

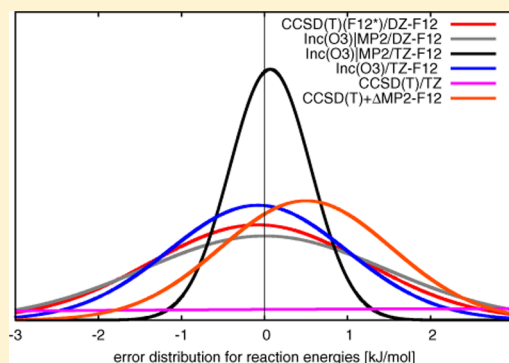
Incremental CCSD(T)(F12*)/IMP2: A Black Box Method To Obtain Highly Accurate Reaction Energies

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S Supporting Information

ABSTRACT: In this work we present a new partitioning scheme for the incremental approach in combination with the efficient (F12*) approximation for explicitly correlated coupled cluster (*J. Chem. Phys.* **2010**, *132*, 231102). Furthermore we establish a black-box truncation scheme which provides chemical accuracy for the absolute energies of 81 molecules and 51 reaction energies. The errors in the absolute CCSD(T)/cc-pVTZ-F12 energies due to the local approximations are characterized by mean = −0.24 kJ/mol, σ = 0.49 kJ/mol, mae = 0.37 kJ/mol, rmsd = 0.54 kJ/mol, and range = 3.63 kJ/mol. For the reaction energies we find mean = 0.07 kJ/mol, σ = 0.49 kJ/mol, mae = 0.33 kJ/mol, rmsd = 0.49 kJ/mol, and range = 2.40 kJ/mol. On the basis of these findings it is evident that the incremental scheme provides highly accurate CCSD(T) energies of benchmark quality.



1. INTRODUCTION

Today's workhorse in quantum chemistry is density functional theory (DFT), which usually provides qualitatively correct results at low computational cost. When using modern density functionals, DFT-methods frequently provide also quantitatively correct results.^{1–3} However, there are still some cases where different density functionals deliver different results and therefore an alternative method for the computation is desirable. Furthermore it is very important to have different techniques at hand, when solving the electronic Schrödinger equation with approximate methods. If these techniques rely on different approximations, it is unlikely, that they break down for the same system and therefore a good agreement of the results gives a strong evidence for a correct theoretical value.

One method to compute highly accurate energies is coupled cluster singles doubles with perturbative triples excitations (CCSD(T)), if it is combined with an appropriate one particle basis set. Because of the unfavorable scaling of CCSD(T) with the system-size, the application of this method is restricted to small systems, or to medium sized systems in combination with a too small basis set at the cost of lower accuracy.

Since the accurate computation of large molecular systems is of very high interest, a huge number of approximate coupled cluster methods were proposed during the past decades.^{4–33} The computational costs of these methods were reduced by different strategies like the fragmentation of molecular orbitals (FMO),^{8,9,34–36} the electrostatically embedded many-body expansion,^{37–40} the divide-and-conquer scheme,^{18,41,42} the cluster-in-molecule method (CIM)^{17,20,43–46} as well as the Pulay type local correlation methods.^{4,5,47–49,49–52} The latter local correlation methods suffer from the so-called domain-error, which may introduce discontinuities in the potential energy

surface.⁵³ This discontinuity problem can be solved by merging the domains⁵⁴ or the use of bump functions.^{10,11} It was recently shown that explicitly correlated F12 terms can be used to remove the domain error.^{49,50}

A very promising method to obtain highly accurate coupled cluster energies at significantly reduced cost is the application of pair natural orbitals (PNOs).⁵⁵ Within this framework Neese and co-workers proposed a series of highly efficient and reliable coupled cluster methods.^{30–32,56–58}

A complete coverage of the literature on local correlation methods is beyond the scope of this work. For a good introduction to local correlation methods we refer to the review of Gordon et al.^{19,28} and to the *Phys. Chem. Chem. Phys.* special issue on fragment and localized orbital methods in electronic structure theory^{34,35,42,52,59–62} as well as to the references therein.

The second complication associated with coupled cluster methods is the slow convergence of the energy with respect to the one particle basis set.⁶³ It was shown that coupled cluster methods can provide the solution of the electronic Schrödinger equation with excellent accuracy, if large one-particle basis sets are used.⁶⁴ A small basis set of triple- ζ quality is not sufficient to obtain high accuracy. One can improve the convergence of the total energy by a complete basis set extrapolation^{65,66} or by the application of explicitly correlated methods.^{66–81}

In this work we use explicit correlation to obtain results close to the complete basis set limit and apply the incremental scheme of Stoll^{82–84} to increase the applicability of the highly efficient and accurate CCSD(T)(F12*) method.⁸⁰ The incremental scheme is a generalization of the Bethe–Goldstone

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expansion as introduced to quantum chemistry by Nesbet.^{85–87} The basic idea of this method is to partition the system of interest into small fragments called domains. The total energy of the system is then obtained by computations of domains, pairs of domains, triples of domains, and so forth, until the desired accuracy is obtained. This basic principle has been successfully used in the past to model one-, two-, and three-dimensional periodic,^{88–99} as well as molecular^{33,100–106} systems. The performance of the approach was also investigated for CCSD first order properties¹⁰⁷ and a special core–valence correlation treatment.^{108,109}

In this contribution we use the CCSD(T)(F12*)/cc-pVTZ-F12 method to obtain highly accurate benchmark results for 51 reaction energies. With this data we analyze the accuracy obtained by the incremental series, when using a modified partitioning scheme for the construction of the one-site domains. The accuracy of the scheme is also analyzed for the absolute energies of 81 small to medium sized molecules with different electronic structure. The limiting factor of the molecular size was the feasibility of the standard CCSD(T)(F12*) calculation in the cc-pVTZ-F12 basis set. Finally we propose a computational setup, which can be used in a black box manner, that is, there is no need for a manual adaption of the truncation parameters.

2. THEORY

2.1. Incremental Scheme. In an incremental calculation the total system is partitioned into disjointed sets of localized occupied orbitals. We call these subsets one-site domains.^{13,110,111} These domains form the basis for the computation of the total energy. For the first order one computes the correlation energies for each domain separately and sums them up. To correct for the

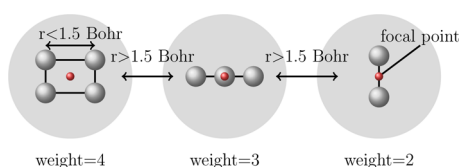


Figure 1. Construction of the merged orbitals by connectivity. With this step we merge the LMOs of multiple bonds or core orbitals to their focal point and assign a proper weight factor. We use the centers of charge as vertices of a graph and draw a connecting line between a pair, if the distance of the centers of charge is smaller than 1.5 Bohr. All vertices connected by a line are collected in a merged orbital domain. The weight of the new domain is the number of orbitals, and the new location is the focal point.

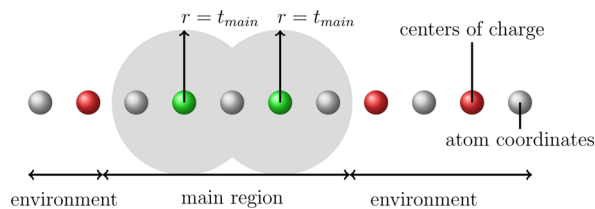


Figure 2. Schematic construction of the domain-specific basis set in 2 dimensions. The centers of charge of a domain are given in green. One selects the important part of a domain by the gray area. The area is determined by drawing circles with the radius t_{main} around every center of charge of the 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. The environment is treated with a small SV basis set. In real molecular systems t_{main} is the radius of a sphere, and we select the important part by a volume analogous to the gray area.

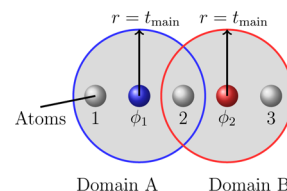


Figure 3. In organic molecules it can frequently happen that ϕ_1 and ϕ_2 are bonding orbitals of two different domains, but sharing the same atom (2). We select atom 2 for the important part in Domain A and in Domain B, since the basis functions located on atom 2 are important to describe both ϕ_1 and ϕ_2 .

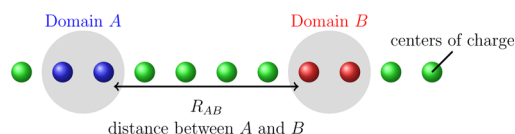


Figure 4. Graphical representation of the distance screening. If the distance of two domains is larger than t_{dist} the increment is neglected. The distance between two domains is defined as the smallest distance between the centers of charge in A to the those in B. Since the magnitude of the increments usually decays with the order, we shrink t_{dist} with increasing order ($t_{\text{dist}}(i) = f/(i-1)^2$, where i is the actual order and f the truncation parameter.).

nonadditivity of the total energy it is necessary to include also higher order terms. These terms are computed from pairs, triples, and so forth of domains, until the desired accuracy is reached.^{13,82} To avoid a double counting of correlation energy contributions, one has to subtract all permutations of lower order terms in the computation of a given increment. One can express this conveniently, by using a set theory notation:

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

where $\mathcal{P}(\mathbb{D})$ is the power set of the set of the domains \mathbb{D} . The restriction to 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. Partitioning Scheme. To partition the orbitals of an arbitrary system into domains, we previously used METIS graph partitioning¹¹² as described in ref 13. The partitioning with the old scheme was not satisfactory in all cases, and therefore we implemented a modified version to overcome the previous drawbacks. The first problem when partitioning a set of occupied orbitals using the charge centers is that the orbitals of a double bond can end up in different domains. The same problem occurs for triple bonds or core orbitals of an atom. We avoid this by merging the local orbitals into sets of close orbitals using a distance criterion. This step is implemented as a graph partitioning by connectivity (see Figure 1). Next we use the procedure in ref 13 to create an initial guess for the one-site domains. In this step the size of the domains is used as a parameter (dsp). In this work we use a fixed value of 4 orbitals in all calculations. Now we do a pairwise refinement of the initial domains, for all domain pairs. Since the domains change with each step, we iterate until the domains are self-consistent.

Table 1. Statistical Measures for the Incremental Absolute CCSD(T)(F12*)/cc-pVDZ-F12 Energies in kJ/mol, Using a Test Set of 87 Molecules^a

| f | t_{main} | μ | σ | mae | rmsd | max | min | max abs error | range |
|--------------------------------|-------------------|-------|----------|------|------|-------|--------|---------------|-------|
| Inc.(O3)-CCSD(T)(F12*) | | | | | | | | | |
| 25 | 2.5 | −0.69 | 2.34 | 1.20 | 2.43 | 10.34 | −14.60 | 14.60 | 24.94 |
| 25 | 3.0 | −0.73 | 2.30 | 1.24 | 2.40 | 10.34 | −13.90 | 13.90 | 24.24 |
| 30 | 2.5 | −0.70 | 2.52 | 1.26 | 2.60 | 10.68 | −16.52 | 16.52 | 27.20 |
| 30 | 3.0 | −0.75 | 2.48 | 1.30 | 2.57 | 10.68 | −15.82 | 15.82 | 26.50 |
| 30 | 3.5 | −0.55 | 3.53 | 1.41 | 3.55 | 18.96 | −23.24 | 23.24 | 42.21 |
| 30 | 4.0 | 1.26 | 7.07 | 1.62 | 7.14 | 63.69 | −7.42 | 63.69 | 71.10 |
| 35 | 2.5 | −0.75 | 2.79 | 1.31 | 2.87 | 10.65 | −19.92 | 19.92 | 30.57 |
| 35 | 3.0 | −0.80 | 2.74 | 1.35 | 2.84 | 10.65 | −19.13 | 19.13 | 29.78 |
| Inc.(O3)-CCSD(T)(F12*)/MP2-F12 | | | | | | | | | |
| 25 | 2.5 | −0.32 | 0.72 | 0.52 | 0.78 | 1.36 | −3.17 | 3.17 | 4.53 |
| 25 | 3.0 | −0.36 | 0.73 | 0.55 | 0.81 | 1.33 | −3.25 | 3.25 | 4.58 |
| 30 | 2.5 | −0.27 | 0.68 | 0.48 | 0.73 | 1.37 | −2.93 | 2.93 | 4.30 |
| 30 | 3.0 | −0.32 | 0.70 | 0.52 | 0.76 | 1.33 | −3.01 | 3.01 | 4.34 |
| 30 | 3.5 | −0.33 | 0.99 | 0.53 | 1.04 | 1.11 | −7.89 | 7.89 | 9.00 |
| 30 | 4.0 | 0.02 | 1.56 | 0.59 | 1.55 | 5.10 | −11.49 | 11.49 | 16.58 |
| 35 | 2.5 | −0.25 | 0.65 | 0.47 | 0.70 | 1.37 | −2.63 | 2.63 | 3.99 |
| 35 | 3.0 | −0.30 | 0.67 | 0.50 | 0.73 | 1.33 | −2.67 | 2.67 | 4.00 |

^aThe distance truncation by $t_{\text{dist}}(i) = f/(i - 1)^2$ has only a very small effect. The truncation of the virtual space with t_{main} has a larger effect. The most critical molecule with respect to the obtained accuracy is anthracene.

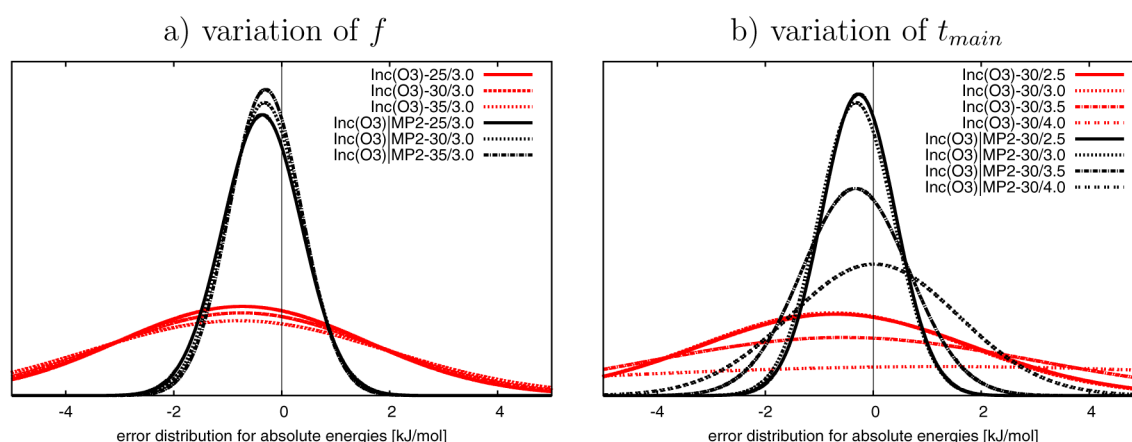


Figure 5. Error distributions for different choices of $t_{\text{dist}}(i) = f/(i - 1)^2$ and t_{main} in Bohr based on the data in Table 1. The red graphs are the error distributions of the incremental CCSD(T)(F12*)/cc-pVDZ-F12 expansions, and the black graphs correspond to the MP2 corrected ones. The first value in the legends refers to f and the second to t_{main} (Inc.(O3)- f/t_{main}). The change of f has only a very small effect, whereas the t_{main} has a larger impact. Surprisingly the increase of t_{main} from 2.5 to 4.0 Bohr increases the error, which is somewhat counterintuitive (see text). All MP2 corrected error distributions (black) are more compact than the uncorrected ones (red). Therefore the MP2 correction improves the overall accuracy.

The refinement of a pair is performed by the unification of the two domains into the set \mathbb{D}_{ij} and the selection of the two orbitals ϕ_a and ϕ_b with the largest distance. Now we sort the set \mathbb{D}_{ij} by the distance to ϕ_a . Next we create a new domain \mathbb{D}_i and add the orbitals of \mathbb{D}_{ij} to this domain. We start at ϕ_a and stop, if the distance to orbital ϕ_b becomes smaller than the distance to ϕ_a , or the maximum domain-size (dsp) is exceeded. This procedure works very well and can partition the system into useful domains (vide infra). Since the partitioning step is performed using the centers of charge of the local orbitals, it is quite independent of the one-particle basis set. Therefore we do the partitioning in a small basis set like STO-3G^{113–115} or SV.¹¹⁶ The advantage of this procedure is that the computation of the correlation energy is independent from the solution of the Hartree–Fock problem in the full basis set and therefore one can solve both parts separately.

2.3. Domain-Specific Basis Set. A way to reduce the virtual space for the calculation of the correlation energy in a domain is the domain-specific basis set approximation. Within this approximation we classify the atoms of the molecule into two classes: main region and environment. The idea of the approximation is that virtual orbitals far from the correlated orbitals of the domain are not needed in the computation of the correlation energy. The systematic classification into the two classes is achieved by the parameter t_{main} (see Figure 2). With this parameter the atoms close to the occupied localized orbitals of the domain are classified as important for the computation of the correlation energy. The selected atoms are treated with the large original basis set whereas the rest is treated with the small environment basis set (SV).

With this procedure it is clear that neighboring domains can share atoms within the important part. We think that this is a good choice, since a good description of a chemical bond

usually requires AOs from all involved atoms (c.f. Figure 3). However one should note that the incremental scheme can repair for some deficiencies in the wave function, as demonstrated by the success of the zero buffer approximation by Zhang and Dolg.³³

Within this framework one has to construct orthogonal localized orbitals in the new basis set. This can be done by a Hartree–Fock calculation in the new basis set and a subsequent template localization.¹¹⁷ When using this technique the domains can be uniquely mapped from the small basis (SV) to the larger domain-specific basis set, as the procedure worked sufficiently well for all cases studied so far. The additional Hartree–Fock calculations are currently performed for the whole system using the domain-specific basis set. This step takes usually only few minutes per domain and is negligible compared to the time required in the coupled cluster part.

2.4. Distance Screening. Considering eq 1 the number of calculations \mathcal{N} grows with

$$\mathcal{N} = \sum_{i=1}^O \binom{|D|}{i}$$

However, it is not necessary to compute all increments, since the increments decay with increasing order and with the spatial distance of the underlying one-site domains (Figure 4). 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.^{110,115}

2.5. Parallelization. The incremental scheme is an inherently parallel method. Therefore it was parallelized in a master and slave structure.¹³ For an efficient use of modern multicore machines a double parallel treatment similar to the one proposed by Fedorov and co-workers¹¹⁸ 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.

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

2.7. MP2 Error Correction. It was previously demonstrated, that the error of an incremental CCSD(T) calculation can be significantly reduced with a MP2-based energy correction:^{116,119,120}

$$E_{\text{corr}}^{\text{inc}}(\text{CCSD(T)}|\text{MP2}) = E_{\text{corr}}^{\text{inc}}(\text{CCSD(T)}) - [E_{\text{corr}}^{\text{inc}}(\text{MP2}) - E_{\text{corr}}(\text{MP2})] \quad (3)$$

Similar schemes to reduce the error were proposed by other authors.^{27,121–125} Please note that we use the MP2-F12 value for the error correction throughout this work. The acronym -F12 is left out when referring to the error correction, to simplify the notation.

2.8. Statistical Measures. To perform the statistical analysis of the errors $\Delta_i = E_i^{\text{approx}} - E_i^{\text{ref}}$ introduced by local approximations, we use the following statistical measures:

$$\text{mean deviation: } \mu = \frac{1}{n} \sum_{i=1}^n \Delta_i$$

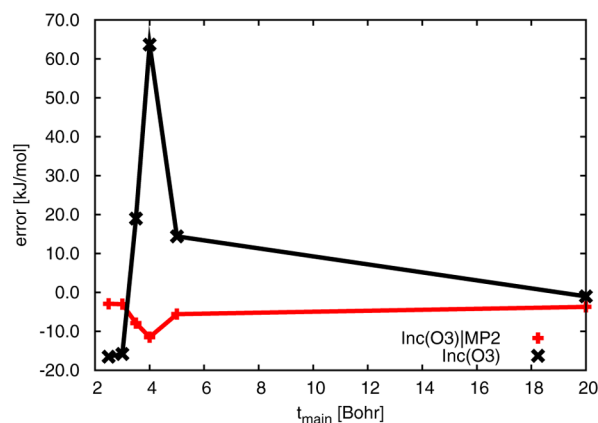


Figure 6. Error of the Inc.(O3)-CCSD(T)(F12*) and Inc.(O3)-CCSD(T)(F12*)|MP2-F12 absolute energies for anthracene using different values of t_{main} . Anthracene is the worst case in our study. The MP2 correction improves the accuracy in general and compensates the large errors for intermediate values of t_{main} . When t_{main} is chosen to 2.5 or 3.0 Bohr we obtain high accuracy for the Inc.(O3)-CCSD(T)-(F12*)|MP2-F12 method.

$$\text{standard deviation: } \sigma = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (\Delta_i - \mu)^2}$$

$$\text{root mean square deviation: } \text{rmsd} = \sqrt{\frac{1}{n} \sum_{i=1}^n \Delta_i^2}$$

$$\text{mean absolute error: } \text{mae} = \frac{1}{n} \sum_{i=1}^n |\Delta_i|$$

$$\text{maximum deviation: } \text{max} = \max_i \Delta_i$$

$$\text{minimum deviation: } \text{min} = \min_i \Delta_i$$

$$\text{maximum absolute deviation: } \text{max abs error} = \max_i |\Delta_i|$$

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

2.9. Computational Details. The coupled cluster calculations were performed with a development version of the TURBOMOLE program package.^{69,80,126–128} In the environment the SV¹²⁹ basis set in combination with the appropriate RI basis set¹³⁰ for density fitting was used in all calculations. The required data such as MO-coefficients, overlap, overlap of two basis sets and dipole integrals was obtained from a modified version of the ricc2 module.¹³¹ In the explicitly correlated calculations we used a Slater type correlation factor as proposed by Ten-no.¹³² In TURBOMOLE the Slater type function is represented by a linear combination of six Gaussians.¹³³ Furthermore, we applied the cc-pVDZ-F12 and cc-pVTZ-F12 basis sets of Peterson^{134,135} using the corresponding CABS¹³⁶ and the recommended exponents in the correlation factor ($0.9 a_0^{-1}$ and $1.0 a_0^{-1}$). The details of the explicitly correlated MP2-F12¹²⁸ and CCSD(T)(F12*)^{69,137} are ansatz 2, approximation B¹³⁸ and the fixed amplitude approach.¹³⁹ The geometries were optimized with the BP86/def2-TZVP^{129,140–142} method using the RI-approximation as implemented in TURBOMOLE.^{143–145} The obtained structures were characterized as minima by analyzing the Hessian matrix.¹⁴⁶

Table 2. Errors in the Absolute Energies Due to Local Approximations in Incremental CCSD(T)(F12*) Expansions Using the cc-pVDZ-F12 and cc-pVTZ-F12 Basis Sets^a

| no. | molecule | cc-pVTZ-F12 | | cc-pVDZ-F12 | |
|-----|---|---------------|--------------|---------------|--------------|
| | | CCSD(T)(F12*) | inc | CCSD(T)(F12*) | inc |
| | | energy a.u. | error kJ/mol | energy a.u. | error kJ/mol |
| 1 | (C ₃ H ₇ S) ₂ | −1032.261530 | −1.13 | −1032.206393 | −1.37 |
| 2 | C ₄ H ₉ SO ₃ H | −781.479833 | −0.58 | −781.414755 | −0.68 |
| 3 | C ₄ H ₉ SO ₂ H | −706.291076 | −0.92 | −706.236467 | −1.17 |
| 4 | propylthiophene | −670.119140 | −1.24 | −670.072920 | −2.12 |
| 5 | C ₂ H ₅ CCICHCH ₃ | −655.414608 | −0.07 | −655.374752 | −0.18 |
| 6 | OS(C ₂ H ₅) ₂ | −631.119080 | −0.47 | −631.075465 | −0.51 |
| 7 | S(C ₂ H ₅) ₂ | −555.977756 | −0.16 | −555.944949 | −0.21 |
| 8 | dihydroanthracene | | | −539.848108 | −1.81 |
| 9 | anthracene | | | −538.641908 | −3.01 |
| 10 | C ₃ H ₇ SH | −516.723326 | −0.22 | −516.695673 | −0.28 |
| 11 | Me ₇ Et-cyclobutane | | | −510.213599 | −0.10 |
| 12 | Me ₈ -cyclobutane | | | −470.965974 | 0.60 |
| 13 | cyclopentadienyletropyne | | | −463.659106 | −0.95 |
| 14 | C ₁₂ H ₁₂ | | | −463.623673 | −0.67 |
| 15 | CO(NHC ₃ H ₇) ₂ | −460.549869 | −0.91 | −460.486934 | −1.06 |
| 16 | C ₆ H ₁₃ CO ₂ H | −425.125007 | −0.63 | −425.066219 | −0.80 |
| 17 | ethylpivalat | −425.117632 | −1.38 | −425.058615 | −1.31 |
| 18 | HCO ₂ C ₅ H ₁₁ | −385.840319 | −0.31 | −385.786730 | −0.36 |
| 19 | naphtaline | −385.304890 | −2.69 | −385.256269 | −2.68 |
| 20 | ethyl-γ-butyrolactone | −384.650026 | −0.20 | −384.596934 | −0.19 |
| 21 | methyl-δ-valerolactone | −384.646118 | −0.29 | −384.592948 | −0.51 |
| 22 | hexandione | −384.635885 | −0.42 | −384.583154 | −0.31 |
| 23 | C ₃ H ₇ CO ₂ C ₂ H ₃ | −384.624284 | −0.77 | −384.571305 | −0.64 |
| 24 | C ₄ H ₉ NHCONH ₂ | −382.046215 | −0.66 | −381.993831 | −0.83 |
| 25 | C ₄ H ₉ NO ₂ | −362.536686 | −0.40 | −362.485776 | −0.47 |
| 26 | C ₄ H ₉ ONO | −362.531453 | −0.53 | −362.480584 | −0.80 |
| 27 | tetramethylpentane | −354.490774 | 0.02 | −354.442928 | 0.12 |
| 28 | n-nonane | −354.490247 | −0.45 | −354.442431 | −0.53 |
| 29 | trimethylbenzene | −349.669856 | 0.46 | −349.624673 | 1.32 |
| 30 | pentandiol | −347.793677 | −0.46 | −347.744140 | −0.40 |
| 31 | propylfurane | −347.495830 | −0.29 | −347.448985 | −0.22 |
| 32 | C ₄ H ₉ CO ₂ H | −346.614846 | −0.48 | −346.566559 | −0.58 |
| 33 | HCON(C ₂ H ₅) ₂ | −326.725008 | 0.15 | −326.680270 | −0.02 |
| 34 | C ₄ H ₉ NCO | −325.514802 | −0.46 | −325.471075 | −0.59 |
| 35 | C ₃ H ₇ NO ₂ | −323.282275 | −0.47 | −323.236624 | −0.38 |
| 36 | C ₆ H ₁₂ O | −310.665821 | −0.15 | −310.622874 | −0.11 |
| 37 | diethyloxirane | −310.643181 | −0.23 | −310.600110 | −0.30 |
| 38 | butandiol | −308.538998 | −0.18 | −308.494735 | −0.08 |
| 39 | (C ₂ H ₄ OH) ₂ | −308.527555 | −0.45 | −308.483393 | −0.57 |
| 40 | (C ₂ H ₅ O) ₂ | −308.434143 | −0.29 | −308.389469 | −0.28 |
| 41 | C ₃ H ₇ CO ₂ H | −307.359711 | −0.27 | −307.316674 | −0.30 |
| 42 | C ₂ H ₅ CO ₂ CH ₃ | −307.344879 | −0.28 | −307.301647 | −0.27 |
| 43 | dimethylpyrrole | −288.395902 | 0.60 | −288.357994 | 1.33 |
| 44 | C ₂ H ₅ CCNCHCH ₃ | −288.374572 | −0.21 | −288.337750 | −0.35 |
| 45 | C ₃ H ₇ CONH ₂ | −287.489665 | −0.29 | −287.450157 | −0.31 |
| 46 | methylpyridine | −287.189625 | −0.85 | −287.152714 | −1.09 |
| 47 | C ₃ H ₇ NCO | −286.259966 | −0.26 | −286.221484 | −0.33 |
| 48 | methylcyclohexane | −274.781808 | 0.44 | −274.745022 | 0.29 |
| 49 | trimethyl-ethyl-ethene | −274.754264 | 0.34 | −274.717666 | 0.60 |
| 50 | Heptene | −274.747928 | −0.12 | −274.711352 | −0.17 |
| 51 | eq-methylcyclohexene | −273.556587 | 0.43 | −273.520588 | 0.42 |
| 52 | ax-methylcyclohexene | −273.472572 | 0.17 | −273.436203 | 0.15 |
| 53 | pentanol | −272.626796 | −0.35 | −272.588669 | −0.48 |
| 54 | methylcyclohexa-1,3-diene | −272.329246 | 0.20 | −272.293888 | 0.31 |
| 55 | methylcyclohexa-1,4-diene | −272.325324 | −0.02 | −272.289960 | −0.16 |
| 56 | C ₄ H ₉ CHO | −271.415389 | −0.15 | −271.378284 | −0.17 |
| 57 | propyloxirane | −271.380780 | −0.11 | −271.342948 | −0.17 |

Table 2. continued

| no. | molecule | cc-pVTZ-F12 | | cc-pVDZ-F12 | |
|-----|--|---------------|--------------|---------------|--------------|
| | | CCSD(T)(F12*) | inc | CCSD(T)(F12*) | inc |
| | | energy a.u. | error kJ/mol | energy a.u. | error kJ/mol |
| 58 | toluene | −271.152712 | −1.00 | −271.117908 | −1.37 |
| 59 | C ₃ H ₇ CHCO | −270.183978 | −0.29 | −270.147709 | −0.26 |
| 60 | methylfurane | −268.989706 | 0.75 | −268.953294 | 1.18 |
| 61 | heptatriyne | −268.553437 | −0.15 | −268.520349 | −0.18 |
| 62 | H ₂ C−C ₅ −CH ₂ | −268.530596 | −0.55 | −268.497252 | −0.72 |
| 63 | C ₂ H ₅ CO ₂ H | −268.104447 | −0.07 | −268.066664 | −0.05 |
| 64 | methylimidazole | −265.184506 | −0.01 | −265.149739 | −0.06 |
| 65 | methylpyrazole | −265.163527 | 0.10 | −265.128635 | 0.03 |
| 66 | methylpyrrole | −249.136395 | 0.01 | −249.103692 | 0.14 |
| 67 | C ₂ H ₅ CONH ₂ | −248.234798 | −0.08 | −248.200535 | −0.07 |
| 68 | neo-hexane | −236.730203 | 0.94 | −236.698086 | 1.05 |
| 69 | dimethylbutane | −236.727830 | 0.06 | −236.695687 | 0.26 |
| 70 | 2-methylpentane | −236.727494 | −0.05 | −236.695385 | −0.02 |
| 71 | 3-methylpentane | −236.726484 | −0.20 | −236.694368 | −0.19 |
| 72 | <i>n</i> -hexane | −236.726042 | −0.36 | −236.693959 | −0.52 |
| 73 | tetramethylethene | −235.499509 | 0.52 | −235.468110 | 0.81 |
| 74 | 3-hexene | −235.495898 | −0.10 | −235.464591 | −0.15 |
| 75 | 1-hexene | −235.492862 | −0.08 | −235.461532 | −0.10 |
| 76 | hexyne | −234.244198 | −0.26 | −234.213672 | −0.35 |
| 77 | dimethyloxirane | −232.132837 | 0.03 | −232.100247 | 0.08 |
| 78 | C ₄ H ₉ NH ₂ | −213.505771 | −0.27 | −213.476612 | −0.34 |
| 79 | diethylamine | −213.497422 | −0.10 | −213.468229 | −0.14 |
| 80 | C ₃ H ₇ CN | −211.088503 | −0.08 | −211.061507 | −0.10 |
| 81 | <i>trans</i> -2-pentene | −196.241179 | −0.19 | −196.215109 | −0.29 |
| 82 | <i>cis</i> -2-pentene | −196.239336 | −0.12 | −196.213223 | −0.19 |
| 83 | 1-pentene | −196.237816 | −0.05 | −196.211733 | −0.02 |
| 84 | pentadiene | −195.014373 | 0.02 | −194.988979 | 0.02 |
| 85 | 2-pentyne | −194.995546 | −0.05 | −194.970281 | −0.08 |
| 86 | 1-pentyne | −194.989145 | −0.08 | −194.963868 | −0.10 |
| 87 | C ₂ H ₅ NH ₂ | −134.996052 | −0.00 | −134.977394 | 0.00 |

^aFor the truncation of the incremental series we applied third order, $f = 30$ Bohr, $t_{\text{main}} = 3.0$ Bohr and applied the MP2 correction.

Table 3. Statistical Analysis of the Errors in the Absolute CCSD(T)(F12*) Energies Introduced by Local Approximations^a

| basis set | μ | σ | mae | rmsd | max | min | max abs error | range |
|-----------------------|-------|----------|------|------|------|-------|---------------|-------|
| cc-pVDZ-F12 total set | −0.32 | 0.69 | 0.52 | 0.76 | 1.33 | −3.01 | 3.01 | 4.34 |
| cc-pVDZ-F12 | −0.27 | 0.62 | 0.47 | 0.59 | 1.33 | −2.68 | 2.68 | 4.01 |
| cc-pVTZ-F12 | −0.24 | 0.49 | 0.37 | 0.54 | 0.94 | −2.69 | 2.69 | 3.63 |

^aThe details for the incremental scheme are given in Table 2.

3. RESULTS

3.1. Test Set. To demonstrate that our incremental method works also for chemically interesting problems, we study the absolute energies of 81 molecules and 51 reaction energies similar to those in ref 49. and ref 32. We increased the size of the molecules, to obtain significant results with the incremental scheme. For a meaningful testing of the approximations in the incremental expansion medium sized molecules are needed, since the incremental series truncates trivially with the exact result for too small molecules. Furthermore the molecules should not be too large, to keep the full CCSD(T)(F12*)/cc-pVTZ-F12 or at least the cc-pVDZ-F12 computation feasible.

3.2. Variation of the Truncation Parameters. Now we search for the optimal set of truncation parameters, to be used for a black box truncation scheme. To validate the truncations applied in our scheme with respect to the introduced thresholds, we compare the results for different choices of the parameters f and t_{main} for a third order expansion. The second

order incremental expansion is not accurate on average. To perform this analysis on a solid basis, we computed the statistical parameters μ , σ , mae, rmsd, max, min, max abs error, and range for 87 absolute energies (Table 1).

In Figure 5 we present the change of the error in the incremental series, when different truncation parameters are used. The corresponding error measures are explicitly given in Table 1. Considering the variation of f we see only very small changes (Figure 5a). The changes in the accuracy are in general larger for the variation of t_{main} . The increase of the statistical error with an increase of t_{main} as given in Figure 5b is unexpected. For the worst case example anthracene we investigated the error introduced by different choices of t_{main} in more detail (Figure 6). If small values of 2.5 and 3.0 Bohr are used the accuracy is high. For intermediate values the error increases, and for large values the error becomes small again. Within this context we note that the virtual space depends also on the order of an increment, and in higher order increments

Table 4. Reaction Energies in kJ/mol for Different Quantum Chemical Methods^a

| no. | reaction | CCSD(T)(F12*) | CCSD(T)(F12*) | MP2-F12/B | Inc.(O3)lMP2 | Inc.(O3)lMP2 |
|-----|--|---------------|---------------|-------------|--------------|--------------|
| | | cc-pVTZ-F12 | cc-pVDZ-F12 | cc-pVTZ-F12 | cc-pVDZ-F12 | cc-pVTZ-F12 |
| 1 | C ₆ H ₁₂ O + 2 H ₂ O ₂ → ethyl-γ-butyrolactone + 3 H ₂ O | −631.46 | −634.17 | −667.63 | −634.25 | −631.50 |
| 2 | C ₄ H ₉ NH ₂ + 3 H ₂ O ₂ → C ₄ H ₉ NO ₂ + 4 H ₂ O | −604.44 | −606.82 | −660.63 | −606.95 | −604.57 |
| 3 | C ₄ H ₉ CHO + H ₂ O ₂ → C ₄ H ₉ CO ₂ H + H ₂ O | −374.02 | −374.80 | −394.07 | −375.20 | −374.36 |
| 4 | C ₄ H ₉ SO ₂ H + H ₂ O ₂ → C ₄ H ₉ SO ₃ H + H ₂ O | −345.93 | −348.58 | −375.72 | −348.09 | −345.59 |
| 5 | <i>trans</i> -2-pentene + H ₂ O ₂ → pentandiole | −328.70 | −328.14 | −344.65 | −328.25 | −328.96 |
| 6 | toluene + 3 H ₂ → methylcyclohexane | −280.92 | −280.97 | −261.49 | −279.30 | −279.49 |
| 7 | pentanole + H ₂ O ₂ → C ₄ H ₉ CHO + 2 H ₂ O | −267.53 | −269.43 | −284.08 | −269.12 | −267.33 |
| 8 | (C ₂ H ₅ O) ₂ → (C ₂ H ₄ OH) ₂ | −245.25 | −246.60 | −260.38 | −246.89 | −245.42 |
| 9 | 3-hexene + H ₂ O ₂ → diethyloxirane + H ₂ O | −237.04 | −236.29 | −258.76 | −236.44 | −237.16 |
| 10 | S(C ₂ H ₅) ₂ + H ₂ O ₂ → OS(C ₂ H ₅) ₂ + H ₂ O | −221.39 | −223.15 | −244.68 | −223.46 | −221.70 |
| 11 | ax-methylcyclohexene → eq-methylcyclohexene | −220.58 | −221.55 | −217.94 | −221.28 | −220.32 |
| 12 | hexyne + H ₂ → 1-hexene | −195.95 | −195.58 | −185.21 | −195.34 | −195.76 |
| 13 | 2-pentyne + H ₂ → <i>trans</i> -2-pentene | −187.99 | −187.62 | −176.73 | −187.84 | −188.13 |
| 14 | 2-pentyne + H ₂ → <i>cis</i> -2-pentene | −183.15 | −182.67 | −172.00 | −182.78 | −183.22 |
| 15 | 2-pentyne + HCN → C ₂ H ₅ CCNCHCH ₃ | −179.71 | −178.66 | −179.20 | −178.93 | −179.88 |
| 16 | 1-hexene + H ₂ → <i>n</i> -hexane | −155.29 | −155.06 | −158.70 | −155.48 | −155.57 |
| 17 | 1-pentyne + H ₂ O → C ₄ H ₉ CHO | −146.87 | −146.74 | −135.68 | −146.80 | −146.94 |
| 18 | 2 C ₃ H ₇ NH ₂ + COCl ₂ → CO(NHC ₃ H ₇) ₂ + 2 HCl | −136.33 | −133.34 | −130.54 | −134.40 | −137.24 |
| 19 | eq-methylcyclohexene + H ₂ → methylcyclohexane | −134.39 | −134.08 | −136.29 | −134.20 | −134.39 |
| 20 | <i>trans</i> -2-pentene + Cl ₂ → C ₂ H ₅ CClCHCH ₃ + HCl | −131.10 | −133.39 | −143.63 | −133.28 | −130.98 |
| 21 | 2-pentyne + HCl → C ₂ H ₅ CClCHCH ₃ | −125.37 | −125.60 | −124.18 | −125.70 | −125.39 |
| 22 | 1-pentene + ethene → heptene | −108.11 | −107.78 | −117.84 | −107.93 | −108.18 |
| 23 | C ₄ H ₉ CHO + H ₂ → pentanole | −98.13 | −97.19 | −99.47 | −97.50 | −98.33 |
| 24 | dimethyloxirane + H ₂ O → butandiole | −94.14 | −94.42 | −88.28 | −94.58 | −94.35 |
| 25 | methylpyridine + H ₂ → dimethylpyrrole | −84.66 | −83.79 | −88.75 | −81.37 | −83.21 |
| 26 | C ₄ H ₉ NCO + NH ₃ → C ₄ H ₉ NHCONH ₂ | −82.48 | −81.20 | −74.31 | −81.44 | −82.69 |
| 27 | C ₃ H ₇ CN + H ₂ O → C ₃ H ₇ CONH ₂ | −81.02 | −79.09 | −74.26 | −79.30 | −81.22 |
| 28 | propylfuran + H ₂ S → propylthiophene + H ₂ O | −80.91 | −83.34 | −104.58 | −85.23 | −81.87 |
| 29 | diethylamine + CO → HCON(C ₂ H ₅) ₂ | −72.11 | −69.29 | −84.91 | −69.16 | −71.86 |
| 30 | C ₃ H ₇ NCO + H ₂ O → C ₃ H ₇ NH ₂ + CO ₂ | −71.53 | −72.60 | −66.60 | −72.27 | −71.27 |
| 31 | C ₃ H ₇ CO ₂ C ₂ H ₃ → ethyl-γ-butyrolactone | −67.59 | −67.29 | −77.40 | −66.83 | −67.02 |
| 32 | H ₂ C-C ₅ -CH ₂ → heptatriyne | −59.97 | −60.64 | −99.85 | −60.10 | −59.58 |
| 33 | methylpyrazole → methylimidazole | −55.08 | −55.41 | −51.66 | −55.49 | −55.20 |
| 34 | 1-pentene + H ₂ O → pentanole | −49.03 | −48.33 | −49.89 | −48.80 | −49.33 |
| 35 | methylfuran + NH ₃ → methylpyrrole + H ₂ O | −44.62 | −44.89 | −57.65 | −45.93 | −45.37 |
| 36 | C ₃ H ₇ CHCO + H ₂ CO → propyloxirane + CO | −39.44 | −39.28 | −36.04 | −39.20 | −39.27 |
| 37 | pentanole + CO → HCO ₂ C ₅ H ₁₁ | −35.19 | −32.58 | −42.35 | −32.47 | −35.15 |
| 38 | (C ₃ H ₇ S) ₂ + H ₂ → 2 C ₃ H ₇ SH | −29.12 | −30.42 | −17.06 | −29.60 | −28.43 |
| 39 | pentadiene + ethene → ax-methylcyclohexene | −28.19 | −29.78 | −5.63 | −29.91 | −28.34 |
| 40 | hexandione → methyl-δ-valerolactone | −26.87 | −25.71 | −31.43 | −25.91 | −26.74 |
| 41 | C ₂ H ₅ CO ₂ H + methanole → C ₂ H ₅ CO ₂ CH ₃ + H ₂ O | −21.23 | −20.84 | −23.00 | −21.07 | −21.44 |
| 42 | C ₄ H ₉ ONO → C ₄ H ₉ NO ₂ | −13.74 | −13.63 | −33.42 | −13.30 | −13.62 |
| 43 | <i>n</i> -hexane → neo-hexane | −10.92 | −10.83 | −15.70 | −9.26 | −9.63 |
| 44 | methylcyclohexa-1, 4-diene → methylcyclohexa-1, 3-diene | −10.30 | −10.31 | −13.55 | −9.84 | −10.08 |
| 45 | 1-pentene → <i>trans</i> -2-pentene | −8.83 | −8.86 | −10.09 | −9.14 | −8.97 |
| 46 | toluene + H ₂ → methylcyclohexa-1, 3-diene | −6.57 | −6.86 | 14.24 | −5.18 | −5.37 |
| 47 | <i>trans</i> -2-pentene → <i>cis</i> -2-pentene | −4.84 | −4.95 | −4.73 | −5.06 | −4.91 |
| 48 | 3-methylpentane → dimethylbutane | −3.53 | −3.46 | −5.11 | −3.01 | −3.27 |
| 49 | C ₂ H ₅ CO ₂ H + NH ₃ → C ₂ H ₅ CONH ₂ + H ₂ O | −1.73 | −1.50 | −5.65 | −1.52 | −1.74 |
| 50 | <i>n</i> -nonane → tetramethylpentane | −1.38 | −1.30 | −12.32 | −0.66 | −0.92 |
| 51 | C ₃ H ₇ CO ₂ H + NH ₃ → C ₃ H ₇ CONH ₂ + H ₂ O | −0.69 | −0.48 | −4.46 | −0.49 | −0.70 |

^aFor the truncation of the incremental series we applied $f = 30$ Bohr and $t_{\text{main}} = 3.0$ Bohr. Inc.(O3)lMP2 = Inc.-(O3)-CCSD(T)(F12*)lMP2.

the excitation space will be included again. This means more precisely, that we do not neglect the important physics to describe the system of interest.

On the basis of these findings, we conclude that t_{main} should not be modified when trying to improve the accuracy. From our previous investigations we suggest to increase the order of the

incremental series for such purposes. When using a small t_{main} only very few atoms are treated with the large basis set, and the computational setup is similar to the zero buffer approach proposed by Zhang and Dolg.³³

When choosing appropriate values for the truncation parameters, we obtain highly accurate results, as proven by

Table 5. Statistical Measures in kJ/mol^a

| method | μ | σ | mae | rmsd | max | min | max abs error | range |
|---------------------------------------|-------|----------|-------|-------|-------|--------|---------------|-------|
| Inc.(O3)IMP2/TZ ^b | 0.07 | 0.49 | 0.33 | 0.49 | 1.45 | -0.95 | 1.45 | 2.40 |
| CCSD(T)+ Δ MP2/TZ ^c | 0.50 | 1.03 | 0.91 | 1.14 | 2.62 | -2.11 | 2.62 | 4.73 |
| Inc.(O3)/TZ ^b | -0.08 | 1.07 | 0.61 | 1.06 | 3.41 | -4.95 | 4.95 | 8.36 |
| CCSD(T)(F12*)/DZ ^d | -0.08 | 1.29 | 0.92 | 1.28 | 2.99 | -2.71 | 2.99 | 5.70 |
| Inc.(O3)IMP2/DZ ^d | -0.00 | 1.46 | 1.07 | 1.45 | 3.29 | -4.32 | 4.32 | 7.60 |
| CCSD(T)/TZ ^c | 4.20 | 10.63 | 6.23 | 11.33 | 48.04 | -9.36 | 48.04 | 57.40 |
| MP2/TZ ^c | -1.56 | 11.01 | 8.00 | 11.01 | 21.08 | -39.85 | 39.85 | 60.93 |
| Inc.(O3)-MP2-F12/TZ ^b | -5.42 | 15.24 | 11.63 | 16.03 | 22.20 | -55.97 | 55.97 | 78.17 |
| MP2-F12/B/TZ ^b | -5.27 | 15.38 | 11.62 | 16.11 | 22.56 | -56.19 | 56.19 | 78.75 |

^aErrors computed relative to CCSD(T)(F12*)/cc-pVTZ-F12. For the truncation of the incremental series we applied $f = 30$ Bohr and $t_{\text{main}} = 3.0$ Bohr. Inc.(O3)IMP2 = Inc.-(O3)-CCSD(T)(F12*)IMP2. Inc.(O3) = Inc.-(O3)-CCSD(T)(F12*). ^bcc-pVTZ-F12. ^ccc-pVTZ. ^dcc-pVDZ-F12.

the statistical analysis. On the basis of this data, we propose to use fixed values of $f = 30$ Bohr and $t_{\text{main}} = 3.0$ Bohr in combination with a third order expansion and the MP2 correction. When using the incremental scheme in this manner, one can use it as a black-box method, without manually determining any parameter.

3.3. Accuracy. To establish the accuracy of the proposed scheme on a significant basis, we investigated the performance of our scheme for 87 molecules at the CCSD(T)(F12*)/cc-pVDZ-F12 level of theory. For 81 molecules we were also able to compute the energies in the cc-pVTZ-F12 basis set (Table 2). These results were obtained with the optimal truncation scheme (third order, $f = 30$ Bohr, $t_{\text{main}} = 3.0$ Bohr). The complete set of data for the variation of t_{main} and f is given in the Supporting Information.¹⁴⁷ Based on these results we computed the statistical error measures in Table 3. The maximum error of -3.01 kJ/mol in the absolute energies is found for anthracene. This can be realized by the fact that anthracene is a highly delocalized system which can cause problems for local correlation methods in general. However the error is still acceptable. Considering the small σ of 0.69 kJ/mol at the double ζ -level we find 99.7% of the errors to be in a range of 4.14 kJ/mol ($[\mu - 3\sigma, \mu + 3\sigma]$). Since μ is also small, we can conclude that our method provides the CCSD(T)(F12*) energy within chemical accuracy of about 4.18 kJ/mol on average. If we consider the last two lines of Table 3, we find a slight improvement of the accuracy, if we increase the basis set from double to triple- ζ .

3.3.1. Absolute Energies. **3.3.2. Reaction Energies.** The absolute energy is usually not the quantity of interest when using quantum chemical methods to model chemical problems. To test the accuracy of our method also for reaction energies, we computed 55 reaction energies (Tables 4 and 7). The statistical analysis was performed for 51 reaction energies using the CCSD(T)(F12*)/cc-pVTZ-F12 energies. The reactions in Table 7 are not included because we could not perform the reference calculations in the triple- ζ basis set on our hardware. It was already recognized in earlier studies that high accuracy can be obtained with the cc-pVDZ-F12 basis set, if explicitly correlated coupled cluster methods are used.⁸¹ Since the computations in smaller basis sets are rather inexpensive, such a strategy could be an alternative to a local correlation method for medium sized systems and therefore we include these results in our analysis. The errors of the reaction energies for a selected set of methods are presented in Table 6. The complete set of data is compiled in the Supporting Information.¹⁴⁷

To simplify the analysis, we discuss the accuracy of the local approximations proposed in this work based on the statistical

measures in Table 5. In this table we also included the accuracy of MP2-F12/cc-pVTZ-F12, CCSD(T)/cc-pVTZ, and the complete basis set estimate of CCSD(T) using an MP2 increment (eq 4).¹⁴⁸

$$E(\text{CCSD(T)}) + E(\Delta\text{MP2}) = E(\text{CCSD(T)/cc-pVTZ}) + E(\text{MP2-F12/cc-pVTZ-F12}) - E(\text{MP2/cc-pVTZ}) \quad (4)$$

For a convenient comparison of the average accuracy, the methods in Table 5 are sorted with respect to their standard deviation. The best performance is found for the incremental scheme if a cc-pVTZ-F12 basis set is used. A rather high accuracy is also found for eq 4, where the basis set limit of CCSD(T) is estimated by an MP2 increment using MP2-F12/cc-pVTZ-F12. The incremental scheme without the MP2 correction works also quite well, when only considering σ . However, in this case the range is somewhat larger, and the error for the hydrogenation of anthracene is quite large at double- ζ level. The reaction was not included in the test set, since the full calculation in the large triple- ζ basis was infeasible (on our hardware). When using the MP2-correction the error is quite small (1.20 kJ/mol, Table 7).

In agreement with ref 81 it is also found that the CCSD(T)(F12*) method in the double- ζ basis set provides highly accurate results. When combining the incremental scheme and the smaller cc-pVDZ-F12 basis set the accuracy is slightly worse compared to full calculation in the double- ζ basis set. On the other hand a method with a σ of 1.46 kJ/mol can still be classified as highly accurate. When considering the coupled cluster calculations in a small cc-pVTZ basis set, the σ is significantly larger (10.63 kJ/mol). Therefore it is evident, that the small basis set is not sufficient to provide the intrinsic accuracy of the CCSD(T) model. The MP2 model provides an accuracy similar to the CCSD(T)/cc-pVTZ model when using a triple- ζ basis set $\sigma = 11.01$ kJ/mol. In contrast to the coupled cluster method the accuracy of MP2 becomes worse if explicit correlation is used to improve the one particle basis set. This finding is a result of an error compensation of the MP2 method when using a triple- ζ basis set as previously discussed by Helgaker et al.¹⁴⁹ Please note that even if the MP2-F12 model alone is in general not very accurate, it is very well suitable to compute the MP2 CBS energy, which is a basic ingredient in eq 4.

When considering the $[\mu - 3\sigma, \mu + 3\sigma]$ interval for the error, we find that the proposed incremental CCSD(T)(F12*) method is within chemical accuracy of 4.18 kJ/mol. Therefore it is evident, that our model is useful for high accuracy computational chemistry.

Table 6. Errors in the Reaction Energies Relative to CCSD(T)(F12*)/cc-pVTZ-F12 in kJ/mol^a

| no. | reaction | CCSD(T)(F12*) | MP2-F12/B | Inc.(O3)lMP2 | Inc.(O3)lMP2 |
|-----|--|---------------|-------------|--------------|--------------|
| | | cc-pVDZ-F12 | cc-pVTZ-F12 | cc-pVDZ-F12 | cc-pVTZ-F12 |
| 1 | C ₆ H ₁₂ O + 2 H ₂ O ₂ → ethyl-γ-butyrolactone + 3 H ₂ O | -2.71 | -36.17 | -2.79 | -0.04 |
| 2 | C ₄ H ₉ NH ₂ + 3 H ₂ O ₂ → C ₄ H ₉ NO ₂ + 4 H ₂ O | -2.38 | -56.19 | -2.51 | -0.13 |
| 3 | C ₄ H ₉ CHO + H ₂ O ₂ → C ₄ H ₉ CO ₂ H + H ₂ O | -0.78 | -20.05 | -1.18 | -0.34 |
| 4 | C ₄ H ₉ SO ₂ H + H ₂ O ₂ → C ₄ H ₉ SO ₃ H + H ₂ O | -2.65 | -29.80 | -2.17 | 0.34 |
| 5 | <i>trans</i> -2-pentene + H ₂ O ₂ → pentandiole | 0.56 | -15.96 | 0.45 | -0.26 |
| 6 | toluene + 3 H ₂ → methylcyclohexane | -0.04 | 19.44 | 1.62 | 1.44 |
| 7 | pentanole + H ₂ O ₂ → C ₄ H ₉ CHO + 2 H ₂ O | -1.90 | -16.55 | -1.58 | 0.21 |
| 8 | (C ₂ H ₅ O) ₂ → (C ₂ H ₄ OH) ₂ | -1.35 | -15.13 | -1.63 | -0.17 |
| 9 | 3-hexene + H ₂ O ₂ → diethyloxirane + H ₂ O | 0.75 | -21.72 | 0.59 | -0.12 |
| 10 | S(C ₂ H ₅) ₂ + H ₂ O ₂ → OS(C ₂ H ₅) ₂ + H ₂ O | -1.76 | -23.29 | -2.07 | -0.31 |
| 11 | ax-methylcyclohexene → eq-methylcyclohexene | -0.97 | 2.64 | -0.70 | 0.26 |
| 12 | hexyne + H ₂ → 1-hexene | 0.36 | 10.73 | 0.61 | 0.18 |
| 13 | 2-pentyne + H ₂ → <i>trans</i> -2-pentene | 0.36 | 11.26 | 0.15 | -0.14 |
| 14 | 2-pentyne + H ₂ → <i>cis</i> -2-pentene | 0.48 | 11.15 | 0.37 | -0.07 |
| 15 | 2-pentyne + HCN → C ₂ H ₅ CCNCHCH ₃ | 1.06 | 0.52 | 0.78 | -0.16 |
| 16 | 1-hexene + H ₂ → <i>n</i> -hexane | 0.23 | -3.41 | -0.19 | -0.28 |
| 17 | 1-pentyne + H ₂ O → C ₄ H ₉ CHO | 0.13 | 11.19 | 0.07 | -0.07 |
| 18 | 2 C ₃ H ₇ NH ₂ + COCl ₂ → CO(NHC ₃ H ₇) ₂ + 2 HCl | 2.99 | 5.79 | 1.93 | -0.91 |
| 19 | eq-methylcyclohexene + H ₂ → methylcyclohexane | 0.32 | -1.90 | 0.19 | 0.01 |
| 20 | <i>trans</i> -2-pentene + Cl ₂ → C ₂ H ₅ CClCHCH ₃ + HCl | -2.29 | -12.52 | -2.18 | 0.13 |
| 21 | 2-pentyne + HCl → C ₂ H ₅ CClCHCH ₃ | -0.22 | 1.19 | -0.33 | -0.02 |
| 22 | 1-pentene + ethene → heptene | 0.33 | -9.73 | 0.18 | -0.07 |
| 23 | C ₄ H ₉ CHO + H ₂ → pentanole | 0.93 | -1.34 | 0.62 | -0.21 |
| 24 | dimethyloxirane + H ₂ O → butandiole | -0.27 | 5.87 | -0.44 | -0.21 |
| 25 | methylpyridine + H ₂ → dimethylpyrrole | 0.87 | -4.09 | 3.29 | 1.45 |
| 26 | C ₄ H ₉ NCO + NH ₃ → C ₄ H ₉ NHCONH ₂ | 1.28 | 8.18 | 1.04 | -0.20 |
| 27 | C ₃ H ₇ CN + H ₂ O → C ₃ H ₇ CONH ₂ | 1.93 | 6.76 | 1.72 | -0.21 |
| 28 | propylfuran + H ₂ S → propylthiophene + H ₂ O | -2.42 | -23.67 | -4.32 | -0.95 |
| 29 | diethylamine + CO → HCON(C ₂ H ₅) ₂ | 2.82 | -12.80 | 2.95 | 0.25 |
| 30 | C ₃ H ₇ NCO + H ₂ O → C ₃ H ₇ NH ₂ + CO ₂ | -1.07 | 4.94 | -0.74 | 0.26 |
| 31 | C ₃ H ₇ CO ₂ C ₂ H ₃ → ethyl-γ-butyrolactone | 0.30 | -9.81 | 0.75 | 0.57 |
| 32 | H ₂ C-C ₅ -CH ₂ → heptatriyne | -0.67 | -39.88 | -0.13 | 0.39 |
| 33 | methylpyrazole → methylimidazole | -0.33 | 3.42 | -0.41 | -0.11 |
| 34 | 1-pentene + H ₂ O → pentanole | 0.70 | -0.85 | 0.24 | -0.30 |
| 35 | methylfuran + NH ₃ → methylpyrrole + H ₂ O | -0.27 | -13.03 | -1.31 | -0.74 |
| 36 | C ₃ H ₇ CHCO + H ₂ CO → propyloxirane + CO | 0.16 | 3.40 | 0.24 | 0.18 |
| 37 | pentanole + CO → HCO ₂ C ₅ H ₁₁ | 2.61 | -7.16 | 2.72 | 0.04 |
| 38 | (C ₃ H ₇ S) ₂ + H ₂ → 2 C ₃ H ₇ SH | -1.30 | 12.05 | -0.49 | 0.69 |
| 39 | pentadiene + ethene → ax-methylcyclohexene | -1.59 | 22.56 | -1.72 | -0.15 |
| 40 | hexandione → methyl-δ-valerolactone | 1.15 | -4.57 | 0.96 | 0.13 |
| 41 | C ₂ H ₅ CO ₂ H + methanole → C ₂ H ₅ CO ₂ CH ₃ + H ₂ O | 0.38 | -1.77 | 0.16 | -0.21 |
| 42 | C ₄ H ₉ ONO → C ₄ H ₉ NO ₂ | 0.11 | -19.68 | 0.44 | 0.12 |
| 43 | <i>n</i> -hexane → neo-hexane | 0.09 | -4.78 | 1.66 | 1.30 |
| 44 | methylcyclohexa-1, 4-diene → methylcyclohexa-1, 3-diene | -0.01 | -3.25 | 0.46 | 0.22 |
| 45 | 1-pentene → <i>trans</i> -2-pentene | -0.03 | -1.26 | -0.31 | -0.14 |
| 46 | toluene + H ₂ → methylcyclohexa-1,3-diene | -0.29 | 20.81 | 1.39 | 1.20 |
| 47 | <i>trans</i> -2-pentene → <i>cis</i> -2-pentene | -0.11 | 0.11 | -0.22 | -0.07 |
| 48 | 3-methylpentane → dimethylbutane | 0.07 | -1.58 | 0.52 | 0.26 |
| 49 | C ₂ H ₅ CO ₂ H + NH ₃ → C ₂ H ₅ CONH ₂ + H ₂ O | 0.23 | -3.92 | 0.21 | -0.02 |
| 50 | <i>n</i> -nonane → tetramethylpentane | 0.08 | -10.94 | 0.72 | 0.46 |
| 51 | C ₃ H ₇ CO ₂ H + NH ₃ → C ₃ H ₇ CONH ₂ + H ₂ O | 0.21 | -3.78 | 0.20 | -0.01 |

^aFor the truncation of the incremental series we applied $f = 30$ Bohr and $t_{\text{main}} = 3.0$ Bohr. Inc.(O3)lMP2 = Inc.-(O3)-CCSD(T)(F12*)lMP2.

In Table 7 we included 4 critical reactions, where the full CCSD(T)(F12*)/cc-pVTZ-F12 calculation was not feasible on our hardware. Especially the last reaction is a critical test reaction for our method, since anthracene is involved and in addition the conjugated π -system is destroyed in the reaction. Since the error is only 1.2 kJ/mol, we come to

the conclusion that such systems can also be treated with high accuracy.

3.4. Comparison to Other Schemes: Schmittl Cyclization. We selected the Schmittl type^{151–153} reaction to compare the performance of the incremental scheme proposed in this work (Table 8), to the smart implementation

Table 7. Reaction Energies of Critical Reactions in kJ/mol^a

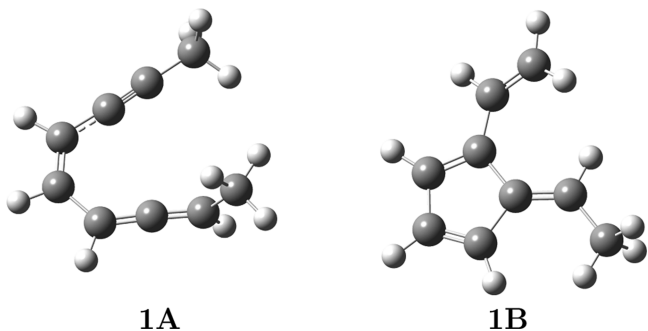
| no. | reaction | CCSD(T)(F12*) | MP2-F12/B | CCSD(T) | Inc.(O3)lMP2 | error ^b |
|-----|---|---------------|-------------|---------|--------------|--------------------|
| | | cc-pVDZ-F12 | cc-pVTZ-F12 | cc-pVTZ | cc-pVDZ-F12 | cc-pVDZ-F12 |
| 1 | tetramethylethene → Me ₈ -cyclobutane | −78.12 | −101.08 | −82.89 | −79.13 | −1.01 |
| 2 | tetramethylethene + trimethyl-ethyl-ethene → Me ₇ Et-cyclobutane | −73.05 | −95.81 | | −74.55 | −1.50 |
| 3 | C ₁₂ H ₁₂ → cyclopentadienyletropyne | −93.03 | −94.97 | −89.59 | −93.31 | −0.28 |
| 4 | anthracene + H ₂ → dihydroanthracene | −86.20 | −74.53 | −85.44 | −85.00 | 1.20 |

^aThe reactions were not included in Table 4 because the full CCSD(T)(F12*) calculation in the cc-pVTZ-F12 basis set was not possible for at least one reactant. The errors are similar to the errors in Table 6. For the truncation of the incremental series we applied third order, $f = 30$ Bohr and $t_{\text{main}} = 3.0$ Bohr. Please note, that C₁₂H₁₂ has a different structure compared to the molecule in ref 150. Therefore the errors in the reaction energies are not directly comparable. Inc.(O3)lMP2 = Inc.(O3)-CCSD(T)(F12*)lMP2. ^bError due to the incremental scheme.

Table 8. Performance of the Proposed Incremental Expansion of the Schmittl Cyclization Shown in Figure 7^a

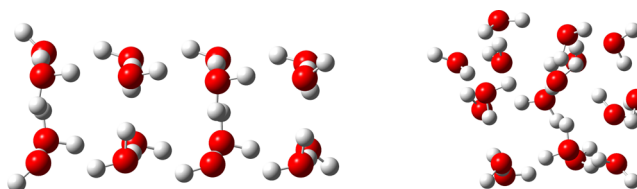
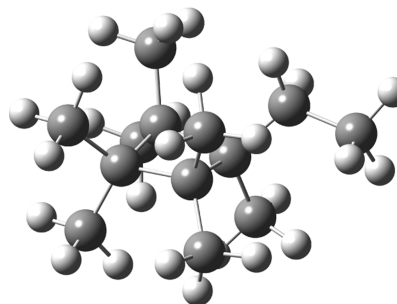
| method | 1A | 1B | ΔE | error |
|-----------------------------------|------------|------------|--------|--------|
| | a.u. | a.u. | kJ/mol | kJ/mol |
| CCSD(T)(F12*) ^b | −348.26793 | −348.34047 | −190.5 | |
| Inc.(O3) ^b | −348.26835 | −348.34144 | −191.9 | −1.4 |
| Inc.(O3)lMP2 ^b | −348.26803 | −348.34084 | −191.2 | −0.7 |
| CCSD(T)/DZ ^c | −347.83868 | −347.91309 | −195.4 | |
| inc-db-B0-CCSD(T)/DZ ^c | −347.83798 | −347.91290 | −196.7 | −1.3 |
| CCSD(T)/TZ ^c | −348.18090 | −348.25208 | −186.9 | |
| inc-db-B0-CCSD(T)/TZ ^c | −348.18061 | −348.25253 | −188.8 | −1.9 |

^aAs basis set the cc-pVDZ-F12 basis set with 360 AO basis functions was applied. The geometries were taken from ref 33. ^bThis work, including CABS singles correction.^{81,154,155} ^cRef 33.

Figure 7. B3LYP structure of the reactants of the Schmittl cyclization^{151–153} studied by Zhang and Dolg.³³

of the incremental scheme proposed by Zhang and Dolg in ref 33. In this reference the authors argue that the SV basis is too small to describe the environment of a domain, when computing an increment. Considering the results of the statistical analysis above it is evident that the accuracy obtained with our scheme is very high.

To support our argumentation, that the SV basis set is sufficient for the description of the environment of a domain, we compare both schemes directly. Comparing the error obtained for the third order incremental CCSD(T)(F12*)/cc-pVDZ-F12 expansion (Inc.(O3)) of −1.4 kJ/mol to the error of the inc3-db-B0 of −1.3 and −1.9 kJ/mol at the cc-pVDZ and cc-pVTZ level, we see that our scheme has a similar accuracy. When using the MP2 corrected incremental series our error drops down to −0.7 kJ/mol. On the basis of these findings, we conclude that the SV basis is sufficient to model the environment in our implementation. Finally we note that the computational effort of the additional Hartree–Fock calculations in the domains

Figure 8. Structure of (H₂O)₁₆ and (H₂O)₁₇ from Xantheas and coworkers.¹⁵⁶Figure 9. BP86/def2-TZVP optimized structure of Me₇Et-cyclobutane.

is negligible compared with the effort of the coupled cluster calculations.

4. TIMING

To demonstrate the efficiency of our approach we selected two different systems: medium sized water clusters in Figure 8 and Me₇Et-cyclobutane in Figure 9. While the first test case is an application to systems where the incremental scheme is converged at second order and therefore especially efficient, the second test case is a more general example.

4.1. Water Clusters. The accurate computation of binding energies is a difficult task for standard computational chemistry methods, since high level methods like CCSD(T) are needed, and the basis set convergence is very slow for these systems. Therefore the choice of an appropriate basis set is of crucial importance in a CCSD(T) calculation for those clusters. Even for the (F12*) model used in this work the binding energy changes by 2 kJ/mol when increasing the basis set from triple- to quadruple- ζ level (see Table 9). Considering the efficiency of the approach we find the wall times to be reduced compared to the incremental (F12) scheme.¹¹⁶ With the incremental (F12*) model we were able to compute the binding energy of the (H₂O)₁₆ cluster with a reduced total and also a reduced wall time compared with that of the massively parallel CCSD(T) calculation of ref 156. With the proposed incremental scheme it is also possible to increase the basis set to quadruple- ζ level

Table 9. Binding Energies (E_b) of Medium Sized Water Clusters^a

| method | cluster | basis size | E_b [kJ/mol] | cores | total time [h] | wall time [h] |
|------------------------------------|----------------------------------|------------|----------------|--------|----------------|-------------------|
| CCSD(T)/AVTZ ^{b,c} | (H ₂ O) ₁₆ | 1472 | -716.1 | 120000 | 399600 | 3.3 |
| frag-CCSD(T)/AVTZ ^{c,d} | (H ₂ O) ₁₆ | 1472 | -716.3 | | 2256 | 19.0 |
| Inc.(O2)IMP2(F12)/DZ ^e | (H ₂ O) ₁₆ | 768 | -679.7 | 248 | 308 | 5.8 ^f |
| Inc.(O2)IMP2(F12*)/DZ ^e | (H ₂ O) ₁₆ | 768 | -678.7 | 288 | 213 | 1.8 ^g |
| Inc.(O3)IMP2(F12)/DZ ^e | (H ₂ O) ₁₆ | 768 | -679.6 | 248 | 1669 | 7.7 ^f |
| Inc.(O3)IMP2/(F12*)DZ ^e | (H ₂ O) ₁₆ | 768 | -678.6 | 256 | 919 | 4.0 |
| Inc.(O2)IMP2(F12)/TZ ^e | (H ₂ O) ₁₆ | 1424 | -685.4 | 248 | 878 | 22.9 ^f |
| Inc.(O2)IMP2(F12*)/TZ ^e | (H ₂ O) ₁₆ | 1424 | -684.3 | 260 | 534 | 6.6 ^g |
| Inc.(O3)IMP2(F12*)/TZ ^e | (H ₂ O) ₁₆ | 1424 | -683.4 | 260 | 2144 | 10.1 |
| Inc.(O2)IMP2(F12*)/QZ ^e | (H ₂ O) ₁₆ | 2480 | -682.6 | 256 | 1883 | 33.0 ^g |
| CCSD(T)/AVTZ ^{b,c} | (H ₂ O) ₁₇ | 1564 | -764.2 | | | |
| Inc.(O2)IMP2(F12)/TZ ^e | (H ₂ O) ₁₇ | 1513 | -729.4 | 272 | 1239 | 29.5 ^f |
| Inc.(O2)IMP2(F12*)/TZ ^e | (H ₂ O) ₁₇ | 1513 | -729.4 | 276 | 790 | 9.0 ^g |
| Inc.(O3)IMP2(F12*)/TZ ^e | (H ₂ O) ₁₇ | 1513 | -729.1 | 276 | 3429 | 14.5 |
| Inc.(O2)IMP2(F12*)/QZ ^e | (H ₂ O) ₁₇ | 2635 | -727.1 | 276 | 2555 | 35.9 ^g |

^aThe incrementally expanded CCSD(T)(F12*)IMP2 (Inc(Oi)IMP2(F12*)) energies are compared to conventional computations and to the results of the CCSD(T)(F12)IMP2 (Inc(Oi)IMP2(F12)) method applied in our previous work. The E_b of the explicitly correlated methods include the CABS singles correction to the Hartree-Fock energy.^{81,154,155} ^bCCSD(T) energy from ref 156; Performed on a supercomputer with 120000 cores. ^cAVTZ = aug-cc-pVTZ. ^dBates et al.,²⁷ local approximations. The MP2 contribution is rate determining. ^eXZ refers to the cc-pVXZ-F12 basis set of Peterson and co-workers.¹³⁴ ^fRef 116. ^gThe MP2-F12 calculation is the time determining step. The MP2-F12 calculation was performed on 12 cores and 90 GB RAM using the SMP parallel MP2-F12 in TURBOMOLE.

Table 10. Timing Analysis of the Proposed Scheme for Me₇Et-cyclobutane at the CCSD(T)(F12*)/cc-pVDZ-F12 Level^a

| calculation step | | time [%] |
|---------------------------|------------------------|---------------|
| integrals | | 45 |
| CCSD | | 35 |
| (T) | | 10 |
| MP2-F12 | | 2 |
| rest | | 12 |
| method | total [h] ^b | wall time [h] |
| standard | 707.6 | 176.9 |
| Inc.(O3)IMP2 ^c | 681.2 | 3.4 |

^aAt the double- ζ -level the dimension of the basis is 624. In the calculation, 13 occupied orbitals were frozen and 39 were active. ^bThe total time is computed from the wall time by multiplication by 4, since the computations were performed on 4 cores. ^c61 nodes were used.

with 2480 contracted AO basis functions. Since the errors from the incremental scheme are smaller than the errors due to the basis set, the total accuracy can be increased by the computation in a larger basis set. Using the proposed incremental method in combination with the cc-pVDZ-F12 basis set (768 contracted AO basis functions) we can compute the binding energy of (H₂O)₁₆ with 0.05% of the computational time used in ref 156. When using the corresponding quadruple- ζ basis set with 2480 functions, we need 0.5% of the time.

4.2. Me₇Et-cyclobutane. To illustrate the performance of our approach for a standard organic molecule, we use Me₇Et-cyclobutane in Figure 9 as an example. For the computation of such a molecule more CPU time is necessary compared to that for the water clusters because the computation of the third order correction is necessary to obtain the required accuracy. At the double- ζ level the total computational time of the standard method and the incremental method is basically equal (Table 10). However, the wall time of the incremental calculation is significantly smaller (3.4 h). Therefore the incremental scheme is an attractive tool for computational chemistry, if CCSD(T) energies are required as a benchmark. To illustrate the

computational cost of the different steps using the current setup we included a detailed timing analysis in Table 10. The computational time is currently determined by the integral and CCSD part of the calculation (80%).

Finally we note that using the incremental scheme the calculation in the cc-pVTZ-F12 basis set (1157 AOs) was still feasible on our hardware—the standard calculation was not. The CCSD(T)(F12*)/cc-pVTZ-F12 energy is -510,2817 hartree when including the CABS-singles correction and using $\gamma = 1.0 a_0^{-1}$.

The nice feature of the incremental scheme is the inherent parallelization which enables us to perform rather large coupled cluster calculations with small wall times. Therefore we conclude that the proposed approach is useful for the computation of high level CCSD(T) energies.

5. CONCLUSION

In this work we established optimal values for the truncation parameters applied in our implementation of the incremental scheme. These values were found by the statistical analysis of the absolute energies of 87 small- and medium-sized molecules. With this optimal truncation scheme it is possible to use our incremental scheme in a complete black-box manner, that is, there is no need for a manual adaption of a truncation parameter. The performance of the approach was analyzed for 51 reaction energies. The statistical errors as measured by mean = 0.07 kJ/mol, σ = 0.49 kJ/mol, mae = 0.33 kJ/mol, rmsd = 0.49 kJ/mol, and max = 1.45 kJ/mol are very small. Therefore we conclude that our scheme provides highly accurate results for relative energies which are a central quantity in computational chemistry.

■ ASSOCIATED CONTENT

Supporting Information

Reaction energies and the corresponding errors for all methods discussed in the text. Furthermore, the absolute energies of the incremental CCSD(T)(F12*) expansions. Finally, all coordinates of the molecular structures are included in atomic units.

This material 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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