

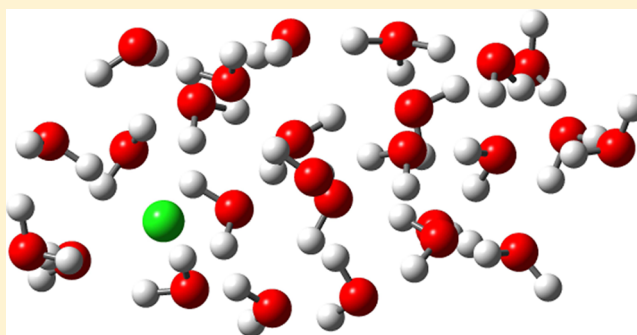
# Incremental CCSD(T)(F12)IMP2-F12—A Method to Obtain Highly Accurate CCSD(T) Energies for Large Molecules

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**S** Supporting Information

**ABSTRACT:** In this work, we apply the recently proposed MP2 correction to incremental energies within the domain-specific basis set approach to incrementally expanded CCSD(T)(F12) energies. The approach is tested for a set of 27 molecules with different electronic structures including water clusters, aqua complexes, aliphatic hydrocarbons, alkenes, alkynes, aromatic systems, and amino acids. The root mean squared deviation of the absolute energies with respect to the standard calculation is 1.7 kJ/mol, the mean absolute deviation is 1.2 kJ/mol, and the range is 4.7 kJ/mol. The wall time of the computations is reduced due to the application of a doubly parallel strategy—the independent coupled cluster calculations are performed on up to 70 nodes in parallel, and in addition the computations on one node are performed with the SMP-parallelized coupled cluster code in TURBOMOLE. Using this strategy, we can perform computations in minutes or hours, instead of days or months. Applying the proposed scheme enables us to routinely treat systems with 50 atoms at the CCSD(T)(F12) level in combination with appropriate basis sets to obtain nearly CBS accuracy. Also, larger systems are still feasible on a standard cluster as demonstrated for  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{25}\text{Cl}^-$  with 80 atoms.



## 1. INTRODUCTION

Today's workhorse in quantum chemistry is density functional theory, which usually yields qualitatively and quantitatively correct results. However, there are cases where the accuracy of DFT is not sufficient and one needs an alternative method like coupled cluster singles doubles with perturbative triples excitations—CCSD(T). Due to the steep scaling of this method with the system size, it is only applicable to very small systems. In order to overcome the scaling drawback of coupled cluster methods in general, a huge number of local coupled cluster methods have been developed over the past decades.<sup>1–27</sup> The goal of low order scaling has been reached by several strategies like the fragmentation of molecular orbitals (FMO) as advocated by Kitaura, Fedorov, and others;<sup>5,6,28–30</sup> the divide-and-conquer scheme of Yang;<sup>15,31,32</sup> the cluster-in-molecule method (CIM);<sup>14,17,33–35</sup> as well as the Pulay type local correlation methods<sup>36</sup> with efficient implementations of Werner and co-workers.<sup>1,2,37,38,39</sup> Within this framework, extensions to local-MRCI<sup>40</sup> and to periodic systems were suggested.<sup>41</sup> The most important error in the Pulay type local correlation approach is the so-called domain error, which can cause large jumps in the potential energy surface.<sup>42</sup> In order to obtain smooth potential energy surfaces, Head-Gordon and co-workers proposed the use of bump functions.<sup>7,8</sup> A different strategy to remove the domain error is to use explicitly correlated F12 terms as proposed by Werner and Adler.<sup>38,39</sup>

A complete coverage of the literature on local correlation methods is beyond the scope of this work, and we refer to the

recent reviews of Gordon et al.<sup>16,25</sup> and to the PCCP special issue on fragment and localized orbital methods in electronic structure theory<sup>28,29,32,41,43–46</sup> as well as to the references therein.

One strategy to extend the applicability of CCSD(T) is the incremental scheme proposed by Stoll.<sup>47–49</sup> It is based on the Bethe-Goldstone expansion as introduced to quantum chemistry by Nesbet.<sup>50–52</sup> Conceptually, the incremental scheme is similar to the FMO scheme, since both expand the energy or a part of it in a many-body series (eq 1). However, the definition of the energy contributions differs from case to case, as well as the way in which the contributions are calculated.

In our previous work, we presented a fully automated implementation of the incremental scheme,<sup>10</sup> introduced the domain-specific basis set approach for efficiency,<sup>53,54</sup> demonstrated the applicability,<sup>55–61</sup> and extended the approach to properties.<sup>62</sup> Since we obtain the CCSD(T) total energy with high accuracy, the proposed method is suitable for computing atomization energies. Also adiabatic interaction energies of molecular clusters, as required in QCE<sup>63,64</sup> calculations, can be computed.

Another problem associated with wave function based correlation methods is the slow convergence of the correlation energy with respect to the one particle basis set. In order to

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obtain high accuracy, one can perform an extrapolation of the energy to the complete basis set limit (CBS)<sup>65</sup> or use modern explicitly correlated methods.<sup>66–79</sup> Since the basis set extrapolation requires large basis sets to obtain the CBS limit accurately, this method becomes very time-consuming due to the unfavorable scaling of post Hartree–Fock methods with respect to the basis set. Such a procedure is usually intractable for large systems. In contrast to this, it is sufficient to apply medium-sized basis sets, when using explicitly correlated methods, and hence one can save significant computational effort.<sup>68,80</sup> For a recent review on explicitly correlated methods, consider ref 81 and the references therein.

In this contribution, we present an incremental CCSD(T)-(F12) method in combination with our recently proposed error correction based on MP2.<sup>82</sup> The approach is tested for a set of 27 benchmark molecules with different electronic structures. The performance of the proposed approach is analyzed with respect to the errors in the absolute energy using the arithmetic mean, the root mean squared deviation (rms), and the range as well as the mean absolute deviation (mad).

## 2. THEORY

**2.1. Incremental Scheme.** In an incremental calculation, the total system is divided into small one-site domains consisting of groups of localized occupied orbitals.<sup>10,55,83</sup> Then one calculates the correlation energies for these domains. In order to include the nonadditivity corrections, one calculates higher order corrections until the desired accuracy is reached. The correlation energy is computed with the incremental series:<sup>10,47</sup>

$$E_{\text{corr}} = \sum_{\mathbb{X} \in \mathcal{P}(\mathbb{D}) \wedge |\mathbb{X}| \leq O} \Delta \varepsilon_{\mathbb{X}} \quad (1)$$

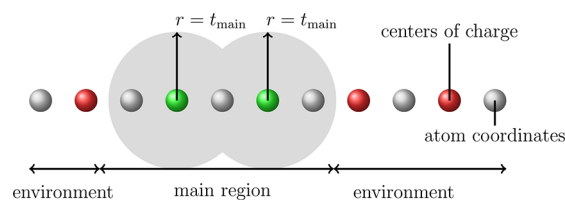
where  $\mathcal{P}(\mathbb{D})$  is the power set of the set of the domains  $\mathbb{D}$ . The restriction on the cardinality of the sets  $\mathbb{X}$  truncates the incremental series at the desired order  $O$ . The general increment is defined as

$$\Delta \varepsilon_{\mathbb{X}} = \varepsilon_{\mathbb{X}} - \sum_{\mathbb{Y} \in \mathcal{P}(\mathbb{X}) \wedge |\mathbb{Y}| < |\mathbb{X}|} \Delta \varepsilon_{\mathbb{Y}} \quad (2)$$

where  $\varepsilon_{\mathbb{X}}$  is the correlation energy of the combined subsystems of  $\mathbb{X}$ .

**2.2. Domain-Specific Basis Set.** One approximation is the usage of a domain-specific basis set, which reduces the virtual space of the environment of a domain. For a systematic determination of the environment, the parameter  $t_{\text{main}}$  is used (see Figure 1). This parameter defines a radius around every occupied localized orbital in the domain. The space defined by all these spheres is the main part, treated with the original large basis set, and the rest is the environment, which is treated with a small basis set (SV in this work). In order to set up an orthogonal set of molecular orbitals in the new basis set, a HF calculation with a successive localization is performed. The orbitals of the domain are identified in the new basis set by mapping the centers of charge of the localized orbitals from one basis to the other. This mapping is not always unique, and we force the orbitals to be as similar as possible within a modified Boys localization procedure (template localization).<sup>84</sup>

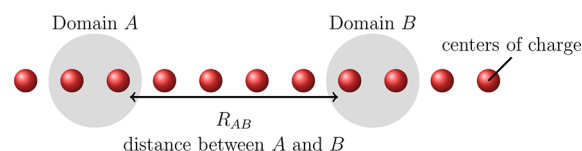
One can view the domain-specific basis set as a way to automatically construct the embedding of a domain. As previously discussed by Stoll et al.,<sup>85</sup> one will need an



**Figure 1.** Construction of the domain-specific basis set. The centers of charge of a domain are given in green. One selects the important part of a domain by the gray area (a volume in 3 dimensions). The area is determined by drawing circles with the radius  $t_{\text{main}}$  around every center of charge of the domain (green circles). Now one uses the large original basis set in the important part, and the rest of the system is defined as environment, which is treated with a small basis set (SV).

embedding scheme if the interaction of the domains with the environment is not negligible. This basic concept of reducing the basis set in the environment by mixed basis sets or pseudopotentials or both was extensively used by Paulus et al., Dolg et al., and Staemmler et al. to increase the computational efficiency of the incremental approach.<sup>43,85–93</sup>

**2.3. Distance Screening.** From eq 1, one can see that the number of calculations grows very fast with respect to the order of the incremental series. Since the increments decay very rapidly with respect to the order of the expansion and with respect to the spatial distance of the underlying one-site domains, one can truncate the series at a low order and neglect the increments with far distant one-site domains (Figure 2).<sup>85</sup>



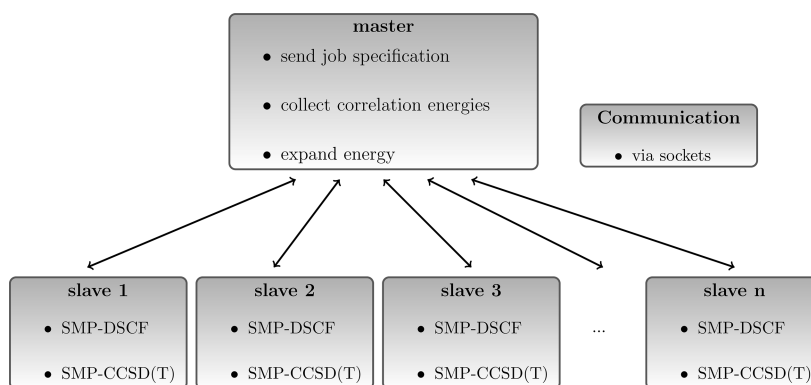
**Figure 2.** Graphical representation of the distance screening. If the distance of two domains is larger than  $t_{\text{dist}}$ , the increment is neglected. The distance between two domains is defined as the smallest distance between the centers of charge in A to those in B. Since the magnitude of the increments usually decays with the order, we shrink  $t_{\text{dist}}$  with increasing order ( $t_{\text{dist}}(i) = (f/(i-1))^2$ , where  $i$  is the actual order and  $f$  is the truncation parameter).

Due to the order and distance decay, one can shrink the truncation distance for neglecting the increments with increasing order. We account for this by applying an order dependent truncation threshold  $t_{\text{dist}}(i) = f/(i-1)^2$ , where  $i$  is the index of the order.<sup>55,94</sup>

**2.4. Parallelization.** The incremental scheme is an inherently parallel method. Therefore, it was parallelized in a master and slave structure.<sup>10</sup> For an efficient use of modern multicore machines, a double parallel treatment similar to the one proposed by Fedorov and co-workers<sup>95</sup> is applied. On a single node, the shared memory version of TURBOMOLE is applied, whereas the different correlation calculations are distributed over the desired number of nodes (see Figure 3).

**2.5. Hardware.** All computations were performed on a cluster of 71 nodes connected by a standard gigabit Ethernet. Each node is equipped with an Intel Xeon E3-1270 3.4 GHz quad-core CPU, 8 GB of RAM, and a single hard disk of 1 TB.

**2.6. MP2 Error Correction.** If we truncate the incremental expansion, we will introduce an error  $\Delta E$ . This error can be corrected using the corresponding error from a computationally less demanding MP2 calculation:



**Figure 3.** Schematic representation of the applied multilevel parallelization scheme. Disk and RAM access on a single node is controlled by TURBOMOLE. Within this scheme, no significant internode communication is required. The additional SCF calculations are required due to the domain-specific basis set (vide supra).

$$\begin{aligned}
 E_{\text{corr}}^{\text{inc}}(\text{CCSD(T)}|\text{MP2}) &= E_{\text{corr}}^{\text{inc}}(\text{CCSD(T)}) - \Delta E(\text{MP2}) \\
 &= E_{\text{corr}}^{\text{inc}}(\text{CCSD(T)}) - [E_{\text{corr}}^{\text{inc}}(\text{MP2}) - E_{\text{corr}}(\text{MP2})] \quad (3)
 \end{aligned}$$

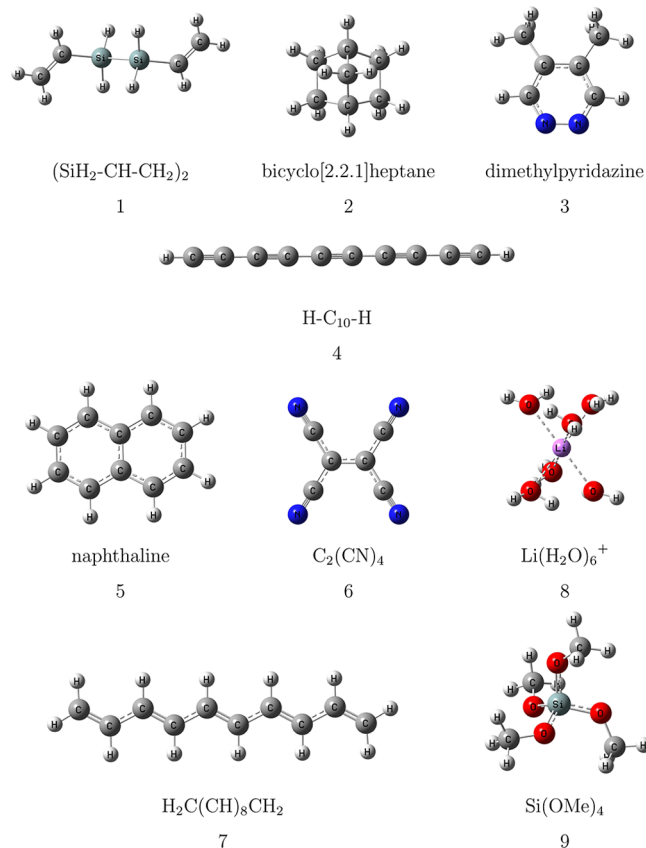
This correction is similar to the QM/QM methods by means of the subtractive scheme.<sup>24,96–100</sup>

**2.7. Computational Details.** The coupled cluster calculations were performed with a development version of the TURBOMOLE program package.<sup>68,79,101–103</sup> In the environment, the SV<sup>104</sup> basis set in combination with the appropriate RI basis set<sup>105</sup> for density fitting was used in all calculations. The required data such as MO coefficients, overlap, overlap of two basis sets, and dipole integrals were obtained from a modified version of the ricc2 module.<sup>106</sup> In the explicitly correlated calculations, we used a Slater type correlation factor as proposed by Ten-no.<sup>107</sup> In TURBOMOLE, the Slater type function is represented by a linear combination of six Gaussians.<sup>108</sup> Furthermore, we applied the cc-pVDZ-F12 basis set of Peterson et al.<sup>109,110</sup> using the corresponding CABS<sup>111</sup> and the recommended exponent of  $0.9 a_0^{-1}$  in the correlation factor. For the cationic aqua complexes, we used the cc-pCVDZ-F12 basis set and an exponent of  $1.4 a_0^{-1}$ . The details of the explicitly correlated MP2-F12<sup>103</sup> and CCSD(T)-(F12)<sup>68,112</sup> are ansatz 2, approximation B,<sup>113</sup> and the fixed amplitude approach.<sup>114</sup> The geometries were obtained with the BP86/SV(P) method<sup>104</sup> using the RI approximation as implemented in TURBOMOLE.<sup>115–117</sup> The obtained structures were characterized as minima by analyzing the Hessian matrix.<sup>118</sup>

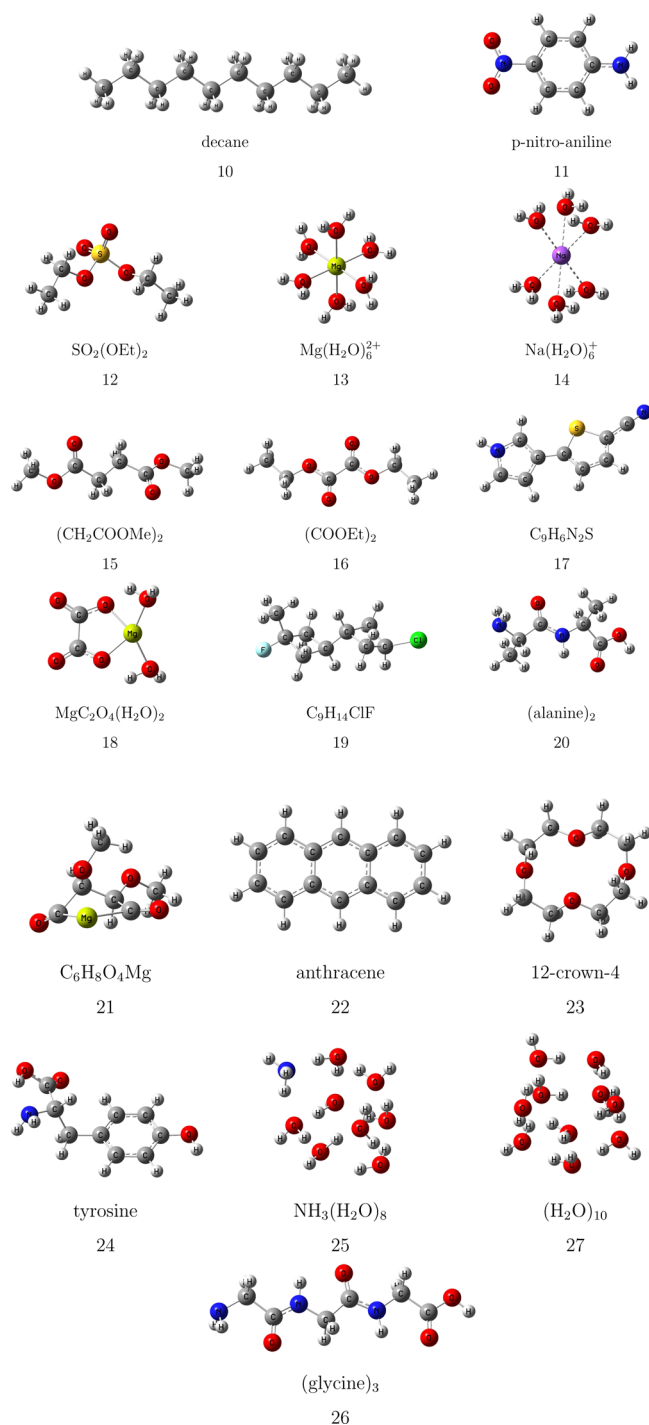
For the calculations using the incremental scheme, we used  $t_{\text{main}} = 3$  Bohr to set up the domain-specific basis set and  $t_{\text{con}} = 3$  Bohr for the truncation of the connectivity matrix in the partitioning step;<sup>10</sup> the domain size parameter (dsp)—a measure for the size of the domains—was set to 4 and  $E_{\text{tresh}} = 10^{-6}$  au<sup>83</sup> to automatically control the target accuracy of the required correlation energies. All energies in the statistics were computed up to third order in the incremental series. The parameter  $f$  for the order dependent distance truncation was set to 30 Bohr (vide supra).

**2.8. Test Set.** The choice of the test set is of critical importance for the analysis of the accuracy. If only molecules are chosen which can be easily handled, we will obtain perfect accuracy. Conversely, if we chose only those molecules which cannot be handled, we end up with a very bad accuracy. One restriction for the choice of the molecules was the size, since

the standard computation had to be feasible on our hardware. Another restriction was that we need proper basis sets for the explicitly correlated methods. Therefore, we restricted the test set to molecules containing only H, Li, Be, C, N, O, F, Na, Mg, Si, S, and Cl atoms. Since one would expect that conjugated  $\pi$ -systems and aromatic systems are difficult to treat with local correlation methods, we included several systems with such structural units. In order to convince the reader that our test set includes molecules of chemical interest as well as species which are not trivially computed with our scheme, the structures of the molecules are shown in the Figures 4 and 5.



**Figure 4.** Structures of the molecules in the chosen test set (part I).



**Figure 5.** Structures of the molecules in the chosen test set (part II). The structure of the water cluster was taken from Piecuch and co-workers.<sup>14</sup>

### 3. RESULTS

The main goal of this work is to establish the accuracy of the recently proposed incremental CCSD(T)IMP2 method. Therefore, we select a broad data set of molecules containing fragments of real life molecules. We did not choose the standard data sets with small molecules, because the incremental scheme requires at least medium-sized molecules to test the accuracy on a meaningful basis. For too small molecules, the incremental series will yield the exact answer, since the highest order will be computed. Due to the size of the

molecules, we had to choose the small cc-pVDZ-F12 basis set in order to compute the reference energies with the standard CCSD(T)(F12) method. We should note that the standard calculations were already quite time-consuming with up to 6 days on four cores. The results of the calculations are summarized in Table 1. For a complete list of the results as well as the coordinates of the molecules, we refer to the Supporting Information.

The errors due to the incremental scheme are visualized in Figure 6. The systems were ordered according to the CCSD(T)(F12) correlation energy. When comparing the plots of the correlation energies, one cannot see a difference between the standard computation and the incrementally expanded ones (left-hand scale). Considering the errors in the incremental expansions, one can see rather large errors for the incremental MP2-F12 and the incremental CCSD(T)(F12). Since the errors are very similar for all 27 systems, one can use the MP2 error to correct the coupled cluster result. To investigate the performance of the MP2 correction for the incrementally expanded CCSD(T)(F12) energies on a solid basis, we performed a statistical analysis using the data in Table 1.

The analysis is based on the following measures of the errors  $x$ :

$$x = E_{\text{inc}} - E_{\text{ref}}$$

where  $E_{\text{inc}}$  is the energy obtained by the incremental scheme and  $E_{\text{ref}}$  is the energy of the reference calculation.

$$\text{range} = x_{\text{max}} - x_{\text{min}}$$

$$\text{mean} = \bar{X} = \frac{1}{n} \sum_{i=1}^n x_i$$

$$\text{rms} = \sqrt{\left( \frac{1}{n} \sum_{i=1}^n x_i^2 \right)}$$

$$\text{mad} = \frac{1}{n} \sum_{i=1}^n |x_i|$$

$$\sigma = \sqrt{\left( \frac{1}{n} \sum_{i=1}^n (x_i - \bar{X})^2 \right)}$$

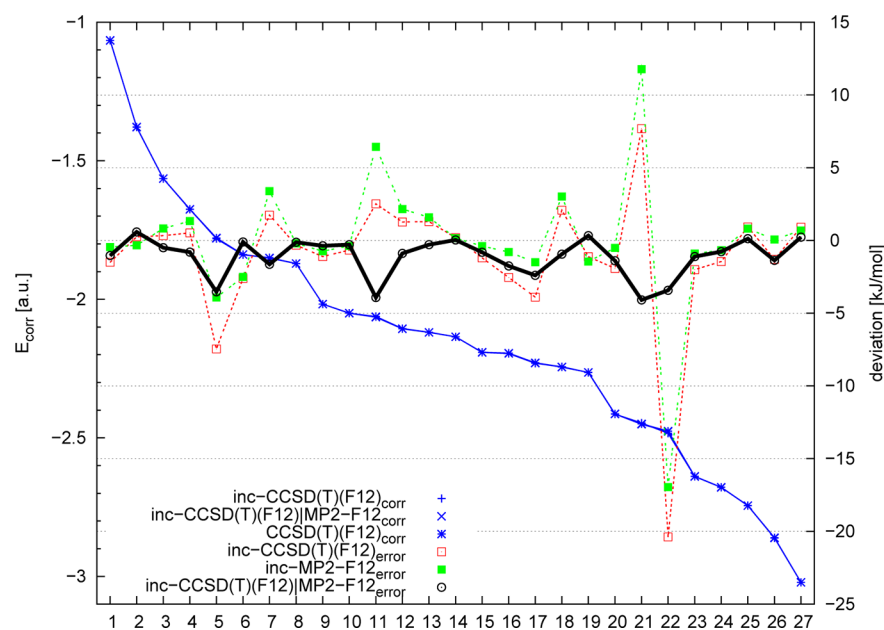
The values of these error measures are given in Table 2. Since the rms and the mad of the incremental MP2-F12 and CCSD(T)(F12) are below 5 kJ/mol, we conclude that these approximations work reasonably well on average, but the range is much too large with ca. 29 kJ/mol. For the MP2 corrected incremental coupled cluster, on the other hand, the range is only 4.7 kJ/mol. Comparing the rms, the mad, and  $\sigma$  we find a significantly smaller value for the CCSD(T)(F12)IMP2 method compared to the incrementally expanded MP2-F12 or CCSD(T)(F12) values. On the basis of this observation, we conclude that the MP2 based error correction scheme works well for chemically relevant species. As a result of our previous investigations, we expect that the MP2 correction can only correct for the deficiencies introduced by the domain-specific basis set approximation but not for higher order effects in the incremental series;<sup>62</sup> i.e. if systems with an intrinsic fourth order contribution are computed, we expect that the fourth order has to be calculated at the coupled cluster level. The results of



**Table 1.** Incrementally Expanded MP2-F12/cc-pVDZ-F12 and CCSD(T)(F12)/cc-pVDZ-F12 Correlation Energies As Well As the Exact Values of the Full Standard Calculation in Atomic Units<sup>a</sup>

no.	system	MP2-F12			CCSD(T)(F12)					inc-ΔMP2, rel. [%]
		inc, au	error, kJ/mol	exact, au	inc, au	error, kJ/mol	inc-ΔMP2, au	error, kJ/mol	exact, au	
1	(SiH <sub>2</sub> -CH-CH <sub>2</sub> ) <sub>2</sub>	-0.99546	-0.5	-0.99528	-1.06592	-1.5	-1.06575	-1.0	-1.06535	100.04
2	bicycloheptane	-1.32091	-0.3	-1.32079	-1.37842	0.2	-1.37829	0.6	-1.37851	99.98
3	dimethylpyridazine	-1.52679	0.8	-1.52711	-1.56435	0.3	-1.56466	-0.5	-1.56447	100.01
4	H-C <sub>10</sub> -H	-1.66502	1.3	-1.66553	-1.67490	0.5	-1.67541	-0.8	-1.67511	100.02
5	naphthaline	-1.73719	-3.9	-1.73569	-1.78130	-7.5	-1.77980	-3.5	-1.77845	100.08
6	C <sub>2</sub> (CN) <sub>4</sub>	-1.83854	-2.5	-1.83758	-1.83941	-2.6	-1.83846	-0.1	-1.83842	100.00
7	H <sub>2</sub> C(CH) <sub>8</sub> CH <sub>2</sub>	-1.77446	3.4	-1.77575	-1.85011	1.7	-1.85140	-1.6	-1.85077	100.03
8	Li(H <sub>2</sub> O) <sub>6</sub> <sup>+</sup>	-1.84970	-0.2	-1.84963	-1.87096	-0.3	-1.87089	-0.1	-1.87084	100.00
9	Si(OMe) <sub>4</sub>	-1.97420	-0.7	-1.97392	-2.01752	-1.1	-2.01724	-0.4	-2.01710	100.01
10	decane	-1.94342	-0.4	-1.94328	-2.05022	-0.7	-2.05007	-0.3	-2.04996	100.01
11	p-nitro-aniline	-2.04304	6.4	-2.04549	-2.06213	2.5	-2.06458	-3.9	-2.06308	100.07
12	SO <sub>2</sub> (OEt) <sub>2</sub>	-2.07607	2.2	-2.07689	-2.10555	1.3	-2.10637	-0.9	-2.10603	100.02
13	Mg(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup>	-2.09945	1.6	-2.10006	-2.11877	1.3	-2.11937	-0.3	-2.11926	100.01
14	Na(H <sub>2</sub> O) <sub>6</sub> <sup>+</sup>	-2.12013	0.2	-2.12019	-2.13528	0.2	-2.13534	0.0	-2.13535	100.00
15	(CH <sub>2</sub> COOMe) <sub>2</sub>	-2.15354	-0.4	-2.15339	-2.19175	-1.2	-2.19160	-0.8	-2.19129	100.01
16	(COOEt) <sub>2</sub>	-2.15750	-0.8	-2.15720	-2.19550	-2.5	-2.19520	-1.8	-2.19453	100.03
17	C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> S	-2.19777	-1.5	-2.19720	-2.23071	-3.9	-2.23013	-2.4	-2.22922	100.04
18	MgC <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub>	-2.24110	3.0	-2.24225	-2.24325	2.1	-2.24440	-0.9	-2.24404	100.02
19	C <sub>9</sub> H <sub>14</sub> ClF	-2.18927	-1.5	-2.18872	-2.26439	-1.1	-2.26384	0.3	-2.26397	99.99
20	(alanine) <sub>2</sub>	-2.36976	-0.5	-2.36956	-2.41430	-1.9	-2.41410	-1.4	-2.41356	100.02
21	C <sub>6</sub> H <sub>8</sub> O <sub>4</sub> Mg	-2.39257	11.8	-2.39705	-2.44644	7.7	-2.45092	-4.1	-2.44936	100.06
22	anthracene	-2.42915	-17.0	-2.42269	-2.48330	-20.4	-2.47684	-3.4	-2.47553	100.05
23	12-crown-4	-2.57043	-0.9	-2.57009	-2.63950	-2.0	-2.63916	-1.1	-2.63873	100.02
24	tyrosine	-2.63739	-0.7	-2.63713	-2.67891	-1.4	-2.67865	-0.8	-2.67836	100.01
25	NH <sub>3</sub> (H <sub>2</sub> O) <sub>8</sub>	-2.73370	0.8	-2.73401	-2.74419	0.9	-2.74450	0.1	-2.74455	100.00
26	(glycine) <sub>3</sub>	-2.82427	0.1	-2.82429	-2.86103	-1.3	-2.86106	-1.4	-2.86053	100.02
27	(H <sub>2</sub> O) <sub>10</sub>	-3.00988	0.7	-3.01014	-3.02113	0.9	-3.02139	0.2	-3.02148	100.00

<sup>a</sup>The corresponding errors are given in kJ/mol. inc-ΔMP2 refers to incremental CCSD(T)(F12)|MP2-F12 and inc to incremental MP2-F12 or CCSD(T)(F12).



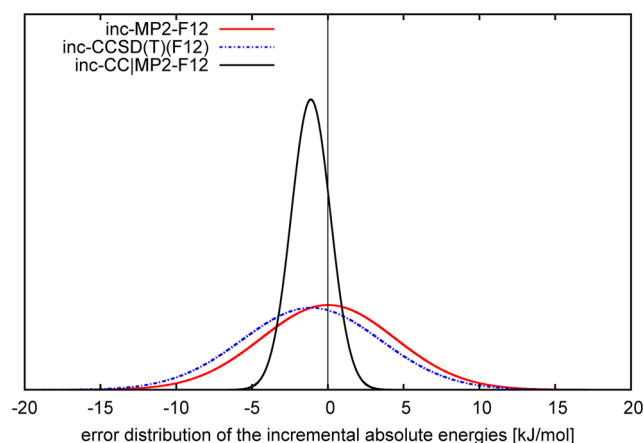
**Figure 6.** Incrementally computed correlation energies and errors of the incrementally expanded correlation energies based on the data in Table 1. The first three plots refer to the scale on the left-hand side and show the correlation energy in atomic units. At this scale, they are all on top of each other. The last three plots refer to the scale on the right-hand side and show the error in the absolute energy in kJ/mol. The bold curve is the CCSD(T)(F12)|MP2-F12 error. The numbering of the molecules 1–27 is the same as in Table 1.

**Table 2.** Statistical Measures for the Errors Due to the Incremental Expansion for MP2-F12, CCSD(T)(F12), and CCSD(T)(F12)|MP2-F12 Energies<sup>a</sup>

	inc-MP2	inc	inc-ΔMP2
range	28.73	28.07	4.67
mean	0.02	−1.10	−1.12
rms	4.42	4.70	1.71
mad	2.37	2.56	1.22
σ	4.42	4.57	1.29

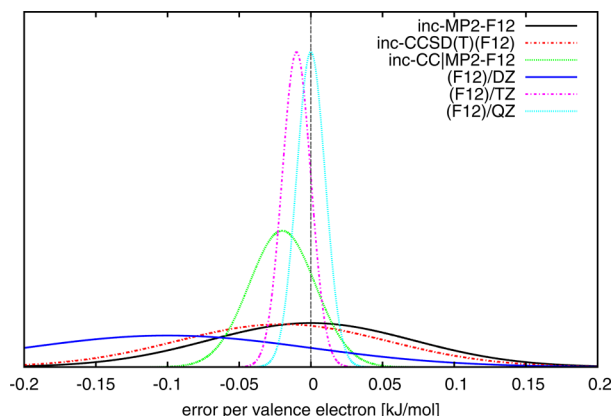
<sup>a</sup>Since the range, the rms, the mad, and the σ are smaller for the MP2 corrected energies, it is evident that the MP2 correction works well. inc-MP2 refers to the incremental MP2-F12, inc to the incremental CCSD(T)(F12), and inc-ΔMP2 to the incremental CCSD(T)(F12)|MP2-F12 result. All values are in kJ/mol.

Table 2 can be visualized if we assume that the error distribution is a Gaussian distribution, which has been done in Figure 7 for the absolute energies. Comparing the shapes of



**Figure 7.** Normal distribution of the errors due to the incremental expansion for the total energies based on the data in Table 1. inc-CC|MP2-F12 refers to the incremental CCSD(T)(F12)|MP2-F12 method.

the error distributions we conclude that the MP2 correction works well. In Figure 8, we used the number of electrons to normalize the errors. The errors per correlated electron can be compared to the errors obtained by Hättig and co-workers<sup>79</sup> for the CBS error in the reaction energies using the CCSD(F12) method. Since we compare errors of reaction energies with errors in the absolute energies and results from different test sets, the result must be interpreted with some care. In reaction energies, some error cancellation may occur, which is not present in the absolute energies. Comparing the error distributions, we find that the incrementally expanded MP2-F12, CCSD(T)(F12), and CCSD(F12)/cc-pVDZ-F12 ones have a similar shape. The main difference is that the error distributions of the incrementally expanded energies are closer to the origin. The error distribution of the CCSD(F12)/cc-pVTZ-F12 is significantly more compact, and using the quadruple-ζ basis set it is essentially a distribution around the origin. Considering the error distribution for the MP2 corrected CCSD(T)(F12) method, we find a more compact distribution compared to the CCSD(F12)/cc-pVDZ-F12 distribution. Comparing the result to the CCSD(F12)/cc-pVTZ-F12 distribution, we find that CCSD(F12)/cc-pVTZ-F12 is more accurate with respect to the basis set limit. On the basis of these findings, we conclude that one can apply the



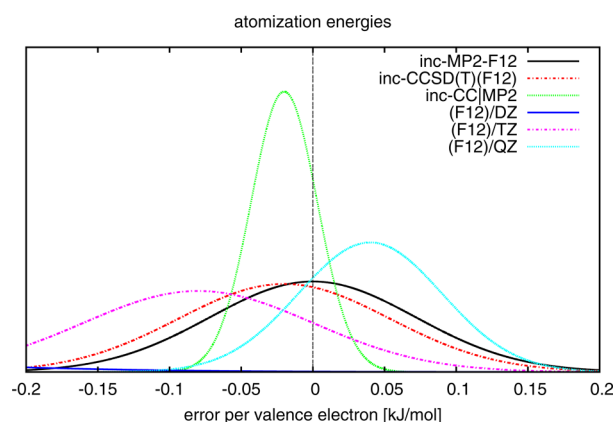
**Figure 8.** Normal distribution of the errors per valence electron due to the incremental expansion for the total energies based on the data in Table 1. The (F12) curves are error distributions per valence electron of the reaction energies of Hättig et al.<sup>79</sup> In this reference, the errors are reported for the CCSD(F12) method with respect to the basis set limit. XZ refers to the cc-pVXZ-F12 basis set series of Peterson and co-workers.<sup>109</sup> We compare the error distribution per valence electron of the absolute energies with the distributions of the reaction energies.

CCSD(T)(F12)|MP2-F12 method in combination with the cc-pVDZ-F12 basis set without a significant loss of accuracy. Assuming a similar error distribution for the incremental expansion at the triple-ζ level, the very high accuracy of the original (F12) method will not be conserved. However, the accuracy of the proposed method is still high. Finally, we note that one can usually obtain the accuracy required to model chemical reaction energies by using a double-ζ-F12 basis set in combination with explicitly correlated methods.<sup>80</sup> The computation of the coupled cluster energy using a triple-ζ basis set becomes extremely time-consuming or even infeasible for larger molecules. With the incremental scheme, such computations are still feasible (vide infra).

Next, we consider the influence of our local approximations on the accuracy of atomization energies (AE) for the investigated molecules. In an atom, all electrons are spatially close and usually strongly interacting. Therefore, it does not make sense to apply local approximations for atoms. One should always compute the whole atom with the standard correlation method. If we now compute the error in the atomization energies  $\Delta E_{\text{AE}}$ , we end up with the error in the correlation energy due to the local approximations  $\Delta E_{\text{inc}}$ :

$$\begin{aligned}\Delta E_{\text{AE}} &= \text{AE}_{\text{inc}} - \text{AE}_{\text{std}} = E_{\text{inc}}^{\text{molecule}} - \sum_i E_i(\text{atom}) \\ &= E_{\text{std}}^{\text{molecule}} + \sum_i E_i(\text{atom}) - E_{\text{inc}}^{\text{molecule}} = E_{\text{inc}}^{\text{molecule}} - E_{\text{std}}^{\text{molecule}} \\ &= \Delta E_{\text{inc}}\end{aligned}$$

where  $\text{AE}_{\text{inc}}$  is the atomization energy from the incremental scheme,  $\text{AE}_{\text{std}}$  is the atomization energy from the standard computation, and  $E_i(\text{atom})$  is the energy of atom  $i$ . In Figure 9, we compare the error distributions due to our local approximations to the errors with respect to the CBS for the atomization energies of Hättig et al.<sup>79</sup> This comparison can again not be rigorously made, since our test set is different from the test set in ref 79. However, we do not have better values to compare with. The CCSD(T)/CBS(56) computations as well as the CCSD(T)(F12)/cc-pVQZ-F12 ones are infeasible for most of the molecules in our test set. If we choose a test set



**Figure 9.** Normal distribution of the errors per valence electron due to the incremental expansion for the total energies based on the data in Table 1. The (F12) curves are error distributions per valence electron of the atomization energies with respect to the complete basis set limit at the CCSD level using explicit correlation.<sup>79</sup> XZ refers to the cc-pVXZ-F12 basis set series of Peterson and co-workers.<sup>109</sup> inc-CCIMP2-F12 refers to the incremental CCSD(T)(F12)|MP2-F12 method.

with too small molecules on the other hand, we will yield too good results with our approach, since the incremental series truncates with the exact result, if the number of domains is smaller than the order of the expansion. The comparison made in Figure 9 is just for a qualitative classification of the accuracy provided by the incremental scheme. Since all of our computations were performed in the cc-pVDZ-F12 basis set, we do not expect to obtain AEs of higher accuracy than the intrinsic accuracy of the CCSD(T)(F12)/cc-pVDZ-F12 method. On the other hand, if the Gaussian distribution is more compact than the distribution of the applied model, we will not introduce a significant error due to our approximation. For the AEs, we find exactly this behavior—the error distributions of the incrementally expanded correlation energies are more compact than the ones for the applied model. The error distribution of the CCSD(T)(F12)|MP2 method is even more compact than the distribution of the CBS error of CCSD(F12) using the cc-pVQZ-F12 basis set. From this finding, it is evident that the incremental CCSD(T)(F12)|MP2 method can be applied to compute high accuracy AEs, if appropriately large basis sets are applied. After all these considerations, one should keep in mind that just the effect of the local approximations has been considered.

#### 4. TIMINGS

Due to the local approximations and the massive parallelization, one can significantly reduce the wall time of lengthy CCSD(T) calculations. With the proposed method, it is possible to obtain highly accurate CCSD(T)(F12) energies within a few hours or less, which would require days, weeks, or months, if at all feasible, on our cluster. In Table 3, we demonstrate the efficiency of our scheme in combination with the obtained accuracy. Comparing the result of the standard coupled cluster calculation in the double- $\zeta$  basis set to the incrementally expanded ones, we find the accuracy to be better than 2 kJ/mol for inc-CCSD(T)(F12) and 0.25 kJ/mol for inc-CCSD(T)(F12)|MP2 energies. Considering the corresponding timings, we find speedups of about 70–600 in the wall times. This water cluster was also computed by Piecuch and Li<sup>119</sup> using their single environment cluster-in-molecule method (SECIM) in

**Table 3.** Efficiency and Accuracy of the Incremental Scheme: Correlation Contribution to the Adiabatic Interaction Energy ( $E_{\text{ad}}^{\text{corr}}$ ) of the Lowest Energy Structure of  $(\text{H}_2\text{O})_{10}$  As Studied in ref 119<sup>a</sup>

method	basis cc-pVXZ-F12	$E_{\text{ad}}^{\text{corr}}$ [kJ/mol]	nodes	total time <sup>b</sup> [h]	wall time [h]
CCSD(T)(F12)	D	−125.9	1	120.1	120.1
inc(2)-CCSD(T)(F12)	D	−127.6	56	8.6	0.2
inc(3)-CCSD(T)(F12)	D	−125.0	31	49.4	1.8
inc(2)-CCSD(T)(F12) MP2	D	−126.0	57	9.2	0.68 <sup>c</sup>
inc(3)-CCSD(T)(F12) MP2	D	−125.7	32	50.1	1.8
inc(2)-CCSD(T)(F12)	T	−131.4	56	21.6	0.5
inc(3)-CCSD(T)(F12)	T	−129.1	51	210.0	5.2
inc(2)-CCSD(T)(F12) MP2	T	−130.0	57	24.8	3.2 <sup>c</sup>
inc(3)-CCSD(T)(F12) MP2	T	−129.7	52	213.1	5.2
inc(2)-CCSD(T)(F12)	Q	−131.3	56	84.9	2.1
inc(3)-CCSD(T)(F12)	Q	−128.9	65	1152.6	23.3
inc(2)-CCSD(T)(F12) MP2	Q	−130.1	57	96.0	11.1 <sup>c</sup>
inc(3)-CCSD(T)(F12) MP2	Q	−129.4	66	1163.7	23.3

<sup>a</sup>In all computations, we used all four cores of the compute nodes. The monomer was optimized with MP2 using cc-pVTZ on H and aug-cc-pVTZ on O. <sup>b</sup>Total time per node. All computations were performed using the SMP parallelization in TURBOMOLE with four cores on each node. <sup>c</sup>The MP2-F12 calculation is the time determining step. The MP2-F12 calculation was performed on four cores using the SMP parallel MP2 in TURBOMOLE. The problem of a time-consuming MP2 can be solved by using a PNO based MP2 scheme.<sup>120,121</sup>

combination with the 6-31++G(d,p) basis set. Since their computations were performed at the CCSD level, on different machines, on a single CPU, and in a different basis set, the absolute timings are not immediately comparable. Using their timings, one can compute a speedup factor of 1.5 in the total time and a factor of 10.2 for the wall time due to the parallelism of their scheme. Considering the timings of a second order expansion, we find a speedup of 13 for the total time and a speedup of 178 for the wall time using our scheme.

As a further demonstration of the efficiency of our approach, we computed the adiabatic interaction energies of  $(\text{H}_2\text{O})_{16}$ (4444a) and  $(\text{H}_2\text{O})_{17}$ (sphere) using the proposed scheme and comparing the results to the CCSD(T)/aug-cc-pVTZ ones of Yoo et al.<sup>122</sup> (see Table 4). Since the absolute energies of the CCSD(T)(F12)/cc-pVDZ-F12 and CCSD(T)/aug-cc-pVTZ differ—the (F12) result is significantly lower—we use the adiabatic interaction energy of the cluster  $E_{\text{ad}}$  to compare the results:

$$E_{\text{ad}} = E(\text{cluster}) - \sum_i E_i(\text{monomers}) \quad (4)$$

The geometries of the clusters were taken from ref 122, and the monomer was optimized at the MP2 level using the aug-cc-pVTZ basis set for O and the cc-pVTZ basis set for H. Because of the fact that adiabatic interaction energies converge very

Table 4. Adiabatic Interaction Energies ( $E_{\text{ad}}$ ) of Large Water Clusters<sup>a</sup>

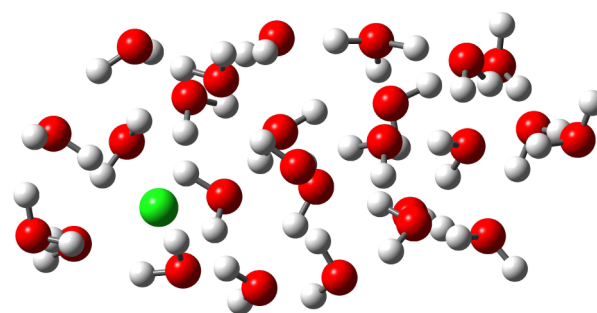
method	cluster	$E_{\text{ad}}$ [kJ/mol]	cores	total time [h]	wall time [h]
CCSD(T)/aug-cc-pVTZ <sup>b</sup>	(H <sub>2</sub> O) <sub>16</sub>	−716.1	120000	399600	3.3
fragment-CCSD(T)/aug-cc-pVTZ <sup>c</sup>	(H <sub>2</sub> O) <sub>16</sub>	−716.3		2256	19.0
inc(2)-CCSD(T)(F12)/DZ <sup>d</sup>	(H <sub>2</sub> O) <sub>16</sub>	−682.8	244	285	1.5
inc(3)-CCSD(T)(F12)/DZ <sup>d</sup>	(H <sub>2</sub> O) <sub>16</sub>	−677.7	244	1646	7.7
inc(2)-CCSD(T)(F12)IMP2-F12/DZ <sup>d</sup>	(H <sub>2</sub> O) <sub>16</sub>	−679.7	248	308	5.8 <sup>e</sup>
inc(3)-CCSD(T)(F12)IMP2-F12/DZ <sup>d</sup>	(H <sub>2</sub> O) <sub>16</sub>	−679.6	248	1669	7.7
inc(2)-CCSD(T)(F12)/TZ <sup>d</sup>	(H <sub>2</sub> O) <sub>16</sub>	−687.5	244	786	3.9
inc(2)-CCSD(T)(F12)IMP2-F12/TZ <sup>d</sup>	(H <sub>2</sub> O) <sub>16</sub>	−685.4	248	878	22.9 <sup>e</sup>
CCSD(T)/aug-cc-pVTZ <sup>b</sup>	(H <sub>2</sub> O) <sub>16</sub>	−764.2		no timing given in ref 122	
fragment-CCSD(T)/aug-cc-pVTZ <sup>c</sup>	(H <sub>2</sub> O) <sub>17</sub>	−764.2		no timing given in ref 24	
inc(2)-CCSD(T)(F12)/DZ <sup>d</sup>	(H <sub>2</sub> O) <sub>17</sub>	−727.4	276	394	1.8
inc(3)-CCSD(T)(F12)/DZ <sup>d</sup>	(H <sub>2</sub> O) <sub>17</sub>	−723.7	276	2666	10.5
inc(2)-CCSD(T)(F12)IMP2-F12/DZ <sup>d</sup>	(H <sub>2</sub> O) <sub>17</sub>	−725.2	280	426	7.8 <sup>e</sup>
inc(3)-CCSD(T)(F12)IMP2-F12/DZ <sup>d</sup>	(H <sub>2</sub> O) <sub>17</sub>	−725.2	280	2697	10.5
inc(2)-CCSD(T)(F12)/TZ <sup>d</sup>	(H <sub>2</sub> O) <sub>17</sub>	−731.3	268	1121	5.2
inc(2)-CCSD(T)(F12)IMP2-F12/TZ <sup>d</sup>	(H <sub>2</sub> O) <sub>17</sub>	−729.4	272	1239	29.5 <sup>e</sup>

<sup>a</sup>The incrementally expanded CCSD(T)(F12) is compared to the conventional computation with respect to accuracy and efficiency.  $E_{\text{ad}}$  of the explicitly correlated methods includes the CABS singles correction to the Hartree–Fock energy.<sup>80,124,125</sup> <sup>b</sup>Taken from ref 122. This computation was performed on a supercomputer using 120 000 cores. <sup>c</sup>The result of Bates et al.<sup>24</sup> using local approximations. The MP2 contribution is the time determining step. <sup>d</sup>XZ refers to the cc-pVXZ-F12 basis set of Peterson and co-workers.<sup>109</sup> <sup>e</sup>The MP2-F12 calculation is the time determining step. The MP2-F12 calculation was performed on four cores using the SMP parallel MP2-F12 in TURBOMOLE.

slowly with respect to the one particle basis set,<sup>59–61</sup> we expect that the CCSD(T)(F12)/cc-pVDZ-F12 calculation yields a higher accuracy than the standard CCSD(T)/aug-cc-pVTZ calculation. On the basis of our previous calculations of adiabatic interaction energies for water clusters of this size, we expect the basis set superposition error to be on the order of 40 kJ/mol for a conventional calculation in the small aug-cc-pVTZ basis set.<sup>123</sup> Comparing the conventional CCSD(T) energies to the F12 results for (H<sub>2</sub>O)<sub>16</sub>, we find that the CCSD(T)/aug-cc-pVTZ result is lower by 31–38 kJ/mol. As discussed above, this is most likely due to the basis set superposition error. Furthermore, it was demonstrated that the errors of a conventional CCSD(T)/aug-cc-pVTZ calculation are larger than the errors from a CCSD(T)(F12)/cc-pVDZ-F12 calculation.<sup>79–81</sup> On the basis of the statistic analysis above, we expect that the errors due to the local approximations are also small. Therefore, we conclude that the adiabatic interaction energies based on the CCSD(F12)IMP2-F12 method of the current work are more accurate than the ones based on the data of ref 122. Comparing the computational effort of both approaches, it is clearly evident that the strategy proposed in this work requires less effort. In the worst case, we needed 0.41% and, in the best case, 0.07% of the CPU time of ref 122. In the work of Bates et al.,<sup>24</sup> a many body expansion in combination with an MP2 based error correction was applied to compute the CCSD(T) energy. Since the approach is similar to our scheme, the timings of both approaches are comparable. Finally, we conclude that it is now possible to compute such high level coupled cluster energies for large systems on a small cluster of standard PCs, rendering such computations to a routine task.

## 5. LARGE SYSTEM

Finally, we calculated a model system for the solvation of HCl in (H<sub>2</sub>O)<sub>26</sub>. In the computed species, the hydrochloric acid is deprotonated, forming a Cl<sup>−</sup> anion and a H<sub>3</sub>O<sup>+</sup> cation (Figure 10). Due to this fact, this model system is a critical test for describing two separated charges with the incremental scheme.

Figure 10. BP86/SV(P) optimized structure of H<sub>3</sub>O<sup>+</sup> (H<sub>2</sub>O)<sub>25</sub>Cl<sup>−</sup>.

As one can see from the results of the incremental MP2-F12 expansions in Table 5, one can obtain highly accurate

Table 5. Convergence of the Incrementally Expanded MP2-F12, CCSD(T)(F12), and CCSD(T)(F12)IMP2-F12 Correlation Energies for H<sub>3</sub>O<sup>+</sup> (H<sub>2</sub>O)<sub>25</sub>Cl<sup>−</sup> (atomic units)

order	MP2-F12		CCSD(T)(F12)		CCSD(T)(F12)IMP2-F12	
	ith order $E$	error	ith order $E$		ith order $E$	
1	−7.870879	0.395688	−7.892999		−8.288687	
2	−8.266305	0.000263	−8.286937		−8.287200	
3	−8.265745	0.000822	−8.287002		−8.287824	
exact	−8.266567					

correlation energies with the incremental scheme also for large systems. Considering the convergence of the incremental scheme at the coupled cluster level, we may conclude that the accuracy is similar to MP2-F12. Therefore, it is evident that the proposed scheme can also be applied for large systems with the same thresholds applied for the smaller systems above.

## 6. CONCLUSION

In this article, we investigated the performance of an MP2 corrected explicitly correlated incremental coupled cluster



method with respect to accuracy and efficiency. It was found that the MP2 correction improves the range, the mad, the rms, and the variance for our test set of 27 molecules with different electronic structures. On the basis of the Gaussian distributions for the errors per correlated electron, we did not find significant errors due to the approximations in the incremental scheme for calculations in the cc-pVDZ-F12 basis set. In the cc-pVTZ-F12 basis set, the local approximations slightly affect the result when comparing the error in the absolute energy to the CCSD(F12) basis set error for relative energies. On the other hand, the range for errors in the correlation energies is 4.7 kJ/mol, the mad is 1.2 kJ/mol, and the rms is 1.7 kJ/mol, which should be sufficient for applications in chemistry. In our future work, we will concentrate on the implementation of efficient incremental schemes adapted for the computation of relative energies.

Considering the efficiency of the proposed approach, we demonstrated a reduction of the wall time by a factor of 70–600 for the water decamer; i.e., we were able to compute a 5 day computation in 11 min. Furthermore, we computed the coupled cluster energy of  $(\text{H}_2\text{O})_{16}$  in a few hours on our cheap, low end PC cluster. A recently published coupled cluster calculation for this water cluster took 3.3 h on 120 000 cores using a large supercomputer.

The largest CCSD(T)(F12) computation of this work was  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{25}\text{Cl}^-$  with 80 atoms in the cc-pVDZ-F12 basis set with 1296 AO basis functions. While this is already a considerable size for an explicitly correlated coupled cluster calculation, it is not the limit of the applicability of our code.

Finally, we conclude that it is now possible to compute highly accurate explicitly correlated coupled cluster energies for large molecular systems with the incremental scheme using readily available computer clusters.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information includes the optimized geometries in xyz format and the tables monitoring the convergence of the incremental series for CCSD(F12), the fixed-RI-MP2-F12/2B contribution, CCSD(T)(F12), MP2, MP2-F12, and CCSD-(T)(F12)/MP2-F12. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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### Notes

The authors declare no competing financial interest.

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