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A simple F12 geminal correction in multi-reference perturbation theory

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Abstract

We propose a simple F12 geminal correction in multi-reference perturbation theory. An explicitly correlated term is introduced in the external excitations of the first order wave function in an internally contracted manner. By the use of the s- and p-wave cusp conditions, the F12 correction is expressed as the expectation value of a two-body effective operator, which reduces to the MP2-F12/A*(SP) energy in the single reference limit. The performance of the F12 multi-reference perturbation method is demonstrated for C, CH_2, O_2, and SiC_3.

1. Introduction

One of the main obstacles to accurate electronic structure calculations is the slow convergence of the correlation energy with respective to the size of one-electronic basis set. The cusp conditions [1–3] suggest that the first order wave function in the $1/Z$ expansion is expressed as a product of linear r_{12} and unperturbed wave function at a small inter-electronic distance,

$$\psi = \frac{r_{12}}{2(s+1)}\Phi + O(r_{12}^2), \tag{1}$$

where s takes 0 and 1 for singlet and triplet pairs, respectively. The cusp behavior at coalescence is poorly represented by products of orbitals, while the situation is ameliorated substantially by introducing terms explicitly dependent on the inter-electronic distances into the wave function. Various methods have been proposed in explicitly correlated electronic structure theory. Above all, the resolution of the identity (RI) approximation for many-electron integrals [4] introduced by Kutzelnigg and Klopper in R12 theory has offered practical computational methods applicable to many-electron systems. The R12 methods have been implemented at various levels of theories [4–8]. Recently, there have been several developments [9] involving the use of short-ranged correlation factors like the Slater-type geminal (STG) $f_{12} = \exp(-\gamma r_{12})$ [10,11]. The F12 variants with the short-ranged factors turned out to give very much improved results as compared to the original R12 methods [12–16]. The objective of this Letter is to introduce a simple F12 correction in multi-reference perturbation theory (MRPT). In the following section, the formulation of the theory is presented. We present numerical results in Section 3. Conclusions are given in Section 4.

2. F12 correction in MRPT

Let us consider a complete active space self-consistent field (CASSCF) reference wave function $|0\rangle$ and its first order correction $|1\rangle$ orthogonal to $|0\rangle$. The correction may be divided into the contributions in the internal (int), semi-internal (sem), and external (ext) subspaces [17],

$$|1\rangle = |1_{\mathrm{int}}\rangle + |1_{\mathrm{sem}}\rangle + |1_{\mathrm{ext}}\rangle, \tag{2}$$

whose convergences with respect to the size of one-particle basis are rather different. In the atomic case, the partial wave expansions of the internal and semi-internal contributions to the correlation energy terminate at $L_{\mathrm{occ.}}$ and $3L_{\mathrm{occ.}}$ for the maximum angular momentum of the occupied

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orbitals $L_{\mathrm{occ.}}$, while the external one does not break off. Thus, we introduce an F12 term in the external contribution,

$$|1\rangle = |\tilde{1}\rangle + \Omega_f|0\rangle, \tag{3}$$

where $|\tilde{1}\rangle$ is expanded into a selection of configuration state functions $|K\rangle$ spanned by the one-electronic basis set,

$$|\tilde{1}\rangle = \sum_K |K\rangle \tilde{C}_K, \tag{4}$$

the F12 external wave operator is in the general form,

$$\Omega_f = \frac{1}{2}\sum_{\alpha\beta}\sum_{ij}\sum_{pq} c_{ij}^{pq}\langle\alpha\beta|f_{12}|pq\rangle E_{\alpha i}E_{\beta j}, \tag{5}$$

E_{pq} are the unitary group generators, and $i, j, \ldots$ denote the union of the core and valence orbitals to be correlated, $\alpha, \beta, \ldots$ secondary orbitals in the complete basis, and $p, q, \ldots$ general orbitals in the given basis set. The wave operator (5) accelerates the convergence in an manner and bears a close resemblance with the pq-pair function Ansatz of Dahle et al. [18] in the single reference case, which can be reduced to various forms of Ansätze by constraints to the amplitudes $\{c_{ij}^{pq}\}$. In this particular work, we do not optimize the amplitudes but employ the simplest form fulfilling the s- and p-wave cusp conditions,

$$c_{ij}^{pq} = \frac{1}{4}(3\delta_{ip}\delta_{jq} + \delta_{iq}\delta_{jp}), \tag{6}$$

in conjunction with STG,

$$f_{12} = -\frac{r_c}{2}\exp\left(-\frac{r_{12}}{r_c}\right), \tag{7}$$

where r_c is the length-scale parameter. This is equivalent to the expressions [10,19],

$$\Omega_f = \frac{1}{2}\sum_{\alpha\beta}\sum_{ij}\langle\alpha\beta|\overline{G}_{12}|ij\rangle E_{\alpha i}E_{\beta j}, \tag{8}$$

$$\overline{G}_{12} = \frac{1}{4}f_{12}(3 + p_{12}), \tag{9}$$

where p_{12} is a permutation operator to interchange the spatial coordinates.

Let us choose $|K\rangle$ to be orthonormal and to diagonalize the zeroth order Hamiltonian in the given basis set,

$$\langle K|H_0|L\rangle = E_K^{(0)}\delta_{KL}. \tag{10}$$

The minimization of the Hylleraas energy functional,

$$E^{(2)} = \langle 1|\overline{H}_0|1\rangle + 2Re\langle 1|V|0\rangle, \tag{11}$$

$$\overline{H}_0 = H_0 - E^{(0)}, \tag{12}$$

with respect to $\{\tilde{C}_K\}$ leads to the second order energy expression with an F12 correction,

$$E^{(2)} = E^{(2)}_{\mathrm{conv.}} + \Delta E^{(2)}_{\mathrm{F12}}, \tag{13}$$

where $E^{(2)}_{\mathrm{conv.}}$ is the conventional second order energy without the F12 term and

$$\Delta E^{(2)}_{\mathrm{F12}} = -\Delta E^{(2)}_B + \Delta 2E^{(2)}_V, \tag{14}$$

$$\Delta E^{(2)}_B = \langle F|\overline{H}_0|F\rangle - \sum_K \langle F|\overline{H}_0|K\rangle\frac{\langle K|\overline{H}_0|F\rangle}{E_K^{(0)} - E^{(0)}}, \tag{15}$$

$$\Delta E^{(2)}_V = \langle 0|V\Omega_f|0\rangle - \sum_K \langle 0|V|K\rangle\frac{\langle K|\overline{H}_0|F\rangle}{E_K^{(0)} - E^{(0)}}, \tag{16}$$

$$|F\rangle = \Omega_f|0\rangle. \tag{17}$$

In this work, we employ a couple of approximations. First, we use the analogy of the extended Brillouin condition (EBC) that assumes the zeroth order Hamiltonian closed in $|K\rangle$,

$$\frac{\langle K|\overline{H}_0|F\rangle}{E_K^{(0)} - E^{(0)}} \overset{\mathrm{EBC}}{\cong} \langle K|F\rangle. \tag{18}$$

Secondly, the remaining products $\overline{H}_0\Omega_f$ in (15) are approximated by the operator,

$$\bar{\kappa} = \frac{1}{2}\sum_{\alpha\beta}\sum_{ij}\langle\alpha\beta|\bar{\kappa}_{12}|ij\rangle E_{\alpha i}E_{\beta j}, \tag{19}$$

where $\bar{\kappa}_{12}$ is the commutator between the kinetic energy operators and the generator,

$$\bar{\kappa}_{12} = -\frac{1}{2}[\nabla_1^2 + \nabla_2^2,\ \overline{G}_{12}]. \tag{20}$$

Consequently, the F12 correction becomes

$$\Delta E^{(2)}_{\mathrm{F12}} = \sum_{ijkl}\Gamma^{(0)}_{ijkl}\eta^{kl}_{ij}, \tag{21}$$

where $\Gamma^{(0)}$ is the second order reduced density matrix of $|0\rangle$,

$$\Gamma^{(0)}_{ijkl} = \frac{1}{2}\langle 0|E_{ik}E_{jl} - \delta_{kj}E_{il}|0\rangle, \tag{22}$$

the effective operator η is given by

$$\eta^{kl}_{ij} = \langle ij|(\bar{\kappa}_{12} + 2r_{12}^{-1})(Q'_1Q'_2 - Q_1Q_2)\overline{G}_{12}|kl\rangle, \tag{23}$$

Q'_n and Q_n are projection operators,

$$Q'_n = \sum_\alpha |\alpha(n)\rangle\langle\alpha(n)|, \tag{24}$$

$$Q_n = \sum_a |a(n)\rangle\langle a(n)|, \tag{25}$$

and the summation index a runs over the secondary orbitals in the given basis. In the single reference limit, the present $E^{(2)}$ reduces to the MP2-F12/A*(SP) energy [11]. The contribution with $Q'_1Q'_2$ actually involves three-electron integrals. They can be estimated directly [20], but yet the use of the RI approximation [4] or numerical quadratures [19] is computationally more advantageous.

3. Results and discussion

We present some numerical results of the F12 correction. Except for the application to SiC_3, parent second order perturbation energies are obtained from the state-specific second order multi-reference Møller-Plesset

(MRMP2) method [21,22], which is the special case of the multi-configurational quasi-degenerate perturbation theory (MC-QDPT) [23] for multi-roots. In MRMP2 calculations, we use the canonical orbitals of the spin-averaged Fock operator based on the full valence CASSCF wave function. Basis set convergences are examined using aug-cc-pVXZ [24–26]. Unlike the latest implementation of the single reference MP2-F12 methods [11], the current MRMP2-F12 method implemented in an old program terminal is capable of handling up to g-basis functions, and h-functions are not included in calculations for $X = 5$. All of the two- and three-electron integrals are calculated using the numerical quadrature [19] with the parameters, $n_R = 48$, $n_\theta = 12$ and $n_\phi = 24$, based on the polar coordinate.

3.1. Excitation energy of the carbon atom

The ground (^{3}P) and first excited (^{1}D) states of the carbon atom are calculated. Each of the states is optimized state-specifically in the D_{2h} point group symmetry. Fig. 1 shows the convergence behaviors of the state energies. We examined two values of the exponent of STG, $\gamma = 1.0$ and $\gamma = 1.5$, in the MRMP2-F12 calculations, where the exponent is related with the length-scale parameter as $\gamma = 1/r_c$. Nevertheless, the state energies are insensitive to γ except for aug-cc-pVDZ. The basis set dependencies obtained from the MRMP2-F12 method are much smaller than those without the F12 correction. Table 1 summarizes the calculated excitation energies. The MRMP2-F12 excitation energy is likely to be saturated at aug-cc-pVTZ, while there is room for a further reduction to the limit in the conventional MRMP2 result even at aug-cc-pV5Z. The best estimate of the excitation energy from the F12 correction is slightly smaller than the experimental value 1.26 eV, and the most of the deviation is due to the intrinsic error of the perturbation theory.

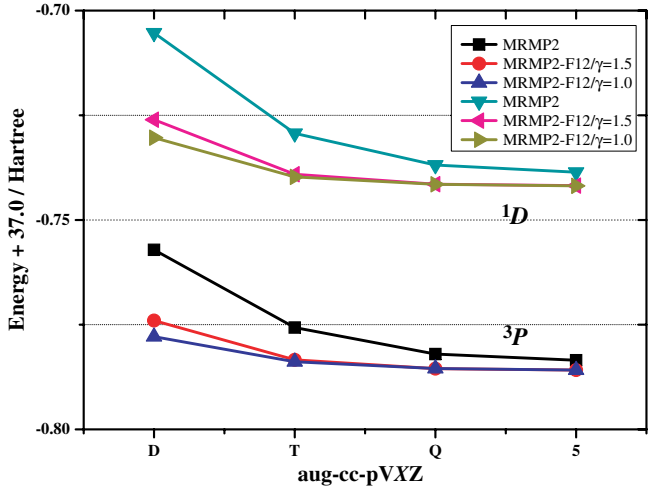

Fig. 1. Calculated energies of the ground (^{3}P) and excited (^{1}D) states of the carbon atom.

Table 1
Excitation energy of the C atom (eV)[a]

aug-cc-pVXZ	MRMP2	MRMP2-F12	
		$\gamma = 1.0$	$\gamma = 1.5$
$X = $ D	1.41	1.31	1.29
$X = $ T	1.26	1.21	1.20
$X = $ Q	1.23	1.20	1.20
$X = 5$[b]	1.22	1.20	1.20

[a] The experimental excitation energy is 1.26 eV.
[b] Without h-functions.

3.2. Atomization energy of CH_2

The second example is the atomization energy of $CH_2(^1A_1)$. Henceforth, the exponent of STG is 1.5. The geometrical parameters $R_{CH} = 1.1068$ Å and $\angle HCH = 102.03°$ optimized at CCSD(T)/cc-pCVQZ [27] are used. Table 2 lists the calculated atomization energies. The increment from aug-cc-pVDZ to aug-cc-pVTZ in the MRMP2-F12 atomization energy is 14 kJ/mol, while most of the amount is originating from the CASSCF reference contribution. The difference between aug-cc-pVTZ and aug-cc-pVQZ in the MRMP2-F12 values diminishes significantly, while the corresponding value is as large as 8 kJ/mol without the F12 correction. The best estimate of the atomization energy from the MRMP2-F12 method with aug-cc-pVQZ is smaller than the experimental value 757.1 kJ/mol by ca. 30 kJ/mol indicating a large intrinsic error of the MR-MP2 method.

3.3. Potential energy curve of O_2

We calculate the potential energy curve of the ground state of O_2 ($^3\Sigma_g^-$). Fig. 2 shows the result. The basis set dependence of the curves in the MRMP2-F12 result is much smaller than that without the F12 correction. Actually, most of the differences in the MRMP2-F12 curves come from the reference energies. It will be shown that the dynamic correlation energy of the MRMP2-F12 method is insensitive to the basis set. Table 3 lists the calculated equilibrium bond lengths and dissociation energies. The MRMP2 bond lengths are almost the same as the corresponding CASSCF ones, and yet the F12 correction somewhat improves the accuracy. The dynamic correlation effects are crucial for the dissociation energy; the CASSCF energies are less than the experimental value by more than 1 eV. The deviation of the MRMP2 energy with aug-cc-pVQZ is only 0.014 eV. Nevertheless, the basis set limit

Table 2
Atomization energy of CH_2 (kJ/mol)[a]

aug-cc-pCVXZ	CASSCF	MRMP2	MRMP2-F12
$X = $ D	639.5	681.1	713.1
$X = $ T	654.9	715.0	727.1
$X = $ Q	656.3	722.6	728.3

[a] The experimental atomization energy is 757.1 kJ/mol.

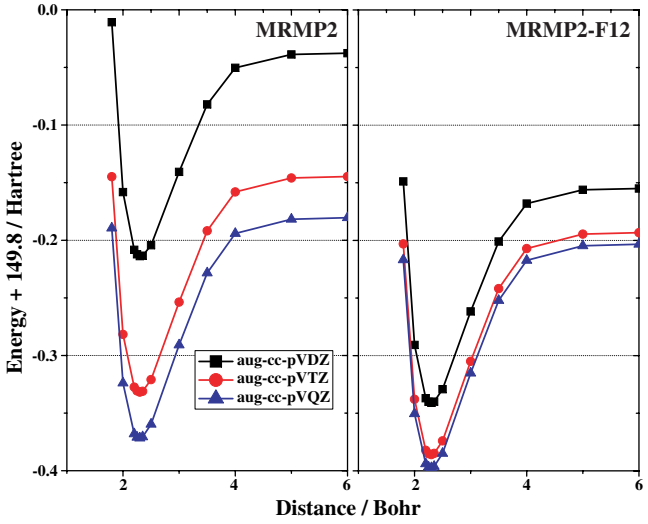

Fig. 2. Potential energy curves of O_2 from the MRMP2 and MRMP2-F12 methods.

Table 3
Equilibrium bond lengths and dissociation energies of O_2

aug-cc-pV*XZ*	r_e (Å)	D_e (eV)
CASSCF		
$X = D$	1.221	3.951
$X = T$	1.219	4.093
$X = Q$	1.216	4.123
MRMP2		
$X = D$	1.226	4.806
$X = T$	1.219	5.106
$X = Q$	1.215	5.227
MRMP2-F12		
$X = D$	1.216	5.069
$X = T$	1.215	5.256
$X = Q$	1.213	5.301
Experiment	1.207	5.213

of MRMP2 is likely to be lower by ~0.1 eV according to the result with the F12 correction. We analyze the components of the dynamic correlation energies at $R_{OO} = 2.35$ Bohr in Fig. 3. As we mentioned in the previous section, the basis set dependence of the semi-internal contribution is very small. The absolute value of the external energy from the orbital expansion increases with the size of the basis set, while the geminal component in the F12 correction decreases. As a result, the total amount of the external energy in MRMP2-F12 is conserved perfectly irrespective of the cardinal number of the basis set.

3.4. Isomers of SiC_3

The global minimum of SiC_3 has been investigated using the CCSD(T) [28,29] and MCQDPT [30,31] levels of theories. These authors have examined a linear isomer in triplet and two rhomboidal isomers in singlet labeled as 1t, 2s, and 3s, respectively [29]. The previous MC-QDPT study

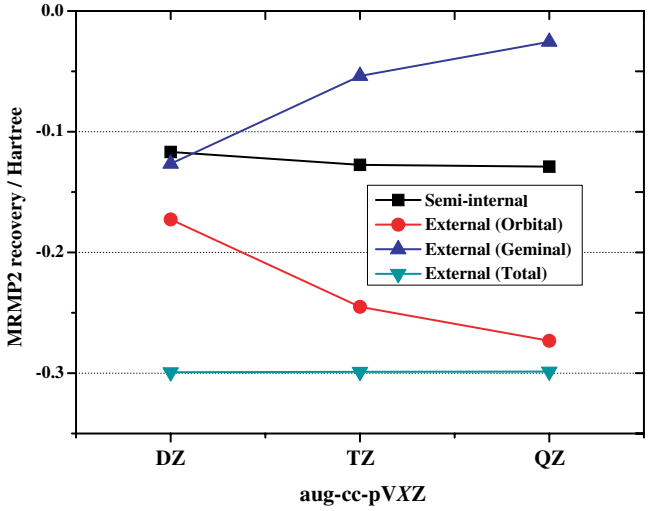

Fig. 3. Components of dynamic correlation energy of O_2.

showed that an erroneous energy ordering is led to by the use of a small basis set along with spin-averaged orbital energies [31]. In particular, the latter causes the intruder state problem for the 1t isomer. To avoid this, we employ the second order Z-averaged perturbation theory (ZAPT2) [32] for the high-spin state isomer, and the F12 correction is obtained based on the restricted open shell Hartree–Fock (ROHF) wave function. The singlet isomers are calculated at the corresponding single reference MP2-F12/A*(SP) method [11]. We use the geometrical parameters optimized at CCSD(T)/cc-pCVQZ [29]. Fig. 4 shows the basis set dependence of the energies of the isomers. The profiles of the F12 methods are much less sensitive to the basis. Table 4 lists the calculated 2s–3s and 2s–1t splittings. The result of RHF/ROHF indicates the electron correlation is crucial for quantitative splittings. The 2s–3s splitting is not sensitive to the choice of the basis set, and the results of MP2 and MP2-F12 are similar. Contrarily, the 2s–1t splitting

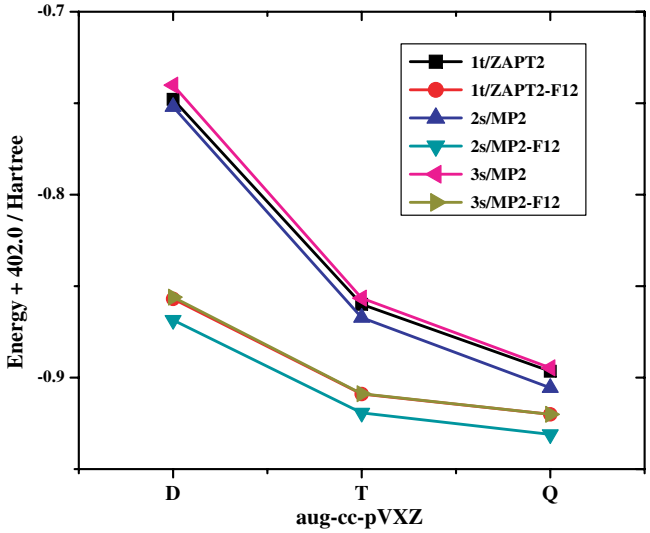

Fig. 4. Calculated energies of the SiC_3 isomers.

Table 4
2s–1t and 2s–3s splittings of the SiC_3 isomers (kcal/mol)

aug-cc-pV*XZ*	2s–1t	2s–3s
RHF/ROHF		
$X = D$	1.52	2.65
$X = T$	1.33	2.08
$X = Q$	1.85	2.50
MP2/ZAPT2		
$X = D$	2.55	7.41
$X = T$	4.56	6.69
$X = Q$	5.68	6.84
MP2-F12/ZAPT2-F12		
$X = D$	7.29	7.86
$X = T$	6.46	6.57
$X = Q$	6.87	6.88
CCSD(T)/cc-pCVQZ[a]	7.5	6.2
MCQDPT/aug-cc-pVQZ[b]	6.7	5.3

[a] Ref. [29].
[b] Ref. [31].

from the MP2/ZAPT2 methods increases with the size of the basis very much. The use of the F12 methods gives quantitatively correct values entirely in agreement with CCSD(T) [29] and MCQDPT [31].

4. Conclusions

We have proposed and tested a simple F12 correction for multi-reference perturbation theory. The F12 terms are is introduced to the external component in the internally contracted manner, and the F12 correction is expressed as the expectation value of the effective two-body operator η. The F12 correction has been tested on the excitation energy of the carbon atom, the atomization energy of CH_2, the potential energy curve of O_2, and the energies of SiC_3 isomers. The convergence behaviors indicate the particular efficiency of the present F12 correction. It is expected that the present (internally contracted) Ansatz to external excitations will likewise work well in other multi-reference methods.

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