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## A simple and efficient CCSD(T)-F12 approximation

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A new explicitly correlated CCSD(T)-F12 approximation is presented and tested for 23 molecules and 15 chemical reactions. The F12 correction strongly improves the basis set convergence of correlation and reaction energies. Errors of the Hartree-Fock contributions are effectively removed by including MP2 single excitations into the auxiliary basis set. Using aug-cc-pVTZ basis sets the CCSD(T)-F12 calculations are more accurate and two orders of magnitude faster than standard CCSD(T)/aug-cc-pV5Z calculations. © 2007 American Institute of Physics.

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The painfully slow convergence of the electron correlation energy with respect to the basis set size can be dramatically improved by including terms into the wave function that depend explicitly on the interelectronic distances.<sup>1,2</sup> In recent years, much progress has been made in improving the accuracy and efficiency of such explicitly correlated methods<sup>3–18</sup> and in making them applicable to rather large molecules.<sup>15–17</sup> Most of this work was restricted to second-order Møller-Plesset perturbation theory, but recently also practical explicitly correlated coupled-cluster (CC) methods have been developed. Based on earlier work of Noga *et al.*,<sup>19,20</sup> Fliegl *et al.*<sup>21,22</sup> proposed a CCSD(T)(F12) model, which differs from the exact theory by the neglect of terms that are quadratic in the explicitly correlated amplitudes. This year, Tew *et al.*<sup>23</sup> demonstrated that with augmented triple-zeta basis sets this method yields correlation energies and reaction energies that are as accurate as standard calculations with augmented quintuple-zeta basis sets. They stated that such calculations are about three times as expensive as conventional CCSD(T) calculations. In this communication we present a method that is even more efficient and accurate.

The general ansatz for closed-shell CCSD-F12 wave functions with single and double excitations,

$$\Psi_{\text{CCSD}} = e^{\hat{T}_1 + \hat{T}_2} \Psi_{\text{HF}}, \quad (1)$$

employs excitation operators

$$\hat{T}_1 = t_a^i \hat{E}_{ai}, \quad (2)$$

$$\hat{T}_2 = T_{ab}^{ij} \hat{E}_{ai} \hat{E}_{bj} + T_{\alpha\beta}^{ij} \hat{E}_{\alpha i} \hat{E}_{\beta j}. \quad (3)$$

Here and in the following, summation over repeated dummy indices is implied. The indices  $i, j, \dots$  refer to occupied orbitals  $a, b$  to virtual (external) orbitals, and  $\alpha, \beta$  to a complete orbital basis set.  $t_a^i$  and  $T_{ab}^{ij}$  are, respectively, the conventional singles and doubles amplitudes. In F12 theory, the additional amplitudes  $T_{\alpha\beta}^{ij}$  are approximated as

$$T_{\alpha\beta}^{ij} = \langle \alpha\beta | \hat{Q}_{12} \hat{F}_{12} | kl \rangle T_{kl}^{ij}, \quad (4)$$

where the projector

$$\hat{Q}_{12} = 1 - |rs\rangle\langle rs| - |mx\rangle\langle mx| - |xm\rangle\langle xm| \quad (5)$$

ensures strong orthogonality of the explicitly correlated terms to the Hartree-Fock reference function as well as to the conventional double excitations.<sup>3,6,17,24–26</sup> The indices  $r, s$  denote the full orbital (MO) basis, and  $x$  the complementary auxiliary (CA) orbital basis.<sup>6,17</sup> Note that  $T_{\alpha\beta}^{ij} = 0$  if both  $\alpha$  and  $\beta$  belong to the orbital basis, or if at least one of them corresponds to an occupied orbital.

As first proposed by Ten-no<sup>11</sup> and subsequently used by several authors,<sup>7,10,12–14,16,17</sup> the correlation factor  $\hat{F}_{12}$  is taken to be a simple Slater function,

$$F(r_{12}) = \exp(-\beta r_{12}). \quad (6)$$

In practice, we approximate the Slater function by a linear combination of Gaussians.<sup>7,17</sup>

The above ansatz is orbital invariant. It suffers, however, from geminal basis set superposition errors,<sup>17,27</sup> and for larger molecules also numerical instabilities occur. These problems can be avoided by using the “diagonal” ansatz,<sup>17,25</sup> in which only the terms for  $kl=ij$  and  $kl=ji$  are kept. This ansatz is not orbital invariant and only size consistent when localized orbitals are used. With localized orbitals it yields more accurate results than the more general orbital invariant ansatz.<sup>17</sup> Even simpler is the diagonal fixed amplitude ansatz by Ten-no,<sup>11</sup> in which  $T_{ii}^{ii} = t_s$ ,  $T_{ij}^{ij} = \frac{1}{2}[t_s + t_r]$ , and  $T_{ji}^{ij} = \frac{1}{2}[t_s - t_r]$  ( $i \neq j$ ). All other amplitudes  $T_{kl}^{ij}$  are zero. The fixed parameters  $t_s = -1/(2\beta)$  and  $t_r = -1/(4\beta)$  follow from the cusp conditions<sup>28,29</sup> for singlet and triplet pairs, respectively. This ansatz, which is orbital invariant, size consistent, and free of geminal superposition errors, has been used in the current work. For simplicity, we will in the following still write  $T_{kl}^{ij}$ , but it will always be assumed that  $kl$  is restricted as defined above.

The CCSD-F12 residual equations for the doubles amplitudes  $T_{ab}^{ij}$  can be straightforwardly derived by using the ansatz in Eq. (3). However, this requires resolution of the identity (RI) approximations in many places and does not

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lead to a numerically stable method. In addition, if the amplitudes  $T_{kl}^{ij}$  are fully optimized, an extended set of CC equations has to be solved. In order to overcome these problems, Fliegl *et al.*<sup>21</sup> have introduced various approximations; in particular, they kept only linear terms in  $T_{kl}^{ij}$ . In the current work, we propose even simpler approximations, which turn out to work equally well.

First, if the diagonal fixed amplitude ansatz is used, no equations need to be solved for the amplitudes  $T_{kl}^{ij}$ . It remains, however, the question of how to compute the energy. For fully optimized amplitudes the CCSD energy is simply

$$E_{\text{corr}} = K_{ab}^{ij}[2\bar{T}_{ab}^{ij} - \bar{T}_{ba}^{ij}] + V_{kl}^{ij}[2T_{kl}^{ij} - T_{lk}^{ij}], \quad (7)$$

with

$$\bar{T}_{ab}^{ij} = T_{ab}^{ij} + t_a^i t_b^j, \quad K_{ab}^{ij} = \langle ij | r_{12}^{-1} | ab \rangle,$$

and

$$V_{kl}^{ij} = \langle ij | r_{12}^{-1} \hat{Q}_{12} \hat{F}_{12} | kl \rangle.$$

This expression is linear in the amplitudes, and therefore errors of the amplitudes affect the energy in first order. This is critical if the fixed amplitude ansatz is applied in which the amplitudes  $T_{kl}^{ij}$  are not optimized. It turns out, however, that the error is very small if the energy is optimized with respect to the exponent  $\beta$  of the correlation factor. In other words, when  $\beta$  is optimized, the optimized amplitudes  $T_{ij}^{ij}$  and  $T_{ji}^{ij}$  are very close to the fixed values from the cusp conditions, and Eq. (7) should give accurate results. This is demonstrated in Fig. 1 for the H<sub>2</sub>O molecule.

Unfortunately, the optimum value of  $\beta$  varies for different molecules and basis sets. For the aug-cc-pVTZ (AVTZ) basis the optimal values lie roughly between  $1.1a_0^{-1}$  for pure hydrocarbons and  $1.5a_0^{-1}$  for molecules containing mainly oxygen atoms. In order to reduce the dependence on  $\beta$ , we have chosen to replace the second term in Eq. (7) by the MP2-F12 Hylleraas functional, i.e.,  $V_{kl}^{ij}$  is replaced by  $V_{kl}^{ij} + R_{kl}^{ij}$ , where  $R_{kl}^{ij}$  is the residual for the explicit part of the MP2-F12 equations. In the case of MP2-F12, this energy expression is accurate to second order in errors of the amplitudes  $T_{kl}^{ij}$  and, therefore, much less sensitive to the choice of  $\beta$  and  $T_{kl}^{ij}$ . This can also be seen in Fig. 1.

In our CCSD(T)-F12a approximation the residuals  $R_{kl}^{ij}$  are computed using the complementary auxiliary basis set approach<sup>6</sup> and approximation 3C. This approximation is based on the MP2-R12/C method by Kedžuch *et al.*<sup>30</sup> and our implementation is described in detail in Ref. 17. The only difference to Ref. 17 is that the CCSD amplitudes replace the MP2 amplitudes in the term  $C_{ab}^{kl} T_{ab}^{ij}$ . The second approximation concerns the contributions of the explicitly correlated terms to the CC equations for the singles and doubles amplitudes. The simplest approximation would be to neglect these entirely and to compute the correlation energy as sum of the CCSD(T) correlation energy and the MP2-F12 correction (i.e., the difference of the pure MP2-F12 and MP2 energies). It has been noted that, usually, the basis set dependence of MP2 is stronger than that of CCSD(T), and that,

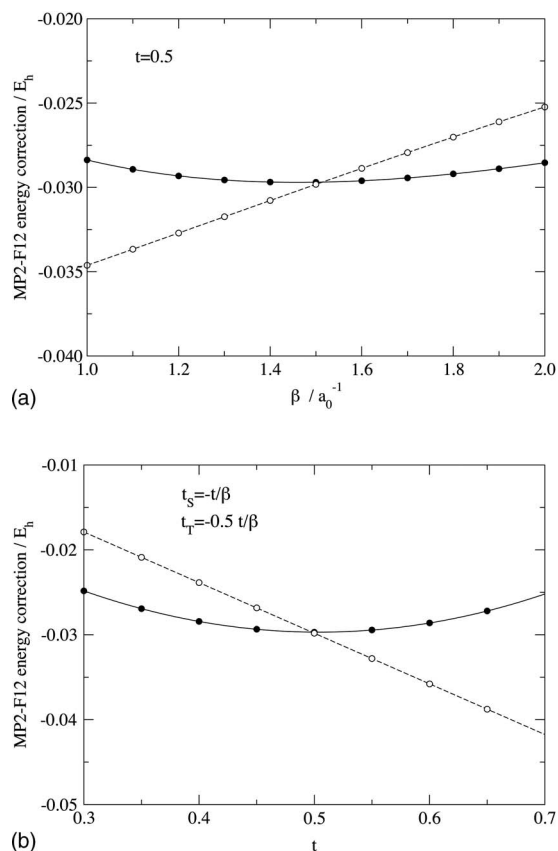


FIG. 1. Dependence of the MP2-F12 energy correction of H<sub>2</sub>O on the choice of  $\beta$  (upper panel) and the fixed amplitudes  $t_s = -t/\beta$  and  $t_r = -t/(2\beta)$  for  $\beta = 1.5a_0^{-1}$  (lower panel); basis AVTZ. The full lines represent the energy computed by the Hylleraas functional, the dashed lines (open symbols) the first-order approximation (see text).

therefore, such a correction has limited accuracy. Nevertheless, already this approximation works quite well (see supplementary material<sup>35</sup>).

A better approximation can be made by including the most important explicitly correlated contributions into the CCSD residuals. The conventional CCSD residuals  $R_{ab}^{ij}$  can be written in matrix form as

$$\mathbf{R}_{\text{CC}}^{ij} = \mathbf{R}_{\text{MP2}}^{ij} + \mathbf{K}(\mathbf{D}^{ij}) + \alpha_{ij,kl} \bar{\mathbf{T}}^{kl} + \mathbf{G}^{ij} + \mathbf{G}^{ji\dagger}, \quad (8)$$

where  $\mathbf{R}_{\text{MP2}}^{ij}$  is the MP2 residual,  $\mathbf{K}(\mathbf{D}^{ij})$  are external exchange operators which account for the contributions of the three- and four-external integrals (see Ref. 31 for definitions and details<sup>39</sup>). The explicit form of the quantities  $\alpha_{ij,kl}$  and  $\mathbf{G}^{ij}$  involve products of integral and amplitude matrices. In our method we assume that the explicitly correlated terms contribute only to the terms that are linear in the amplitude matrices. Furthermore, we make a “hybrid approximation”<sup>5,17</sup> in which we neglect all contributions of the CA basis set  $\{x\}$ . This leads to the correction

$$\Delta \mathbf{R}_{\text{F12a}}^{ij} = [\mathbf{W}^{kl} - \mathbf{K}(\mathbf{F}^{kl}) + \mathbf{C}^{kl}] T_{kl}^{ij}, \quad (9)$$

where  $W_{ab}^{kl} = \langle kl | \hat{F}_{12} r_{12}^{-1} | ab \rangle$  and

$$[\mathbf{K}(\mathbf{F}^{kl})]_{ab} = \langle ab | r_{12}^{-1} | rs \rangle \langle rs | \hat{F}_{12} | kl \rangle. \quad (10)$$

The matrices  $\mathbf{C}^{kl}$  arise from  $\mathbf{R}_{\text{MP2}}^{ij}$ ; thus, they are the same as in MP2-F12 theory.<sup>17</sup> The remaining two terms arise from

TABLE I. Convergence of the valence-shell CCSD(T) correlation energy of H<sub>2</sub>O as a function of the basis set (in  $-mE_h$ )

Basis	Orbital	(F12) <sup>a</sup>	F12a <sup>b</sup>	F12b <sup>b</sup>
AVDZ	232.71	296.09	299.58	293.15
AVTZ	282.04	304.56	306.82	302.42
AVQZ	297.93	307.12	308.78	306.20
AV5Z	303.32	307.81	308.93	307.40
AV6Z	305.43			

<sup>a</sup>CCSD(T)(F12) values from Ref. 23,  $\beta=1.3a_0^{-1}$ .

<sup>b</sup> $\beta=1.3a_0^{-1}$ . The v5ZJKFIT (Ref. 37) and AV5Z/MP2FIT (Ref. 38) bases have been used for RI and DF, respectively.

the explicitly correlated contributions to the external exchange operators  $\mathbf{K}(\mathbf{D}^{ij})$ , where we have approximated the projector in Eq. (5) as  $\hat{Q}_{12}=1-|rs\rangle\langle rs|$ . As in the CCSD(T)(F12) method of Tew *et al.*,<sup>23</sup> no direct contributions of the explicitly correlated terms to the triples are included.

A similar term as in Eq. (9) occurs in the CCSD-F12 residual  $R_{kl}^{ij}$ . If this is included and the energy contribution of  $R_{kl}^{ij}$  is still computed as  $[2T_{kl}^{ij}-T_{lk}^{ij}]R_{kl}^{ij}$ , one obtains an additional energy correction,

$$\Delta E = (2T_{kl}^{ij} - T_{lk}^{ij})\text{tr}[(\mathbf{W}^{kl} - \mathbf{K}(\mathbf{F}^{kl}))\mathbf{D}^{ji}]. \quad (11)$$

We denote the approximation that includes this correction as CCSD(T)-F12b. This contribution roughly doubles the effect of the coupling of the conventional and explicit parts. It is not *a priori* clear whether this will improve the accuracy, since many further terms in the  $R_{kl}^{ij}$  residual are neglected, and the resulting energy functional is an approximation by itself.<sup>40</sup> In fact, as will be shown below, it leads to a worsening of the convergence of the correlation energies with basis set size.

The contributions in Eqs. (9) and (10) can be computed with negligible additional effort together with the operators  $\mathbf{K}(\mathbf{D}^{ij})$  as  $\mathbf{K}(\mathbf{D}^{ij} - \tilde{\mathbf{F}}^{ij})$ , where  $\tilde{\mathbf{F}}^{ij} = \mathbf{F}^{kl}T_{kl}^{ij}$ . The internal-external parts of the modified external exchange operators also contribute to the singles residuals. They are evaluated in the AO basis,<sup>31</sup> and therefore no additional transformed integrals are required. Thus, as compared to a conventional CCSD(T) calculation, the only additional effort is to perform a MP2-F12 calculation beforehand. All required integrals for the MP2-F12 calculation are evaluated using efficient

density-fitting (DF) approximations, as described in previous works.<sup>4,7,16,17</sup> In the Hartree-Fock and CCSD(T) calculations no density-fitting approximations were used.

In order to test the method we have studied the same 15 reactions as Tew *et al.*<sup>23</sup> These involve 23 molecules with first- and second-row atoms. Only the valence electrons were correlated and MP2/aug-cc-pVTZ geometries were used. Reference values were computed using the standard CCSD(T) and augmented correlation consistent basis sets (aug-cc-pVnZ).<sup>32</sup> The results up to quintuple zeta are identical to the values reported by Tew *et al.* In addition, for the smaller molecules we were also able to use aug-cc-pV6Z basis sets. For the second-row atoms, the aug-cc-pV(n+d)Z basis sets<sup>33</sup> with one additional tight *d* shell have been used. For simplicity, in the following we will denote these basis sets AVnZ. The basis set limits were estimated by two-point fits of the CCSD(T) correlation energies to the extrapolation formula<sup>34</sup>  $E_n = E_{\text{CBS}} + An^{-3}$ . Results obtained with  $n=4, 5$  and  $5, 6$  will be denoted CBS[45] and CBS[56], respectively.

The convergence of the valence-shell correlation energy for H<sub>2</sub>O is shown in Table I for the AVnZ basis sets and  $\beta = 1.3a_0^{-1}$ . The convergence of the CCSD(T)-F12a method is found to be faster than that of the CCSD(T)(F12) approximation of Tew *et al.*<sup>23</sup> and more similar to the basis set convergence of MP2-F12. The CCSD(T)-F12a AVQZ and AV5Z values are close to the CBS[45] estimate (308.97 $mE_h$ ) but slightly overestimate the CBS[56] value (308.34 $mE_h$ ). On the other hand, the CCSD(T)-F12b approximation appears to underestimate the correlation energies. Using the AVTZ basis the CCSD(T)-F12a and CCSD(T)-F12b approximations yield 99.5% and 98.1% of the CBS[56] basis set limit. On average, 99.2% and 97.6%, respectively, of the CBS[45] values were obtained for the 23 molecules.

The mean and maximum absolute errors of the Hartree-Fock (HF) and correlation energy contributions to the reaction energies are presented in Table II (for individual values see supplementary material<sup>35</sup>). As HF reference values we took the AV5Z results. It is found that for the AVTZ basis set the mean and maximum HF errors are significantly larger than those of the CCSD(T)-F12a correlation contributions. However, the HF basis set error can be almost entirely removed by adding an MP2 singles energy correction  $\Delta E_s = 2t_{\alpha}^i f_{\alpha}^i$ , obtained by allowing single excitations into the CA orbital space. This means solving  $f_{\alpha}^i = t_{\alpha}^k f_{\alpha}^k - f_{\alpha}^{\beta} f_{\alpha}^{\beta}$ , where  $\alpha, \beta$

TABLE II. Mean absolute (MAD), root mean square (RMS), and maximum absolute (MAX) errors of Hartree-Fock and CCSD(T) correlation energy contributions to the reaction energies in kJ/mol. The AVTZ basis set was used for all F12 calculations.

Error	HF			CCSD(T)		
	AVTZ	AVTZ <sup>a</sup>	AV5Z	(F12) <sup>b</sup>	F12a <sup>c</sup>	F12b <sup>c</sup>
MAD	1.77	0.28	0.58	0.68	0.38	0.54
RMS	2.75	0.36	0.86	0.90	0.55	0.61
MAX	6.42	0.86	2.15	1.62	1.69	1.01

<sup>a</sup>Including singles corrections, see text.

<sup>b</sup>CCSD(T)(F12) values from Ref. 23,  $\beta=1.3a_0^{-1}$ .

<sup>c</sup> $\beta=1.0a_0^{-1}$ . The vQZJKFIT (Ref. 37) and AVQZ/MP2FIT (Ref. 38) bases have been used for RI and DF, respectively.

run over the virtual and CA orbitals (this is entirely distinct from the CCSD calculation). If this correction is applied, the accuracy of the HF contribution is again comparable to that of the correlation energy contributions.

For the correlation contributions, the CBS[56] values have been taken as reference whenever available, otherwise the CBS[45] ones (using the CBS[56] values slightly reduces the errors). The parameter  $\beta$  has been chosen to be  $1.0a_0^{-1}$ . In the current tests this value yielded best results, but the dependence of the errors on the choice of  $\beta$  was found to be rather weak on the average.<sup>35</sup> The results in Table II demonstrate that our CCSD(T)-F12a approximation yields even better accuracy than the CCSD(T)(F12) method of Tew *et al.*,<sup>23</sup> and the reaction energies obtained with the AVTZ basis are better than quintuple-zeta quality. The mean absolute error of the total CCSD(T)-F12a reaction energies (including HF and  $\Delta E_s$ ) amounts to 0.4 kJ/mol, the maximum error to 1.0 kJ/mol. For the CCSD(T)-F12b approximation the corresponding values are 0.6 and 1.4 kJ/mol, respectively.

Finally, we mention that the MP2-F12 calculation, which precedes the CCSD(T) one, takes only a relatively small amount of time. For the largest case in the present study, namely, the CH<sub>3</sub>CHO molecule, the total CPU time (using MOLPRO,<sup>36</sup> including integral evaluation and HF) was 3856 s (AMD Opteron 2.6 GHz; no symmetry has been used). Of this time, the DF-MP2-F12 took 334 sec, i.e., less than 10%. Thus, for almost no additional cost, results of at least CCSD(T)/AV5Z quality are obtained. The corresponding standard CCSD(T)/AV5Z calculations would require about 100 times more time and disk space.

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<sup>35</sup>See EPAPS Document No. E-JCPSA6-127-027745 for detailed results for individual reactions. This document can be reached through a direct link in the online article's HTML reference section or via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>).

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<sup>39</sup>Note that we moved some parts of the  $\mathbf{G}^{ij}$  of Ref. 31 to  $\mathbf{R}_{\text{MP2}}^{ij}$ ; also, the matrices  $\mathbf{C}^{ij}$  of Ref. 31 are denoted by  $\tilde{\mathbf{T}}^{ij}$  here in order to avoid confusion with the matrices  $\mathbf{C}^{ij}$  in the MP2-F12 theory of Ref. 17.

<sup>40</sup>Strictly, a Lagrangian functional should be used and then the  $\Lambda$  vector would replace the amplitudes. The effect of including further terms into the residuals  $R_{kl}^{ij}$  is currently investigated in our laboratory.