$\text{SF-}[2]_{R12}$: A spin-adapted explicitly correlated method applicable to arbitrary electronic states

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The [2]_{R12} method [M. Torheyden and E. F. Valeev, J. Chem. Phys. **131**, 171103 (2009)] is an explicitly correlated perturbative correction that can greatly reduce the basis set error of an arbitrary electronic structure method for which the two-electron density matrix is available. Here we present a spin-adapted variant (denoted as SF-[2]_{R12}) that is formulated completely in terms of spin-free quantities. A spin-free cumulant decomposition and multi-reference generalized Brillouin condition are used to avoid three-particle reduced density matrix completely. The computational complexity of SF-[2]_{R12} is proportional to the sixth power of the system size and is comparable to the cost of the single-reference MP2-R12 method. The SF-[2]_{R12} method is shown to decrease greatly the basis set error of multi-configurational wave functions. © *2011 American Institute of Physics*. [doi:10.1063/1.3664729]

I. INTRODUCTION

Explicitly correlated R12 methods (known in their modern form as F12 methods)[1–3] are a promising approach to reduce the basis set error of quantum many-body electronic-structure methods. Conventional many-body methods represent wave functions (or other many-electron objects such as Green's function or reduced density matrix) exclusively in terms of products of one-electron functions; such representations emulate the analytic structure of the exact wave function inefficiently and converge to the basis set limit in atoms as $(L + 1)^{-3}$, where L is the maximum angular momentum of the basis. R12 methods[4,5] augment the conventional wave functions by a few terms characterized by explicit dependence on the interelectronic distances, r_{ij}, thereby accounting for the proper wave function behavior at short r_{ij},[6,7] and yielding a much improved $(L + 1)^{-7}$ basis set convergence rate. Unlike the more general explicitly correlated wave functions, R12 methods avoid three-body (9-dimensional) and higher-body integrals by an approximate resolution-of-the-identity; the effect of the extra explicitly correlated terms on the computational cost is therefore small. R12 methods, when combined with high-level correlation models,[8–11] can achieve very high accuracy with a modest basis set. Often using a double-zeta basis can match the accuracy of a conventional quadruple-zeta basis.

Following their introduction by Kutzelnigg in 1985,[4,5] the R12 approach was promptly implemented in all major wave function methods by Klopper, Noga, Kutzelnigg, and Gdanitz.[4,5,12–14] Essential improvements of the R12 methodology have occurred in the last decade[15–22] and established the modern R12 methods that are characterized by (1) non-linear dependence on r_{ij}, via exponentially decaying correlation factor $f(r_{ij})$ (hence the name "F12 methods"), (2) resolution-of-the-identity of three- and four-electron integrals

in terms of a separate (auxiliary) Gaussian basis set, numerical quadrature, or both, (3) use of cusp conditions to specify expansion coefficients of explicitly correlated terms, and (4) use of specialized F12-specific basis sets.

Up to now, intense efforts have been focused on R12 variants of single-reference many-body methods, where the wave function is expanded from one reference (Hartree-Fock) determinant. However, chemistry and physics of some ground electronic states (for example, in biradicals, stretched bonds, transition metal compounds) and most excited states contain multiple configurations of large amplitudes, due to exact or near-exact degeneracies. For such problems, multi-reference (MR) methods are often more suitable because their ansätze explicitly take into account the multi-configurational nature of the states in the zeroth-order approximation. For the same reasons as the single-reference methods, conventional MR methods also suffer slow convergence of correlation energy with respect to the basis set. The R12 idea can also be applied to these methods to overcome the slow convergence.

The first MR-R12 method developed was R12-MRCI (and R12-MR-ACPF) of Gdanitz[23,24] using linear r_{12} correlation factors and based on the old R12 technology; the mandatory use of large orbital basis sets limited applications to extreme-accuracy computations of atoms and small molecules.

Ten-no was first to introduce a generally applicable MR-R12 method based on the modern R12 technology. His MRMP2-F12 method[25] used the framework of the second-order multi-reference Møller-Plesset method.[26] In contrast to Gdanitz's work, Ten-no was first to use *internally contracted* geminal functions produced by the action of a geminal generator to a complete active space self-consistent field (CASSCF) wave function with fixed coefficients; internal contraction allows to avoid the numerical difficulties posed by the non-contracted formulation. For simplicity, MRMP2-F12 utilized some additional approximations inspired by the single-reference R12 theory; only a

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CASSCF 2-RDM was required to compute the F12 correction. For single-determinantal references MRMP2-F12 reduces to the MP2-R12/A* method. In atoms the MRMP2-F12 converges to the basis set limit as $(L + 1)^{-5}$.

Later Torheyden and Valeev proposed a generally applicable second-order R12 correction, termed as $[2]_{R12}$,[27] which is *a posteriori* correction to an arbitrary electronic structure method, single- and multi-configurational. Similar to MRMP2-F12, $[2]_{R12}$ uses internally contracted geminal functions but obtained from a more extensive ansatz (see below). A set of systematic approximations was used to avoid the need for high-rank density matrices; thus only 2-RDM of the reference wave function was required. For single-determinantal references $[2]_{R12}$ reduces to a close analog of the MP2-R12/C method. In atoms $[2]_{R12}$ converges to the basis set limit as $(L + 1)^{-7}$. As a proof of principle, the initial applications of $[2]_{R12}$ in Ref. 27 utilized reference wave functions that already included some dynamical correlation, such as multi-reference configuration interaction (MRCI).

Recently, Shiozaki and Werner developed CASPT2-F12 and MRCI-F12 (and MRACPF-F12) methods;[28,29] these methods were generalized to multi-state variants in which multiple reference functions are explicitly correlated, to deal with conical intersections and avoided crossings.[30] The methods used internally contracted geminal functions. Unlike MRMP2-F12 and $[2]_{R12}$, Shiozaki and Werner introduced the geminal functions *a priori*, i.e., the conventional correlation contributions to the wave function were optimized in presence of geminal functions.

This work focuses on the $[2]_{R12}$ method, whose appeal is its relative simplicity and general applicability: it can be applied to any electronic state for which the 2-RDM is available. As a proof of concept, the authors correlated the whole MRCI wave function using the geminal terms. This leads to relatively high computational cost, since all orbitals in the so-called orbital basis set (OBS) are treated as occupied orbitals. A less expensive alternative is to correlate only the dominant contribution of $|\Psi_{\text{MRCI}}\rangle$. The simplest choice may be the CASSCF wave function, i.e., $|0\rangle = |\Psi_{\text{CASSCF}}\rangle$. The resulting cost of the R12 correction is comparable to that of MP2-R12. In addition, the original $[2]_{R12}$ (termed hereafter as SO-$[2]_{R12}$ to distinguish from the spin-free version) is formulated in spin-orbital basis due to the use of a spin-orbital Fock operator. In this work, we developed a spin-free $[2]_{R12}$ method (denoted as SF-$[2]_{R12}$) and documented its performance on several prototypical cases. To avoid the need for high-rank RDM, we propose a different approximation scheme, inspired by the single-reference R12 methods. We also considered whether it is possible to decouple the conventional and geminal parts of the wave function by using solely the CASSCF wave function for the R12 correction.

II. METHODOLOGY

We construct a perturbative expansion in the same way as in the SO-$[2]_{R12}$. Given an abstract single- or multi-reference zeroth-order wave function $|0\rangle$, the basis error correction for the energy is computed by evaluating the second-order Hylleraas functional

$$\mathcal{H}^{(2)} = 2\langle 0|\hat{H}|\psi^{(1)}\rangle + \langle \psi^{(1)}|\hat{H}^{(0)}|\psi^{(1)}\rangle. \quad (1)$$

The first order wave function $|\psi^{(1)}\rangle$ is written as an internally contracted R12 geminal function, defined by

$$
\begin{aligned}
|\psi^{(1)}\rangle &= \hat{\Omega}^{(1)}|0\rangle \\
&= \frac{1}{2} t_{rs}^{pq} \big(r_{\alpha'\beta'}^{rs} E_{pq}^{\alpha'\beta'} + 2 r_{\alpha'x}^{rs} E_{pq}^{\alpha'x} \\
&\quad - 2 r_{\alpha'k}^{rs} (\Gamma^{(-1)})_j^i \, \Gamma_{pq}^{jk} E_i^{\alpha'} \big) |0\rangle.
\end{aligned}
\quad (2)
$$

In this work $p/q/r/s/t/u/v/w$ refer to the orbitals correlated by the R12 geminals; $i/j/k$ denote occupied orbitals (core or active); κ/λ represent the orbitals in the formal complete basis set (CBS) of infinite dimension; $x/y/z$ stand for the orbitals in the so-called OBS, i.e., the usual computational basis set; α'/β' denote orbitals in CBS orthogonal to OBS orbitals (in practice α'/β' are approximated by the complementary auxiliary basis set (CABS) orbitals constructed using the standard CABS+ procedure of Valeev[16]). Summation is implied in each term over indices that appear twice. E denotes a spin-free substitution operator,

$$E_\kappa^\lambda = \sum_{\sigma=\uparrow,\downarrow} a_{\kappa_\sigma}^{\lambda_\sigma}, \qquad E_{rs}^{pq} = \sum_{\substack{\sigma=\uparrow,\downarrow \\ \tau=\uparrow,\downarrow}} a_{r_\sigma s_\tau}^{p_\sigma q_\tau}, \quad (3)$$

and r is the matrix element of the correlation factor

$$r_{\alpha'\beta'}^{rs} = \int \int \phi_{\alpha'}(\mathbf{r}_1)\phi_{\beta'}(\mathbf{r}_2) f(r_{12}) \phi_r(\mathbf{r}_1)\phi_s(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2. \quad (4)$$

Here Γ denotes the spin-free RDM: $\Gamma_r^s = \langle 0|E_r^s|0\rangle$, $\Gamma_{rs}^{pq} = \langle 0|E_{rs}^{pq}|0\rangle$. Notice that Eq. (2) becomes equivalent to its spin-orbital counterpart in Ref. 27 by using inverse of the spin-orbital, rather than the spin-free, 1-RDM.

The difference between ansatz (2) and Ten-no's ansatz in MRMP2-F12 is due to the *semi-internal* excitations, i.e., the double excitations in which one of the electrons remains in the occupied space. These terms can be eliminated from our ansatz by restricting the sums over x and y to include only unoccupied orbitals only (hence eliminating the last term in Eq. (2) completely). As shown by Ten-no,[25] semi-internal excitations are relatively unimportant for at least valence CASSCF references as in atoms semi-internal excitations can only involve unoccupied orbitals of angular momentum up to $3L_{\text{occ}}$. Although for p-elements conventional CASPT2 or MRCI will already describe these effects in a basis set with at least $L = 3$ (e.g., cc-pVTZ), for heavy elements the description of these effects in terms of orbital products could become too burdensome. Furthermore, because our goal is to design the $[2]_{R12}$ method to be applicable with arbitrary reference wave functions, for which semi-internal excitations can be important, these terms are kept in our ansatz.

SO-$[2]_{R12}$ (Ref. 27) employed the spin-dependent Fock operator as $\hat{H}^{(0)}$; therefore $\mathcal{H}^{(2)}$ was expressed in terms of spin-orbital RDMs. To avoid spin-dependence in SF-$[2]_{R12}$

we use the spin-averaged Fock operator,

$$\hat{F}_N = \left(h_\lambda^\kappa + \Gamma_r^s \left(g_{\lambda s}^{\kappa r} - \frac{1}{2} g_{s\lambda}^{\kappa r} \right) \right) E_\kappa^\lambda - E_0 = F_\lambda^\kappa E_\kappa^\lambda - E_0,$$
(5)

$$\hat{H}^{(0)} = \hat{P}\hat{F}_N\hat{P} + (1 - \hat{P})\hat{F}_N(1 - \hat{P}), \ (\hat{P} = |0\rangle\langle 0|),$$
(6)

where *h/g* are the matrix elements of one- and two-particle Hamiltonians (without antisymmetrization), and E_0 is the expectation value of the Fock operator with respect to $|0\rangle$: $E_0 = F_\lambda^\kappa \Gamma_\kappa^\lambda$. Subscript *N* denotes the normal-ordering in the Mukherjee-Kutzelnigg sense.[31]

With these definitions Eq. (1) involves up to the 4-particle RDM. To reduce the operation and storage complexities, in SO-[2]$_{R12}$ 3- and 4-RDMs were avoided via the cumulant approximation;[31,32] in combination with screening approximations only 1- and 2-RDM are necessary to evaluate the SO-[2]$_{R12}$ correction, with operation count proportional to the sixth power of the system size. Although the results looked encouraging, there are doubts about the reliability of cumulant approximation in the strong-correlation regime.[33–35] Here we explore a slightly different route to reduce the extent to which the cumulant approximation is employed.

Let us first rewrite the geminal-geminal coupling term in the Hylleraas functional by extracting a commutator,

$$\mathcal{H}^{(2)} = 2\langle 0|\hat{H}\hat{\Omega}^{(1)}|0\rangle + \langle \psi^{(1)}|([\hat{F}_N, \hat{\Omega}^{(1)}] + \hat{\Omega}^{(1)}\hat{F}_N)|0\rangle.$$
(7)

The appearance of 4-RDM is due to the term $\langle \psi^{(1)}|\hat{\Omega}^{(1)}\hat{F}_N|0\rangle$. In single-reference R12 methods, this term vanishes if we invoke the Brillouin condition and assume the generalized Brillouin condition (GBC).[36] In the context of multi-reference R12 methods, GBC was also used by Ten-no.[25] In this spirit, we propose to neglect completely this term instead of employing cumulant approximation. That is,

$$\mathcal{H}^{(2)} \approx 2\langle 0|\hat{H}\hat{\Omega}^{(1)}|0\rangle + \langle \psi^{(1)}|[\hat{F}_N, \hat{\Omega}^{(1)}]|0\rangle.$$
(8)

This is the key difference from the initial formulation of [2]$_{R12}$. With this approximation, 4-RDM is eliminated and only the RDM of rank 3 and lower are needed. To approximate 3-RDM we expand it in cumulant form developed by Kutzelnigg and co-workers[37] and discard the 3-particle cumulant

$$\Gamma_{Q_1 Q_2 Q_3}^{P_1 P_2 P_3} = \Lambda_{Q_1 Q_2 Q_3}^{P_1 P_2 P_3} + \Gamma_{Q_1}^{P_1}\Gamma_{Q_2}^{P_2}\Gamma_{Q_3}^{P_3} - \frac{1}{2}\Gamma_{Q_2}^{P_1}\Gamma_{Q_1}^{P_2}\Gamma_{Q_3}^{P_3}(\mathbf{3})$$

$$+ \frac{1}{4}\Gamma_{Q_2}^{P_1}\Gamma_{Q_3}^{P_2}\Gamma_{Q_1}^{P_3}(\mathbf{2}) + \Gamma_{Q_1}^{P_1}\Lambda_{Q_2 Q_3}^{P_2 P_3}(\mathbf{3})$$

$$- \frac{1}{2}\Gamma_{Q_2}^{P_1}\Lambda_{Q_1 Q_3}^{P_2 P_3}(\mathbf{6}).$$
(9)

Λ denotes spin-free cumulant and the numbers in parentheses denote the numbers of similar expression from permutations. Thereby $\mathcal{H}^{(2)}$ can be expressed in terms of only spin-free 1- and 2-RDMs. Furthermore, within the screening approximation,[27] $\mathcal{H}^{(2)}$ becomes

$$\mathcal{H}^{(2)} = \mathcal{V} + \mathcal{B}_0 + \mathcal{X} + \Delta, \text{ where}$$
(10)

$$\mathcal{V} = t_{rs}^{pq}\Gamma_{pq}^{xy}\left(g_{xy}^{\kappa\lambda}r_{\kappa\lambda}^{rs} - g_{xy}^{tu}r_{tu}^{rs} - g_{xy}^{\alpha't}\Gamma_t^u r_{\alpha'u}^{rs} \right),$$
(11)

$$\mathcal{B}_0 = t_{rs}^{pq}t_{tu}^{vw}\Gamma_{vw}^{rs}\left(r_{pq}^{\mu\lambda}f_\lambda^\kappa r_{\mu\kappa}^{tu} - r_{pq}^{zy}f_y^x r_{zx}^{tu} - r_{pq}^{yx}f_x^{\alpha'}r_{\alpha'y}^{ut} \right.$$

$$\left. -r_{pq}^{\alpha'y}f_{\alpha'}^x r_{xy}^{tu} - \frac{1}{2}r_{pq}^{\beta'y}\Gamma_y^x f_{\beta'}^{\alpha'}r_{\alpha'x}^{tu} - \frac{1}{2}r_{pq}^{\alpha'y}\Gamma_y^x f_x^\kappa r_{\alpha'\kappa}^{tu} \right),$$
(12)

$$\mathcal{X} = -t_{rs}^{pq}t_{tu}^{vw}\left(\Gamma_{vx}^{rs}f_w^x \right)\left(r_{\kappa\lambda}^{tu}r_{pq}^{\kappa\lambda} - r_{yz}^{tu}r_{pq}^{yz} - \frac{1}{2}r_{y\alpha'}^{tu}\Gamma_z^y r_{pq}^{z\alpha'} \right),$$
(13)

$$\Delta = -\left(r_{\alpha'\kappa}^{tu}f_x^\kappa t_{tu}^{vw} \right)$$

$$\times \left[\left(t_{rs}^{pq}r_{pq}^{\alpha'y} \right)\left(\Gamma_v^s \left(-\frac{1}{2}\Gamma_{wy}^{xr} + \frac{1}{2}\Gamma_w^x\Gamma_y^r - \frac{1}{2}\Gamma_w^r\Gamma_y^x \right) \right.\right.$$

$$+ \Gamma_w^s \left(-\frac{1}{2}\Gamma_{yv}^{xr} + \Gamma_v^r\Gamma_y^x - \frac{1}{4}\Gamma_y^r\Gamma_v^x \right) + \Gamma_v^r \left(\Gamma_{wy}^{xs} - \Gamma_y^s\Gamma_w^x \right)$$

$$\left.\left. + \Gamma_w^r \left(-\frac{1}{2}\Gamma_{vy}^{xs} + \frac{1}{2}\Gamma_y^s\Gamma_v^x \right) \right) \right].$$
(14)

The equation is derived by using the Python program TEE.PY,[38] which can evaluate matrix elements of products of second-quantized operators using generalized Wick theorem.[31,51–53] The geminal coefficients t_{rs}^{pq} are fixed to satisfy the first-order cusp condition (the so-called SP ansatz)[19]

$$t_{rs}^{pq} = \frac{3}{8}\delta_r^p\delta_s^q + \frac{1}{8}\delta_s^p\delta_r^q.$$
(15)

The most expensive term is $t_{rs}^{pq}t_{tu}^{vw}\Gamma_{vw}^{rs}r_{pq}^{\mu\lambda}f_\lambda^\kappa r_{\mu\kappa}^{tu}$, whose evaluation in the framework of approximation C[39] scales as $C^2X^3 + C^4X^2$, with *C* and *X* the numbers of R12 correlated orbitals and CABS orbitals, respectively.

The general SF-[2]$_{R12}$ framework is applicable to arbitrary many-body methods as long as the 1- and 2-RDMs are available, similarly to SO-[2]$_{R12}$(e.g., when applied to the Hartree-Fock wave function the method reduces of a close analog of the MP2-R12/C method). Our immediate desire is to use SF-[2]$_{R12}$ to correct for the basis set incompleteness of MRCI, MRPT, and emerging MRCC methods. However, such wave functions expressed in basis sets of double-zeta quality and larger already include substantial amount of dynamical correlation, hence many orbitals will be *weakly occupied*. Geminal correlation of weakly occupied orbital pairs will therefore be an unnecessary computational burden. Therefore practical computations with SF-[2]$_{R12}$ should use only strongly occupied orbitals in the definition of geminals. For example, given a MRCI wave function one could compute natural orbitals and truncate at some occupancy threshold; the SF-[2]$_{R12}$ correction would be computed with the 1- and 2-RDMs transformed to the truncated natural orbital set.

In the current work we pursue a simpler option: namely, the CASSCF wave function is used directly as the reference. With this choice the cost of SF-[2]$_{R12}$ is similar to that of a

single-reference MP2-R12 method. Therefore, the additional computation time induced by the SF-$[2]_{R12}$ correction is fairly small. When necessary we will denote the choice of the reference function in parentheses, e.g., SF-$[2]_{R12}$(CAS).

Recent investigations of single-reference and multi-reference R12 methods have revealed that the correlation energy basis error has been efficiently reduced so that the basis error in the reference energy starts to dominate[1,25,27,28,30] (for MR methods based on CASSCF, we define the correlation energy as the difference between the total energy and the CASSCF reference energy). Therefore it is imperative to correct the basis set error of the correlation energy (two-electron basis set incompleteness) along with that of the reference energy (one-electron basis set incompleteness). For that purpose, Kong and Valeev have proposed a perturbative approach,[40] dubbed as $[2]_S$, in which the basis set error of CASSCF is corrected using (internally contracted) single excitations from the CASSCF reference wave function into the CABS space ("CABS singles"). Recently, a configuration interaction approach was proposed by Shiozaki and Werner for the same purpose.[30] Since the coupling of the CABS singles and R12 geminals is expected to be weak, the values of $[2]_S$ and SF-$[2]_{R12}$ corrections are simply added together.

III. COMPUTATIONAL DETAILS

The Hylleraas functional was evaluated using the standard R12 technology with an exponential correlation factor,[20] $f(r_{12}) = -\exp(-\gamma r_{12})/\gamma$, fit to 6 Gaussian geminals. In the benchmark calculations, when the aug-cc-pVXZ basis[41] (abbreviated as "aXZ") was employed as OBS, $\gamma = 1.5$ was used; with the cc-pVXZ-F12 basis[21] (abbreviated as "XZF") of Peterson as OBS, the recommended values for γ were adopted. The XZF and aXZ orbital basis sets were augmented with the cc-pVXZ-F12/OptRI basis[22] and the uncontracted cc-pV6Z basis,[42] respectively, to support CABS. The

two-point X^{-3} extrapolation[43] was used to estimate the CBS limit for correlation energies. For HF, the extrapolation was based on aQZ and a5Z; for N_2, it was based on aTZ and aQZ. The MRCI (without internal contraction) was based on CASSCF, with core orbitals frozen in MRCI. All R12 calculations utilized the massively parallel quantum chemistry (MPQC) program,[44] with MRCI and CASSCF wave functions computed with the Psi3 suite.[45] All two-electron integrals in the R12 part of the computation were approximated with robust density fitting.[18]

IV. RESULTS AND DISCUSSION

As a first test of SF-$[2]_{R12}$, we computed the potential energy surfaces of the HF and N_2 molecules. These bond breaking prototypes display transitions between weak correlation and strong correlation regimes. The results are shown in Figs. 1 and 2; the corresponding non-parallelity errors (NPE) are tabulated in Table I. NPE is defined as the difference between the maximum and the minimum errors (with respect to the CBS limits from extrapolation) in the computed bond distance ranges (see Table I for further details). As easily seen from Fig. 1 the significant improvement due to the perturbative correction is evident. We can quantify the accuracy of the energy relative to the reference estimate with NPE. In aDZ basis, the inclusion of $[2]_S$ and SF-$[2]_{R12}$ reduces the error from 10.35 kcal/mol to 0.84 kcal/mol, even slightly better than that of aQZ. In aTZ basis, the error is further reduced to 0.35 kcal/mol, similar to the a5Z result. As already mentioned, once SF-$[2]_{R12}$ accounts for the basis set error of correlation energy, the basis error of the CASSCF energy itself becomes prominent. Addition of the $[2]_S$ correction effectively reduces the latter; the role of the $[2]_S$ correction is particularly important at short bond distances (compare the two R12-corrected datasets in Fig. 1). For HF, including $[2]_S$ further lowers the NPE by a factor of 5.
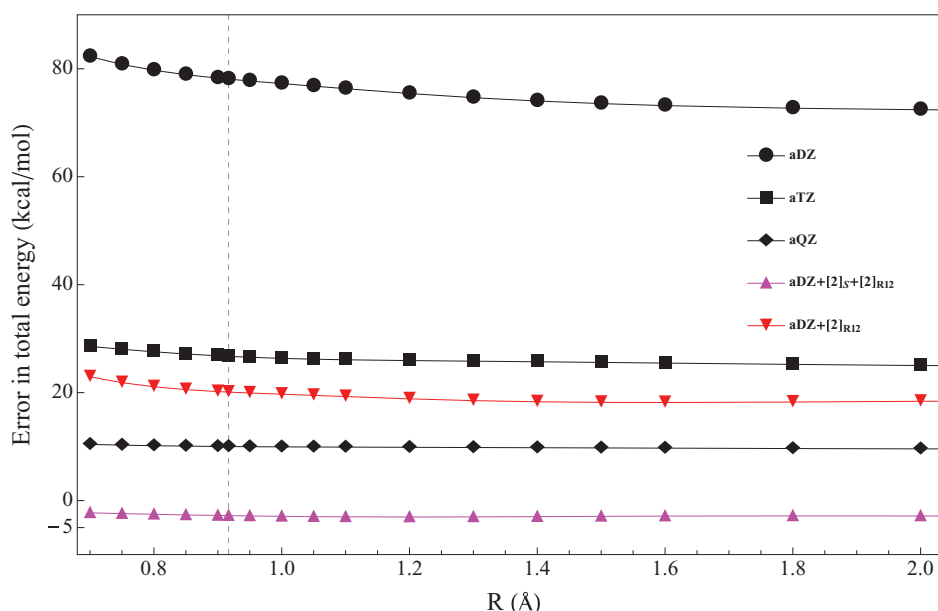

FIG. 1. The basis set error of the valence MRCI energy for HF molecule with respect to its CBS limit (obtained from extrapolation). aXZ stands for the aug-cc-pVXZ basis. The dashed line marks the equilibrium geometry (R = 0.9168 Å).
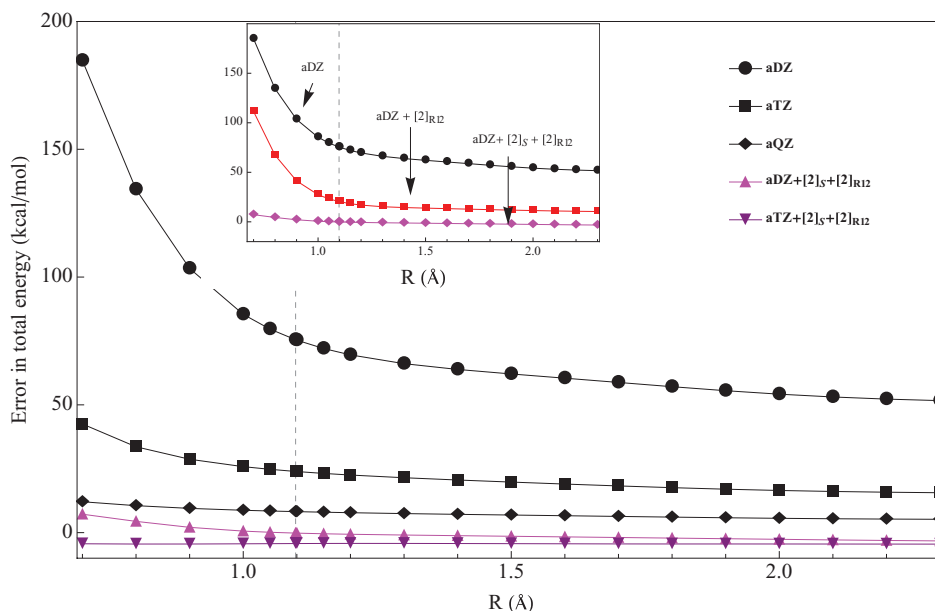
FIG. 2. The basis set error of the valence MRCI energy for N$_2$ molecule with respect to its CBS limit (obtained from extrapolation). aXZ stands for the aug-cc-pVXZ basis. The dashed line marks the equilibrium geometry (R = 1.09768 Å).

We observed similar improvement for N$_2$. Corrections SF-[2]$_{R12}$ and [2]$_S$ reduce the NPE of aDZ MRCI to the aQZ level; for aTZ, the perturbation correction reduces the error to 0.38 kcal/mol, much smaller than that of aQZ. The error for aDZ, even with SF-[2]$_{R12}$, is quite large, but it shall not be attributed to the error in correlation energy. As the inset in Fig. 2 demonstrates, the large error in the (SF-[2]$_{R12}$ corrected) total energy comes from the error in the reference energy, especially in the short distance region, as is clear from the large difference between the two lower curves. The introduction of [2]$_S$ significantly improves both the absolute and the relative energies. This illustrates the effect of [2]$_S$ and the importance of balanced reduction of the basis set errors of reference and correlation energies.

Both the current method SF-[2]$_{R12}$(CAS) and MRMP2-F12 (Ref. 25) are *posteriori* corrections. As we noted above, the two approaches are closely related; however, they involve different sets of approximations. Their performance is compared in Table II, which shows the excitation energies (^{1}D-^{3}P) of carbon atom and the atomization energy of CH$_2$ (^{1}A$_1$ state)[25] computed with SF-[2]$_{R12}$(CAS) and MRMP2-F12. For the C atom excitation energy, the two methods differ by 0.024 eV in aDZ, but the difference decreases to as small as 0.001 eV in aQZ. For the atomization energy of CH$_2$, the results are also very similar; in aQZ, the difference is around 0.7 kJ·mol^{-1}(about 0.007 eV). Considering the rather differ-

ent approximations introduced in each method, the similarity of the results is remarkable. More testing is needed, however, to make stronger conclusions about the similarities between our SF-[2]$_{R12}$(CAS) method and Ten-no's MRMP-F12 method.

Our last example concerns the basis set error of the adiabatic excitation energy (T$_e$) from the lowest triplet to the lowest singlet state of methylene, $E(\tilde{a}\ ^1A_1) - E(\tilde{X}\ ^3B_1)$. The results are tabulated in Table III, in which the MRCI-F12 data of Shiozaki and Werner are also listed for comparison. On one hand, even in DZF, SF-[2]$_{R12}$ reduces the basis error from 0.048 eV to a very small value of 0.003 eV, even better than the quality in QZF; moreover, the correlation energy contribution to T$_e$ quickly converges, once SF-[2]$_{R12}$ is included. For example, with SF-[2]$_{R12}$, the difference between TZF and QZF is as small as 0.001 eV, in contrast to 0.01 eV without the correction. Therefore, the convergence (to the SF-[2]$_{R12}$ basis limit) is greatly accelerated. On the other hand, compared to the CBS limit value, we notice that SF-[2]$_{R12}$ overestimates the CBS limit of the correlation energy; for example, in QZF, the SF-[2]$_{R12}$ corrected T$_e$ is −0.075 eV, 0.008 eV lower than the estimated CBS value. Although not shown here, the overestimation also occurs for each individual state, not just for the energy differences. It is clear from the table that even with SF-[2]$_{R12}$, the rapid initial convergence to the CBS limit becomes slow in the asymptotic limit.

TABLE I. Nonparallelity error (NPE) of valence MRCI energies with respect to their complete basis set limits, based on the data from 0.7 Å to the most stretched geometry (a bond distance of 7 Å for HF and 10 Å for N$_2$). For HF, it is (8e, 5o); for N$_2$, it is (10e, 8o). "aXZ" refers to the aug-cc-pVXZ basis set. The unit is kcal/mol.

	aDZ	aTZ	aQZ	a5Z	aDZ+[2]$_{R12}$	aTZ+[2]$_{R12}$	aDZ+[2]$_S$+[2]$_{R12}$	aTZ+[2]$_S$+[2]$_{R12}$
HF	10.35	3.79	0.91	0.39	4.76	1.48	0.84	0.35
N$_2$	134.20	27.34	7.06		101.43	11.68	11.10	0.38

TABLE II. Comparison between $[2]_{R12}$ and MRMP-F12. "corr" denotes the correlation energy contribution to the properties under investigation. "F12" denotes the pure F12 contribution of MRMP-F12 (excluding the MRMP2 correlation energy). For all calculations, the $2s$ and $2p$ valence orbitals define the active space. The core orbitals are optimized in state-specific CASSCF computations and then frozen in the MRMP2. The geometry of CH_2 (C_{2v} symmetry), the MRMP2, and MRMP-F12 energies are taken from Ref. 25: $R_{CH} = 1.1068$ Å, and $\angle HCH = 102.03°$. "aXZ" refers to the aug-cc-pVXZ basis set.

	CASSCF	MRMP2	corr	corr+F12	corr+$[2]_{R12}$
		C atom excitation energy (eV): ^1D -^3P			
aDZ	1.595	1.409	−0.186	−0.290	−0.314
aTZ	1.513	1.262	−0.250	−0.307	−0.310
aQZ	1.513	1.228	−0.284	−0.314	−0.315
		CH_2 ($^1A_1$ state) atomization energy (kJ mol^{-1})			
aD	639.5	681.1	41.6	73.6	73.9
aT	654.9	715.0	60.0	72.2	71.6
aQ	656.3	722.7	66.4	72.1	71.4

In comparison, MRCI-F12 (Ref. 28) converges to the exact limit more quickly. The major difference of SF-$[2]_{R12}$(CAS) from MRCI-F12, in which the conventional correlation is optimized in the presence of the explicit correlation, is the decoupled treatment of the two components of the correlation effect. The R12 correction is based purely on CASSCF and is independent of the correlation model (MRCI, MRPT, etc.). Essentially, the "interference effect" between the correlation methods and basis-set hierarchies[46,47] is not taken into account in SF-$[2]_{R12}$(CAS).

Here we are specifically interested in the "interference" terms in the energy that come from the interaction of the conventional correlation part of the wave function, $|\Psi_{conv}\rangle$, and the R12 counterpart, $|\Psi_{R12}\rangle$. There are two types of such interference terms. The first, a more benign one, is from the coupling through the zeroth-order (Fock) operator, $\langle\Psi_{conv}|\hat{H}^{(0)}|\Psi_{R12}\rangle$. This coupling term is included in the Hylleraas functional for the second-order energy and hence is taken into account in MRMP2-F12; the effect of this coupling is relatively small. The more troublesome is the coupling through the first-order operator, i.e., $\langle\Psi_{conv}|\hat{H}^{(1)}|\Psi_{R12}\rangle$. This term converges as slowly as the correlation energy itself, i.e., as $(L + 1)^{-3}$. It is not accounted in the second-order energy expression, and thus requires at least a third-order treatment. Neither of these terms is accounted in our

SF-$[2]_{R12}$(CAS) method, but these terms are accounted in the SF-$[2]_{R12}$ method based on a correlated reference, such as MRCI.

To estimate the magnitude of the interference effect we computed the MP2 and CCSD basis set errors with MP2-R12 and d-CCSD(2)$_{\overline{R12}}$ (Ref. 48) for the two states and the results are contained in Table III (only R12 contributions to T_e are shown). Comparison of the two sets of data spotlights the interference effect: the difference converges quite slowly and even at QZF, the difference is still as large as 0.019 eV. This effect should and does extend to MR methods and it accounts for the major difference between SF-$[2]_{R12}$ and MRCI-F12. We emphasize that the issue under discussion is not inherent in the general theory SF-$[2]_{R12}$; it emerges only because we are investigating the particular variant SF-$[2]_{R12}$(CAS) and employ the uncorrelated CASSCF reference functions (in the sense that the dynamical correlation is missing). Work to account for the interference effect within our scheme is currently underway. In the end, we stress that even the estimated MRCI CBS limit still differs from the experimental value by about 0.04 eV, much larger than the interference effect at TZF or QZF. Thence judging from the particular case study, even with CASSCF references, practically SF-$[2]_{R12}$ is a very reasonable approximation to the more rigorous MRCI-F12, if other high order effects are not considered.

TABLE III. Comparison between $[2]_{R12}$ and MRCI-F12 for the singlet-triplet separation of CH_2 in eV: $^1A_1$ - $^3B_1$. "corr" denotes the correlation energy contribution to the properties under investigation. "F12" denotes the pure F12 contribution of MRCI-F12 (excluding the MRCI correlation energy). For all calculations, the $2s$ and $2p$ valence orbitals define the active space. The core orbitals are optimized in state-specific CASSCF computations and then frozen in the MRCI. The geometries, MRCI/MRCI-F12 (the SFIX version) energies and CBS limits are taken from Ref. 28 (Table IV). "XZF" refers to the cc-pVXZ-F12 basis set. "DMC" stands for diffusion quantum Monte Carlo. MP2-R12 and CCSD(2)$_{\overline{R12}}$ refer to purely the R12 contributions (excluding the conventional contributions).

	CASSCF	MRCI	corr	corr+F12	corr+$[2]_{R12}$	CCSD(2)$_{\overline{R12}}$	MP2-R12
DZF	0.457	0.438	−0.019	−0.054	−0.070	−0.034	−0.093
TZF	0.437	0.391	−0.047	−0.065	−0.074	−0.012	−0.046
QZF	0.436	0.379	−0.057	−0.067	−0.075	−0.006	−0.027
CBS	0.435	0.368	−0.067				
Expt.[a]	0.406						
DMC[b]	0.406(4)						

[a]Reference 49.
[b]Reference 50.

V. SUMMARY

Here we presented a spin-free variant of the universal explicitly correlated correction [2]$_{R12}$ that was originally proposed by Torheyden and Valeev in a spin-orbital form. Evaluation of the 3- and 4-RDM is avoided by adopting the Brillouin conditions of single-reference R12 methods, and by cumulant and screening approximations. To account for the basis set error of the reference wave function, we additively include the perturbative [2]$_S$ correction of Kong and Valeev. The SF-[2]$_{R12}$ approach is technically simple: no modification of the standard wave function is introduced and the effect of geminal terms is evaluated perturbatively. The performance of SF-[2]$_{R12}$ was evaluated on prototypical bond breaking processes, the C atom excitation energy, the atomization energy of CH_2, and the singlet-triplet separation of methylene. The R12 correction in our approach robustly reduces the basis set error and accelerates the convergence to the CBS limit.

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