $|I\rangle$ and $|S^a\rangle$ are internal and singly external configuration state functions (CSFs), respectively. The internal configuration space $\{I\}$ includes all configurations built from occupied orbitals which can be created by applying double excitations to the individual reference configurations. All possible spin couplings are taken into account. Similarly, the space $\{S\}$ includes all $N - 1$ electron functions generated by two orbital annihilations and one internal orbital creation from any reference configuration. Thus, this class includes true single excitations as well as semi-internal double excitations (i.e., double excitations with one excitation into active orbitals and one into virtual orbitals). For more details see Refs. 1 and 2.

The configuration space with two electrons in the external orbital subspace is spanned by internally contracted configurations,¹ which are generated by applying two spin-summed one-electron excitation operators \hat{E}_i^a ,

$$\hat{E}_i^a = \sum_{\rho=\{\alpha, \beta\}} \eta_{a\rho}^\dagger \eta_{i\rho}, \quad (2)$$

to an arbitrary fixed reference wave function $|0\rangle$

$$|\Psi_{\text{ref}}\rangle \equiv |0\rangle = t_R^{(0)} |R\rangle. \quad (3)$$

The reference configurations are a subset of the internal configurations $\{R\} \subset \{I\}$. Note that their coefficients t_R are fully relaxed in the MRCI wave function, but kept fixed to their original values in the definition of the internally contracted double excitations. The reference coefficients $t_R^{(0)}$ as well as the orbitals are optimized in a preceding multiconfiguration self-consistent field (MCSCF) or CASSCF calculation.

The spin-coupled contracted doubly external configurations are defined as

$$|\Phi_{ijp}^{ab}\rangle = \frac{1}{2} (\hat{E}_i^a \hat{E}_j^b + p \hat{E}_i^b \hat{E}_j^a) |0\rangle \quad (i \geq j). \quad (4)$$

The parity $p = \pm 1$ corresponds to singlet and triplet coupling of the external electrons, respectively. In the remainder of this paper, implied summations involving singlet or triplet pair indices ijp or klq are restricted as shown in Eq. (1). For a unique set of configurations the restriction $a \geq b$ would be sufficient, but in order to obtain an efficient formulation in terms of matrix multiplications it is convenient to use all a, b . This implies for the amplitudes $T_{ab}^{ijp} = pT_{ba}^{ijp}$.

Normally, the internal contraction causes very small errors, except in cases when the character of the reference function very strongly changes in the correlation calculation. This can happen in the vicinity of avoided crossings or conical intersections. In such cases it is necessary to use the union of internally contracted configurations generated from two or more reference states. For details and extensions to electronically excited states see Ref. 51.

The advantage of using internally contracted configurations is that their number is independent of the number of reference configurations. This eliminates the most severe bottleneck of the standard uncontracted MRCI methods, in which all double excitations relative to all individual reference configurations are taken into account. However, the contracted configurations have a complicated structure and are neither normalized nor orthogonal

$$\langle \Phi_{ijp}^{ab} | \Phi_{klq}^{cd} \rangle = \frac{1}{2} (\delta_{ac} \delta_{bd} + p \delta_{ad} \delta_{bc}) S_{ijp,klq}, \quad (5)$$

$$S_{ijp,klq} = \delta_{pq} \langle 0 | \hat{E}_{kl}^{ij} + p \hat{E}_{lk}^{ij} | 0 \rangle. \quad (6)$$

Orthogonal configurations $|\Phi_{Dp}^{ab}\rangle$ can be obtained by symmetrical orthogonalization

$$|\Phi_{Dp}^{ab}\rangle = \sum_{i \geq j} U_{Dp,ijp} |\Phi_{ijp}^{ab}\rangle \quad (7)$$

where $\mathbf{U} = \mathbf{S}^{-1/2}$. Here the two- and three-electron excitation operators are defined as

$$\hat{E}_{kl}^{ij} = \sum_{\rho=\alpha,\beta} \eta_{i\rho}^\dagger \hat{E}_l^j \eta_{k\rho}, \quad (8)$$

$$\hat{E}_{lmn}^{ijk} = \sum_{\rho=\alpha,\beta} \eta_{i\rho}^\dagger \hat{E}_{mn}^{jk} \eta_{l\rho}, \quad (9)$$

and furthermore the spin-coupled two-electron excitation operator as

$$\hat{E}_{ijp}^{\kappa\lambda} = \frac{1}{2} (\hat{E}_{ij}^{\kappa\lambda} + p \hat{E}_{ji}^{\kappa\lambda}). \quad (10)$$

In principle, it is also possible to define internally contracted internal and singly external configurations. However, their orthogonalization would in general require the diagonalization of the third and fourth-order density matrices (3RDM and 4RDM), respectively, which might cause a bottleneck in calculations for larger molecules. Moreover, fifth or (for non-CAS reference functions) sixth-order density matrices would be needed to compute the Hamiltonian matrix elements. In the current work we therefore leave the internal ($|I\rangle$) and singly external ($|S^a\rangle$) CSFs uncontracted, as originally proposed by Werner and Knowles.¹ Another way to avoid higher order

RDMs is to classify the internal and semi-internal configurations according to the number of holes in the closed-shell (inactive) orbital subspace of the reference function. It is then possible to contract all internal and semi-internal configurations that depend at most on two active orbital labels, so that at most the 2RDM is needed for the overlap and the 4RDM for the Hamiltonian (in this case the RDMs only depend on the active orbital labels). This scheme, which can speed up calculations by one order of magnitude or more, has first been applied by Celani and Werner⁵² for CASPT2, and has recently been implemented for MRCI in our laboratory.⁵³ Its extension to MRCI-F12 will be considered in future work.

B. Ansatz for MRCI-F12

We employ a similar ansatz for the MRCI-F12 wave function as we used earlier for CASPT2-F12. The MRCI wave function Eq. (1) is augmented by internally contracted geminal terms

$$\Psi_{\text{MRCI-F12}} = \Psi_{\text{MRCI}} + t_{\text{F12}} \hat{Q} \hat{F} |0\rangle, \quad (11)$$

where the geminal excitation operator \hat{F} is defined as

$$\hat{F} = \mathcal{F}_{\alpha\beta}^{ijp} \hat{E}_{ijp}^{\alpha\beta} + \mathcal{F}_{\alpha\beta}^{ijk} \hat{E}_{ijk}^{\alpha\beta}. \quad (12)$$

$\mathcal{F}_{\alpha\beta}^{ijp}$ are two-electron integrals over the Slater-type geminal function⁵ multiplied by fixed amplitudes t_{ijp} ,

$$\mathcal{F}_{\alpha\beta}^{ijp} = \frac{1}{2} t_{ijp} (F_{\alpha\beta}^{ij} + p F_{\alpha\beta}^{ji}), \quad (13)$$

$$\begin{aligned} F_{\alpha\beta}^{ij} &= \langle ij | F_{12} | \alpha\beta \rangle \\ &= \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_\alpha(\mathbf{r}_1) \phi_\beta(\mathbf{r}_2) F_{12} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2), \end{aligned} \quad (14)$$

$$t_{ijp} = \begin{cases} \frac{1}{2} (1 + \delta_{ij})^{-1} & (p = +1) \\ \frac{1}{4} (1 - \delta_{ij}) & (p = -1). \end{cases} \quad (15)$$

The coefficient t_{F12} in Eq. (11) can be chosen in two ways: In intermediate normalization ($\langle \Psi | 0 \rangle = 1$) the value $t_{\text{F12}} = 1$ satisfies the first-order cusp conditions [fixed amplitude ansatz (FIX), or SP ansatz].⁵⁴ Alternatively, one can determine the value of t_{F12} variationally; in this case the intermediate normalization condition is not required (scaled fixed amplitudes, or SFIX). We have implemented and tested both options. The FIX ansatz is size consistent (if combined with a size consistent conventional wave function) and orbital invariant. The SFIX ansatz is still orbital invariant and size extensive, but not size consistent. In the current context, this is not an important issue, since the MRCI method is not size consistent anyway. One could also optimize the amplitudes t_{ijp} fully (using $t_{\text{F12}} = 1$), which would correspond to the diagonal (D) ansatz in MP2-F12.²³ Since the diagonal ansatz is not orbital invariant, and size consistent only with localized orbitals, we do not further consider it in this work. Note that our definition of $\mathcal{F}_{\alpha\beta}^{ijp}$ differs from its single-reference analog by a factor of 1/2 so that

$$\mathcal{F}_{\alpha\beta}^{ijp} \hat{E}_{ijp}^{\alpha\beta} = \frac{1}{2} \mathcal{F}_{\alpha\beta}^{ij} \hat{E}_{ij}^{\alpha\beta}, \quad (16)$$

which is consistent with the rest of the equations. The spin uncoupled effective geminal amplitudes for singly external configurations are

$$\begin{aligned} \mathcal{F}_{\alpha k}^{ij} &= (\mathcal{F}_{\alpha k}^{ij,1} + \mathcal{F}_{\alpha k}^{ij,-1})(1 + \delta_{ij}) \\ &= \langle \alpha k | F_{12} | mn \rangle t_{mn}^{ij}, \end{aligned} \quad (17)$$

$$t_{mn}^{ij} = \frac{3}{8} \delta_{im} \delta_{jn} + \frac{1}{8} \delta_{in} \delta_{jm}. \quad (18)$$

In our program the F_{12} correlation factor is approximated by a fit to a linear combination of six Gaussian geminals

$$F_{12} = -\gamma^{-1} \exp(-\gamma r_{12}) \approx \sum_{i=1}^6 c_i \exp(-\alpha_i r_{12}^2). \quad (19)$$

The coefficients c_i and exponents α_i are determined by a weighted fit, as described in Ref. 23. Throughout this work, the length parameter γ is set to 1.0 a_0^{-1} .

The strong-orthogonality projector \hat{Q} is required to keep the geminal terms orthogonal to the conventional wave function. It can be expressed as

$$\hat{Q} = \hat{Q}_{\alpha\beta,ij} - \hat{Q}_{ab,ij} + \hat{Q}_S \equiv \hat{Q}_P + \hat{Q}_S, \quad (20)$$

in which $\hat{Q}_{\alpha\beta,ij}$ projects onto the infinite space spanned by all internally contracted double excitations $|\Phi_{ijp}^{\alpha\beta}\rangle$ and $\hat{Q}_{ab,ij}$ removes the configuration space that is already present in the conventional MRCI. **The doubly external contribution of $\hat{Q}_P \hat{F}|0\rangle$ can be rewritten in terms of internally contracted configurations as**

$$\hat{Q}_P \hat{F}|0\rangle = \Phi_{ijp}^{x'y'} \mathcal{F}_{x'y'}^{ijp} + 2\Phi_{ijp}^{x'a} \mathcal{F}_{x'a}^{ijp}, \quad (21)$$

where x', y' label the complete complementary orbital space. The summations over the complete space x', y' can be eliminated and replaced by analytical integrals in the most important terms. In terms where this is not possible, the complete CO space is approximated by the finite CABS space, i.e. the indices x', y' are replaced by x, y .

The singles projector \hat{Q}_S is defined as

$$\hat{Q}_S = |S^x\rangle \langle S^x| [1 - |\Phi_i^x\rangle \langle \Phi_j^x| \boldsymbol{\gamma}^{-1}]_j, \quad (22)$$

where $\gamma_{ij} = \langle 0 | \hat{E}_{ij}^i | 0 \rangle$ is the 1-RDM and $\boldsymbol{\gamma}^{-1}$ is its inverse. Its purpose of \hat{Q}_S is twofold: $|S^x\rangle \langle S^x|$ projects from the space of internally contracted geminal excitations to the uncontracted space of CSFs with one electron in the CABS space. This makes it possible to use the same coupling coefficients as in the conventional MRCI. In contrast to the doubly external contributions, it will for these terms not be possible to remove summations over the complete space x' , and therefore we use the finite CABS space from the beginning. As will be shown later, the energy contributions of these configurations converge quickly with basis set size, and the restriction to the CABS space is not a severe approximation. This is due to the fact that for atoms the semi-internal energy contribution saturates with RI functions of angular momentum quantum numbers up to $3l_{\text{occ}}$ (l_{occ} is the maximum angular momentum

TABLE II. Definition of the coupling coefficients used in the MRCI-F12 formalism. All quantities are independent of the external indices a, b , and there is no implied summation over repeated indices within the brackets. The coupling coefficients are the same as used in the conventional MRCI.

pair-pair:	$\alpha_{mn}(ijp, klq) = \delta_{pq} \langle 0 \hat{E}_{klm}^{ijm} + p \hat{E}_{lkn}^{ijm} 0 \rangle$ $\beta_{mn}(ijp, klq) = \langle 0 \hat{E}_{mlk}^{ijn} + p \hat{E}_{lmk}^{ijn} + q \hat{E}_{mkl}^{ijn} + pq \hat{E}_{kml}^{ijn} 0 \rangle$ $\gamma(ijp, klq) = \delta_{pq} f_{mn} \langle 0 \hat{E}_{klm}^{ijm} + p \hat{E}_{lkn}^{ijm} 0 \rangle$
single-single:	$\alpha_{mn}(S, T) = \langle S^a \hat{E}_n^m T^a \rangle$ $\beta_{mn}(S, T) = \langle S^a \hat{E}_{mb}^a T^b \rangle$ $\gamma(S, T) = f_{mn} \langle S^a \hat{E}_n^m T^a \rangle$
pair-single:	$\sigma_k(ijp, S) = \langle \Phi_{ijp}^{ab} \hat{E}_k^b S^a \rangle$ $\alpha_{kmn}(ijp, S) = \langle \Phi_{ijp}^{ab} \hat{E}_{kn}^{bm} S^a \rangle$
pair-internal:	$\sigma_{mn}(ijp, I) = \frac{1}{2} \langle 0 \hat{E}_{mn}^{ij} + p \hat{E}_{nm}^{ij} I \rangle$
single-internal:	$\sigma_k(S, I) = \langle S^a \hat{E}_k^a I \rangle$ $\alpha_{kmn}(S, I) = \langle S^a \hat{E}_{kn}^{am} I \rangle$
pair-ref.:	$\sigma_{mn}(ijp, 0) = \frac{1}{2} \langle 0 \hat{E}_{mn}^{ij} + p \hat{E}_{nm}^{ij} 0 \rangle$
single-ref.:	$\sigma_k(S, 0) = \langle S^a \hat{E}_k^a 0 \rangle$ $\alpha_{kmn}(S, 0) = \langle S^a \hat{E}_{kn}^{am} 0 \rangle$

quantum number in the occupied space),⁴⁵ and RI basis sets contain such higher angular momentum functions.

The projector in brackets removes the contributions of internally contracted single excitations $|\Phi_i^x\rangle = \hat{E}_i^x | 0 \rangle$, which cannot easily be separated from the space of semi-external double excitations $|\Phi_{ij}^{xk}\rangle = \hat{E}_{ij}^{xk} | 0 \rangle$.⁴⁶ The inverse of the 1RDM occurs because the internally contracted singles are nonorthogonal

$$\langle \Phi_i^x | \Phi_j^y \rangle = \delta_{xy} \gamma_{ij}. \quad (23)$$

The singles geminal part can now be written as

$$\hat{Q}_S \hat{F}|0\rangle = |S^x\rangle \mathcal{F}_x^S \quad (24)$$

with

$$\mathcal{F}_x^S = (\delta_{ST} - D_m^S D_m^T) \alpha_{ikj}(T, 0) \mathcal{F}_{xk}^{ij}, \quad (25)$$

$$D_m^S = \sigma_n(S, 0) (\boldsymbol{\gamma}^{-1/2})_{mn}. \quad (26)$$

The coupling coefficients $\sigma_i(S, 0)$ and $\alpha_{ikj}(S, 0)$ are defined in Table II. We note that in our previous communication on CASPT2-F12 (Ref. 48) the singles were not projected out exactly but only approximately by using a normal ordered excitation operator $\{\hat{E}_{ij}^{\alpha k}\} = \hat{E}_i^{\alpha k} - \hat{E}_i^{\alpha} \gamma_{kj} + \frac{1}{2} \gamma_{ki} \hat{E}_j^{\alpha}$.⁵⁵ As is shown in the supplementary material,⁵⁶ the differences between both approaches are only significant for small (double- ζ) basis sets.

In summary, the geminal parts as written in Eqs. (21) and (24) have the same form as the corresponding singles and doubles contributions in the standard MRCI wave function, except that the CO or CABS orbitals are used and the amplitudes T_{ab}^{ijp} and t_a^S are replaced by the fixed effective geminal amplitudes $\mathcal{F}_{x'y'}^{ijp}$, $\mathcal{F}_{x'a}^{ijp}$, and \mathcal{F}_x^S . Since all density matrices and coupling coefficients are independent of the virtual orbitals, they are the same for the conventional and explicitly correlated terms, and thus the contributions of the geminal

terms to the residual expressions are completely analogous to the conventional ones. The only exceptions are the terms in which the summations over the complete CA space are replaced by analytical integrals. This will be discussed in Secs. II C and II D.

C. The energy expectation value and amplitude equations

The MRCI-F12 energy expectation value can be written as

$$E = \frac{\langle \Psi_{\text{MRCI}} | \hat{H} | \Psi_{\text{MRCI}} \rangle + 2A t_{\text{F12}} + B t_{\text{F12}}^2}{\langle \Psi_{\text{MRCI}} | \Psi_{\text{MRCI}} \rangle + X t_{\text{F12}}^2}, \quad (27)$$

where

$$A = \langle \Psi_{\text{MRCI}} | \hat{H} \hat{Q} \hat{F} | 0 \rangle, \quad (28)$$

$$B = \langle 0 | \hat{F}^\dagger \hat{Q} \hat{H} \hat{Q} \hat{F} | 0 \rangle, \quad (29)$$

$$X = \langle 0 | \hat{F}^\dagger \hat{Q} \hat{F} | 0 \rangle. \quad (30)$$

The pure MRCI contributions are of course the same as in the conventional case described in Ref. 1 and need no further discussion. Defining

$$A_{ab}^{Dp} = \langle \Phi_{Dp}^{ab} | \hat{H} \hat{Q} \hat{F} | 0 \rangle, \quad (31)$$

$$A_a^S = \langle \Phi_a^S | \hat{H} \hat{Q} \hat{F} | 0 \rangle, \quad (32)$$

$$A_I = \langle I | \hat{H} \hat{Q} \hat{F} | 0 \rangle, \quad (33)$$

one obtains

$$A = t_I A_I + t_a^S A_a^S + T_{ab}^{Dp} A_{ab}^{Dp}. \quad (34)$$

Explicit expressions for the quantities A_I , A_a^S , A_{ab}^{Dp} , B , and X will be presented in Sec. II D.

The amplitude equations for the FIX ansatz are obtained by differentiation of the Lagrangian $L = E + 2\lambda(\langle 0 | \Psi \rangle - 1)$ with respect to the amplitudes t_I , t_a^S , and T_{ab}^{Dp} . The second term takes care of the intermediate normalization condition $\langle 0 | \Psi \rangle = 1$, which must be implied for the FIX ansatz. In this case the coefficient $t_{\text{F12}} = 1$ is kept fixed. This yields

$$\langle \Phi_{Dp}^{ab} | \hat{H} | \Psi_{\text{MRCI}} \rangle + A_{ab}^{Dp} t_{\text{F12}} - E T_{ab}^{Dp} = 0, \quad (35)$$

$$\langle S^a | \hat{H} | \Psi_{\text{MRCI}} \rangle + A_a^S t_{\text{F12}} - E t_a^S = 0, \quad (36)$$

$$\langle I | \hat{H} | \Psi_{\text{MRCI}} \rangle + A_I t_{\text{F12}} - \lambda t_I^{(0)} - E t_I = 0, \quad (37)$$

in which E is the MRCI-F12 expectation value as given above. These equations can be solved by subspace residual minimization of Eqs. (35)–(37) with iterative updates. Explicit expressions for the matrix elements $\langle \Phi_{Dp}^{ab} | \hat{H} | \Psi_{\text{MRCI}} \rangle$, $\langle S^a | \hat{H} | \Psi_{\text{MRCI}} \rangle$, and $\langle I | \hat{H} | \Psi_{\text{MRCI}} \rangle$ can be found in Ref. 1.

For the SFIX ansatz, in which the coefficient t_{F12} is optimized, we do not need to impose intermediate normalization (i.e., we set $\lambda = 0$), but instead the derivative of the Lagrangian with respect to the scaling factor t_{F12} must vanish at convergence

$$A + (B - EX)_{\text{F12}} = 0. \quad (38)$$

TABLE III. Definition of the integrals used in the F12 formalism. The matrices $V_{\alpha\beta}^{ij}$, $B_{ij,kl}$ and $X_{ij,kl}$ are the same as in the closed-shell single-reference MP2-F12 theory. $B_{ij,kl}$ is evaluated using the so called approximation C (Refs. 22 and 23). The working equations can be found in Ref. 23.

$$\begin{aligned} J_{\kappa\lambda}^{kl} &= \langle \kappa\kappa | r_{12}^{-1} | \lambda\lambda \rangle \\ K_{\kappa\lambda}^{kl} &= \langle \kappa\lambda | r_{12}^{-1} | kl \rangle \\ F_{\kappa\lambda}^{kl} &= \langle \kappa\lambda | r_{12}^{-1} F_{12} | kl \rangle \\ W_{\kappa\lambda}^{kl} &= \langle \kappa\lambda | r_{12}^{-1} F_{12}^2 | kl \rangle \\ F_{ij,kl}^2 &= \langle ij | F_{12}^2 | kl \rangle \\ V_{\kappa\lambda}^{ij} &= \langle \kappa\lambda | r_{12}^{-1} \hat{Q}_{12} F_{12} | ij \rangle = W_{\kappa\lambda}^{ij} - K_{\kappa\lambda}^{rs} F_{rs}^{ij} - K_{\kappa\lambda}^{ox} F_{ox}^{ij} - K_{\kappa\lambda}^{xo} F_{xo}^{ij} \\ X_{ij,kl} &= \langle ij | F_{12} \hat{Q}_{12} F_{12} | kl \rangle = F_{ij,kl}^2 - F_{rs}^{ij} F_{rs}^{kl} - F_{ox}^{ij} F_{ox}^{kl} - F_{xo}^{ij} F_{xo}^{kl} \\ B_{ij,kl} &= \langle ij | F_{12} \hat{Q}_{12} (\hat{f}_1 + \hat{f}_2) \hat{Q}_{12} F_{12} | kl \rangle \\ \mathcal{F}_{\kappa\lambda}^{ijp} &= \frac{1}{2} t_{ijp} (F_{\kappa\lambda}^{ij} + p F_{\kappa\lambda}^{ji}) \\ \mathcal{V}_{\kappa\lambda}^{ijp} &= \frac{1}{2} t_{ijp} (V_{\kappa\lambda}^{ij} + p V_{\kappa\lambda}^{ji}) \\ \mathcal{W}_{\kappa\lambda}^{ijp} &= \frac{1}{2} t_{ijp} (W_{\kappa\lambda}^{ij} + p W_{\kappa\lambda}^{ji}) \\ \mathcal{X}_{ijp,klq} &= \frac{1}{2} \delta_{pq} t_{ijp} t_{klq} (X_{ij,kl} + p X_{ji,kl}) \\ \mathcal{B}_{ijp,klq} &= \frac{1}{2} \delta_{pq} t_{ijp} t_{klq} (B_{ij,kl} + p B_{ji,kl}) \end{aligned}$$

In this case the residual equations represent an eigenvalue problem that can be solved iteratively by a Davidson-like method (see Ref. 1 for details).

D. Matrix elements for MRCI-F12

In second quantization the molecular Hamiltonian is defined as

$$\hat{H} = h_{\kappa\lambda} \hat{E}_{\lambda}^{\kappa} + \frac{1}{2} K_{\kappa\lambda}^{\mu\nu} \hat{E}_{\mu\nu}^{\kappa\lambda} \quad (39)$$

where $h_{\kappa\lambda}$ is the sum of kinetic and external potential terms and $K_{\kappa\lambda}^{\mu\nu} = \langle \kappa\lambda | r_{12}^{-1} | \mu\nu \rangle$ are the two-electron repulsion integrals. Further integrals, which are needed in later expressions, are summarized in Table III.

As an example for the derivation of the matrix elements A , B , and X defined in the previous section we consider the pair contribution to the term $\langle 0 | \hat{H} \hat{Q}_P \hat{F} | 0 \rangle$. Using Eq. (21) we obtain

$$\begin{aligned} \langle 0 | \hat{H} \hat{Q}_P \hat{F} | 0 \rangle &= \sigma_{kl} (ijp, 0) (K_{kl}^{\alpha\beta} \mathcal{F}_{\alpha\beta}^{ijp} - K_{kl}^{ab} \mathcal{F}_{ab}^{ijp}) \\ &= \frac{1}{2} t_{ijp} \sigma_{kl} (ijp, 0) (\langle kl | r_{12}^{-1} \hat{Q}'_{12} F_{12} | ij \rangle \\ &\quad + p \langle kl | r_{12}^{-1} \hat{Q}'_{12} F_{12} | ji \rangle), \quad (40) \end{aligned}$$

where \hat{Q}'_{12} is a two-electron projector

$$\begin{aligned} \hat{Q}'_{12} &= |\alpha\beta\rangle\langle\alpha\beta| - |ab\rangle\langle ab| \\ &= |x'y'\rangle\langle x'y'| + |ax'\rangle\langle ax'| + |x'a\rangle\langle x'a| \\ &= 1 - |rs\rangle\langle rs| - |ox'\rangle\langle ox'| - |x'o\rangle\langle x'o|. \quad (41) \end{aligned}$$

In the last equality we have used the RI, $|\kappa\lambda\rangle\langle\kappa\lambda| = 1$. The unit operator (1) leads to analytical integrals

$\langle ij|r_{12}^{-1}F_{12}|mn\rangle$, and thus the double summation over the infinite space is eliminated. In the last two terms, which usually give only small contributions, the summation over the complete complementary space x' must be approximated by the finite CABS space x , and the two-electron projector \hat{Q}'_{12} is then replaced by

$$\hat{Q}_{12} = 1 - |rs\rangle\langle rs| - |ox\rangle\langle ox| - |xo\rangle\langle xo|. \quad (42)$$

This is exactly the same as in single-reference MP2-F12 theory. Using the integrals defined in Table III the result can now be compactly written as

$$\langle 0|\hat{H}\hat{Q}_P\hat{F}|0\rangle = \mathcal{V}_{kl}^{ijp}\sigma_{kl}(ijp, 0). \quad (43)$$

The corresponding singles contribution reads

$$\langle 0|\hat{H}\hat{Q}_S\hat{F}|0\rangle = [\sigma_k(S, 0)h_{kx} + \alpha_{kmn}(S, 0)J_{kx}^{mn}] \mathcal{F}_x^S. \quad (44)$$

Similar arguments yield

$$X = \mathcal{X}_{ijp,klq}S_{ijp,klq} + \mathcal{F}_x^S \mathcal{F}_x^S. \quad (45)$$

The matrices A_{ab}^{Dp} are evaluated in the basis of nonorthogonal configurations Φ_{ijp}^{ab} and subsequently transformed to the orthogonal basis

$$A_{ab}^{Dp} = \frac{1}{2}U_{Dp,ijp}(A_{ab}^{ijp} + pA_{ba}^{ijp}), \quad (46)$$

where

$$A_{ab}^{ijp} = S_{ijp,klq}[\gamma_{ab}^{klq} + 2h_{ax}\mathcal{F}_{xb}^{klq} + 2K_{ab}^{xm}\mathcal{F}_x^S\sigma_m(klq, S)] \\ + [2J_{ax}^{mn}\alpha_{mn}(ijp, klq) + K_{ax}^{mn}\beta_{mn}(ijp, klq)] \mathcal{F}_{xb}^{klq}. \quad (47)$$

The contributions to the internal and singles residuals are

$$A_a^S = [\delta_{ST}h_{ax} + J_{ax}^{mn}\alpha_{mn}(S, T) + K_{ax}^{mn}\beta_{mn}(S, T)] \mathcal{F}_x^T \\ + 2\mathcal{F}_{ax}^{ijp}[h_{xk}\sigma_k(ijp, S) + J_{xk}^{mn}\alpha_{kmn}(ijp, S)] \\ + 2\mathcal{V}_{ak}^{ijp}\sigma_k(ijp, S), \quad (48)$$

$$A_I = [h_{kx}\sigma_k(S, I) + J_{kx}^{mn}\alpha_{kmn}(S, I)] \mathcal{F}_x^S \\ + \mathcal{V}_{mn}^{ijp}\sigma_{mn}(ijp, I). \quad (49)$$

The coupling coefficients σ , α , and β are defined in Table II. They are exactly the same as used in the conventional MRCI.

The explicit expressions for the geminal–geminal term B can be derived from the conventional matrix element $\langle \Psi_{\text{MRCI}}|\hat{H}|\Psi_{\text{MRCI}}\rangle$ (cf. Ref. 1) by replacing the amplitudes T_{ab}^{ijp} and t_a^S by the geminal amplitudes $\mathcal{F}_{\alpha\beta}^{ijp}$ and \mathcal{F}_x^S , respectively. In most terms, the summations over the infinite virtual space cannot be removed and must be approximated by double RI approximations. An example is the term

$$\left(\mathcal{F}_{x'y'}^{ijp}K_{x'z'}^{mn}\mathcal{F}_{z'y'}^{klq} + 2\mathcal{F}_{ay'}^{ijp}K_{az'}^{mn}\mathcal{F}_{z'y'}^{klq} \right. \\ \left. + \mathcal{F}_{x'b}^{ijp}K_{x'z'}^{mn}\mathcal{F}_{z'b}^{klq} + \mathcal{F}_{ay'}^{ijp}K_{ac}^{mn}\mathcal{F}_{cy'}^{klq} \right) \beta_{mn}(ijp, klq). \quad (50)$$

In some terms resolutions of the identity can be used to eliminate the double RIs, the most important one being

$$\langle ijp|F_{12}\hat{Q}_{12}r_{12}^{-1}\hat{Q}_{12}F_{12}|klq\rangle S_{ijp,klq} \\ = [\langle ijp|F_{12}r_{12}^{-1}F_{12}|klq\rangle - \mathcal{F}_{rs}^{ijp}(\mathcal{V}_{rs}^{klq} + \mathcal{W}_{rs}^{klq}) \\ - 2\mathcal{F}_{xo}^{ijp}(\mathcal{V}_{xo}^{klq} + \mathcal{W}_{xo}^{klq})] S_{ijp,klq}. \quad (51)$$

Even though the full implementation of these expressions is in principle feasible, it involves many multiple RI approximations and integrals over up to two CABS orbitals. These terms would not only be expensive to evaluate, but would also require very large RI basis sets for numerical stability. This is the same situation as for exact CCSD-F12 methods. In the next two sections we therefore introduce approximations for the B and A terms. If only B is approximated, one obtains a model that corresponds to the (F12*) approximation in coupled cluster theory. If also the coupling terms A are approximated, one arrives at approximation MRCI-F12b which has been implemented in the current work.

E. Approximation MRCI(F12*)

In this section we introduce an approximation for the geminal–geminal term B . A similar approximation has been used before in the CCSD-F12b,^{9,28} CCSD(F12),^{57,58} and CCSD(F12*)¹³ methods.

The geminal–geminal block B is approximated by replacing $\hat{H} - E_0$ with $\hat{H}^{(0)} - E^{(0)}$, where $\hat{H}^{(0)}$ is the zeroth-order Hamiltonian used in CASPT2

$$\hat{H}^{(0)} = \hat{P}_0\hat{f}\hat{P}_0 + (1 - \hat{P}_0)\hat{f}(1 - \hat{P}_0) \quad (52)$$

with $\hat{P}_0 = |0\rangle\langle 0|$, $E_0 = \langle 0|\hat{H}|0\rangle$, and $E^{(0)} = \langle 0|\hat{f}|0\rangle$. The Fock operator is defined as

$$\hat{f} = \left[h_{\kappa\lambda} + \gamma_{ij} \left(J_{\kappa\lambda}^{ij} - \frac{1}{2}K_{\kappa\lambda}^{ij} \right) \right] \hat{E}_{\lambda}^{\kappa} \equiv f_{\kappa\lambda} \hat{E}_{\lambda}^{\kappa}. \quad (53)$$

Thus, the geminal–geminal block of the Hamiltonian is approximated as

$$B \approx (E_0 - E^{(0)})X + \langle 0|\hat{F}^{\dagger}\hat{Q}\hat{f}\hat{Q}\hat{F}|0\rangle. \quad (54)$$

The matrix element over the Fock operator is

$$\langle 0|\hat{F}^{\dagger}\hat{Q}\hat{f}\hat{Q}\hat{F}|0\rangle = \mathcal{B}_{ijp,klq}S_{ijp,klq} + \mathcal{X}_{ijp,klq}\gamma(ijp, klq) \\ + 4\mathcal{F}_x^S [f_{ak}\mathcal{F}_{xa}^{ijp} + f_{yk}\mathcal{F}_{xy}^{ijp}] \sigma_k(ijp, S) \\ + \mathcal{F}_x^S f_{xy}\mathcal{F}_y^S + \gamma(S, T)\mathcal{F}_x^S \mathcal{F}_x^T. \quad (55)$$

F. Approximation MRCI-F12b

In the previous section we have shown how the geminal–geminal term B can be efficiently approximated. The A coupling terms still involve the computation and storage of the three-external integrals K_{ab}^{kx} and are expensive to evaluate. In the following, we introduce an additional approximations which avoids also these problems. This corresponds to the F12b approximation in CC theory.^{9,28}

Apart from the V_{rs}^{ijp} terms, all contributions of two-electron integrals to the A matrix elements are neglected and the one-electron matrix elements h_{rs} are replaced by f_{rs} (the same approximation is made in CASPT2-F12⁴⁸). In addition, the CABS contributions to the V_{rs}^{ij} matrix elements are neglected and \mathcal{V}_{rs}^{ijp} is approximated as

$$\tilde{\mathcal{V}}_{rs}^{ijp} = \frac{1}{2} t_{ijp} (\tilde{V}_{rs}^{ij} + p \tilde{V}_{rs}^{ji}), \quad (56)$$

$$\tilde{V}_{rs}^{ij} = W_{rs}^{ij} - K_{rs}^{tu} F_{tu}^{ij}. \quad (57)$$

The coupling terms then simplify to

$$A_{ab}^{ijp} \approx S_{ijp,klq} [\tilde{\mathcal{V}}_{ab}^{klq} + 2 f_{ax} \mathcal{F}_{xb}^{klq}], \quad (58)$$

$$A_a^S \approx 2 \tilde{\mathcal{V}}_{ak}^{ijp} \sigma_k(ijp, S) + f_{ax} \mathcal{F}_x^S + 2 \mathcal{F}_{ax}^{ijp} f_{xk} \sigma_k(ijp, S). \quad (59)$$

The evaluation of the integrals K_{ab}^{kx} and J_{ax}^{mn} is thus avoided and the computational effort is strongly reduced. Note that the amplitude equation for the internal coefficients [Eq. (49)] is not approximated, since it directly contributes to the energy.

G. Variants with size consistency corrections

Davidson's correction⁵⁹ to MRCI energies, that accounts approximately for contributions of higher order excitations and reduces the size consistency errors, has been implemented for MRCI-F12 in the same way as in the conventional MRCI method. The correction is defined as

$$\Delta E_{+Q} = (E - E_0)(c_0^{-2} - 1), \quad (60)$$

where c_0 is the coefficient of the reference function in the (normalized) MRCI-F12 wave function. One can either use the fixed reference function, yielding

$$c_0 = \frac{1}{\sqrt{N}} \langle 0 | \Psi_{\text{MRCI-F12}} \rangle = \frac{1}{\sqrt{N}} \sum_{I \in \{R\}} t_I^{(0)} t_I, \quad (61)$$

in which $N = \langle \Psi_{\text{MRCI-F12}} | \Psi_{\text{MRCI-F12}} \rangle$ (Q1 correction in Ref. 3). This may fail in the vicinity of conical intersections, since then states may strongly mix and c_0 may get small, leading to a strong overestimation of the correction. This problem can be avoided by using instead of the coefficients $t_I^{(0)}$ the relaxed reference coefficients t_I . Renormalization of the relaxed reference function then yields

$$c_0^2 = \frac{1}{N} \sum_{I \in \{R\}} t_I^2 \quad (62)$$

(Q0 correction in Ref. 3). This correction is used by default unless otherwise stated.

Replacing the expectation value of MRCI-F12 methods by

$$E = E_0 + \frac{\langle \Psi_{\text{MRCI-F12}} | H - E_0 | \Psi_{\text{MRCI-F12}} \rangle}{\langle 0 | 0 \rangle + g_a \langle \Psi_i | \Psi_i \rangle + g_e \langle \Psi_e | \Psi_e \rangle} \quad (63)$$

leads to the MRACPF-F12 methods, in which

$$|\Psi_i\rangle = (1 - \hat{P}_0) t_I |I\rangle, \quad (64)$$

$$|\Psi_e\rangle = t_a^S |S^a\rangle + T_{ab}^{ijp} |\Phi_{ijp}^{ab}\rangle + t_{F12} \hat{Q} \hat{F} |0\rangle. \quad (65)$$

In the MRACPF model,⁵⁰ g_a and g_e are set to

$$g_a = 1, \quad (66)$$

$$g_e = 2/n, \quad (67)$$

where n is the number of correlated electrons. MR averaged quadratic coupled cluster⁶⁰ (MRAQCC-F12) and MRCEPA(0)-F12 (linear coupled electron pair approximation) can be obtained by using a different set of g_a and g_e values. Since their working equations are very similar to those of MRCI-F12, they are not repeated here.

III. RESULTS

The method described in the previous sections has been implemented in the developer version of the MOLPRO suite of *ab initio* programs.⁶¹ In all calculations reported in this paper approximation F12b has been used. For the sake of simplicity the suffix b will be omitted in the following. Unless otherwise noted, Davidson's correction (Q0) was applied in all calculations presented in the following, since it reduces the size consistency errors of the MRCI and MRCI-F12 methods and in most cases leads to significantly improved results (with and without F12 correction). All integrals with CABS indices, as well as all those needed to compute V , X , and B in Table III, are computed using density fitting.¹⁸ The Fock matrix elements (except for f_{mn} in Table II) are also evaluated using density fitting. All other integrals are computed exactly. The CBS values are calculated by applying Helgaker's formula⁶² to the total energies computed by aug-cc-pV5Z and 6Z, assuming that the CASSCF contribution is well converged at the aug-cc-pV6Z basis set.

The singlet-triplet separation of methylene (CH_2) has been computed by the above described MRCI-F12 method, as well as other MR methods using the full valence and larger active spaces. The full-valence active space consists of (3,2,1,0) orbitals in a_1 , b_2 , b_1 , a_2 symmetries, while the larger active space, which formally includes in addition the C(3s, 3p, 3d) AOs, has (7,4,3,1) orbitals. Peterson's correlation consistent double, triple and quadruple ζ F12 basis sets^{63,64} (cc-pVXZ-F12 for the OBS and cc-pVXZ-F12/OptRI for the CABS, denoted hereafter as VXZ-F12, $X = \{D, T, Q\}$) are used. For density fitting, we have used the corresponding aug-cc-pVXZ/MP2FIT and cc-pVXZ/JKFIT basis sets ($X = T$ for VDZ-F12 and VTZ-F12, and $X = Q$ for VQZ-F12).^{65,66} An even-tempered diffuse function per angular momentum has been added to cc-pVXZ/JKFIT basis.²⁴ The total energies of the singlet and triplet states of CH_2 are summarized in Table IV, and the singlet-triplet separations are presented in Table V. In order to demonstrate the convergence of the energy with respect to the basis set (Table IV), we have fixed the geometry to $r_{\text{CH}} = 2.1023 a_0$ ($2.0413 a_0$) and $\angle_{\text{HCH}} = 101.71^\circ$ (134.22°) for the 1A_1 (3B_1) states, respectively. However, for computing the singlet-triplet splittings (Table V) the geometries have

TABLE IV. The reference and correlation energies of singlet and triplet methylene in E_h at fixed geometries (see text). MRCI and MRCI-F12 values include Davidson's correction (+Q0).

OBS	CASSCF	CASPT2	CASPT2-F12	MRCI	MRCI-F12 (FIX)	MRCI-F12 (SFIX)
Singlet, (3,2,1,0) active space						
VDZ-F12	-38.95368	-0.08233	-0.10545	-0.09896	-0.11619	-0.11652
VTZ-F12	-38.95735	-0.09554	-0.10639	-0.11256	-0.11916	-0.11964
VQZ-F12	-38.95811	-0.10111	-0.10667	-0.11703	-0.12002	-0.12036
CBS56	-38.95832	-0.10666	—	-0.12052	—	—
Triplet, (3,2,1,0) active space						
VDZ-F12	-38.97048	-0.08814	-0.10938	-0.09827	-0.11426	-0.11452
VTZ-F12	-38.97341	-0.10090	-0.11063	-0.11085	-0.11685	-0.11725
VQZ-F12	-38.97413	-0.10605	-0.11096	-0.11492	-0.11760	-0.11789
CBS56	-38.97432	-0.11103	—	-0.11806	—	—
Singlet, (7,4,3,1) active space						
VDZ-F12	-39.02901	-0.01911	-0.03808	-0.02306	-0.04022	-0.04029
VTZ-F12	-39.03562	-0.02909	-0.03776	-0.03393	-0.04070	-0.04080
VQZ-F12	-39.03687	-0.03343	-0.03792	-0.03798	-0.04116	-0.04125
CBS56	-39.03720	-0.03792	—	-0.04142	—	—
Triplet, (7,4,3,1) active space						
VDZ-F12	-39.04687	-0.01877	-0.03608	-0.02168	-0.03727	-0.03734
VTZ-F12	-39.05252	-0.02849	-0.03642	-0.03189	-0.03805	-0.03814
VQZ-F12	-39.05366	-0.03258	-0.03661	-0.03565	-0.03849	-0.03858
CBS56	-39.05394	-0.03667	—	-0.03875	—	—

been optimized for each method and basis set. The optimized geometries can be found in Supplementary Material.⁵⁶ The MRCI-F12 correlation energies have achieved 1 kcal/mol accuracy (compared to their CBS limits) with as small as the VTZ-F12 basis set. The singlet–triplet separation is also converged to a few tenth of a mE_h at the triple- ζ basis set. The experimental value corrected for the zero-point vibration energy and relativity is 9.1 ± 0.2 kcal/mol,⁶⁷ which agrees well with our MRCI-F12 values for the (7,4,3,1) active space.

We have also examined the dependence of the F12 energies with respect to the size of RI basis sets, which is shown in Table VI. The reference values were computed using the huge RI basis set of Klopper.¹⁶ The errors arising from the incompleteness of RI basis sets in MRCI-F12 were found of the same order as in the CCSD-F12 method, which legitimates the direct use of the CABS orbitals for the semi-internal terms [see Eq. (22)].

Another example is the dissociation energy of the ozone molecule in its electronic ground state to a triplet oxygen molecule and a triplet oxygen atom [$O_3(^1A_1) \rightarrow O_2(^3\Sigma_g^-) + O(^3P)$]. The ozone molecule has a strong multiconfiguration character. The experimental value for D_e is 26.1 kcal/mol.⁶⁸ The geometries of O_3 and O_2 have been optimized for each method and basis set using numerical gradients. The optimized geometrical parameters for CASSCF, CASPT2, MRCI, and MRACPF with and without F12 terms are listed in Table VII. MRCI-F12 with the double- ζ basis set already gives equilibrium geometries accurate to 0.01 Å and $< 0.1^\circ$, which halves the error of the MRCI method. With the triple- ζ basis set, the obtained bond lengths are found to agree within 0.003 Å with the experimental values.⁶⁹ The dissociation energies computed using these optimized geometries are also compiled in Table VII. Obviously, F12 treatments greatly accelerate their convergence with respect to the basis size. The MRCI-F12

TABLE V. The singlet–triplet separation of methylene in kcal/mol. The geometries have been optimized for all combinations of methods and basis sets. MRCI and MRCI-F12 values include Davidson's correction (+Q0).

OBS	CASSCF	CASPT2	CASPT2-F12	MRCI	MRCI-F12 (FIX)	MRCI-F12 (SFIX)
(3,2,1,0) active space						
VDZ-F12	10.58	14.19	13.02	10.12	9.34	9.29
VTZ-F12	10.12	13.44	12.73	9.01	8.62	8.57
VQZ-F12	10.11	13.16	12.75	8.73	8.54	8.51
CBS56		12.79		8.49		
(7,4,3,1) active space						
VDZ-F12	11.21	11.01	9.96	10.35	9.36	9.35
VTZ-F12	10.61	10.23	9.76	9.33	8.94	8.93
VQZ-F12	10.54	10.00	9.71	9.07	8.86	8.85
CBS56		9.72		8.83		

TABLE VI. The errors due to the incompleteness of the RI insertion (in μE_h). The singlet CH_2 is computed by the VDZ-F12 basis set for OBS and various RI basis sets. Klopper's huge RI basis set^a is used as a reference.

RI	MRCI-F12	CCSD-F12b
aVDZ/JKFIT	-39.0	-25.1
aVTZ/JKFIT	-36.6	-32.0
aVQZ/JKFIT	-26.6	-25.9
aVSZ/JKFIT	-22.2	-21.0
VDZ-F12/OPTRI	6.5	3.4

^aReference 16.

value with the triple- ζ basis set deviates only by 0.9 kcal/mol from the experimental value, and the quadruple- ζ basis set reproduces it within 0.2 kcal/mol. The SFIX ansatz slightly outperforms the FIX ansatz, especially in calculations with small basis sets. The conventional MRCI method is off by 3 kcal/mol with the triple- ζ basis set and by 1.2 kcal/mol even with the quadruple- ζ basis set. MRACPF-F12 gives quantitatively similar results to MRCI-F12.

Next, the geometries and spectroscopic constants of several first-row hydrides and homonuclear diatomics have been

TABLE VII. The dissociation energy (in kcal/mol) and optimized geometry of ozone and oxygen molecules in angstrom and degree. MRCI and MRCI-F12 values include Davidson's correction (+Q0).

Method	OBS	D_e	Ozone		Oxygen
			r_{OO}	\angle_{OOO}	r_{OO}
CASSCF	VDZ-F12	9.01	1.289	116.6	1.222
	VTZ-F12	10.27	1.281	116.8	1.216
	VQZ-F12	10.55	1.280	116.8	1.215
CASPT2	VDZ-F12	14.91	1.299	116.6	1.225
	VTZ-F12	18.99	1.284	116.7	1.214
	VQZ-F12	20.82	1.282	116.7	1.213
	CBS56	22.04	1.280	116.8	1.211
CASPT2-F12	VDZ-F12	20.16	1.290	116.5	1.219
	VTZ-F12	21.66	1.281	116.7	1.212
	VQZ-F12	22.08	1.280	116.7	1.211
MRCI	VDZ-F12	17.62	1.293	116.6	1.224
	VTZ-F12	22.72	1.279	116.8	1.214
	VQZ-F12	24.86	1.276	116.8	1.212
	CBS56	26.12	1.273	116.8	1.210
MRCI-F12 (FIX)	VDZ-F12	22.91	1.284	116.6	1.218
	VTZ-F12	25.23	1.275	116.8	1.211
	VQZ-F12	25.96	1.273	116.8	1.210
MRCI-F12 (SFIX)	VDZ-F12	23.43	1.283	116.6	1.217
	VTZ-F12	25.38	1.274	116.8	1.211
	VQZ-F12	26.01	1.273	116.8	1.210
ACPF	VDZ-F12	17.54	1.294	116.6	1.224
	VTZ-F12	22.62	1.279	116.7	1.214
	VQZ-F12	24.76	1.277	116.8	1.212
	CBS56	26.03	1.274	116.8	1.210
ACPF-F12 (FIX)	VDZ-F12	22.79	1.285	116.6	1.218
	VTZ-F12	25.13	1.275	116.8	1.211
	VQZ-F12	25.87	1.274	116.8	1.210
Experiment		26.1	1.272	116.8	1.208

^aTaken from Ref. 68.

calculated. Core orbitals are doubly occupied and not correlated. We have used the full valence active spaces for the homonuclear diatomics, while four orbitals which formally correspond to the $3s$ and $3p$ orbitals of C–F are added for the hydrides. Dunning's cc-pVXZ and aug-cc-pVXZ basis sets^{70,71} for H and C–F, respectively, are used for OBS (abbreviated by VXZ and aVXZ in Table VIII) and Weigend's cc-pVXZ/JKFIT and (aug-)cc-pVXZ/MP2FIT basis sets^{65,66} for auxiliary basis sets. Table VIII compiles the equilibrium bond lengths, harmonic frequencies and dissociation energies. The equilibrium bond lengths and harmonic frequencies were calculated by fitting the potential energy curves with polynomials of rank 8. The experimental values are taken from Refs. 72 and 73. For the equilibrium bond lengths, which are quite insensitive to the basis set, the F12 treatments reduce the error at the double or triple- ζ level by a factor of 2. The harmonic frequencies are improved significantly by the F12 treatment; the triple- ζ calculations reproduce the corresponding CBS values typically within 10 cm^{-1} , which is in contrast to the conventional MRCI method whose basis-set errors can amount to 25 cm^{-1} or more. Moreover, the improvements by the F12 factor for the dissociation energies are remarkable. The pure correlation contributions [i.e., the difference of MRCI(-F12) energies and CASSCF energies] quickly converge to the CBS limit: the errors in the correlation contributions are less than 1 kcal/mol using the aug-cc-pVTZ basis set, while one often observes errors of more than 5 kcal/mol for MRCI with the same basis set. In many cases, the remaining errors of MRCI-F12 calculations are parallel to those of CASSCF, suggesting that the future development of a "CABS singles" correction²⁴ to CASSCF is necessary to further reduce the errors.

Finally, we have examined the reaction barriers and the exothermicity of the $\text{F} + \text{H}_2$ reaction by the MRCI-F12 method. These quantities are known to be strongly dependent on the basis set.³ The geometries optimized by the MRCI method with the aug-cc-pV5Z basis set were used (see Ref. 3 for details). Only the $1^2A'$ ground state was considered in the CASSCF, MRCI, and MRCI-F12 calculations (the $2^2A'$ and $1^2A''$ states, which are degenerate with the $1^2A'$ at the $\text{F} + \text{H}_2$ asymptote, have very little effect on the energy differences considered here, even though they cannot be neglected at intermediate geometries, see Refs. 74 and 75). The active space is spanned by $2a'-9a'$, $1a''$, and $2a''$ orbitals. The $1a'$ orbital is not correlated in the MRCI and MRCI-F12 calculations. The aug-cc-pVXZ basis sets for F and the cc-pVXZ set for H are used as OBS^{70,71} [diffuse functions on H introduce significant basis-set superposition errors and are therefore omitted³]. For Davidson's correction, we have employed the Q1 variant [cf. Eq. (61)], as recommended in Ref. 3. MRCI-F12 with the quadruple- ζ basis set is already converged to a few hundredth of a kcal/mol as compared to its CBS limit. In contrast, the conventional MRCI method requires the aug-cc-pV6Z basis set (or more) to achieve the same accuracy. As one can observe, the CASSCF and correlation contributions have errors of different signs and partly cancel with each other; probably this is the source of the small humps in the convergence of the MRCI-F12 reaction barriers. The core correlation, relativistic, non Born–Oppenheimer, and spin-orbit contributions, which are not considered in this work, amount to +0.442 and

TABLE VIII. The equilibrium bond lengths r_e (in angstrom), harmonic frequencies ω_e (in cm^{-1}), and dissociation energies D_e (in kcal/mol) of first-row hydrides and homonuclear diatomics. MRCI and MRCI-F12 values include Davidson's correction (+Q0). MRCI-F12 has been performed with the SFIX ansatz.

OBS	CASSCF	MRCI	MRCI-F12	CASSCF	MRCI	MRCI-F12	CASSCF	MRCI	MRCI-F12
CH, $X^2\Pi$		r_e (Expt. 1.120)			ω_e (Expt. 2858.5)			D_e (Expt. 83.9)	
aVDZ / VDZ	1.139	1.141	1.135	2825.0	2819.1	2849.3	74.1	77.1	81.1
aVTZ / VTZ	1.123	1.123	1.121	2827.2	2835.9	2843.1	76.1	82.2	83.6
aVQZ / VQZ	1.122	1.121	1.120	2840.7	2847.3	2851.1	76.3	83.4	83.9
aV5Z / V5Z	1.122	1.120	1.120	2841.6	2850.6	2852.1	76.4	83.7	84.0
CBS56	—	1.120	—	—	2851.9	—	—	84.0	—
NH, $X^3\Sigma^-$		r_e (Expt. 1.036)			ω_e (Expt. 3282.3)			D_e (Expt. n/a)	
aVDZ / VDZ	1.054	1.053	1.047	3212.1	3209.8	3259.5	72.2	74.8	80.4
aVTZ / VTZ	1.045	1.041	1.039	3226.3	3254.1	3269.0	73.3	80.5	82.4
aVQZ / VQZ	1.044	1.038	1.038	3233.2	3270.9	3275.8	73.6	82.1	82.9
aV5Z / V5Z	1.044	1.038	1.038	3234.4	3274.4	3276.6	73.6	82.5	82.9
CBS56	—	1.037	—	—	3277.0	—	—	82.9	—
OH, $X^2\Pi$		r_e (Expt. 0.970)			ω_e (Expt. 3737.8)			D_e (Expt. 106.6)	
aVDZ / VDZ	0.980	0.980	0.972	3700.3	3685.4	3725.8	95.8	99.4	104.6
aVTZ / VTZ	0.975	0.974	0.972	3714.0	3711.3	3725.5	96.7	104.5	106.4
aVQZ / VQZ	0.974	0.971	0.971	3723.1	3729.8	3733.2	96.9	106.2	107.0
aV5Z / V5Z	0.973	0.971	0.971	3724.8	3733.4	3734.2	96.9	106.7	107.1
CBS56	—	0.971	—	—	3734.9	—	—	107.1	—
HF, $X^1\Sigma^+$		r_e (Expt. 0.917)			ω_e (Expt. 4138.3)			D_e (Expt. 141.6)	
aVDZ / VDZ	0.924	0.924	0.921	4116.8	4085.9	4120.9	129.5	133.9	138.9
aVTZ / VTZ	0.921	0.921	0.920	4145.9	4120.2	4130.6	130.1	139.1	140.9
aVQZ / VQZ	0.919	0.918	0.918	4153.3	4136.4	4136.9	130.4	140.8	141.5
aV5Z / V5Z	0.919	0.918	0.918	4154.2	4137.3	4137.5	130.4	141.2	141.6
CBS56	—	0.917	—	—	4136.6	—	—	141.6	—
C ₂ , $X^1\Sigma_g^+$		r_e (Expt. 1.243)			ω_e (Expt. 1854.7)			D_e (Expt. 146±3)	
aVDZ	1.267	1.274	1.262	1843.2	1800.7	1844.2	139.0	128.3	137.9
aVTZ	1.255	1.253	1.248	1839.1	1828.9	1844.5	142.5	139.4	143.0
aVQZ	1.254	1.248	1.246	1841.7	1843.6	1850.2	143.2	142.8	144.3
aV5Z	1.253	1.247	1.246	1842.2	1847.9	1851.2	143.3	143.7	144.5
CBS56	—	1.246	—	—	1851.1	—	—	144.6	—
N ₂ , $X^1\Sigma_g^+$		r_e (Expt. 1.098)			ω_e (Expt. 2358.6)			D_e (Expt. 228.4)	
aVDZ	1.117	1.123	1.115	2339.6	2300.1	2343.9	207.0	201.8	217.3
aVTZ	1.105	1.106	1.103	2335.9	2324.5	2341.9	212.0	218.0	224.8
aVQZ	1.104	1.102	1.101	2339.2	2339.9	2347.2	213.2	223.8	226.8
aV5Z	1.104	1.101	1.101	2340.4	2345.2	2348.9	213.3	225.5	227.1
CBS56	—	1.101	—	—	2348.7	—	—	227.2	—
O ₂ , $X^3\Sigma_g^-$		r_e (Expt. 1.208)			ω_e (Expt. 1580.2)			D_e (Expt. 120.6)	
aVDZ	1.221	1.225	1.215	1542.8	1536.3	1575.2	91.2	107.5	114.9
aVTZ	1.218	1.217	1.213	1536.5	1550.0	1567.4	94.4	115.1	118.3
aVQZ	1.215	1.212	1.210	1547.8	1571.9	1579.8	95.1	118.1	119.6
aV5Z	1.215	1.211	1.210	1548.1	1575.9	1580.3	95.1	118.9	119.7
CBS56	—	1.210	—	—	1581.2	—	—	119.7	—
F ₂ , $X^1\Sigma_g^+$		r_e (Expt. 1.412)			ω_e (Expt. 916.6)			D_e (Expt. 39.0)	
aVDZ	1.490	1.454	1.430	658.3	815.6	861.7	16.1	30.3	33.4
aVTZ	1.459	1.420	1.413	736.3	906.7	922.5	19.1	35.9	37.3
aVQZ	1.459	1.415	1.412	731.7	911.5	919.0	19.1	36.9	37.6
aV5Z	1.458	1.413	1.412	733.7	917.1	921.1	19.1	37.2	37.6
CBS56	—	1.411	—	—	921.7	—	—	37.5	—

−0.365 kcal/mol for the reaction barrier and exothermicity, respectively.³

The computational cost of MRCI-F12 per iteration is almost identical to that of MRCI. The overhead for the additional integral evaluations and the computation of the F12

energy contributions is usually small: for O₃ in C_s symmetry with the full valence active space, MRCI-F12 took 2920 s (wall time) with the VTZ-F12 basis set, whereas MRCI took 2860 s with the same basis set. Timings were measured on an AMD Opteron 2380 workstation (2.5 GHz, 1 core).

TABLE IX. The reaction barriers and exothermicity of the F + H₂ reaction in kcal/mol. MRCI and MRCI-F12 values include Davidson's correction (+Q1).

OBS	CASSCF	MRCI	MRCI-F12 (FIX)	MRCI-F12 (SFIX)
Barrier (bent)				
aVTZ	7.304	1.795	1.291	1.333
aVQZ	7.427	1.433	1.298	1.294
aV5Z	7.475	1.385	1.310	1.310
aV6Z ^a	7.481	1.352		
CBS56		1.307		
Barrier (linear)				
aVTZ	6.165	2.064	1.772	1.800
aVQZ	6.273	1.850	1.791	1.790
aV5Z	6.320	1.854	1.818	1.819
aV6Z ^a	6.326	1.838		
CBS56		1.817		
Exothermicity				
aVTZ	34.848	30.640	31.960	31.766
aVQZ	34.959	31.674	32.126	32.071
aV5Z	34.906	31.832	32.086	32.048
aV6Z ^a	34.902	31.916		
CBS56		32.032		

^aThe MRCI-F12 calculations with aV6Z were not performed since there are no auxiliary basis sets available.

IV. CONCLUSIONS

We have developed an explicitly correlated MRCI-F12 method, which provides results with near MRCI/CBS limit accuracy and quantitative agreement with the experimental values already with medium-size basis sets. The doubly external configurations generated by the geminal excitations are internally contracted, while the singly external configurations remain uncontracted. In order to reduce the computational cost and to improve the numerical stability, approximations are made for the geminal-geminal block and for the geminal-conventional coupling terms. These are similar to the F12b approximation in the single reference CC-F12 theories.²⁸ In this approximation, the computational cost of MRCI-F12 is almost the same as that of MRCI with the same basis set, while the basis set dependence is much improved. As a side product, we have also implemented MRACPF-F12 and related methods.

The applicability of the MRCI-F12 method presented here is the same as that of the underlying conventional MRCI method. It can be used for strongly correlated or degenerate electronic structures, and is a powerful tool to compute, for instance, global PES's for small systems or the energetics of reactions involving transition metal compounds. An extension to excited electronic states, including the possibility to treat avoided crossings and conical intersections, will be presented in a separate publication. The efficiency and applicability of the method to larger molecules can be increased by contracting further configuration classes, as proposed by Celani and Werner for CASPT2.⁵² Recently, a new MRCI program based on this scheme has been developed in our group,⁵³ and its extension to MRCI-F12 will be considered in the near future.

Our study shows that most of the remaining basis set incompleteness errors are due to the surprisingly slow con-

vergence of the CASSCF energy with basis set size. A correction to the CASSCF energy, similar to the CABS singles correction²⁴ in single-reference cases, is therefore highly desirable and will be presented in a future publication.

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