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Explicitly correlated second-order Møller–Plesset perturbation theory for unrestricted Hartree–Fock reference functions with exact satisfaction of cusp conditions

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We formulated and implemented explicitly correlated second-order Møller–Plesset perturbation theory for unrestricted Hartree–Fock reference functions with exact satisfaction of the cusp conditions. For this purpose the geminal basis was augmented by spin-flipped functions. Numerical tests for the correlation energies of several open shell systems have shown faster convergence toward the complete basis set limit when the spin-flipped geminals are included. We also performed benchmark calculations of atomization energies for a set of 16 molecules. © 2009 American Institute of Physics. [DOI: 10.1063/1.3212884]

I. INTRODUCTION

Most of the orbital based methods in quantum chemistry exhibit painfully slow convergence of correlation energies toward the complete basis set (CBS) limit—the corresponding rate of the error is proportional to $(L_{\max} + 1)^{-3}$,¹ where L_{\max} is the highest angular momentum of the given one-electron basis. This is caused by the fact that the behavior of the wave function in the vicinity of interelectronic coalescence cannot be described well in terms of products of one-particle basis functions. The introduction of linear- r_{12} terms² into the expansion of wave functions improves the convergence behavior to $(L_{\max} + 1)^{-7}$ (Ref. 3) due to the more accurate description of the behavior around the coalescence point.^{4,5} During the past several years, there has been extensive advancement in explicitly correlated methods,⁶ such as the introduction of auxiliary basis sets,^{7,8} use of numerical quadratures,⁹ and density fitting^{10,11} for evaluation of many-electron integrals, nonlinear correlation factors,^{12–14} local correlated methods,^{15–17} and approximate coupled-cluster (CC) methods.^{18,19} The diagonal orbital invariant *Ansatz* based on the s - and p -wave cusp conditions^{4,5} (SP *Ansatz*)⁹ has been employed in various F12 (Refs. 20–25) methods. More recently, full CC-F12 methods beyond the standard approximation^{26–28} and CC linear response theory²⁹ have been implemented by the use of automated code synthesis techniques.

For treatment of open shell molecules, explicitly correlated multireference configuration interaction (MRCI-R12) calculations were demonstrated by Gdanitz and co-worker^{30–32} and MP2-R12 and CCSD-R12 methods based on the unrestricted Hartree–Fock (UHF) as well as restricted open shell Hartree–Fock (ROHF) references were developed by Noga and co-workers.^{33,34} More recent advances involve

MRMP2-F12 method by Ten-no³⁵ and restricted MP2 (RMP2-F12) method for high spin states by Knizia and Werner.³⁶ Some calculations for atomization energies have been carried out.^{37–40} Most of the explicitly correlated methods for open shell systems, previously described in the literature, are formulated with pair functions as products of the F12 factor and occupied spin orbitals as those in the unitary invariant *Ansatz*.⁴¹ Recently we have suggested that the previous *Ansätze* without the use of the rational generator⁹ cannot fully satisfy the cusp conditions,²⁴ but it can be circumvented by the inclusion of a spin-flipped geminal (SFG) basis.²⁴ Very recently, Knizia *et al.*⁴² extended the simplified CCSD(T)-F12x approximations to open shell systems with such a basis within the use of ROHF reference functions.

In this paper, we report on a formulation and implementation of the MP2-F12 method for UHF reference functions (UMP2-F12) with extended *Ansätze* that includes a SFG basis. The implementation of this method is performed within the framework of the diagonal (SP and IJII) *Ansätze*.²⁰ Numerical results for the correlation energies of several open shell systems show the improvement in accuracy when SFG basis is introduced. Benchmark calculation for atomization energies of 16 molecules shows that the inclusion of SFG basis improves the accuracy for both of the *Ansätze*.

II. THEORY

A. General considerations

Henceforth, the spatial parts of the spin-up occupied, virtual, and general orbitals are denoted by i, j, \dots, a, b, \dots , and p, q, \dots , respectively. The corresponding parts of the spin-down orbitals are denoted by $\bar{i}, \bar{j}, \dots, \bar{a}, \bar{b}, \dots$, and \bar{p}, \bar{q}, \dots . In addition, we use up and down arrows for alpha and beta spin functions, respectively, as $k_1(\vec{x}) = \varphi_k(\vec{r})\alpha$.

The Hylleraas energy functional for the UHF reference function is

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$$H[\{u_{i_1 j_1}, u_{\bar{i}_1 \bar{j}_1}, u_{i_1 \bar{j}_1}\}] = \sum_{i < j} e_{ij} + \sum_{\bar{i} < \bar{j}} e_{\bar{i}\bar{j}} + \sum_i \sum_{\bar{j}} e_{i\bar{j}}, \quad (1)$$

with the pair energies

$$e_{ij} = \langle u_{i_1 j_1} | (\hat{F}_{12} - \varepsilon_i - \varepsilon_j) | u_{i_1 j_1} \rangle + 2 \langle u_{i_1 j_1} | r_{12}^{-1} | i_1 j_1 \rangle \quad (2)$$

and similar expressions for $e_{\bar{i}\bar{j}}$ and $e_{i\bar{j}}$, where $\hat{F}_{12} = \hat{F}_1 + \hat{F}_2$ is a sum of Fock operators and the double vertical lines denote the antisymmetrization of pair functions. The pair functions take the forms

$$u_{i_1 j_1}(\vec{x}_1, \vec{x}_2) = \sum_{k,l} \hat{Q}_{12} t_{ij}^{kl} f_{12} k_{\uparrow}(\vec{x}_1) l_{\uparrow}(\vec{x}_2) + \sum_{a,b} C_{ij}^{ab} a_{\uparrow}(\vec{x}_1) b_{\uparrow}(\vec{x}_2), \quad (3a)$$

$$u_{\bar{i}_1 \bar{j}_1}(\vec{x}_1, \vec{x}_2) = \sum_{\bar{k}, \bar{l}} \hat{Q}_{12} t_{\bar{i}\bar{j}}^{\bar{k}\bar{l}} f_{12} \bar{k}_{\downarrow}(\vec{x}_1) \bar{l}_{\downarrow}(\vec{x}_2) + \sum_{\bar{a}, \bar{b}} C_{\bar{i}\bar{j}}^{\bar{a}\bar{b}} \bar{a}_{\downarrow}(\vec{x}_1) \bar{b}_{\downarrow}(\vec{x}_2), \quad (3b)$$

$$C_{ij}^{ab} = - \sum_{k,l} \frac{\langle k_{\uparrow} l_{\uparrow} | (\hat{F}_{12} - \varepsilon_i - \varepsilon_j) | a_{\uparrow} b_{\uparrow} \rangle t_{ij}^{kl}}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} - \frac{\langle ij | ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}, \quad (7a)$$

$$C_{\bar{i}\bar{j}}^{\bar{a}\bar{b}} = - \sum_{\bar{k}, \bar{l}} \frac{\langle \bar{k}_{\downarrow} \bar{l}_{\downarrow} | (\hat{F}_{12} - \varepsilon_{\bar{i}} - \varepsilon_{\bar{j}}) | \bar{a}_{\downarrow} \bar{b}_{\downarrow} \rangle t_{\bar{i}\bar{j}}^{\bar{k}\bar{l}}}{\varepsilon_{\bar{a}} + \varepsilon_{\bar{b}} - \varepsilon_{\bar{i}} - \varepsilon_{\bar{j}}} - \frac{\langle \bar{i}\bar{j} | \bar{a}\bar{b} \rangle}{\varepsilon_{\bar{a}} + \varepsilon_{\bar{b}} - \varepsilon_{\bar{i}} - \varepsilon_{\bar{j}}}, \quad (7b)$$

$$C_{i\bar{j}}^{\bar{a}b} = - \sum_{k, \bar{l}} \frac{\langle k_{\uparrow} \bar{l}_{\downarrow} | f_{12} (\hat{F}_{12} - \varepsilon_i - \varepsilon_{\bar{j}}) | a_{\uparrow} \bar{b}_{\downarrow} \rangle t_{i\bar{j}}^{k\bar{l}} + \langle \bar{l}_{\uparrow} k_{\downarrow} | f_{12} (\hat{F}_{12} - \varepsilon_i - \varepsilon_{\bar{j}}) | a_{\uparrow} \bar{b}_{\downarrow} \rangle t_{i\bar{j}}^{\bar{l}k}}{\varepsilon_a + \varepsilon_{\bar{b}} - \varepsilon_i - \varepsilon_{\bar{j}}} - \frac{\langle i\bar{j} | \bar{a}b \rangle}{\varepsilon_a + \varepsilon_{\bar{b}} - \varepsilon_i - \varepsilon_{\bar{j}}}. \quad (7c)$$

Note that the last term in the numerator of Eq. (7c) cannot be expressed in the commutator form as $[f_{12}, \hat{F}_{12}]$ since the spin-flipped spin orbitals are not eigenfunctions of the Fock operator. Generally, it is important to keep the spin factors within the Dirac brackets when the spin-dependent operators, such as \hat{F}_{12} and \hat{Q}_{12} in UHF, are present.

B. Intermediates

We introduce the intermediates that are necessary for the energy expressions in the diagonal (SP and IJJ) *Ansätze*.

$$u_{i_1 \bar{j}_1}(\vec{x}_1, \vec{x}_2) = \sum_k \sum_{\bar{l}} [\hat{Q}_{12} t_{i\bar{j}}^{k\bar{l}} f_{12} k_{\uparrow}(\vec{x}_1) \bar{l}_{\downarrow}(\vec{x}_2) + \hat{Q}_{12} t_{i\bar{j}}^{\bar{l}k} f_{12} \bar{l}_{\downarrow}(\vec{x}_1) k_{\uparrow}(\vec{x}_2)] + \sum_{a, \bar{b}} C_{i\bar{j}}^{a\bar{b}} a_{\uparrow}(\vec{x}_1) \bar{b}_{\downarrow}(\vec{x}_2), \quad (3c)$$

with $f_{12} = f(r_{12})$. The strong orthogonality projector^{43,44} is

$$\hat{Q}_{12} = (\mathbf{1} - \hat{O}_1)(\mathbf{1} - \hat{O}_2), \quad (4)$$

where \hat{O}_n is the projection operator onto the space of the occupied spin orbitals in the UHF reference,

$$\hat{O}_n = \sum_i |i_{\uparrow}(\vec{x}_n)\rangle \langle i_{\uparrow}(\vec{x}_n)| + \sum_{\bar{j}} |\bar{j}_{\downarrow}(\vec{x}_n)\rangle \langle \bar{j}_{\downarrow}(\vec{x}_n)|, \quad (5)$$

and we use the Slater-type geminal^{12,20}

$$f_{12} = -\frac{1}{\gamma} \exp(-\gamma r_{12}). \quad (6)$$

It should be noted that the second term on the right-hand side (rhs) of Eq. (3c) with the SFG basis $f_{12} \bar{l}_{\downarrow}(\vec{x}_1) k_{\uparrow}(\vec{x}_2)$ is absent in the original unitary invariant *Ansatz*.⁴¹ We have shown that SFG is originating from the multiplication of the permutation operator⁹ in the rational generator and is crucial for fulfilling the cusp conditions for the UHF reference.²⁴ Expressions for the amplitudes of the products of virtual orbitals in Eqs. (3a)–(3c) can be obtained by the minimization of $H[\{u_{i_1 j_1}, u_{\bar{i}_1 \bar{j}_1}, u_{i_1 \bar{j}_1}\}]$.

Henceforth, we will also assume that the generalized Brillouin condition holds

$$[\hat{F}_{12}, \hat{Q}_{12}] \approx 0. \quad (8)$$

For the expression of the UMP2-F12 correlation energy, it is convenient to introduce the intermediates

$$V_{ij}^{kl} = \langle k_{\uparrow} l_{\uparrow} | \frac{1}{r_{12}} \hat{Q}_{12} f_{12} | i_1 j_1 \rangle - \sum_{a,b} \phi_{ij}^{ab} \langle ab | \frac{1}{r_{12}} | kl \rangle \quad (9)$$

(and similar expressions for $V_{\bar{i}\bar{j}}^{\bar{k}\bar{l}}$ and $V_{i\bar{j}}^{\bar{k}\bar{l}}$) and

$$V_{ji}^{kl} = \langle k_{\uparrow} \bar{l}_{\downarrow} | \frac{1}{r_{12}} \hat{Q}_{12} f_{12} | \bar{j}_{\uparrow} i_{\downarrow} \rangle - \sum_{a,\bar{b}} \frac{\langle \bar{j}_{\uparrow} i_{\downarrow} | f_{12} (\hat{F}_{12} - \varepsilon_i - \varepsilon_{\bar{j}}) | a_{\uparrow} \bar{b}_{\downarrow} \rangle}{\varepsilon_a + \varepsilon_{\bar{b}} - \varepsilon_i - \varepsilon_{\bar{j}}} \langle a\bar{b} | \frac{1}{r_{12}} | k\bar{l} \rangle, \quad (10)$$

where

$$\phi_{ij}^{ab} = \frac{\langle i_{\uparrow} j_{\downarrow} | [f_{12}, \hat{F}_{12}] | a_{\uparrow} b_{\downarrow} \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}. \quad (11)$$

We also use

$$B_{ij}^{kl} = \langle k_{\uparrow} l_{\downarrow} | [\hat{F}_{12}, f_{12}] \hat{Q}_{12} f_{12} | i_{\uparrow} j_{\downarrow} \rangle - \sum_{a,\bar{b}} \phi_{ij}^{ab} \langle a_{\uparrow} b_{\downarrow} | [\hat{F}_{12}, f_{12}] | k_{\uparrow} l_{\downarrow} \rangle \quad (12)$$

(and ones for $B_{ij}^{k\bar{l}}$ and $B_{ij}^{\bar{k}l}$) and

$$B_{ij}^{\bar{k}l} = \langle i_{\uparrow} \bar{j}_{\downarrow} | [\hat{F}_{12}, f_{12}] \hat{Q}_{12} f_{12} | \bar{l}_{\uparrow} k_{\downarrow} \rangle - \sum_{a,\bar{b}} \phi_{ij}^{a\bar{b}} \langle a_{\uparrow} \bar{b}_{\downarrow} | (\hat{F}_{12} - \varepsilon_i - \varepsilon_{\bar{j}}) f_{12} | \bar{l}_{\uparrow} k_{\downarrow} \rangle, \quad (13a)$$

$$B_{ji}^{\bar{k}l} = \langle \bar{j}_{\uparrow} i_{\downarrow} | f_{12} \hat{F}_{12} \hat{Q}_{12} f_{12} | \bar{l}_{\uparrow} k_{\downarrow} \rangle - \sum_{a,\bar{b}} \langle \bar{j}_{\uparrow} i_{\downarrow} | f_{12} \hat{F}_{12} | a_{\uparrow} \bar{b}_{\downarrow} \rangle \frac{\langle a_{\uparrow} \bar{b}_{\downarrow} | (\hat{F}_{12} - \varepsilon_i - \varepsilon_{\bar{j}}) f_{12} | \bar{l}_{\uparrow} k_{\downarrow} \rangle}{\varepsilon_a + \varepsilon_{\bar{b}} - \varepsilon_i - \varepsilon_{\bar{j}}} - (\varepsilon_i + \varepsilon_{\bar{j}}) \langle \bar{j}_{\uparrow} i_{\downarrow} | f_{12} \hat{Q}_{12} f_{12} | \bar{l}_{\uparrow} k_{\downarrow} \rangle - \sum_{a,\bar{b}} \frac{\langle \bar{j}i | f_{12} | a\bar{b} \rangle \langle a_{\uparrow} \bar{b}_{\downarrow} | (\hat{F}_{12} - \varepsilon_i - \varepsilon_{\bar{j}}) f_{12} | \bar{l}_{\uparrow} k_{\downarrow} \rangle}{\varepsilon_a + \varepsilon_{\bar{b}} - \varepsilon_i - \varepsilon_{\bar{j}}}. \quad (13b)$$

All matrix elements of the B and V intermediates resemble those in the closed-shell case, and their evaluation is described in detail elsewhere.²⁰ In Eqs. (10) and (13a), there is a new element $\langle a_{\uparrow} \bar{b}_{\downarrow} | (\hat{F}_{12} - \varepsilon_i - \varepsilon_{\bar{j}}) f_{12} | \bar{l}_{\uparrow} k_{\downarrow} \rangle$ which can be calculated using the identity

$$(\hat{F}_{12} - \varepsilon_i - \varepsilon_{\bar{j}}) f_{12} = -(\varepsilon_i + \varepsilon_{\bar{j}}) f_{12} + [\hat{F}_{12}, f_{12}] + f_{12} \hat{F}_{12}. \quad (14)$$

The integrals over the last term of the rhs of Eq. (14) can be calculated by the use of the resolution of the identity (RI),

$$\langle a_{\uparrow} \bar{b}_{\downarrow} | f_{12} \hat{F}_{12} | \bar{l}_{\uparrow} k_{\downarrow} \rangle = \sum_p \varepsilon_p \langle \bar{l} | p \rangle \langle p k | f_{12} | a\bar{b} \rangle + \sum_{\bar{q}} \varepsilon_{\bar{q}} \langle k | \bar{q} \rangle \langle \bar{l} \bar{q} | f_{12} | a\bar{b} \rangle. \quad (15)$$

The convergence of the expansion is very fast due to the fact that RI basis should be saturated only up to maximum angular momentum of the occupied orbitals for each spin case. The first term on the rhs of Eq. (13b) can be evaluated in the same way as in the closed-shell case²⁰ with the aid of RI. The computational cost of the present method is about four times more expensive than the closed-shell implementation^{9,20}

since each type of molecular integrals should be evaluated for four different combinations of spin indices.

C. Geminal amplitudes

The SP *Ansatz* from the coalescence conditions,⁹ which is diagonal orbital invariant, has been used in various explicitly correlated methods.²⁰⁻²⁵ Recently, Köhn introduced the extended SP *Ansätze* for the perturbational triples²⁸ and CCSD-LRT.²⁹ Knizia *et al.*⁴² used the *Ansatz* for open shell systems with ROHF reference functions. The geminal amplitudes of the SP *Ansatz*²⁴ are

$$t_{ij}^{ij} = \bar{t}_{ij}^{\bar{j}\bar{i}} = t_{ij}^{\bar{j}\bar{i}} = \frac{3}{8}, \quad (16a)$$

$$t_{ij}^{ji} = \bar{t}_{ij}^{\bar{i}\bar{j}} = t_{ij}^{\bar{i}\bar{j}} = \frac{1}{8}, \quad (16b)$$

$$t_{ii}^{\bar{i}\bar{i}} = \bar{t}_{ii}^{\bar{i}\bar{i}} = \frac{1}{2}, \quad (16c)$$

which can be obtained by the application of the rational generator with s - and p -wave cusp conditions⁹ to the UHF reference function. The presence of the SFG amplitudes $t_{ij}^{\bar{i}\bar{j}}$ is novel and the present *Ansatz* is reduced to the usual SP *Ansatz* in the closed-shell limit.

The minimization of the Hylleraas energy functional (1) with respect to the diagonal geminal amplitudes yields

$$t_{ij}^{ij} = -\frac{V_{ij}^{ij}}{B_{ij}^{ij}}, \quad (17a)$$

$$\bar{t}_{ij}^{\bar{j}\bar{i}} = -\frac{V_{ij}^{\bar{j}\bar{i}}}{B_{ij}^{\bar{j}\bar{i}}}, \quad (17b)$$

$$t_{ij}^{\bar{j}\bar{i}} = -\frac{V_{ij}^{\bar{j}\bar{i}} + B_{ij}^{\bar{j}\bar{i}} \bar{t}_{ij}^{\bar{j}\bar{i}}}{B_{ij}^{\bar{j}\bar{i}}}, \quad (17c)$$

$$\bar{t}_{ii}^{\bar{i}\bar{i}} = -\frac{V_{ii}^{\bar{i}\bar{i}} B_{ii}^{\bar{i}\bar{i}} - V_{ii}^{\bar{i}\bar{i}} \bar{t}_{ii}^{\bar{i}\bar{i}}}{B_{ii}^{\bar{i}\bar{i}} B_{ii}^{\bar{i}\bar{i}} - (B_{ii}^{\bar{i}\bar{i}})^2}. \quad (17d)$$

Note that the amplitudes from Eqs. (17c) and (17d) are solutions of a system of linear equations. The denominator of Eq. (17d) can be close to zero if the spin-up and spin-down orbitals become similar to each other. In this case, we need a threshold below which the system of equations for the corresponding $t_{ij}^{\bar{j}\bar{i}}$ and $\bar{t}_{ij}^{\bar{j}\bar{i}}$ can be considered as linearly dependent and the corresponding spin-flipped amplitude should be set to zero. This *Ansatz* with SFG basis is denoted by the IJJ⁺ *Ansatz* to distinguish from the IJJ one in which all the spin-flipped amplitudes from Eq. (17d) are zero. The geminal amplitudes of the spin-antiparallel pairs in the IJJ *Ansatz* are

TABLE I. Correlation energies (in mE_h) of individual electronic pairs of N atom calculated with SP *Ansatz*.

L_{\max}	1	2	3	4	5	6	CBS
$\alpha\alpha$ pairs							
1s2s	-0.483	-0.503	-0.505	-0.505	-0.505	-0.505	-0.51
1s2p	-1.191	-1.367	-1.379	-1.380	-1.380	-1.380	-1.38
2s2p	-2.160	-2.326	-2.430	-2.439	-2.441	-2.441	-2.44
2p2p	-5.917	-8.146	-8.268	-8.281	-8.284	-8.284	-8.28
$\beta\beta$ pairs							
1s2s	-0.905	-0.922	-0.924	-0.924	-0.924	-0.924	-0.92
$\alpha\beta$ pairs							
1s1s	-40.481	-40.834	-40.866	-40.869	-40.869	-40.869	-40.87
1s2s	-2.243	-2.330	-2.340	-2.341	-2.341	-2.341	-2.34
2s1s	-2.151	-2.250	-2.261	-2.262	-2.262	-2.262	-2.26
2s2s	-12.207	-13.184	-13.293	-13.312	-13.316	-13.317	-13.32
2p1s	-1.030	-2.015	-2.091	-2.099	-2.101	-2.101	-2.101
2p2s	-14.843	-21.160	-21.614	-21.673	-21.684	-21.686	-21.69
Total	-133.89	-165.06	-167.53	-167.83	-167.89	-167.90	-167.92
%	79.7	98.3	99.8	99.9	100.0	100.0	100.0

$$t_{ij}^{\bar{i}\bar{j}} = -\frac{V_{ij}^{\bar{i}\bar{j}}}{B_{ij}^{\bar{i}\bar{j}}}, \quad (18)$$

$$+ B_{ji}^{\bar{i}\bar{k}\bar{j}\bar{i}} t_{mn}^{\bar{i}\bar{k}\bar{j}\bar{i}} + 2V_{ij}^{\bar{k}\bar{l}\bar{k}\bar{l}} + 2V_{ij}^{\bar{j}\bar{k}\bar{l}\bar{j}}). \quad (19)$$

Using the intermediates B and V defined previously, the second-order energy can be expressed as

$$E_{\text{UMP2-F12}} = E_{\text{UMP2}} + \sum_{i,j,k,l} \left(\sum_{m,n} \frac{1}{2} B_{ij}^{kl} t_{ij}^{mn} t_{mn}^{kl} + V_{ij}^{kl} t_{ij}^{kl} \right) + \sum_{\bar{i},\bar{j},\bar{k},\bar{l}} \left(\sum_{\bar{m},\bar{n}} \frac{1}{2} B_{\bar{i}\bar{j}}^{\bar{k}\bar{l}} t_{\bar{i}\bar{j}}^{\bar{m}\bar{n}} t_{\bar{m}\bar{n}}^{\bar{k}\bar{l}} + V_{\bar{i}\bar{j}}^{\bar{k}\bar{l}} t_{\bar{i}\bar{j}}^{\bar{k}\bar{l}} \right) + \sum_{\bar{i},\bar{j},\bar{k},\bar{l}} \left(\sum_{\bar{m},\bar{n}} (B_{\bar{i}\bar{j}}^{\bar{k}\bar{l}} t_{\bar{i}\bar{j}}^{\bar{m}\bar{n}} t_{\bar{m}\bar{n}}^{\bar{k}\bar{l}} + 2B_{\bar{i}\bar{j}}^{\bar{i}\bar{k}\bar{m}\bar{n}} t_{\bar{i}\bar{j}}^{\bar{i}\bar{k}\bar{m}\bar{n}}) \right)$$

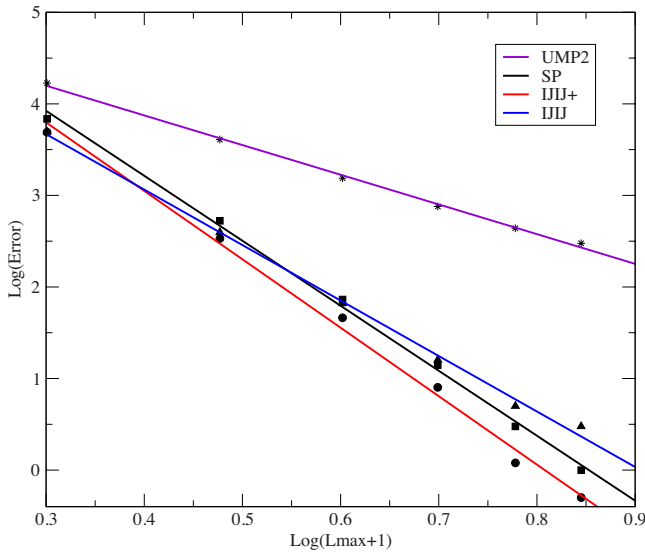


FIG. 1. Errors in the $2s_1 2p_1$ pair energy using subsets of the $20s14p11d9f7g5h3i$ basis.

III. RESULTS AND DISCUSSION

Henceforth, we use the value of Slater exponent $\gamma=1.5$ in all our F12 calculations. For the evaluation of many-electron integrals we used a spherical grid of 9216 points per atom. Molecular geometries are taken from Ref. 45, except for the $\text{CH}_2(^3B_1)$, whose geometry is taken from Ref. 46.

A. Convergence rates

In order to investigate the convergence rates of the correlation energy toward the CBS limit for different *Ansätze*, we calculate the UMP2-F12 energies of N atom using the subsets of the near saturated $20s14p11d9f7g5h3i$ basis.⁷ The

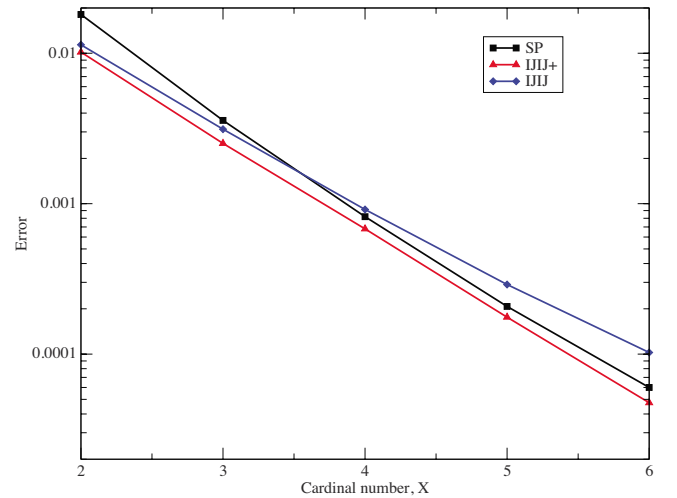


FIG. 2. Mean absolute error of the correlation energies as a function of the cardinal number in the aug-cc-pCVXZ hierarchy.

TABLE II. Correlation energies of high spin molecules calculated with different basis sets (atomic unit).

	aug-cc-pCVDZ	aug-cc-pCVTZ	aug-cc-pCVQZ	aug-cc-pCV5Z	aug-cc-pCV6Z	Near CBS
N						
SP	-0.156 67	-0.165 84	-0.167 42	-0.167 79	-0.167 88	
IJJ ⁺	-0.161 61	-0.166 49	-0.167 53	-0.167 81	-0.167 89	-0.167 92
IJJ	-0.161 06	-0.166 23	-0.167 42	-0.167 77	-0.167 86	
CH ₂ (³ B ₁)						
SP	-0.176 39	-0.184 41	-0.185 96	-0.186 26	-0.186 33	
IJJ ⁺	-0.180 56	-0.185 03	-0.186 05	-0.186 28	-0.186 33	-0.186 35
IJJ	-0.180 13	-0.184 78	-0.185 96	-0.186 23	-0.186 31	
CN						
SP	-0.401 83	-0.418 43	-0.421 68	-0.422 38	-0.422 56	
IJJ ⁺	-0.410 95	-0.419 80	-0.421 85	-0.422 44	-0.422 58	-0.422 63
IJJ	-0.409 65	-0.419 10	-0.421 60	-0.422 31	-0.422 52	
O ₂						
SP	-0.589 40	-0.613 72	-0.618 37	-0.619 45	-0.619 70	
IJJ ⁺	-0.602 87	-0.615 33	-0.618 56	-0.619 49	-0.619 72	-0.619 81
IJJ	-0.600 30	-0.614 09	-0.618 07	-0.619 26	-0.619 61	

CBS values of the second-order pair energies are calculated from the extrapolations of the IJJ⁺ energies of $L=5$ and 6 on the assumption that the convergence rates are proportional to $(L_{\max}+1)^{-7}$.

The pair energies from the SP *Ansatz* are listed in the Table I. UMP2-F12(SP) recovers 99.8% of the second-order energy with $L_{\max}=3$. For each *Ansatz*, the convergence rate can be asymptotically estimated as $(L_{\max}+1)^{-m}$. We plot the error versus $(L_{\max}+1)$ pair using logarithmic coordinates for the $2s_{\downarrow}2p_{\uparrow}$ pair in Fig. 1. The corresponding values of m are 3.2, 6.9, 6.1, and 7.4 for UMP2, UMP2-F12(SP), UMP2-F12(IJJ), and UMP2-F12(IJJ⁺), respectively. The observed convergence rates of the IJJ and IJJ⁺ *Ansätze* are somewhat better than those expected from the partial wave expansion, 5 and 7. The convergence rates are improved by the inclusion of SFG, especially in constructing the SP *Ansatz*, where the exact satisfaction of the cusp conditions is critical. For the IJJ and IJJ⁺ *Ansätze*, the effects of SFG are less critical due to the variational nature of the method, albeit the difference in the convergence rate is still significant. It is expected that

a similar behavior is observed for the unitary invariant *Ansätze*,⁴¹ which is not treated in this paper.

B. Correlation energies

The correlation energies of the open shell systems N, CH₂, CN, and O₂ are calculated using the aug-cc-pCVXZ basis⁴⁷⁻⁴⁹ with $X=D, T, Q, 5,$ and 6 . The results are given in Table II. The CBS limits are estimated by using the two-point (56) extrapolation scheme of F12 (Ref. 50) for the IJJ⁺ energies. The mean absolute errors over the four molecules are also displayed in Fig. 2. The differences of the IJJ⁺ and IJJ energies demonstrate the effect of the inclusion of SFG. The IJJ⁺ energy of O₂ is closer to CBS than the IJJ one by $2.5mE_h$ with aug-cc-pCVDZ. The SP and IJJ⁺ *Ansätze* give more accurate correlation energies than IJJ especially for large cardinal numbers since the cusp conditions can be satisfied exactly for those *Ansätze* by the inclusion of the SFG basis.

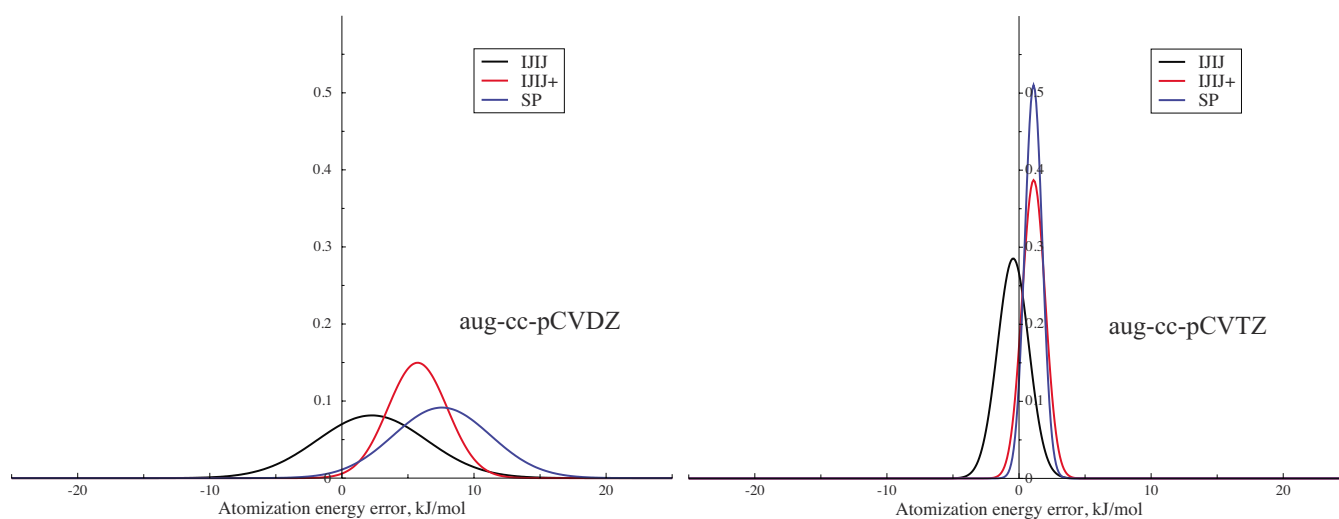


FIG. 3. Normal distribution functions for the atomization energy for molecules from Table II.

TABLE III. Atomization energies (kJ/mol).

	aug-cc-pCVDZ			aug-cc-pCVTZ			CBS
	SP	IJJ ⁺	IJJ	SP	IJJ ⁺	IJJ	
H ₂	-86.64	-87.43	-87.43	-89.53	-89.53	-89.53	-89.79
HF	-204.26	-204.53	-209.78	-207.15	-207.15	-209.25	-207.68
F ₂	-337.90	-338.16	-348.66	-339.74	-339.74	-343.94	-340.52
N ₂	-520.90	-522.74	-525.36	-527.46	-525.63	-527.20	-527.46
CO	-412.73	-413.00	-416.93	-414.04	-414.04	-416.14	-415.35
CH ₂ (¹ A ₁)	-202.95	-204.26	-205.05	-208.72	-208.73	-209.25	-209.78
H ₂ O	-336.59	-337.38	-340.53	-342.10	-342.10	-343.68	-342.89
NH ₃	-397.50	-399.34	-400.65	-406.16	-405.38	-406.16	-406.69
CH ₄	-368.62	-371.77	-372.55	-377.55	-377.55	-378.07	-378.60
HCN	-519.59	-522.47	-524.57	-528.51	-527.73	-529.04	-529.56
HNO	-557.65	-558.71	-563.17	-564.48	-563.43	-565.80	-565.27
CH ₂ O	-524.57	-525.89	-529.83	-531.13	-531.14	-533.24	-532.71
C ₂ H ₂	-497.79	-503.30	-504.88	-510.39	-510.92	-511.97	-512.76
H ₂ O ₂	-591.00	-592.83	-599.14	-598.88	-598.88	-602.02	-600.45
C ₂ H ₄	-570.78	-576.03	-577.61	-582.86	-583.14	-584.17	-584.70
CO ₂	-704.68	-705.73	-712.82	-708.89	-709.15	-712.82	-710.99
Statistical measures							
$\bar{\Delta}$	7.57	5.73	2.27	1.1	1.1	-0.44	
$\Delta_{\text{abs}}^{\text{max}}$	14.97	9.46	8.14	2.37	1.84	3.42	
$\bar{\Delta}_{\text{abs}}$	7.57	5.73	3.97	1.1	1.29	0.94	
$\bar{\Delta}_{\text{std}}$	3.68	2.25	4.14	0.66	0.87	1.18	

C. Atomization energies

The effect of SFG is also examined for the atomization energies of the set of 16 molecules studied by Bak *et al.*⁵¹ The standard diagonal *Ansätze* based on spin-free pair functions are used for closed-shell molecules. Table III shows the MP2 contributions to the atomization energies along with statistical measures based on the CBS values from the (56) extrapolation. The corresponding normal distribution functions are displayed in Fig. 3. The SP and IJJ⁺ calculations both give smaller standard deviations than IJJ without SFG with the aug-cc-pCVDZ basis. On the other hand, the smallest mean error of the IJJ *Ansatz* is likely to be an artifact due to the unbalanced treatment of the constituting atoms. It is noted that the cusp conditions can be fulfilled in the IJJ calculations only for molecules. The UMP2-F12(IJJ) method tends to underestimate the atomization energies with aug-cc-pCVTZ compared to the corresponding CBS values. The error of the Hartree–Fock (HF) contribution is more significant than the correlation contribution with aug-cc-pCVDZ, i.e., the mean absolute error of the HF contribution is 20.5 kJ/mol. For the result of the aug-cc-pCVTZ result, all of the *Ansätze* provide atomization energies more accurate than 4 kJ/mol. Nevertheless, Fig. 3 exhibits the inclusion of SFG in SP and IJJ⁺ leads to more accurate atomization energies as it is especially visible for aug-cc-pCVTZ. The mean absolute error of the HF contribution with this basis is ~ 2.5 kJ/mol, which is again larger than that of the correlation contribution. Thus a separate treatment of orbital relaxation⁵² is needed for the improvement of overall accuracy as concluded previously.

IV. CONCLUSIONS

In this paper, we have implemented UMP2-F12 methods which satisfy the cusp conditions exactly. It was numerically exhibited that the introduction of SFG in accord with the coalescence conditions enables us to calculate more accurate second-order correlation energies of high spin molecules. The atomization energies of a set of 16 molecules were also calculated to assess the effect of SFG. A statistical analysis of the errors has shown that the presence becomes more prominent with more extensive basis set. The use of SFG in other *Ansätze* and in the development of CC-F12 methods for open shell molecules will be reported in the near future.

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