

# Accurate Calculations of Intermolecular Interaction Energies Using Explicitly Correlated Coupled Cluster Wave Functions and a Dispersion-Weighted MP2 Method<sup>†</sup>

Oliver Marchetti and Hans-Joachim Werner\*

Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Received: June 25, 2009; Revised Manuscript Received: August 17, 2009

Explicitly correlated coupled-cluster calculations of intermolecular interaction energies for the S22 benchmark set of Jurečka, Šponer, Černý, and Hobza (*Chem. Phys. Phys. Chem.* **2006**, 8, 1985) are presented. Results obtained with the recently proposed CCSD(T)-F12a method and augmented double- $\zeta$  basis sets are found to be in very close agreement with basis set extrapolated conventional CCSD(T) results. Furthermore, we propose a dispersion-weighted MP2 (DW-MP2) approximation that combines the good accuracy of MP2 for complexes with predominately electrostatic bonding and SCS-MP2 for dispersion-dominated ones. The MP2-F12 and SCS-MP2-F12 correlation energies are weighted by a switching function that depends on the relative HF and correlation contributions to the interaction energy. For the S22 set, this yields a mean absolute deviation of 0.2 kcal/mol from the CCSD(T)-F12a results. The method, which allows obtaining accurate results at low cost, is also tested for a number of dimers that are not in the training set.

## Introduction

Intermolecular interactions play an important role in many chemical systems. For example, hydrogen bonding  $\pi$ -stacking interactions between nucleic acid base pairs are crucial for the folding of nucleic acids, such as DNA and RNA. The theoretical prediction of interaction potentials between nucleic acid base pairs and other systems has therefore been the focus of many recent papers.<sup>1–16</sup> A particular challenge is the accurate prediction of dispersion energies, which dominate  $\pi$ -stacking interactions. The calculation of dispersion interactions is difficult because they are pure electron correlation effects, which cannot be described by simple methods such as Hartree–Fock or standard density functional theory.

The CCSD(T) method (coupled-cluster with single and double excitations and perturbative treatment of triple excitations) is currently considered to be the most accurate method to compute intermolecular interaction energies. However, due to the steep scaling of the computational cost with molecular size (the triples contribution scales as  $O(N^7)$ , where  $N$  is a measure of the molecular size), such calculations can be performed only for systems of quite limited size. Furthermore, large orbital basis sets are needed, in particular when dispersion interactions are considered. An alternative possibility to accurately compute interaction energies is the use of symmetry-adapted intermolecular perturbation theory, either in its original form<sup>17,18</sup> or in combination with density functional theory,<sup>19–24</sup> but also for these methods the computational cost is rather high.

Various approximations have been proposed in the literature to overcome this problem. One possibility is to use density functional theory with additional empirical terms for the dispersion interaction,<sup>25–29</sup> but even though it has been demonstrated that this works reasonably well, the accuracy is difficult to predict and cannot be systematically improved. A more rigorous way is to use second-order Møller–Plesset perturbation theory (MP2) or local MP2 (LMP2).<sup>4,9,30–32</sup> These methods are known to work very well for most hydrogen bonded (electrostatic-

dominated) systems,<sup>2</sup> but usually overestimate the dispersion interaction significantly. The latter problem can be much reduced by the spin-component-scaled variant (SCS-MP2) of Grimme,<sup>33</sup> but unfortunately, this method underestimates the interaction energies of hydrogen bonded systems.<sup>4,6,9,34</sup> Attempts to reoptimize the scaling factors in SCS-MP2 for intermolecular interactions have also been reported,<sup>6</sup> but the improvements were limited, and the resulting scaling factors were physically unreasonable. Very recently, Pitonak et al.<sup>15</sup> have proposed using the average of MP2 and MP3 for computing interaction energies. This is based on the observation that MP3 underestimates dispersion interactions about as much as MP2 overestimates them. In fact, the accuracy of this so-called MP2.5 approach is quite good for both dispersion- and electrostatic-dominated systems, but the drawback is that MP3 scales as  $O(N^6)$  and is much more expensive than MP2.

In the current paper, we present two new methods for the accurate prediction of intermolecular interactions. Recently, we have demonstrated that the convergence of MP2 interaction energies with respect to the basis set is dramatically improved by using the explicitly correlated MP2-F12 method.<sup>13</sup> Here, we extend this to explicitly correlated coupled-cluster theory. We will show that the recently proposed explicitly correlated CCSD(T)-F12a approximation<sup>35,36</sup> already yields with augmented double- $\zeta$  basis sets interaction energies that are more accurate than standard CCSD(T) results obtained with augmented quadruple- $\zeta$  basis sets. This reduces the cost for a given dimer by 2 orders of magnitude. However, it does not change the  $O(N^7)$  cost scaling of the perturbative triples correction, which is essential to obtain accurate results.

To be able to compute reasonably accurate interaction energies for larger systems, we propose a new variant of the SCS-MP2 method in which the scaling factors depend on the type of interaction: for systems with predominately electrostatic interactions or hydrogen bonds the method reduces to MP2, whereas for predominately dispersion-bonded systems it approaches SCS-MP2, thus combining the advantages of the two methods. It will be shown that this method, which is denoted dispersion-weighted MP2 (DW-MP2) yields results that are at

<sup>†</sup> Part of the “Walter Thiel Festschrift”.

\* Corresponding author. E-mail: werner@theochem.Uni-Stuttgart.de.

least as accurate as the MP2.5 approximation<sup>15</sup> at the cost of a single MP2 calculation.

## Methods

**The CCSD(T)-F12a Method.** The MP2-F12 and CCSD(T)-F12 methods used in the present work have been described in detail earlier.<sup>35–38</sup> We will therefore only briefly summarize some aspects that are relevant in the current work. The MP2-F12 and CCSD-F12 wave functions are defined as

$$\Psi_{\text{MP2-F12}} = (1 + \hat{T}_2)\Phi_{\text{HF}} \quad (1)$$

$$\Psi_{\text{CCSD-F12}} = \exp(\hat{T}_1 + \hat{T}_2)\Phi_{\text{HF}} \quad (2)$$

where  $\hat{T}_1$  and  $\hat{T}_2$  are defined as

$$\hat{T}_1 = \sum_i^{\text{Val}} \sum_a^{\text{Virt}} \hat{E}_{ai} t_a^i \quad (3)$$

$$\hat{T}_2 = \frac{1}{2} \sum_{ij}^{\text{Val}} \left[ \sum_{ab}^{\text{Virt}} \hat{E}_{ai} \hat{E}_{bj} T_{ab}^{ij} + \sum_{\alpha\beta}^{\text{complete}} \hat{E}_{\alpha} \hat{E}_{\beta} \mathcal{F}_{\alpha\beta}^{ij} \right] \quad (4)$$

$$\mathcal{F}_{\alpha\beta}^{ij} = \sum_{kl}^{\text{Val}} \langle \alpha\beta | \hat{Q}_{12} F_{12} | kl \rangle T_{kl}^{ij} \quad (5)$$

with

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

The operator  $\hat{T}_1$  is the same as in ordinary coupled-cluster theory.  $\hat{E}_{ai}$  are the usual spin-summed one-particle excitation operators from occupied valence orbitals  $i, j, \dots$  (Val) to virtual orbitals  $a, b, \dots$  (Virt), and  $t_a^i$  are the corresponding excitation amplitudes. In the current work, excitations from core orbitals are excluded. The first term in  $\hat{T}_2$  describes the conventional double excitations. In addition, the second term includes functions that depend explicitly on the interelectronic distance,  $r_{12}$ . Here  $\alpha, \beta$  run formally over a complete orthogonal space. In the following, we assume that this contains as a subset the occupied and virtual molecular orbitals.  $\hat{Q}_{12}$  is a strong orthogonality projector that keeps the explicitly correlated terms orthogonal to the conventional part of the wave function (for details, see, e.g., refs 37 and 39). The projector is approximated using the union of the orbitals basis and a complementary auxiliary basis set (CABS).<sup>36,37,40</sup> All many-electron integrals then factorize into sums of products of two-electron integrals that can be evaluated efficiently using density fitting approximations.<sup>41</sup>

The amplitudes  $T_{kl}^{ij}$  of the explicitly correlated terms can be determined from the wave function cusp conditions:<sup>42,43</sup>

$$T_{kl}^{ij} = \frac{3}{8} \delta_{ik} \delta_{jl} + \frac{1}{8} \delta_{jk} \delta_{il} \quad (7)$$

Alternatively, they can be optimized in the MP2-F12 or CCSD-F12 methods. Unless otherwise noted, we will in the

current paper use the fixed amplitude ansatz.<sup>36,37,43</sup> In this case, no additional amplitude equations need to be solved.

In the CCSD-F12a method, the CCSD-F12 equations for the amplitudes  $T_{ab}^{ij}$  are approximated by keeping only terms that are linear in the amplitudes  $T_{kl}^{ij}$ . Furthermore, beyond second-order perturbation theory, all contributions of the complementary auxiliary orbital space are neglected. Extensive previous benchmarks<sup>36,44</sup> for atomization energies, reaction energies, ionization potentials, electron affinities, equilibrium structures, and vibrational frequencies have demonstrated that the CCSD(T)-F12a method with double or triple- $\zeta$  basis sets already yields results that are very close to the CCSD basis set limits.

Perturbative contributions of triple excitations can be taken into account as in a standard CCSD(T) calculation. These do not directly include explicitly correlated terms, and therefore, the basis set incompleteness errors of the triples contribution is not reduced by the F12-method. A rough estimate of the basis set limit of the (T) contribution can be obtained by assuming that the fraction of correlation energy obtained with the given basis is the same for the MP2 correlation energy and the (T) contribution. The corrected value can then be obtained by simple scaling<sup>36</sup>

$$\Delta E_{(T^*)} = \Delta E_{(T)} \frac{E_{\text{MP2-F12}}}{E_{\text{MP2}}} \quad (8)$$

When computing counterpoise corrected interaction energies, the ratio  $E_{\text{MP2-F12}}/E_{\text{MP2}}$  is slightly different for the monomers and the dimer, and this leads to a size consistency error. This problem can be avoided by using the same factor for each molecule. In the current work, we determine the ratio for the dimer and use it for the monomers as well. This procedure is size-consistent and, as will be shown later, leads to a significant improvement of the computed CCSD(T)-F12 interaction energies. As indicated in eq 8, an asterisk is used to indicate that the triples energy has been scaled; that is, the approximation is denoted CCSD(T\*)-F12.

**The DW-MP2 Method.** As outlined in the Introduction, the MP2 method works well for hydrogen bonded systems, whereas the SCS-MP2 method gives accurate results for predominately dispersion bonded complexes. Unfortunately, neither of these two methods works for all types of systems. This leads to the idea to use a “dispersion-weighted” (DW) average of MP2 and SCS-MP2,

$$\Delta E_{\text{DW-MP2}} = w \Delta E_{\text{MP2}} + (1 - w) \Delta E_{\text{SCS-MP2}} \quad (9)$$

where the weight factor,  $w$ , is system dependent. It should approach 1 for systems in which the bonding is mainly of electrostatic nature (including H-bonds) and 0 for purely dispersion bonded systems. The method proposed here to determine the weight is based on the fact that for purely dispersion-bonded systems, the (HF) contribution is repulsive (since dispersion is a pure electron correlation effect), but for electrostatic interactions, including hydrogen bonded systems, HF is attractive and qualitatively correct. Thus, the weight can be described by the switching function

$$w = \frac{1}{2} [1 + \tanh(a + br)] \quad (10)$$

where  $a$  and  $b$  are fitting parameters that determine the position and width of the switching function, and

$$r = \frac{\Delta E_{\text{HF}}}{\Delta E_{\text{MP2-F12}}} \quad (11)$$

is the ratio of the Hartree–Fock (HF) and MP2-F12 binding energies. For predominately dispersion-bonded systems,  $r < 0$ , and thus,  $w$  will be small (assuming that  $a$  is small and  $b$  is positive), whereas for electrostatic-dominated systems, the opposite is the case. The parameters  $a$ ,  $b$  are determined by a least-squares fit of the MP2-F12 interaction energies to the CCSD(T\*)-F12a results for the S22 benchmark set of Hobza et al. (see section entitled DW-MP2-F12 Results). We have also tested an extended approach in which the SCS-MP2 scaling parameters are reoptimized in both the  $\Delta E_{\text{MP2}}$  and the  $\Delta E_{\text{SCS-MP2}}$  contributions (leading to a total of six fitting parameters), but this did not lead to a significant improvement in the overall statistics. Thus, it appears that the simple two-parameter approach is close to the optimum of what can be achieved on the basis of MP2.

### Computational Details

All calculations were carried out using the MOLPRO package of ab initio programs.<sup>45</sup> The counter-poise (CP) correction<sup>46</sup> was employed to reduce basis set superposition errors (BSSE). Even though the explicitly correlated calculations recover a large fraction of the correlation energy and the BSSE is therefore significantly smaller than in standard calculations, the CP correction is still necessary, mainly to reduce the BSSE of the HF contribution.

To evaluate the accuracy of the CCSD(T\*)-F12a calculations, conventional CCSD(T) calculations were performed using augmented correlation consistent valence triple- $\zeta$  (aug-cc-pVTZ) and quadruple- $\zeta$  (aug-cc-pVQZ) basis sets.<sup>47</sup> It was found that omission of the diffuse functions at the hydrogen atoms has hardly any effect on the extrapolated interaction energies. Therefore, these functions were omitted. This not only reduces the computational effort but also BSSE effects. These mixed basis sets will be denoted AVTZ' and AVQZ'.

The complete basis set (CBS) limit was estimated by extrapolating the correlation energies using  $E_n = E_{\text{CBS}} + An^{-3}$ , where  $n$  is the cardinal number of the basis set, and  $E_{\text{CBS}}$  and  $A$  are determined by fitting to the energies for  $n = 3$  and  $n = 4$ . The HF contributions were not extrapolated, and the AVQZ' values were used together with the extrapolated correlation energies. The corresponding extrapolated CCSD(T) results will be denoted CCSD(T)/CBS[34]. We note that CBS[34] extrapolation is often not considered sufficient to compute highly accurate energy differences, and the use of at least quadruple- and quintuple- $\zeta$  basis sets (CBS[45]) is normally recommended. Unfortunately, quintuple- $\zeta$  CCSD(T) calculations were not feasible for the relatively large systems studied here. However, in our previous work<sup>13</sup> we computed both MP2/CBS[34] and MP2/CBS[45] interaction energies and found that the differences were very small. In addition, other authors considered CBS[34] extrapolation sufficient for intermolecular interaction energies.<sup>2,15</sup>

The explicitly correlated calculations were performed using the full aug-cc-pVDZ (AVDZ) and aug-cc-pVTZ (AVTZ) basis sets. As resolution of the identity (RI) and density fitting (DF) basis sets, we used the VTZ/JKFIT and AVTZ/MP2FIT basis sets, respectively, for both orbital basis sets. In the AVDZ calculations, the  $g$ -functions in these basis sets were omitted.

The CABS singles correction proposed in ref 35 (see also ref 38) was applied in all explicitly correlated calculations. This substantially improves the accuracy of the HF contributions and is particularly important to obtain reliable results using the AVDZ orbital basis. As in our previous work,<sup>13</sup> the exponent  $\gamma$  in the geminal was chosen to be  $1.0 a_0^{-1}$ .

### Results

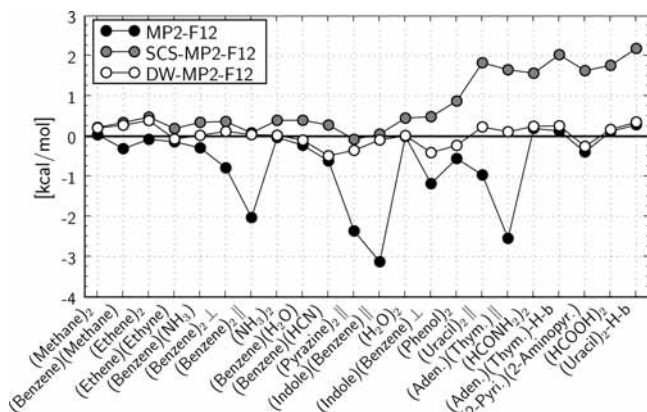
The computed CP-corrected interaction energies for the S22 benchmark<sup>2</sup> set are summarized in Table 1. All calculations were performed at the original geometries for the S22 set, which can be found in the Supporting Information of ref 2. Many of these geometries were optimized at the MP2 level, and therefore, the CCSD(T) binding energies at the CCSD(T) structures would be larger. This is particularly true for dispersion-bonded systems, such as the benzene dimer, for which MP2 significantly overestimates the binding energy and leads to intermolecular distances that are too short.<sup>1,3–5,13</sup> More accurate calculations for the benzene dimer can be found in refs 4, 5, and 13.

**CCSD(T\*)-F12a Results.** We first consider the CCSD(T\*)-F12a values. Due to the size of the systems, CCSD(T)/CBS[34] estimates could be obtained for only 11 of the 22 dimers, and therefore, the following discussion is restricted to this subset. As seen in Table 1, the CCSD(T\*)-F12a interaction energies are very close to the CCSD(T)/CBS[34] reference values. Even for the small AVDZ basis, the mean absolute deviation (MAD) amounts to only 0.05 kcal mol<sup>-1</sup>, and the maximum deviation (MAX) is 0.17 kcal mol<sup>-1</sup>. With the AVTZ basis, the MAD (MAX) values are reduced to 0.014 (0.03) kcal mol<sup>-1</sup>. According to previous experience,<sup>36</sup> it is quite likely that the CCSD(T\*)-F12a/AVTZ values are more accurate than the CCSD(T)/CBS[34] results.

The dramatic improvement in the interaction energies by the explicit correlation treatment is illustrated in Figure 1. The figure clearly demonstrates that the CCSD(T\*)-F12a/AVDZ results are much more accurate than the conventional CCSD(T)/AVQZ' values, and on the scale of the figure, the CCSD(T\*)-F12a/AVTZ and CCSD(T)/CBS[34] values are virtually identical. As already mentioned, the CABS singles correction is very important to reach this excellent accuracy. Without it, the accurate correlation contributions would be spoiled by large errors of the HF contributions; the MAD (MAX) values for the CCSD(T\*)-F12a/AVDZ values without the singles correction are 0.20 (0.854) kcal mol<sup>-1</sup>. Furthermore, we note that the scaling correction of the triples energy reduces the MAD (MAX) values from 0.134 (0.380) to 0.05 (0.17) kcal mol<sup>-1</sup> (basis AVDZ, including CABS singles correction).

In the cases where the CCSD(T\*)-F12a values could be obtained with the AVTZ basis, the corresponding AVDZ results agree with those for AVTZ within 0.1 kcal/mol. Slightly larger errors occur only when the interaction energies are very large (e.g., formic acid dimer) or when the electron correlation contributions are very large. For example, in the pyrazine dimer, the correlation contribution amounts to about  $-8.5$  kcal/mol. In this case, the CCSD(T\*)-F12a/AVDZ value deviates from the AVTZ value by  $-0.24$  kcal/mol, which might be due to the well-known overestimation of the F12a correlation energy for small basis sets.<sup>35,36</sup> Even larger correlation contributions are seen for the last three dispersion-bound systems, and most likely, the absolute values of the AVDZ binding energies are also slightly too large in these cases, despite the fact that they are in very good agreement with the estimated CBS limits of Jurečka et al.<sup>2</sup> It should be noted that for the largest systems, the latter have been obtained only from CCSD(T)/cc-pVDZ calculations





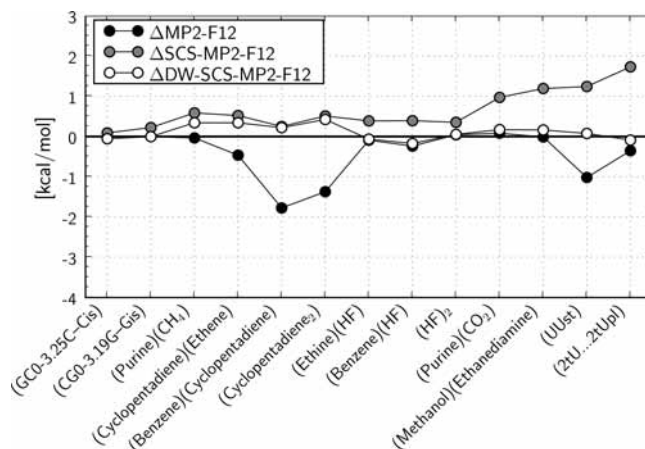
**Figure 3.** Errors of MP2-F12, SCS-MP2-F12, and DW-MP2-F12 interaction energies relative to the CCSD(T\*)-F12 results for the S22 test set (basis aug-cc-pVDZ).

discussion of the DW-MP2-F12 results to the AVDZ basis set. All calculations are explicitly correlated. The two parameters  $a$  and  $b$  of the method, which determine the location and width of the switching function, are determined by fitting the DW-MP2-F12/AVDZ interaction energies of the S22 set to the CCSD(T\*)-F12a ones obtained with the same basis set. The resulting values are  $a = 0.15276$ ,  $b = 1.89952$ . These values are quite insensitive to the basis set. They can also be used with the AVTZ basis set. It should be noted, however, that the diffuse functions in the basis sets are essential to obtain accurate results. Without diffuse functions, the errors of the HF contributions are large, and this affects the ratio in eq 11.

Figure 3 shows the deviations of the MP2-F12, SCS-MP2-F12, and DW-MP2-F12 interaction energies from those of CCSD(T\*)-F12a (all values for basis AVDZ). Although the MP2-F12 method strongly overestimates the binding for the dispersion bonded systems and SCS-MP2-F12 underestimates the binding energies for hydrogen bonded systems, the DW-MP2-F12 shows a much improved accuracy and uniformly small errors for all systems.

One might argue that the good performance of the DW-MP2 method is due to the fact that the two parameters have been optimized for the systems under consideration. We have therefore considered 13 additional dimers (T13 set), which are listed in Table 2. The deviations from the CCSD(T\*)-F12/AVDZ reference values are shown in Figure 4.

The same parameters as before have been used. A statistical analysis is presented in Table 3. The improvement is similar to



**Figure 4.** Errors of MP2-F12, SCS-MP2-F12, and DW-MP2-F12 interaction energies relative to the CCSD(T\*)-F12 results for the T13 set (basis aug-cc-pVDZ).

**TABLE 3: Statistical Analysis of the DW-MP2 Results<sup>a</sup> (in kcal/mol; basis aug-cc-pVDZ)**

	S22	T13
MP2-F12		
RMS	1.17	0.71
MAD	0.74	0.43
MAX	-3.12	-1.77
SCS-MP2-F12		
RMS	1.08	0.80
MAD	0.81	0.65
MAX	2.18	1.73
DW-MP2-F12		
RMS	0.24	0.21
MAD	0.20	0.17
MAX	-0.49	0.42

<sup>a</sup> Parameters optimized for all dimers from the S22 text (see text):  $a = 0.15276$ ,  $b = 1.89952$ . The mean absolute deviations (MAD), maximum deviations (MAX), and root mean square deviations (RMS) from the CCSD(T\*)-F12a/AVDZ values are given.

that for the S22 set. In both cases, the MAD values are 0.2 kcal mol<sup>-1</sup>, and the maximum errors are below 0.5 kcal mol<sup>-1</sup>. We have also found that inclusion of these dimers in the training set would not lead to significantly different results.

**TABLE 2: MP2-F12, SCS-MP2-F12, and DW-MP2-F12 Interaction Energies (in kcal/mol) for the T13 Test Set<sup>a</sup>**

dimer	geometry	CCSD(T*)-F12	HF	MP2-F12	SCS-MP2-F12	DW-MP2-F12	$w^c$
GC0-3.25 C-Cis	<i>b</i>	2.970	4.142	2.914 (-0.055)	3.060 (0.090)	2.915 (-0.055)	0.997
CG0-3.19 G-Gis	<i>b</i>	1.141	2.368	1.139 (-0.003)	1.364 (0.223)	1.139 (-0.003)	1.000
purine·CH <sub>4</sub>	<i>c</i>	-2.138	0.427	-2.173 (-0.035)	-1.551 (0.587)	-1.795 (0.343)	0.391
cyclopentadiene·ethene	<i>d</i>	-2.487	1.403	-2.951 (-0.464)	-1.965 (0.522)	-2.144 (0.342)	0.182
cyclopentadiene·benzene	<i>d</i>	-2.792	5.444	-4.566 (-1.775)	-2.542 (0.250)	-2.571 (0.221)	0.014
cyclopentadiene dimer	<i>d</i>	-3.285	4.098	-4.657 (-1.371)	-2.775 (0.510)	-2.861 (0.424)	0.046
ethine·HF	<i>d</i>	-4.260	-2.892	-4.351 (-0.091)	-3.872 (0.388)	-4.324 (-0.065)	0.944
benzene·HF	<i>d</i>	-4.281	-2.178	-4.519 (-0.238)	-3.888 (0.393)	-4.453 (-0.172)	0.894
(HF) <sub>2</sub>	<i>d</i>	-4.487	-3.856	-4.442 (0.045)	-4.134 (0.353)	-4.434 (0.053)	0.973
purine·CO <sub>2</sub>	<i>c</i>	-5.897	-2.923	-5.813 (0.084)	-4.925 (0.972)	-5.726 (0.171)	0.902
methanol·ethanediamine	<i>d</i>	-7.477	-2.896	-7.488 (-0.012)	-6.284 (1.193)	-7.314 (0.163)	0.855
UUst	<i>b</i>	-7.607	0.547	-8.624 (-1.017)	-6.363 (1.243)	-7.530 (0.077)	0.516
2tU...2tU pl	<i>b</i>	-12.427	-5.467	-12.780 (-0.353)	-10.697 (1.731)	-12.516 (-0.089)	0.873

<sup>a</sup> The AVDZ basis set was used. Deviations from the CCSD(T\*)-F12a/AVDZ values are in parentheses. The Hartree-Fock and all F12 values include the CABS singles correction. <sup>b</sup> Geometries from the JSCH2005 set, ref 2. <sup>c</sup> Geometries optimized using RI-MP2/def2-TZVPP; Vogiatzis and Klopper, private communication. <sup>d</sup> Geometries optimized using LMP2/AVTZ; this work. <sup>e</sup> The weight factor  $w$  in eq 9.

## Conclusions

We have shown that the explicitly correlated CCSD(T\*)-F12a method yields highly accurate dimer interaction energies already with small basis sets. Augmented double- $\zeta$  basis sets are sufficient to achieve an accuracy of better than 0.2 kcal mol<sup>-1</sup> for all dimers in the S22 test set. This is significantly better than standard calculations with the aug-cc-pVQZ basis set, but at the same time 1–2 orders of magnitude less expensive (the savings increase with system size, since the additional cost for the explicit correlation treatment scales with  $O(N^5)$ , whereas CCSD(T) scales with  $O(N^7)$ , where  $N$  is a measure of the system time). This makes it possible to accurately treat larger systems than with the standard CCSD(T) method. The current CCSD(T\*)-F12a/AVTZ values for the S22 set are likely to be the most accurate reference values available so far. It should be noted, however, that they have been computed using the recommended MP2 geometries for the S22 set, which have mostly been optimized at the MP2 level and may significantly differ from CCSD(T) geometries, in particular for dispersion-bonded systems. Thus, in these cases, the true binding energies would be larger. Furthermore, monomer relaxation effects have not been taken into account.

As a pragmatic computationally inexpensive alternative to the CCSD(T\*)-F12 method, we have proposed a dispersion-weighted variant of the SCS-MP2-F12 method. This yields a weighted average of the standard MP2-F12 and SCS-MP2-F12 results in which the weights depend on the ratio of the Hartree-Fock and MP2-F12 values of the interaction energies. This yields much improved accuracy for both the S22 training and for an additional set of 13 dimers, which were not used for fitting the two parameters on which the method depends.

Despite the good performance of the DW-MP2-F12 method for dimer binding energies, it should be noted that the DW-MP2 method is specifically designed to compute dimer interaction energies. It cannot be reasonably used for other energetic quantities, such as reaction energies or reaction barriers. Moreover, the method is not really extensive. If, for instance, dispersion- and hydrogen bonded dimers would be treated in one calculation, compromise values for the weights of MP2 and SCS-MP2 would result. The same could happen if one large system contains both dispersion and electrostatic interactions taking place in different locations. To achieve extensivity, it would be desirable to determine the SCS scaling factors independently for different localized orbital pairs. Further work is in progress along these lines.

**Acknowledgment.** This work has been supported by the Deutsche Forschungsgemeinschaft with the priority program 1145 and by the Fonds der Chemischen Industrie.

## References and Notes

- (1) Sinnokrot, M. S.; Sherrill, C. D. *J. Phys. Chem. A* **2004**, *108*, 10200.
- (2) Jurečka, P.; Šponer, J.; Černý, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985–1993.
- (3) Lee, E. C.; Kim, D.; Jurečka, P.; Tarakeshwa, P.; Hobza, P.; Kim, K. S. *J. Phys. Chem. A* **2007**, *111*, 3446–3457.
- (4) Hill, J. G.; Platts, J. A.; Werner, H.-J. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4072–4078.

- (5) Janowski, T.; Pulay, P. *Chem. Phys. Lett.* **2007**, *447*, 27–32.
- (6) Hill, J. G.; Platts, J. A. *J. Chem. Theory Comput.* **2007**, *3*, 80–85.
- (7) Kabelac, M.; Valdes, H.; Sherer, E. C.; Cramer, C. J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5000–5008.
- (8) Valdes, H.; Pluháčková, K.; Pitonák, M.; Řezáč, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2747–2757.
- (9) Hill, J. G.; Platts, J. A. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2785–2791.
- (10) Hill, J. G.; Platts, J. A. *J. Chem. Phys.* **2008**, *129*, 134101.
- (11) Gkionis, K.; Platts, J. A.; Hill, J. G. *Inorg. Chem.* **2008**, *47*, 3893–3902.
- (12) Bachorz, R. A.; Bischoff, F. A.; Hoefener, S.; Klopper, W.; Ottiger, P.; Leist, R.; Frey, J. A.; Leutwyler, S. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2758–2766.
- (13) Marchetti, O.; Werner, H.-J. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3400–3409.
- (14) Grimme, S.; Mueck-Lichtenfeld, C.; Antony, J. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3327–3334.
- (15) Pitonák, M.; Neogrady, P.; Černý, J.; Grimme, S.; Hobza, P. *ChemPhysChem* **2009**, *10*, 282–289.
- (16) Grafenstein, J.; Cremer, D. *J. Chem. Phys.* **2009**, *130*, 124105.
- (17) Jeziorski, B.; Moszynski, R. *Chem. Rev.* **1994**, *94*, 1887–1930.
- (18) Szalewicz, K.; Patkowski, K.; Jeziorski, B. *Struct. Bonding (Berlin)* **2005**, *116*, 43–117.
- (19) Hesselmann, A.; Jansen, G. *Chem. Phys. Lett.* **2003**, *367*, 778–784.
- (20) Hesselmann, A.; Jansen, G.; Schütz, M. *J. Chem. Phys.* **2005**, *122*, 014103.
- (21) Hesselmann, A.; Jansen, G.; Schütz, M. *J. Am. Chem. Soc.* **2006**, *128*, 11730–11731.
- (22) Misquitta, A. J.; Podeszwa, R.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **2005**, *123*, 214103.
- (23) Misquitta, A. J.; Szalewicz, K. *J. Chem. Phys.* **2005**, *122*, 214109.
- (24) Podeszwa, R.; Bukowski, R.; Szalewicz, K. *J. Chem. Theory Comput.* **2006**, *2*, 400–412.
- (25) Grimme, S. *J. Comput. Chem.* **2004**, *25*, 1463–1473.
- (26) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- (27) Antony, J.; Grimme, S. *Phys. Chem. Chem. Phys.* **2006**, *8*, 5287–5293.
- (28) Grimme, S.; Antony, J.; Schwabe, T.; Mueck-Lichtenfeld, C. *Org. Biomol. Chem.* **2007**, *5*, 741–758.
- (29) Schwabe, T.; Grimme, S. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3397–3406.
- (30) Saebø, S.; Tong, W.; Pulay, P. *J. Chem. Phys.* **1993**, *98*, 2170–2175.
- (31) Hartke, B.; Schütz, M.; Werner, H.-J. *J. Chem. Phys.* **1998**, *239*, 561–572.
- (32) Schütz, M.; Rauhut, G.; Werner, H.-J. *J. Phys. Chem. A* **1998**, *102*, 5997–6003.
- (33) Grimme, S. *J. Chem. Phys.* **2003**, *118*, 9095–9102.
- (34) Antony, J.; Grimme, S. *J. Phys. Chem. A* **2007**, *111*, 4862–4868.
- (35) Adler, T. B.; Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2007**, *127*, 221106.
- (36) Knizia, G.; Adler, T. B.; Werner, H.-J. *J. Chem. Phys.* **2009**, *130*, 054104.
- (37) Werner, H.-J.; Adler, T. B.; Manby, F. R. *J. Chem. Phys.* **2007**, *126*, 164102.
- (38) Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2008**, *128*, 154103.
- (39) Klopper, W.; Samson, C. C. M. *J. Chem. Phys.* **2002**, *116*, 6397–6410.
- (40) Valeev, E. F. *Chem. Phys. Lett.* **2004**, *395*, 190–195.
- (41) Manby, F. R. *J. Chem. Phys.* **2003**, *119*, 4607–4613.
- (42) Pack, R. T.; Byers Brown, W. *J. Chem. Phys.* **1966**, *45*, 556–559.
- (43) Ten-no, S. *Chem. Phys. Lett.* **2004**, *398*, 56–61.
- (44) Rauhut, G.; Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2009**, *130*, 054105.
- (45) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; et al. MOLPRO, version 2009.1, a package of ab initio programs, 2009; see <http://www.molpro.net> (accessed Sept 30 2009).
- (46) Bernardi, F.; Boys, S. F. *Mol. Phys.* **1970**, *19*, 553–556.
- (47) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6806.