

Incremental Scheme for Intermolecular Interactions: Benchmarking the Accuracy and the Efficiency

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ABSTRACT: In this work, we introduce a method to automatically compute the basis set superposition error (BSSE) for large clusters and introduce a correction scheme to improve the accuracy of incrementally expanded coupled cluster energies (CCSD(T)) using the domain-specific basis set approach. The key step for the automatic BSSE computation is the automated partitioning of the system. With the proposed scheme, one can compute the BSSE of large clusters or complexes with different fragments and different charges fully automatic. The second proposal is to use the error from an incrementally expanded MP2 calculation to reduce the error in the corresponding incremental CCSD(T) calculation (CCSD(T)|MP2). This scheme improves the accuracy of incremental CCSD(T) expansions using the domain-specific basis set significantly. The performance of the method is analyzed for intermolecular interactions of H_2 and H_2O clusters and for the adiabatic interaction energy of $\text{Zn}(\text{H}_2\text{O})_6^{2+}$. The errors of the expansion are compared to basis set errors and errors introduced by a cheap lower level method, MP2. Using the proposed CCSD(T)|MP2 scheme, the largest error to the exact CCSD(T) calculation is found to be 0.14 kcal/mol for $\text{Zn}(\text{H}_2\text{O})_6^{2+}$. With the incremental scheme, it was possible to increase the basis set of the CCSD(T) calculation for $(\text{H}_2\text{O})_{10}$ to quintuple- ζ level with 2370 basis functions.

1. INTRODUCTION

The accurate treatment of large molecular clusters is the first step of an ab initio treatment of the condensed phase. Because of Grimmes dispersion correction,¹ one can apply density functional theory to weakly bound clusters, too. However, for a highly accurate description, a coupled cluster treatment using large basis sets is still necessary. Because of this fact, a huge number of methods were developed to overcome the scaling behavior of the coupled cluster methods with respect to the system size^{2–27} or to overcome the steep scaling with respect to the basis set^{28,29} or both.^{30–32} For a nice introduction on fragmentation methods and the basic ideas of local correlation methods in general, we refer to the two recent reviews of Gordon et al.^{17,25} and the references therein.

To obtain an efficient CCSD(T) method for large systems, different strategies are applied. Some schemes like the FMO-scheme of Kitaura and Fedorov^{6,7} and the divide-and-conquer of Yang^{16,33} start to approximate the energy at the Hartree–Fock (HF) level, which results in a total linear scaling method. A different strategy is to compute the Hartree–Fock energy with a standard code and to approximate the correlation energy. Despite the fact that this route is not totally linear scaling due to the standard evaluation of the HF energy, one can obtain very efficient and accurate local correlation codes. The reason for the efficiency is that the time required for the HF calculation is negligible as compared to the time of the CCSD(T) calculation. However, if the HF calculation becomes a bottleneck, one could use density fitting³⁴ or linear scaling techniques at SCF level.^{35,36} In this category, the local correlation methods pioneered by Pulay and Saebø³⁷ as well as the efficient implementations of Werner,² Schütz,³ Head-Gordon,^{8,9} and Adler^{30,32} should be mentioned. The early implementations of the Pulay-type local correlation methods suffered from the so-called domain error, which occurred due

to the restriction to local excitation domains. In a recent work, this problem was solved by the inclusion of terms containing the electron–electron distance explicitly.^{32,38} Conceptually different from these approaches is the cluster-in-molecules method (CIM) with the recently introduced variants DECIM and SECIM.^{15,18,39} Here, the significant coupled cluster amplitudes are approximately obtained from the coupled cluster calculation of clusters constructed from the molecule.

Another approach to extend the applicability of CCSD(T), the gold standard method for benchmarks in quantum chemistry, in combination with large basis sets is the incremental scheme proposed by Stoll.^{40–42} It is based on the Bethe–Goldstone expansion as introduced to quantum chemistry by Nesbet.^{43–45} Depending on the application of the many-body series in eq 1, the incremental scheme can be grouped in category one or two. Conceptually, the FMO-scheme is very similar to the incremental expansion, as both expand the energy or a part of the energy in a many-body series like eq 1.

In our previous work, we presented a fully automated implementation of the incremental scheme,¹¹ demonstrated the general applicability,^{46–52} and extended the approach to properties.⁵³ An important feature of the incremental scheme is the fact that the obtained savings are not based on error compensation. However, one can take advantage of error compensation, but this is not a necessary condition to obtain a fast method with high accuracy. In this article, we propose a way to reduce the error in an incremental calculation, we introduce a scheme to automatically calculate the BSSE-corrections for intermolecular clusters, and we evaluate the accuracy of the incremental scheme in the domain-specific basis

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set approach for a series of correlation consistent basis sets. The approach is tested for a series of $(\text{H}_2)_{10}$ and $(\text{H}_2\text{O})_{10}$ clusters and the $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ cluster. The results are critically analyzed by several criteria for the accuracy of the approach. For instance, the errors introduced by the approximation of the correlation energy must be smaller than the error from a HF-calculation. Another criterion is that a lower level correlation method like MP2 should have larger errors than the approximate CCSD(T). For intermolecular clusters, one is usually interested in two numbers, the relative energy of several clusters of the same size and the adiabatic interaction energy, which is the difference of the cluster energy with n units and the n monomers in their relaxed geometry. In this work, the proposed method is tested with respect to these criteria.

In previous studies, the incremental scheme has been applied to rare gas clusters by Stoll et al.^{54–56} and later Røgggen et al.^{57–59} Please note that our implementation of the incremental scheme deviates from these applications due to the fact that we use a small basis set for the atoms in the environment. This means that an orbital in a domain is constructed from AOs of the complete molecule, whereas in ref 56 the orbitals in the correlation treatment are constructed only from atoms in the domain. In a recent work, Müller et al.⁶⁰ tested different embedding techniques for solid argon. Their Hartree–Fock embedding, where the rare gas cluster is embedded with the full environment at HF level for the next neighbor atoms, is similar to the domain-specific basis set. The difference is that in ref 60 all atoms are treated equally, whereas we reduce the basis set in the environment. As discussed in ref 56, one will always need an embedding if the fragments interact by an electrostatic potential. One can view the domain-specific basis set approach as an incremental expansion, where the embedding is automatically constructed from the Hartree–Fock calculation due to the basis functions in the environment of the domain. This concept of reducing the basis set of the environment by mixed basis sets, or pseudopotentials, or both was extensively used by Stoll, Dolg, Fulde, Paulus, and Staemmler to increase the computational efficiency of the approach.^{56,61–68} The basic difference of these embedding schemes from the scheme in ref 69 and in this work is the construction of the embedding, which is fully automatic as compared to a handmade construction. This advantage enabled us to investigate the performance of the scheme for larger sets of systems. On the other hand, a fraction of computational efficiency was lost by the automatic construction of the domain-specific basis set. Please note that this is not a principal problem, because one can include such advanced embedding techniques in the fully automated scheme, and we will improve this in the future.

One of the major error sources in the treatment of intermolecular interactions using the supermolecular approach is the basis set super position error (BSSE).^{70–72} In small or medium sized basis sets, the BSSE can easily be on the order of the interaction energy. Therefore, it is an important quantity to judge the quality of the results. If the BSSE is viewed as a correction, it can be used as a measure of the error introduced with the usage of an incomplete basis set; that is, the BSSE correction vanishes at the complete basis set limit. Because no exact corrections for the BSSE error exist, it is very important to apply large basis sets in quantum chemical calculations to obtain the desired accuracy. A further method to reduce the error in the calculations is the extrapolation to the complete basis set (CBS) limit. A prerequisite for an accurate CBS extrapolation is a sufficiently large basis set. For the two-point

extrapolation of Halkier et al.,⁷³ a basis set of at least triple and quadruple- ζ quality is required. To obtain high accuracy results, even larger basis sets are necessary. Because of the steep scaling of correlation methods like CCSD and CCSD(T), the computational effort usually prohibits the application of these methods to large intermolecular clusters using large basis sets. With the incremental scheme^{11,40,56,66,74–78} using the domain-specific basis set,^{69,79} one can overcome this drawback as demonstrated in this article.

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.^{11,46,80} Then one calculates the correlation energies for these domains. To include the nonadditivity corrections, one calculates higher order corrections (pair corrections $\Delta\epsilon_{ij}$, triples corrections $\Delta\epsilon_{ijk}$, etc.) until the desired accuracy is reached. The correlation energy is computed with the incremental series:^{11,40}

$$E_{\text{corr}} = \sum_i \Delta\epsilon_i + \frac{1}{2!} \sum_{ij} \Delta\epsilon_{ij} + \frac{1}{3!} \sum_{ijk} \Delta\epsilon_{ijk} + \dots$$

$$\Delta\epsilon_i = \epsilon_i \quad \Delta\epsilon_{ij} = \epsilon_{ij} - \Delta\epsilon_i - \Delta\epsilon_j \quad (1)$$

where ϵ_i is the correlation energy of the subsystem i , and ϵ_{ij} is the correlation energy of the subsystem i and j together. To reduce the computational cost, it is necessary to reduce the virtual space of the domains. Within the domain-specific basis set, a small basis set is introduced to describe the environment of a n -site domain, whereas in the main part of the domain the original large basis set is used.^{69,79,81} To determine the environment, the parameter t_{main} is used. This parameter defines a radius around every occupied localized orbital in the domain. The space defined by all of 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). From eq 1, one can see that the number of calculations grows very fast with respect to the order of the incremental series. Because 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.⁵⁶ Because of the order and distance decay, one can use an order-dependent truncation threshold $t_{\text{dist}} = f/(O - 1)^{2.46,81}$.

2.2. Basis Set Superposition Error (BSSE). The computation of BSSE corrections becomes a tedious task if the clusters become large. To calculate the BSSE with the site-site functional counterpoise scheme (SSFC) as introduced by Wells and Wilson,⁷⁰ one has to perform two extra calculations for every fragment, one calculation in the basis set of the whole cluster and one calculation in basis set of the fragment, both in the geometry of the cluster. Therefore, a fully automatic procedure for the computation of the BSSE correction using the SSFC scheme has been implemented.

$$\Delta\text{SSFC} = \sum_i (E_i^i - E_i^{ij\dots}) \quad (2)$$

where ΔSSFC is the BSSE correction, E_i^i is the energy of the monomer i in the basis set of the monomer at the cluster geometry, and $E_i^{ij\dots}$ is the energy of the monomer i in the basis set of the cluster at the cluster geometry. The only information

one needs in addition to eq 2 is the definition of the fragments. The automatic partitioning into single molecules is based on the radii of the atoms. The basic assumption for this partitioning is the fact that bonds within a molecule are shorter than distances between two molecules.

The partitioning is implemented as graph-partitioning just by the connectivity of the atoms. Two atoms are connected, if their distance is lower than the sum of their radii. By the application of this criterion, the total graph of a molecular cluster consists of small connected subgraphs, representing the molecules. In an atomic cluster, the graph breaks down into unconnected vertices. For the proposed procedure, we use van der Waals radii as default parameter, but the values can also be modified, if necessary. The advantage of the new partitioning in comparison with the pilot implementation⁸² is that clusters with different molecular sizes and charges can be treated.

To automatically handle the frozen cores or charges of a fragment, we perform two Boys localizations: one including all orbitals and one including only the correlated orbitals. Now we map the localized orbitals to the fragments of the system, for the frozen core localization and for the all orbital localization. From the difference of the associated LMOs on a fragment, we calculate the number of frozen core orbitals. The charge of the fragment is calculated from the difference of the sum of the atomic charges of a fragment and 2 times the number of the LMOs from the all orbital localization.

If the coupled cluster calculations in the whole basis set become too time-consuming, the recently proposed distance truncation can be used.⁸²

2.3. MP2 Error Correction. If we truncate the incremental expansion, we will introduce an error ΔE . If we know this error, we can subtract it, from the incrementally expanded energy and obtain the exact result back. This is not useful, because we have to compute the total energy, the quantity to be approximated, to get the error.

$$E_{\text{corr}} = E_{\text{corr}}^{\text{inc}} - \Delta E = E_{\text{corr}}^{\text{inc}} - [E_{\text{corr}}^{\text{inc}} - E_{\text{corr}}] \quad (3)$$

However, if we have a good approximation to the error ΔE , it will be possible to reduce the total error of the incremental energy. In this work, we use the error of the MP2 calculation to reduce the error of the incremental CCSD or CCSD(T) correlation energies. The MP2 corrected incremental CCSD(T) correlation energy reads:

$$\begin{aligned} E_{\text{corr}}^{\text{inc}}(\text{CCSD(T)}|\text{MP2}) \\ = E_{\text{corr}}^{\text{inc}}(\text{CCSD(T)}) - \Delta E(\text{MP2}) \\ = E_{\text{corr}}^{\text{inc}}(\text{CCSD(T)}) - [E_{\text{corr}}^{\text{inc}}(\text{MP2}) - E_{\text{corr}}(\text{MP2})] \end{aligned} \quad (4)$$

Alternatively, one can view this equation from a QM/QM point of view, by means of the subtractive scheme:^{24,83–87}

$$\begin{aligned} E_{\text{corr}}^{\text{inc}}(\text{CCSD(T)}|\text{MP2}) \\ = E_{\text{corr}}(\text{MP2}) + E_{\text{corr}}^{\text{inc}}(\text{CCSD(T)}) - E_{\text{corr}}^{\text{inc}}(\text{MP2}) \end{aligned} \quad (5)$$

With a conceptually similar method, Bates et al.²⁴ recently obtained CCSD(T) energies with average deviations of 0.06 kcal/mol for $(\text{H}_2\text{O})_{16}$ and $(\text{H}_2\text{O})_{17}$. The computation of the MP2 energies was never a bottleneck in the calculations so far, because the RI-MP2 was usually on the order of the SCF calculation or even faster.

2.4. Computational Details. The coupled cluster calculations were performed with a development version of the

TURBOMOLE program package.^{88–90} As basis set for the environment, the SV⁹¹ basis set was used in all calculations. In our earlier work,^{69,79} we applied the STO-3G basis set on the hydrogen atoms of the environment. This is computationally more efficient and revealed to be accurate enough. However, it is required to have a RI-basis⁹² set for the correlation methods in TURBOMOLE, and therefore we switched to the smallest basis, where an auxiliary basis set for density fitting was readily available. 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.³¹ For the $(\text{H}_2)_{10}$ clusters, we used the aug-cc-pVXZ ($X = \text{D}, \text{T}, \text{Q}, \text{5}$) basis sets of Dunning^{93,94} in combination with the optimized RI-basis sets.^{92,95,96} For the water clusters, we used the aug-cc-pVXZ basis set on oxygen and the cc-pVXZ on hydrogen ($X = \text{D}, \text{T}, \text{Q}, \text{5}$). We reference to these basis sets as aVXZ' as frequently defined in the literature.^{97,98}

3. RESULTS

3.1. H_2 Clusters. The optimization of the $(\text{H}_2)_{10}$ cluster with RI-B97-d/def-SV(P)^{91,99–102} and RI-MP2/def-SV(P) was not completely successful. After the optimization, a molecular dynamics run at RI-MP2/def-SV(P) level of theory was performed, and we obtained in total ca. 1200 structures. The investigated structures are no stationary points on the PES. On the other hand, the incremental scheme should work on any arbitrary geometry. To extract the information about the performance of the incremental scheme, we decided to use a subset from ca. 1200 different geometries of the cluster to perform a statistical analysis. The clusters were selected after every 50 energy evaluations. In addition to these structures, we added the cluster with the lowest energy and the completely unoptimized cluster no. 1. For these 26 selected geometries, we performed a calculation with the incremental scheme in the aug-cc-pVDZ and the aug-cc-pVTZ basis sets. In addition to this, we study the basis set convergence at the lowest energy structure, for the series of Dunning correlation consistent basis sets aug-cc-pVXZ ($X = \text{D}, \text{T}, \text{Q}, \text{5}$) including a complete basis set extrapolation using the two-point extrapolation scheme of Halkier et al.⁷³

In Figure 1, we plotted the incremental CCSD(T)/aug-cc-pVDZ and aug-cc-pVTZ correlation contributions to the

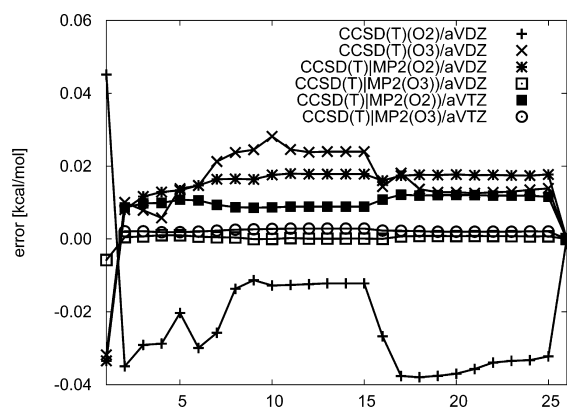


Figure 1. Errors of the incremental correlation contributions to the relative energies of 26 $(\text{H}_2)_{10}$ clusters using the aug-cc-pVDZ and aug-cc-pVTZ basis set. The numbers at the abscissa denote the different $(\text{H}_2)_{10}$ clusters. The energies are relative to the lowest energy cluster 26.

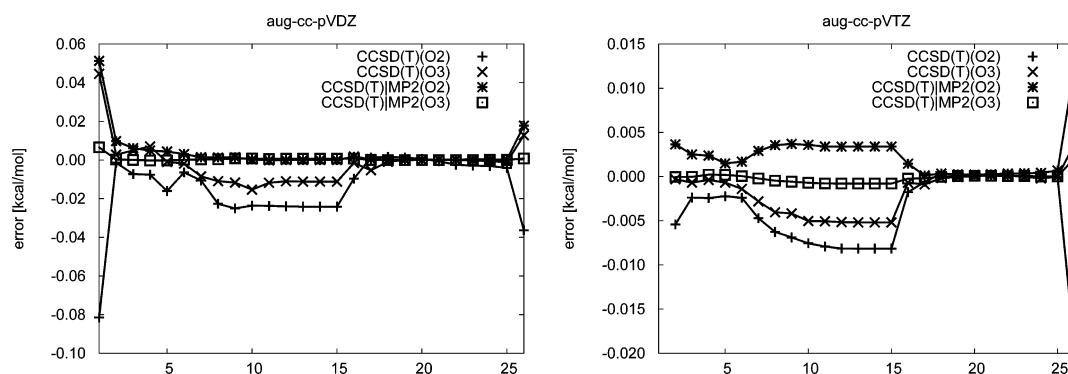


Figure 2. Errors of the incremental correlation contributions to adiabatic interaction energies of 26 $(\text{H}_2)_{10}$ clusters using the aug-cc-pVDZ and basis aug-cc-pVTZ sets.

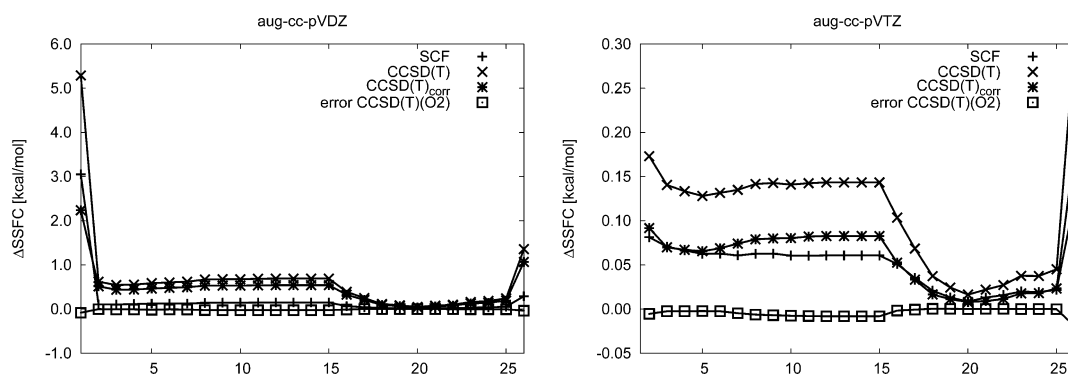


Figure 3. SSFC corrections to the interaction energies for 26 $(\text{H}_2)_{10}$ clusters using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. SCF is the SSFC correction of the Hartree–Fock energy, CCSD(T) refers to the SSFC correction to the CCSD(T) energy, and CCSD(T)_{corr} is the SSFC correction to the CCSD(T) correlation energy. The error of the second-order incremental CCSD(T) expansion is small as compared to the BSSE.

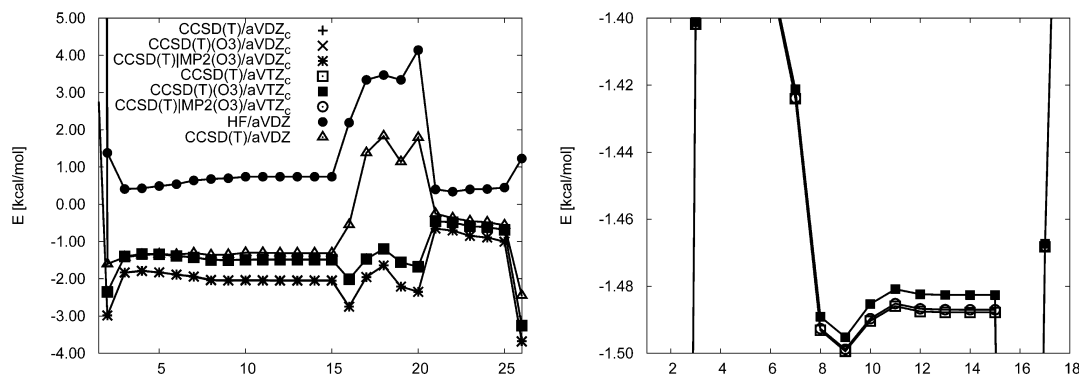


Figure 4. Comparison of various contributions to the adiabatic interaction energies of 26 $(\text{H}_2)_{10}$ clusters using different basis sets. The index *c* denotes the correlation contribution, whereas CCSD(T) includes the HF contribution. The CCSD(T) adiabatic interaction energy (HF+corr.) is +172 kcal/mol for cluster 1. The origin of a large part of the interaction energy is the short H–H-bond length of 0.6 Å in this case. The incrementally expanded CCSD(T) correlation contributions to the adiabatic interaction energies are in excellent agreement to the exact ones. Even if one zooms into the plot by a factor 40, it is hard to recognize the difference between the CCSD(T) and the inc-CCSD(T)IMP2 value. The HF and correlation contributions are on the same order of magnitude for all clusters.

energies relative to the lowest energy structure (cluster 26). The errors of the second-order incremental energies are between -0.04 and 0.05 kcal/mol in the double- ζ basis. At the third-order level, the maximum deviation is slightly reduced and has a different sign. If the above-described MP2-correction is applied, the maximum errors are below 0.02 kcal/mol at second order and below 0.006 kcal/mol at third order. Using the triple- ζ basis set, the errors decrease below 0.015 and 0.003 kcal/mol for the second- and third-order CCSD(T)IMP2 calculations, respectively. Please note that in both cases the

largest deviation in aug-cc-pVDZ basis set comes from the unoptimized cluster 1. This cluster has even a positive correlation contribution to interaction energy of 8.5 kcal/mol. However, we decided to include the cluster in the investigation, because the worst case should not be eliminated from the cluster set.

Figure 2 presents the errors of the correlation energy contributions for various incremental CCSD(T) expansions using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. In general, the error is large for the unoptimized cluster 1 and somewhat

larger for the minimum energy structure (26). Again, the MP2 corrected incremental expansion improves the accuracy, and the MP2 corrected third order is again very close to zero. Comparing the results of the double- and triple- ζ basis sets, we find a reduction of the error of the incremental expansions, if the basis set is increased.

To get an impression of other errors, we computed the SSFC corrections to the adiabatic interaction energies for the 26 $(\text{H}_2)_{10}$ clusters (Figure 3). For most of the clusters, the BSSE correction is between 0.4 and 0.7 kcal/mol, which is huge compared to the errors introduced by the incremental expansion. For a direct comparison of the BSSE to the errors of the incremental expansion, we included the error of the second-order CCSD(T) expansion in Figure 3. As a result, we find that the incremental error is even below the BSSE from the SCF calculation. Extending the basis set from double- ζ to triple ζ reduces the BSSE significantly. In the aug-cc-pVTZ basis set, the BSSE is less than 0.3 kcal/mol for the lowest energy structure as compared to more than 1 kcal/mol at the double- ζ level. On the other hand, the maximum error from a second-order incremental expansion is below -0.04 kcal/mol for this structure, which is significantly smaller.

In Figure 4, the basis set effects are compared to the errors due to the incremental expansion for the interaction energies at the CCSD(T) level. Please note that one cannot distinguish between the incrementally expanded and the exactly calculated CCSD(T) correlation contributions to the interaction energies, indicating a very small error. Comparing the CCSD(T) adiabatic interaction energies at double- and triple- ζ levels, we find a difference of about 0.5 kcal/mol. Because the BSSE corrections and the deviations with respect to the change of the one-particle basis are larger than the errors introduced by the incremental expansion, we conclude that the incremental expansion can be used to compute such weak interactions. A big advantage of the incremental scheme is that one can apply large basis sets for the computation of the energies, which are necessary to obtain highly accurate CCSD(T) correlation energies.

In Table 1, we investigate the effect of the basis set for cluster 26, which has the largest binding energy. The relative errors of the incrementally expanded correlation energy contributions to the adiabatic interaction energies are below 1%. Considering the change of the correlation energy contributions with respect to the basis set, we find significantly larger changes for the double- and triple- ζ basis sets.

To estimate the basis set dependence of the adiabatic interaction energies, we included the exact MP2 values in Figure 5. Please note that the MP2 results differ significantly from the CCSD(T) interaction energies, meaning that one has to apply CCSD(T) for an accurate treatment. However, if we assume that the basis set dependences of CCSD(T) and MP2 are similar, we can estimate the error from the basis set using MP2. Usually, we would regard the MP2-F12/cc-pVQZ-F12 results as the best correlation energy. If one considers the slope of the MP2-F12 interaction energies with respect to the basis set, it seems that the energy is not fully converged with respect to the basis set. Unfortunately, we could not test this, because the corresponding quintuple- ζ basis is not available. On the other hand, the BSSE renders the adiabatic interaction energies too large, which might still be a problem for the conventional MP2 in the aVSZ basis set. Comparing the adiabatic interaction energies at the CBS(45) to the MP2-F12/cc-pVQZ-F12, we find a deviation of 0.026 kcal/mol. Comparing this to the errors

Table 1. Incremental CCSD(T) Correlation Energies and Correlation Energy Contributions to the Adiabatic Interaction Energy of $(\text{H}_2)_{10}$ ^a

order	ith order cont., E_h	$E_{\text{corr}}(i), E_h$	error, kcal/mol	$E_{\text{int}}(i)$, kcal/ mol	error, %
aug-cc-pVDZ, $f = 55$					
2	-0.005591	-0.366515	0.036	-3.638	-0.99
3	-0.000078	-0.366593	-0.013	-3.687	0.35
CCSD(T)IMP2/aug-cc-pVDZ, $f = 55$					
2		-0.366601	-0.018	-3.692	0.48
3		-0.366574	-0.001	-3.675	0.02
aug-cc-pVTZ, $f = 55$					
2	-0.005367	-0.402900	0.019	-3.237	-0.59
3	-0.000036	-0.402937	-0.004	-3.259	0.11
CCSD(T)IMP2/aug-cc-pVTZ, $f = 55$					
2		-0.402950	-0.012	-3.268	0.38
3		-0.402934	-0.002	-3.258	0.06
aug-cc-pVQZ, $f = 55$					
2	-0.005352	-0.410698	0.004	-3.215	-0.11
3	-0.000013	-0.410712	-0.005	-3.223	0.15
CCSD(T)IMP2/aug-cc-pVQZ, $f = 55$					
2		-0.410726	-0.014	-3.232	0.42
3		-0.410707	-0.002	-3.221	0.06
aug-cc-pVSZ, $f = 55$					
2	-0.005349	-0.413137		-3.216	
3	-0.000007	-0.413143		-3.216	
CCSD(T)IMP2/aug-cc-pVSZ, $f = 55$					
2		-0.413136		-3.218	
3		-0.413143		-3.213	
E23					
2	-0.005273	-0.418221	0.012	-3.068	-0.38
3	-0.000019	-0.418239	0.000	-3.079	-0.01
CCSD(T)IMP2 CBS(23)					
2		-0.418255	-0.010	-3.089	0.32
3		-0.418244	-0.003	-3.082	0.09
E34					
2	-0.005341	-0.416389	-0.008	-3.199	0.25
3	0.000003	-0.416386	-0.006	-3.197	0.18
CCSD(T)IMP2 CBS(34)					
2		-0.416400	-0.015	-3.206	0.47
3		-0.416380	-0.002	-3.193	0.06
E45					
2	-0.005346	-0.415695		-3.208	
3	0.000000	-0.415695		-3.207	
CCSD(T)IMP2 CBS(45)					
2		-0.415705		-3.214	
3		-0.415690		-3.204	

^aThe errors are with respect to the exact CCSD(T) calculation using the corresponding basis set or CBS value (cluster 26).

due to the incremental expansions in Table 1, which are below 0.026 kcal/mol except for the calculation in the double- ζ basis set, it is evident that the error due to the many body expansion is not the leading error.

From these considerations, we conclude that the errors resulting from the incremental expansion are lower than the errors introduced by the basis set. At third order, the errors are below 0.006 kcal/mol for incremental CCSD(T), CCSD(T)|MP2, and CBS extrapolated interaction energies. Because the incremental scheme with the domain-specific basis set approach can be used to apply significantly larger basis sets, one can obtain highly accurate results with this approach.

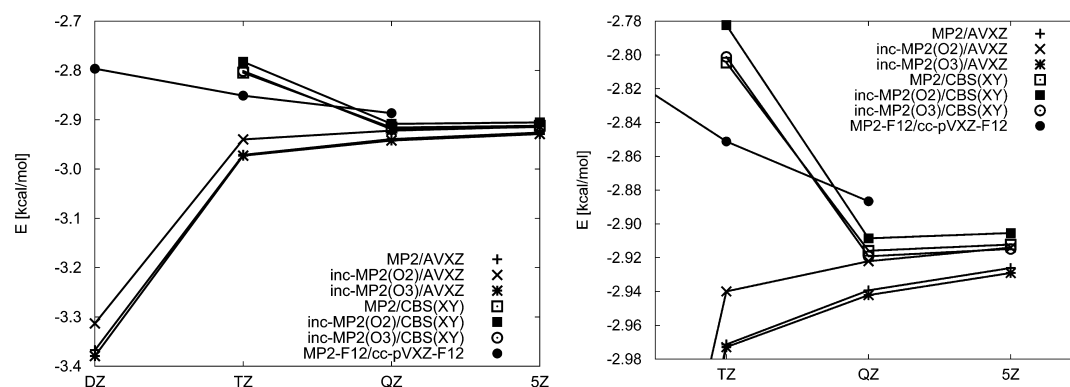


Figure 5. Convergence of the adiabatic interaction energy for the cluster 26 with respect to the basis set. The fixed-RI-MP2-F12/2B calculations were performed with the recommended correlation factor of 0.9, 1.0, and 1.1 a_0^{-1} for the cc-pVDZ-F12, cc-pVTZ-F12, and cc-pVQZ-F12 basis sets, respectively.^{103–108}

Table 2. Mean Absolute Deviation of the Correlation Energy Contributions to the Relative Interaction Energies for the Investigated $(H_2)_{10}$ Clusters for Various Models^a

order	inc-MP2	inc-CCSD	inc-CCSD(T)	inc-CCSD MP2	inc-CCSD(T) MP2
aug-cc-pVDZ					
2	0.042	0.017	0.025	0.025	0.016
3	0.016	0.017	0.017	0.001	0.001
aug-cc-pVTZ					
2	0.025	0.009	0.015	0.016	0.010
3	0.003	0.005	0.005	0.002	0.002

^aThe energies are relative to the lowest energy structure of cluster 26 (kcal/mol).

In Table 2, we present the mean absolute deviations (MAD) of the incremental MP2, CCSD, CCSD(T), as well as the MP2 corrected CCSD|MP2 and CCSD(T)|MP2 correlation energy contributions to the relative energies. From the statistical analysis, we see that a second-order expansion has average deviations of 0.025 kcal/mol for CCSD|MP2 and 0.016 kcal/mol for CCSD(T)|MP2. At the CCSD level, the second-order incremental CCSD|MP2 approach is not an improvement over the incremental CCSD. At the third-order level, the deviations are significantly smaller with ca. 0.001 kcal/mol for both models. In the aug-cc-pVTZ basis set, the average second-order deviations are 0.016 and 0.010 kcal/mol for CCSD|MP2 and CCSD(T)|MP2, respectively. At the third order, the average deviations are 0.002 kcal/mol, which is still significantly smaller than the basis set error (vide supra).

Table 3 presents the mean absolute deviations of the correlation contributions to the adiabatic interaction energies.

Table 3. Mean Absolute Deviations of the Correlation Energy Contributions to the Adiabatic Interaction Energies for the Investigated $(H_2)_{10}$ Clusters for Various Models (kcal/mol)

order	inc-MP2	inc-CCSD	inc-CCSD(T)	inc-CCSD MP2	inc-CCSD(T) MP2
aug-cc-pVDZ					
2	0.019	0.012	0.015	0.007	0.004
3	0.007	0.007	0.007	0.001	0.001
aug-cc-pVTZ					
2	0.006	0.003	0.004	0.003	0.002
3	0.002	0.002	0.002	0.000	0.000

In this case, we find that the incremental CCSD|MP2 and CCSD(T)|MP2 models always improve the results. However, in the aug-cc-pVTZ basis set, the improvement is negligible for CCSD. In the other cases, the error is reduced by a factor of 1.7 (or more). Please note that the third-order deviations of the CCSD|MP2 and CCSD(T)|MP2 models are 0.001 kcal/mol or even smaller for the aug-cc-pVDZ and the aug-cc-pVTZ basis sets, respectively.

3.2. Water Clusters. To compare the accuracy of the incremental approach with the cluster in molecules variants DECIM and SECIM of Piecuch et al., we study the water decamer cluster series of ref 15. Because the computations were made on a different machine, they are not directly comparable. Please note that we were able to compute the full reference calculation with CCSD(T) in a larger basis set faster than the CCSD calculation in ref 109. Therefore, we compare the timings relative to the full computation.

3.2.1. Accuracy. In Figure 6, the errors of the correlation energy contributions to the relative energies for the water

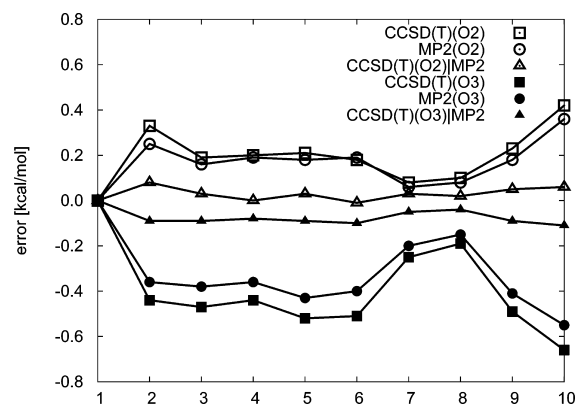


Figure 6. Incremental MP2, CCSD, and CCSD(T) errors of the correlation contributions to the relative energies. The energies are relative to the minimum energy cluster 1. The numbers at the abscissa denote the different water clusters 1–10.

cluster series are given. The largest deviation is 0.67 kcal/mol. Moreover, the errors at third order are in some cases larger than the errors at second order. The reason for this is the introduction of the domain-specific basis set. From a theoretical point of view, this might not be very nice, but the errors are still

small with mean absolute errors of 0.16 kcal/mol at second order and 0.27 kcal/mol at third order for CCSD(T).

If one investigates the contribution of the individual increments, one finds that the distance decay is slightly disturbed if the domain-specific basis set is used to approximate the environment. At large distances, the increments are still negligible, but at medium distances the increments are artificially too large. One reason for this might be the BSSE introduced by the small environment basis set. The comparison of the individual increments with and without the domain-specific basis set shows that the energy of the increments is slightly affected. The higher order increments have a larger magnitude as compared to those computed in the exact environment. The result of this effect can be seen in the errors of the absolute correlation energies in Table 4. The summary of

Table 4. Errors of the Incremental Absolute MP2, CCSD(T) Correlation Energies Using the aVDZ' Basis Set for Cluster 1 (kcal/mol)

env. bas.: <i>f</i> :		aVDZ'	SV	aVDZ'	SV
		30	30	25	25
method	order	error			
MP2	1	47.65	54.55	47.65	54.55
	2	0.11	−0.32	0.11	−0.32
	3	0.00	0.55	0.00	−0.08
CCSD(T)	1	49.90	57.49	49.90	57.49
	2	0.11	−0.34	0.11	−0.34
	3	0.03	0.67	−0.01	−0.10
N_{calc}		165	165	99	99

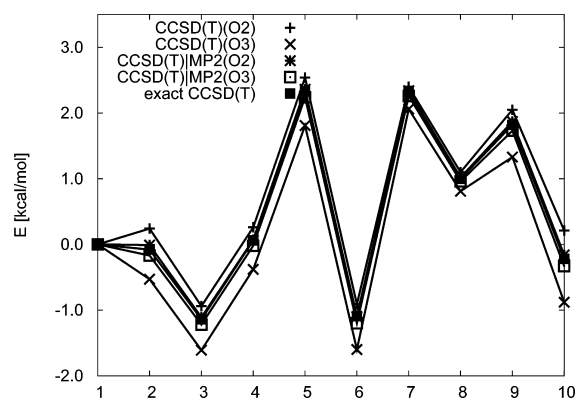


Figure 7. Incremental CCSD(T) correlation contributions to the relative energies of the water cluster series. The CCSD(T)MP2 is the incremental CCSD(T) energy including the error correction using MP2 (vide supra).

the results in Table 4 is that the small basis set in the environment introduces the largest part of the error. Because the basis set effect is similar for MP2 and for CCSD(T), one can effectively remove the error from the domain-specific basis set by a subtraction of the MP2 error. This is frequently used to obtain the complete basis set limit at CCSD(T) level.¹¹⁰ Furthermore, we find, in agreement with our previous results,⁵³ that the MP2 expansion converges faster than the CCSD(T) expansion, if the full basis set is used in the environment. In contrast to this, the convergence behavior of the incremental MP2 and CCSD(T) expansions is similar in the domain-specific basis set. On the basis of the considerations above, it is evident that the MP2 correction works due to a similar

convergence with respect to the one-particle basis set for MP2 and CCSD(T).

One route to obtain the best truncation parameter f is to calculate the incremental expansion without the domain-specific basis set in a smaller basis set and adapt the threshold in a way that only the significant terms are included. For the water decamer 1, this means that the third order could be neglected completely, as one can see from the errors of the incremental CCSD(T) energies using the full basis set in the environment (Table 4). This behavior can change for very large clusters, where the number of third order increments is large and therefore their total contribution to the energy. In the current work, we apply a distance threshold of $f = 30$ Bohr, which turned out to be useful for a broad range of molecules.^{79,81} Even with this choice, we obtain rather accurate results. With a largest error below 1 kcal/mol, one could be happy, but unfortunately the correlation contributions to the relative energies are very small. The largest correlation contribution is 2.32 kcal/mol at the CCSD(T)/aVDZ' level (Figure 7, cluster 5). Therefore, we decided to use the deviation of the relative correlation contributions as an error measure, because this is the approximated number.

Considering the deviations, one finds that the second-order error is in all cases positive, whereas the third-order error is negative. Unfortunately, the error in the third-order energies is higher than the second-order error, but it is still small with a largest deviation of −0.66 kcal/mol. With the MP2 correction proposed in this work, this error can be significantly reduced (vide infra).

Considering the relative energies of the water clusters (Table 5), we have a MAD of 0.2 kcal/mol at second order and 0.4

Table 5. Mean Absolute Deviation (MAD) of the Correlation Energy Contributions to the Relative Energies of the 10 Investigated Water Clusters for Various Models^a

order	inc-MP2	inc-CCSD	inc-CCSD(T)	inc-CCSD/MP2	inc-CCSD(T)/MP2
2	0.17	0.16	0.20	0.03	0.03
3	0.32	0.33	0.40	0.01	0.07

^aThe energies are relative to the minimum energy cluster 1. At Hartree–Fock level, a MAD of 1.01 kcal/mol is found, and using MP2 the MAD is 0.11 kcal/mol. Piecuch et al. report a MAD of 0.17 kcal/mol at CCSD/6-31++G(d,p) level using SECIM(0.0005) and 3.5 kcal/mol using DECIM(0.005,0.01).¹⁰⁹ The energies are in kcal/mol. The basis set is aVDZ'.

kcal/mol at third order for CCSD(T). Using the CCSD(T)MP2 model, the MAD is reduced to 0.03 kcal/mol at second order and to 0.07 kcal/mol at third order. Comparing this to the MAD of the SCF calculation (1.01 kcal/mol), we find that the errors introduced by the incremental scheme are smaller, as they have to be. Comparing the values to the MAD of the MP2 model (0.11 kcal/mol), we find that the MP2 corrected CCSD(T)MP2 model yields better results at second and third order. However, MP2 is a computationally cheap model, and if one can afford a larger basis set, than in a coupled cluster calculation it can lead to higher accuracy. Comparing the MAD of the proposed CCSD(T)MP2 model (0.07 kcal/mol) with the MAD obtained by Piecuch in ref 109 (DECIM 3.5 kcal/mol, SECIM 0.17 kcal/mol), we obtain more accurate results.

The relative errors of the correlation energies are plotted in Figure 6. In this plot, we see that the MP2, CCSD, and CCSD(T) errors behave very similar. This explains why the

error estimate using MP2 is successful. As compared to the computational time for a coupled cluster calculation, the full RI-MP2 calculation can be done at approximately no extra cost.

The correlation contributions to the relative energies of the water cluster series at CCSD(T) level are given in Figure 7 for the exact energy, the second- and third-order incremental expansion CCSD(T)(O2,O3), and the MP2 corrected second- and third-order expansion CCSD(T)IMP2(O2,O3). From this figure, one can see that the MP2 correction significantly improves the accuracy of the incremental expansion, because the corresponding plots are very close to the exact CCSD(T) plot. The largest error is only 0.11 kcal/mol.

In Table 6, we present the MAD of the incremental expansion from the value of the standard calculation. In this

Table 6. MAD of the Correlation Energy Contributions to the Adiabatic Interaction Energies for the Investigated Water Clusters for Various Models^a

order	inc-MP2	inc-CCSD	inc-CCSD(T)	inc-CCSDIMP2	inc-CCSD(T)IMP2
2	0.16	0.35	0.16	0.20	0.02
3	0.22	0.23	0.27	0.01	0.05

^aNeglecting the correlation (Hartree–Fock) results in a MAD of 19.95 kcal/mol, and using MP2 the MAD is 0.69 kcal/mol. The energies are in kcal/mol. The basis set is aVDZ'.

case, the deviations of all incremental expansions are below the MP2 deviation of 0.69 kcal/mol. The CCSDIMP2 has an average second-order deviation of 0.2 kcal/mol and an average third-order deviation of 0.01 kcal/mol. The CCSD(T)IMP2 MAD is 0.02 kcal/mol at second order and 0.05 kcal/mol at third order. It is again unfortunate that the error increases with increasing order, but the error is extremely small.

In Figure 8, we present the incremental CCSD(T) correlation contributions to the adiabatic interaction energies

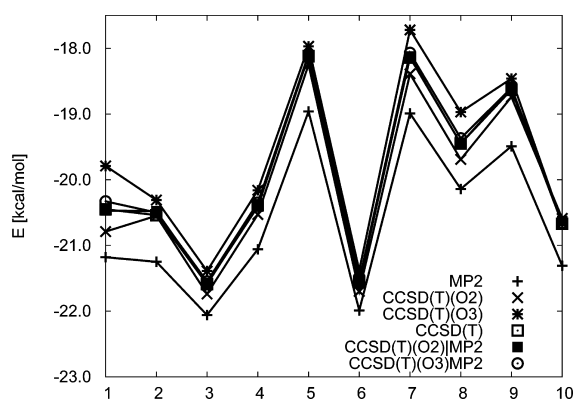


Figure 8. Incremental CCSD(T) correlation contribution to the adiabatic interaction energy for the 10 different water clusters using the aVDZ' basis set.

of the 10 investigated water clusters. In general, one can see that the incrementally expanded energies are close to the exact CCSD(T) value. The MP2 corrected curves are so close to the CCSD(T) curve that it is hard to distinguish them. In contrast to this, the adiabatic interaction energies at the lower MP2 level are about 1 kcal/mol away from the CCSD(T) values.

In Figure 9, we plotted the error of the incrementally expanded adiabatic interaction energies. Because the CCSD-

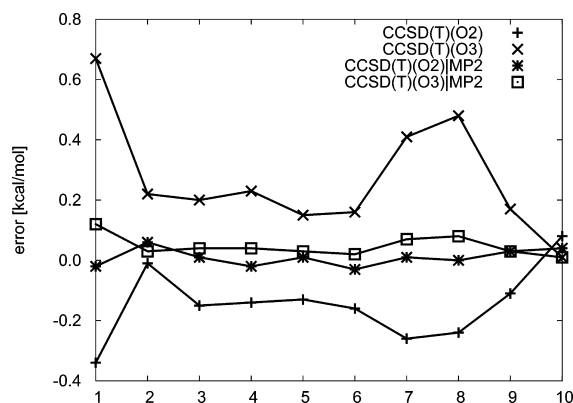


Figure 9. Errors of the incremental CCSD(T)/aVDZ' correlation contributions to the adiabatic interaction energies of the water cluster series.

(T)IMP2 expansions are close to zero and in almost all cases between the uncorrected expansions, we conclude that the model is useful for the description of water clusters. In Figure 10, we computed the adiabatic interaction energy of the water

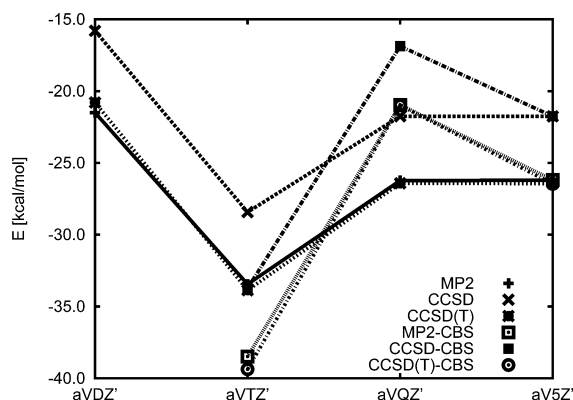


Figure 10. Convergence of the second-order incremental correlation energy contribution to the adiabatic interaction energy with respect to the basis set for the water cluster 1. The energies are not corrected for BSSE, because the computations of the BSSE become computationally very demanding in the large basis sets (aVQZ', aV5Z'). The computation of the BSSE with the SSFC scheme at the aVDZ' level (Figure 11) was already about one day per water cluster (at CHiC).

cluster 1 at different basis set levels along the aVXZ' basis set series. For the CBS estimates, we applied the two-point extrapolation of Halkier and Helgaker et al.⁷³ From this figure, it is evident that the adiabatic interaction energy is largely basis set dependent. The results become stable if the aVQZ' or aV5Z' basis sets are used. The two-point extrapolation is strongly oscillating in the small basis sets, and the total accuracy is spoiled. The reason for this is most likely the BSSE, which is superimposed to the basis set error.¹¹¹ It was previously found that the two-point extrapolation accounts for the error originating from the coulomb cusp, but not for the error originating from the BSSE.^{98,111} Therefore, one should use both schemes to obtain highly accurate results. However, we did not account for the BSSE, because the computation of the BSSE in the aVDZ' basis set took already about one day (at CHiC), and therefore we expect the computation of the BSSE in the aVQZ' and aV5Z' basis sets as computationally too demanding. The CBS(45) is very close to the adiabatic

interaction energy of the aVQZ' and the aVSZ' basis sets, respectively. The computation of the CCSD(T) energy in the aVSZ' basis set with 2370 basis functions can be done on a cluster of cheap standard PCs using the incremental scheme.

Finally, we computed the BSSE for the water clusters in the aVDZ' basis set (Figure 11). Because the BSSE is between 15.1

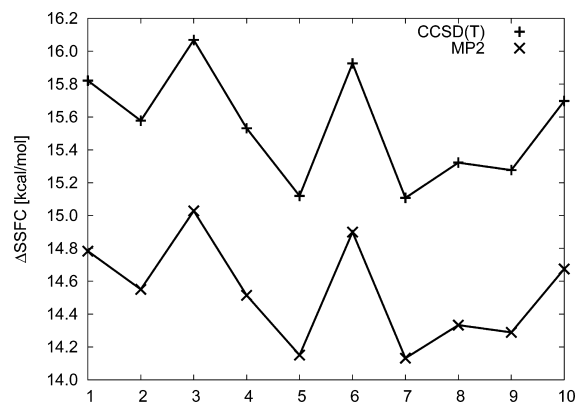


Figure 11. BSSE corrections to the adiabatic interaction energies for the 10 investigated water clusters using the aVDZ' basis set.

and 16.1 kcal/mol, the basis set introduces very large errors in the adiabatic interaction energies and in the relative energies. For instance, the BSSE contribution to the relative energy is up to 0.7 kcal/mol, and the mean absolute BSSE contribution to the relative energies is 0.35 kcal/mol. Comparing this to the largest MAD of the proposed CCSD(T)/MP2 scheme (0.07 kcal/mol), we conclude that the errors due to the incomplete basis set are larger than the errors from the incremental CCSD(T)/MP2 scheme.

3.2.2. Timing. For the incremental third-order CCSD(T)/aVDZ' calculation, the wall time is 2% of the total time using 51 CPUs and 1% for a second-order calculation using 56 CPUs. The total computation time was only 605 min for the second-order calculation and 1833 min for the third-order calculation. The wall times were 18 min on 56 CPUs and 55 min on 51 CPUs for the second- and third-order incremental expansions, respectively. These timings include the wall times of the master process, which consumes essentially no CPU-time. In comparison, the full calculation took 3000 min. A big advantage of the incremental approach is the parallelism and the easy possibility to restart a calculation. These two features are extremely important for the hardware requirements, because no expensive pieces such as infiniband or an uninterrupted power supply are required. The hardware required for incremental coupled cluster calculations can be very cheap standard components.

The total time required for the third-order incremental expansion for the aVTZ' basis set (740 AOs) is 3777 min, and the wall time is 119 min on 56 CPUs. The calculation in the aVQZ' basis (1400 AOs) took 1422 min wall time on 51 CPUs using less than 3 GB RAM per CPU. Please note that the CCSD(T) calculation in the aVSZ' basis set (2370 AOs) was still feasible (Figure 10).

In contrast to the cluster in molecule variants DECIM and SECIM, the current implementation of the incremental scheme is not linear scaling, because the size of the basis in a domain still depends on the size of the system. Furthermore, the SCF step and, in case of the MP2 corrected incremental scheme, the MP2 step are not linear scaling. Therefore, the CIM methods

will be faster for very large systems. However, for medium sized systems, this is not necessarily the case, and we will analyze this in the following. A direct comparison of the CPU-times for the CIM approach of Li and Piecuch et al.¹⁰⁹ and the current work is not directly possible, due to the fact that we use the Dunning basis set (aVDZ', 330 AOs), which is slightly larger than the Pople basis set (6-31++G(d,p), 300 AOs) of ref 109, and we apply CCSD(T) instead of CCSD and our calculations have been made on a different machine. However, the computational effort relative to the full calculation should be comparable.

For the lowest energy structure in the 6-31++G(d,p) basis set, the computational effort relative to the standard calculation is 66.1% in ref 109. In the current work, the third-order incremental expansion requires 61% of the full CPU-time. From Figure 9, one can see that a second-order expansion yields sufficient accuracy, too. The relative computational effort is only 20% in this case. Because of the easy parallelizability of the incremental calculations, we can reduce the wall time to 1%. The relative wall time in ref 109 was still about 10%.

Finally, we note that the computational efficiency of the proposed approach grows with increasing size of the one-particle basis set, due to the better ratio between the size of the basis set in the domain and the full basis set of the molecule. If the obtained accuracy is sufficient for the problem under consideration, the incremental scheme is an attractive alternative to parallel coupled cluster schemes, because the approach uses the inherent parallelism of the incremental series and reduces the scaling behavior of the coupled cluster at the same time. Parallel coupled cluster schemes still suffer from the unfavorable scaling behavior of the coupled cluster methods, which is the origin of the huge CPU times associated with these methods.

3.3. Solvation. One ingredient to compute the solvation energy of a cation in aqueous solution is the interaction energy of the cation with the solvent in gas phase.¹¹² Within the framework of the incremental scheme, it is possible to compute those interaction energies with CCSD(T), also for larger complexes. In Table 7, we demonstrate the performance of the

Table 7. Various Contributions to the Interaction Energy of $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ Using the TZVP Basis Set

method	ΔE , kcal/mol
MP2 _{corr}	−15.1
CCSD(T) _{corr}	−14.6
inc-CCSD(T)(O2) _{corr}	−13.2
inc-CCSD(T)(O3) _{corr}	−14.8
inc-CCSD(T)IMP2(O2) _{corr}	−14.5
inc-CCSD(T)IMP2(O3) _{corr}	−14.7
HF	−322.8
ΔSSFC(CCSD(T))	15.5

incremental scheme for the interaction energy of $\text{Zn}(\text{H}_2\text{O})_6^{2+}$. The errors due to local approximations are below 1 kcal/mol for all incremental methods. If the MP2 correction is applied, the error is 0.14 and −0.11 kcal/mol for the second and third order, respectively. Comparing this to the BSSE correction of 15.5 kcal/mol, we can conclude that the size of the one-particle basis set is more important than the errors due to the many body expansion. Considering the relative errors in the interaction energies of −0.04% and 0.03%, we conclude that the MP2 corrected incremental scheme can provide high-

quality interaction energies for $\text{Zn}(\text{H}_2\text{O})_6^{2+}$. The approach may also be useful for other metals and solvents.

4. CONCLUSION

In this work, we proposed an automated procedure to partition molecular or atomic clusters into fragments necessary for the computation of the basis set superposition error. Furthermore, we proposed a QM/QM like scheme to reduce the error of an incremental CCSD(T) calculation. We demonstrated that the proposed approach yields negligible errors for H_2 and water clusters. With the current approach, it was possible to compute the CCSD(T) energy with quintuple- ζ basis sets for large hydrogen and water clusters. The mean absolute errors of the calculations on water clusters at CCSD(T) level were below 0.11 kcal/mol for the adiabatic interaction energies and the relative energies, respectively. For the $(\text{H}_2)_{10}$ clusters, the mean absolute errors at CCSD(T)/MP2 level were below 0.02 kcal/mol for the relative energies and below 0.01 kcal/mol for the adiabatic interaction energies. The results of this work are encouraging, and therefore we plan to extend the approach to CCSD(F12)(T) in the future.

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Notes

The authors declare no competing financial interest.

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