

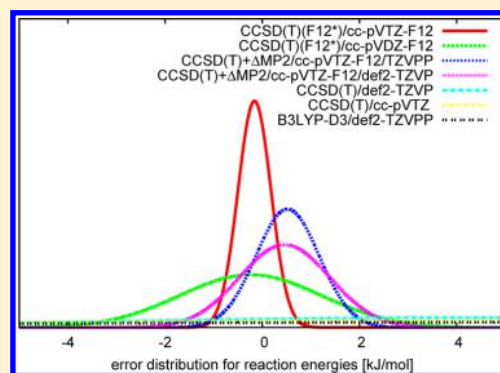
Efficient Calculation of Accurate Reaction Energies—Assessment of Different Models in Electronic Structure Theory

Joachim Friedrich*

Institute for Chemistry, Chemnitz University of Technology, Straße der Nationen 62, 09111 Chemnitz, Germany

Supporting Information

ABSTRACT: In this work we analyze the accuracy and the efficiency of different schemes to obtain the complete basis set limit for CCSD(T). It is found that composite schemes using an MP2 increment to reach the basis set limit provide high accuracy combined with high efficiency. In these composite schemes the MP2-F12/cc-pVTZ-F12 method is suitable to compute the MP2 contribution at the basis set limit. We propose to use the def2-TZVP or the TZVPP basis sets at the coupled cluster level in combination with the cc-pVTZ-F12 basis set at the MP2 level to compute reaction energies close to the basis set limit, if high accuracy methods like CCSD(T)(F12*) or 56-extrapolations are no longer feasible due to the computational effort. The standard deviation of CCSD(T)+ Δ MP2/cc-pVTZ-F12/def2-TZVP and CCSD(T)+ Δ MP2/cc-pVTZ-F12/TZVPP is found to be only 0.93 and 0.65 kJ/mol for a test set of 51 closed shell reactions. Furthermore, we provide a comprehensive list of different computational strategies to obtain CCSD(T) reaction energies with an efficiency and accuracy measure. Finally we analyze how different choices of the exponent in the correlation factor (γ) change the results when using explicitly correlated methods. The statistical results in this study are based on a set of 51 reaction energies in the range of 0.7 to 631.5 kJ/mol.



1. INTRODUCTION

When studying chemical reactions with computational chemistry tools it is frequently necessary to compromise between the accuracy of the computational method and the CPU-time, since high accuracy methods require huge computational resources. For systems with single reference character the coupled cluster singles doubles and perturbative triples method in combination with a large basis set provides the solution of the nonrelativistic electronic Schrödinger equation with sufficient accuracy. Due to the inherent accuracy, this method is part of high accuracy thermochemistry protocols like HEAT,^{1,2} the Wn-series,^{3–6} the correlation consistent composite approach,^{7–10} the FPD scheme,^{11–13} and the focal point method^{14–16} as well as the multicoefficient correlation methods.^{17–19} However, due to the computational demand, the CCSD(T) method is only applicable to small systems or to medium sized systems in rather small basis sets. For standard computational chemistry applications the method of choice is density functional theory which is significantly more efficient than wave function methods and gradients as well as Hessians are readily available. Due to the approximations in state of the art DFT methods one has to accept a larger error in the energy compared to CCSD(T) (for single reference systems). Therefore, CCSD(T) is frequently used as a benchmark method to compute the energy at the DFT geometry. For small systems it is frequently possible to obtain the desired values, but for larger systems it is not, due to the computational demand. To overcome the problem with the computational

resources, different approaches were proposed in the past: the scaling with the system size was reduced by the development of local correlation methods^{20–49} and the requirements on the one-particle basis set were reduced by means of explicit correlation,^{50–57} interference corrected CCSD(T),^{58,59} or composite schemes.^{60–63}

In the composite schemes the coupled cluster calculation is computed in a small basis set. The complete basis set limit (CBS) is reached by an increment from a computationally cheap method like MP2:^{60–67}

$$\begin{aligned} E(\text{CCSD(T)})_{\text{CBS}} &= E(\text{CCSD(T)})_{\text{SB}} \\ &\quad + [E(\text{MP2})_{\text{CBS}} - E(\text{MP2})_{\text{SB}}] \\ &= E(\text{CCSD(T)})_{\text{SB}} + \Delta\text{MP2} \end{aligned} \quad (1)$$

where CBS refers to the complete basis set limit and SB to a small basis set calculation. It is well-known that rather good accuracy is obtained when using a triple- ζ basis set as small basis set.^{16,68–72} We will later reference the energies of the composite method as CCSD(T) + Δ MP2/CBS/SB. For an accurate CBS extrapolation it is still necessary to compute the MP2 energy in a quintuple- ζ basis set, which becomes very time-consuming for large systems. Within the ccCA methodology Mahler and Wilson need more than 60% of the CPU-time for the MP2 step.¹⁰ When using these large basis sets also

Received: January 30, 2015

Published: July 20, 2015



the Hartree–Fock step becomes extremely time-consuming, since one has to deal with several thousand basis functions and the integral screening is not as powerful as in compact double- ζ basis sets. One can overcome this drawback by applying density-fitting in the Hartree–Fock part^{73–75} or by explicitly correlated MP2 (MP2-F12).^{53,76–78} A technical problem associated with these relatively new methods is the choice of the exponent of the correlation factor (γ). This parameter controls the correlation length of the electrons in the system, which might be different for core and valence electrons and significantly change the correlation energy.^{78,79} Furthermore, different values of γ are recommended for different basis sets,^{80,81} and the user does not know which one is a good choice, if mixed basis sets are required due to the availability of the basis sets for the elements in the system. Of course one can solve this by using a huge one-particle basis set and the variation of γ does not significantly affect the accuracy.⁸² This approach is only useful for small systems, since calculations in big basis sets become very demanding for larger systems. Therefore, one is usually forced to use smaller basis sets in computational chemistry applications, and one has to be aware of the potential error sources.

As a computational chemist, one has to face the problem that most applications do not fit into the available computer resources and one is forced to use a compromise between accuracy and applicability. One possibility is to use the previously mentioned local correlation methods. Another possibility is to reduce the basis set of the coupled cluster calculation.^{61,83} In composite schemes frequently a 2–3 extrapolation is used to obtain the MP2-CBS or one uses a double- ζ basis set to compute the CCSD(T) contribution. These values are then used as a benchmark to DFT energies, but the accuracy of the reference is not really clear. This is the starting point for this work, since we provide the errors for several of these strategies. These errors are very important for the interpretation of the results and to judge the quality of the calculation.

Furthermore, we investigate the effect of different choices of γ on the accuracy of 51 reaction energies.⁸⁴ These results are of high importance to evaluate the quality of the high level composite schemes using an MP2-F12 component to estimate the MP2-CBS, in combination with nonoptimal γ -values.^{6,10} Furthermore, we analyze the accuracy and the efficiency of the composite scheme in eq 1 using MP2-F12 in combination with different basis sets as estimate for the complete basis set limit. An interesting feature of such a composite approach is, that geometry optimizations would be readily possible, since MP2 and CCSD(T) gradients are available in several quantum chemistry codes and the gradient for MP2-F12 was recently proposed by Hoefener and Klopper.⁸⁵ Finally we note that the analysis of the errors is restricted to the solution of the electronic Schrödinger equation of single reference systems. For a comparison to experiment one needs to include other effects like the zero-point vibrational energy and depending on the desired accuracy solvent effects, thermal corrections to the enthalpy, the entropy, core correlation, etc. Furthermore, the analysis of this work is restricted to reaction energies and one should be careful when using the data in different situations.

2. COMPUTATIONAL DETAILS

The coupled cluster calculations were performed with a development version of the TURBOMOLE program package.^{50,52,77,86,87} In the explicitly correlated calculations we used

a Slater type correlation factor as proposed by Ten-no.⁸⁸ In TURBOMOLE the Slater type function is represented by a linear combination of six Gaussians.⁷⁸ Furthermore, we applied the cc-pVDZ-F12 and cc-pVTZ-F12 basis sets of Peterson^{80,81} using the corresponding CABS.⁸⁹ The basis sets were taken from the TURBOMOLE basis set library. In some calculations we applied the cc-pVD/TZ basis set of Dunning⁹⁰ in combination with the CBAS of Weigend.⁹¹ The explicitly correlated calculations with the cc-pVTZ basis set were performed with the CBAS to describe the CABS, which is not the optimal choice. For the aug-cc-pVD/TZ^{90,92} basis sets we used the CBAS optimized by Hättig⁹³ and Weigend⁹¹ as well as the CABS of Yousaf and Peterson.⁹⁴ This basis set combination is applied when using the YP-aug-cc-pVD/TZ basis set in TURBOMOLE 6.5.

In the explicitly correlated calculations we corrected the Hartree–Fock reference energy by the CABS-Singles correction proposed by Knizia and Werner.^{95,96} The details of the explicitly correlated MP2-F12,⁷⁷ CCSD(T)(F12), and CCSD(T)(F12*)^{50–52} are ansatz 2, approximation B,⁹⁷ and the fixed amplitude approach.⁷⁶ In all calculations the frozen core approximation was applied. The BP86/def2-TZVP^{98–101} geometries were taken from ref 84. The test set contains 51 reactions with isomerizations, hydrogenations, allylic shifts, and oxidations. The reaction energies in the test set vary from 0.7 to 631.5 kJ/mol.

The DLPNO-CCSD(T),^{38–44} B2PLYP,¹⁰² and the B2GP-PLYP¹⁰³ calculations were performed with the ORCA¹⁰⁴ quantum chemistry program.

One way to obtain highly accurate results is an extrapolation to the complete basis set limit. In this work, the CBS limit for the Hartree–Fock (HF) energy is calculated with the two-point extrapolation of Petersson and co-workers:¹⁰⁵

$$E_{\text{SCF}}^{XY} = \frac{e^{-a\sqrt{Y}}E^X - e^{-a\sqrt{X}}E^Y}{e^{-a\sqrt{Y}} - e^{-a\sqrt{X}}} \quad (2)$$

Where X and Y are the ζ -level and $Y = X + 1$. As recommended the value for the universal constant a is set to 6.30.¹⁰⁵

The CBS limit of the correlation energy is extrapolated with the expression from Helgaker and co-workers:¹⁰⁶

$$E_{\text{corr}}^{XY} = \frac{X^3 E_{\text{corr}}^X - Y^3 E_{\text{corr}}^Y}{X^3 - Y^3} \quad (3)$$

It was recently recognized that the perturbative triples contribution in explicitly correlated coupled cluster calculations is not sufficiently accurate.^{107,108} In order to improve the accuracy of the triples, we use the Schwenke type extrapolation for the triples:¹⁰⁸

$$E_{\text{(T)}}^{\text{CBS(23)}} = E_{\text{(T)}}^{\text{DZ-F12}} + F(E_{\text{(T)}}^{\text{TZ-F12}} - E_{\text{(T)}}^{\text{DZ-F12}}) \quad (4)$$

using $F = 1.431\,442$. Alternatively a fixed scaling factor of 1.0527 was used, as described by Peterson et al.⁸² The reference energy was calculated according to

$$E_{\text{ref}} = E_{\text{HF+CABS-S}}^{\text{QZ-F12}} + \delta E_{\text{MP2-F12}}^{\text{QZ-F12}} + \delta E_{\text{CCSD(F12*)}}^{\text{TZ-F12}} + E_{\text{(T)}}^{\text{CBS(23)}} \quad (5)$$

with

$$E_{\text{HF+CABS-S}} := \text{Hartree Fock including the CABS-singles contribution}$$

Table 1. Reaction Energies of the Test Set (kJ/mol)^a

no.	reaction	CCSD(T)(F12*) TZ-F12	ref
1	$\text{C}_6\text{H}_{12}\text{O} + 2\text{H}_2\text{O}_2 \rightarrow \text{ethyl-}\gamma\text{-butyrolactone} + 3\text{H}_2\text{O}$	-631.46	-630.98
2	$\text{C}_4\text{H}_9\text{NH}_2 + 3\text{H}_2\text{O}_2 \rightarrow \text{C}_4\text{H}_9\text{NO}_2 + 4\text{H}_2\text{O}$	-604.44	-604.10
3	$\text{C}_4\text{H}_9\text{CHO} + \text{H}_2\text{O}_2 \rightarrow \text{C}_4\text{H}_9\text{CO}_2\text{H} + \text{H}_2\text{O}$	-374.02	-373.83
4	$\text{C}_4\text{H}_9\text{SO}_2\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{C}_4\text{H}_9\text{SO}_3\text{H} + \text{H}_2\text{O}$	-345.93	-345.37
5	$\text{trans-2-pentene} + \text{H}_2\text{O}_2 \rightarrow \text{pentandiole}$	-328.70	-328.47
6	$\text{toluene} + 3\text{H}_2 \rightarrow \text{methylcyclohexane}$	-280.92	-280.16
7	$\text{pentanole} + \text{H}_2\text{O}_2 \rightarrow \text{C}_4\text{H}_9\text{CHO} + 2\text{H}_2\text{O}$	-267.53	-267.31
8	$(\text{C}_2\text{H}_5\text{O})_2 \rightarrow (\text{C}_2\text{H}_4\text{OH})_2$	-245.25	-244.89
9	$3\text{-hexene} + \text{H}_2\text{O}_2 \rightarrow \text{diethyloxirane} + \text{H}_2\text{O}$	-237.04	-236.99
10	$\text{S}(\text{C}_2\text{H}_5)_2 + \text{H}_2\text{O}_2 \rightarrow \text{OS}(\text{C}_2\text{H}_5)_2 + \text{H}_2\text{O}$	-221.39	-221.13
11	$\text{ax-methylcyclohexene} \rightarrow \text{eq-methylcyclohexene}$	-220.58	-220.06
12	$\text{hexyne} + \text{H}_2 \rightarrow 1\text{-hexene}$	-195.95	-195.49
13	$2\text{-pentyne} + \text{H}_2 \rightarrow \text{trans-2-pentene}$	-187.99	-187.52
14	$2\text{-pentyne} + \text{H}_2 \rightarrow \text{cis-2-pentene}$	-183.15	-182.72
15	$2\text{-pentyne} + \text{HCN} \rightarrow \text{C}_2\text{H}_5\text{CCNCHCH}_3$	-179.71	-179.47
16	$1\text{-hexene} + \text{H}_2 \rightarrow n\text{-hexane}$	-155.29	-155.15
17	$1\text{-pentyne} + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{CHO}$	-146.87	-146.16
18	$2\text{C}_3\text{H}_7\text{NH}_2 + \text{COCl}_2 \rightarrow \text{CO}(\text{NHC}_3\text{H}_7)_2 + 2\text{HCl}$	-136.33	-135.87
19	$\text{eq-methylcyclohexene} + \text{H}_2 \rightarrow \text{methylcyclohexane}$	-134.39	-134.31
20	$\text{trans-2-pentene} + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{CClCHCH}_3 + \text{HCl}$	-131.10	-130.64
21	$2\text{-pentyne} + \text{HCl} \rightarrow \text{C}_2\text{H}_5\text{CClCHCH}_3$	-125.37	-125.43
22	$1\text{-pentene} + \text{ethene} \rightarrow \text{heptene}$	-108.11	-108.11
23	$\text{C}_4\text{H}_9\text{CHO} + \text{H}_2 \rightarrow \text{pentanole}$	-98.13	-98.21
24	$\text{dimethyloxirane} + \text{H}_2\text{O} \rightarrow \text{butandiole}$	-94.14	-93.94
25	$\text{methylpyridine} + \text{H}_2 \rightarrow \text{dimethylpyrrole}$	-84.66	-84.79
26	$\text{C}_4\text{H}_9\text{NCO} + \text{NH}_3 \rightarrow \text{C}_4\text{H}_9\text{NHCONH}_2$	-82.48	-82.51
27	$\text{C}_3\text{H}_7\text{CN} + \text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_7\text{CONH}_2$	-81.02	-80.93
28	$\text{propylfuran} + \text{H}_2\text{S} \rightarrow \text{propylthiophene} + \text{H}_2\text{O}$	-80.91	-81.36
29	$\text{diethylamine} + \text{CO} \rightarrow \text{HCON}(\text{C}_2\text{H}_5)_2$	-72.11	-72.77
30	$\text{C}_3\text{H}_7\text{NCO} + \text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_7\text{NH}_2 + \text{CO}_2$	-71.53	-71.04
31	$\text{C}_3\text{H}_7\text{CO}_2\text{C}_2\text{H}_5 \rightarrow \text{ethyl-}\gamma\text{-butyrolactone}$	-67.59	-67.52
32	$\text{H}_2\text{C}-\text{C}_5-\text{CH}_2 \rightarrow \text{heptatriyne}$	-59.97	-59.82
33	$\text{methylpyrazole} \rightarrow \text{methylimidazole}$	-55.08	-54.98
34	$1\text{-pentene} + \text{H}_2\text{O} \rightarrow \text{pentanole}$	-49.03	-48.88
35	$\text{methylfuran} + \text{NH}_3 \rightarrow \text{methylpyrrole} + \text{H}_2\text{O}$	-44.62	-44.76
36	$\text{C}_3\text{H}_7\text{CHCO} + \text{H}_2\text{CO} \rightarrow \text{propyloxirane} + \text{CO}$	-39.44	-39.28
37	$\text{pentanole} + \text{CO} \rightarrow \text{HCO}_2\text{C}_5\text{H}_{11}$	-35.19	-35.69
38	$(\text{C}_3\text{H}_7\text{S})_2 + \text{H}_2 \rightarrow 2\text{C}_3\text{H}_7\text{SH}$	-29.12	-27.72
39	$\text{pentadiene} + \text{ethene} \rightarrow \text{ax-methylcyclohexene}$	-28.19	-27.81
40	$\text{hexandione} \rightarrow \text{methyl-}\delta\text{-valerolactone}$	-26.87	-26.99
41	$\text{C}_2\text{H}_5\text{CO}_2\text{H} + \text{methanole} \rightarrow \text{C}_2\text{H}_5\text{CO}_2\text{CH}_3 + \text{H}_2\text{O}$	-21.23	-21.40
42	$\text{C}_4\text{H}_9\text{ONO} \rightarrow \text{C}_4\text{H}_9\text{NO}_2$	-13.74	-13.60
43	$n\text{-hexane} \rightarrow \text{neo-hexane}$	-10.92	-11.06
44	$\text{methylcyclohexa-1,4-diene} \rightarrow \text{methylcyclohexa-1,3-diene}$	-10.30	-10.37
45	$1\text{-pentene} \rightarrow \text{trans-2-pentene}$	-8.83	-8.83
46	$\text{toluene} + \text{H}_2 \rightarrow \text{methylcyclohexa-1,3-diene}$	-6.57	-6.17
47	$\text{trans-2-pentene} \rightarrow \text{cis-2-pentene}$	-4.84	-4.80
48	$3\text{-methylpentane} \rightarrow \text{dimethylbutane}$	-3.53	-3.58
49	$\text{C}_2\text{H}_5\text{CO}_2\text{H} + \text{NH}_3 \rightarrow \text{C}_2\text{H}_5\text{CONH}_2 + \text{H}_2\text{O}$	-1.73	-1.82
50	$n\text{-nonane} \rightarrow \text{tetramethylpentane}$	-1.38	-1.70
51	$\text{C}_3\text{H}_7\text{CO}_2\text{H} + \text{NH}_3 \rightarrow \text{C}_3\text{H}_7\text{CONH}_2 + \text{H}_2\text{O}$	-0.69	-0.76

^aThe reference energies were obtained by eq 5 which includes the HF/cc-pVQZ-F12+CABS-singles contribution, the MP2/cc-pVQZ-F12 correlation energy, the CCSD(F12*)/cc-pVTZ-F12 increment, and the triples from a Schwenke-type extrapolation.

$$\delta E_{\text{MP2-F12}} := \text{MP2} - \text{F12/B correlation energy}$$

$$\delta E_{\text{CCSD(F12*)}} = E_{\text{CCSD(F12*)}} - E_{\text{MP2-F12}}$$

$$\delta E_{\text{(T)}}^{\text{CBS(23)}} = E_{\text{(T)}}^{\text{CBS(23)}} \quad \text{from eq 4}$$

The upper index indicates the basis set (XZ-F12: = cc-pVXZ-F12). The philosophy behind this scheme is to compute every component as accurate as possible. In order to perform the statistical analysis of the errors $\Delta_i = E_i^{\text{approx}} - E_i^{\text{ref}}$ introduced by different approximations to the CBS, we use the following statistical measures:

Table 2. Statistical Measures of the Errors in the Reaction Energies [kJ/mol] Relative to the HF/cc-pVQZ-F12+CABS-Singles (CABS-S)^{95,96,109}

basis	μ	σ	mae	rmsd	max	min	max abs error	range
CBS(34)/cc-pVXZ-F12 ^a	0.00	0.06	0.04	0.05	0.17	−0.11	0.17	0.28
cc-pVQZ-F12	0.02	0.10	0.05	0.10	0.49	−0.13	0.49	0.62
CABS-S/cc-pVTZ-F12	0.01	0.10	0.07	0.10	0.25	−0.20	0.25	0.45
CABS-S/aug-cc-pVTZ	−0.01	0.24	0.17	0.24	0.61	−0.84	0.84	1.45
cc-pVTZ-F12	0.18	0.64	0.38	0.66	3.15	−1.33	3.15	4.48
CABS-S/cc-pVDZ-F12	0.07	0.65	0.45	0.64	2.41	−1.40	2.41	3.81
aug-cc-pVTZ	0.24	1.57	0.97	1.57	7.06	−1.95	7.06	9.02
CABS-S/aug-cc-pVDZ	−0.39	1.71	1.22	1.74	4.26	−6.73	6.73	10.99
CABS-S/cc-pVTZ	0.41	4.00	2.71	3.98	13.54	−7.92	13.54	21.47
CBS(23)/cc-pVXZ ^b	1.66	5.18	2.83	5.39	23.49	−3.53	23.49	27.02
cc-pVDZ-F12	0.57	5.70	3.50	5.67	23.91	−11.79	23.91	35.70
cc-pVTZ	1.84	7.68	4.13	7.82	34.84	−6.66	34.84	41.50
aug-cc-pVDZ	−3.06	10.32	7.03	10.67	41.75	−29.86	41.75	71.61
cc-pVDZ	3.03	24.61	14.06	24.55	107.51	−29.00	107.51	136.51

^aEquation 2 using the cc-pVTZ-F12 and cc-pVQZ-F12 basis sets. ^bEquation 2 using the cc-pVDZ and cc-pVTZ basis sets.

Table 3. Statistical Measures Mean and Standard Deviation As Well As the Uncertainties in These Measures (kJ/mol)^a

method	μ	$\mu(\mu)$	$\sigma(\mu)$	σ	$\mu(\sigma)$	$\sigma(\sigma)$
$\mu_{\text{rand}} = -0.4; \sigma_{\text{rand}} = 0.4$						
CCSD(T)(F12*)/cc-pVTZ-F12	−0.09	−0.489	0.056	0.22	0.455	0.044
CCSD(T)(F12*)/aug-cc-pVTZ	−0.47	−0.866	0.056	0.85	0.936	0.054
MP2-F12/B/cc-pVQZ-F12	−5.27	−5.665	0.056	15.38	15.380	0.056
MP2-F12/B/cc-pVTZ-F12	−5.36	−5.755	0.056	15.27	15.275	0.056
ref		−0.399	0.056		0.398	0.040
$\mu_{\text{rand}} = -0.7; \sigma_{\text{rand}} = 3.1$						
CCSD(T)(F12*)/cc-pVTZ-F12	−0.09	−0.784	0.438	0.22	3.093	0.311
CCSD(T)(F12*)/aug-cc-pVTZ	−0.47	−1.162	0.438	0.85	3.199	0.320
MP2-F12/B/cc-pVQZ-F12	−5.27	−5.960	0.438	15.38	15.669	0.433
MP2-F12/B/cc-pVTZ-F12	−5.36	−6.050	0.438	15.27	15.565	0.433
ref		−0.694	0.438		3.084	0.310
$\mu_{\text{rand}} = -0.7; \sigma_{\text{rand}} = 2$						
CCSD(T)(F12*)/cc-pTZ-F12	−0.09	−0.786	0.282	0.22	2.002	0.201
CCSD(T)(F12*)/aug-cc-pVTZ	−0.47	−1.164	0.282	0.85	2.162	0.214
MP2-F12/B/cc-pVQZ-F12	−5.27	−5.962	0.282	15.38	15.496	0.281
MP2-F12/B/cc-pVTZ-F12	−5.36	−6.052	0.282	15.27	15.392	0.281
ref		−0.696	0.282		1.990	0.200

^aThe values for μ_{rand} and σ_{rand} define the Gaussian distribution of the random numbers. μ and σ are the mean and the standard deviation of the method with a single number as reference. $\mu(\mu)$ and $\sigma(\mu)$ are the mean of the mean as well as the standard deviation of the mean. $\mu(\sigma)$ and $\sigma(\sigma)$ are the mean standard deviation and the standard deviation of the standard deviation. The data is based on the 51 reaction energies in Table 1. If the reference carries a large error as modelled by σ_{rand} and μ_{rand} , we find that the investigated method has basically the same error distribution as the reference. Therefore it is not necessary to converge the basis set error much further than the intrinsic accuracy of CCSD(T).

mean deviation

$$\mu = \frac{1}{n} \sum_{i=1}^n \Delta_i$$

standard deviation

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

root mean square deviation

$$\text{rmsd} = \sqrt{\frac{1}{n} \sum_{i=1}^n \Delta_i^2}$$

mean absolute error

$$\text{mae} = \frac{1}{n} \sum_{i=1}^n |\Delta_i|$$

maximum deviation

$$\text{max} = \max_i \Delta_i$$

minimum deviation

$$\text{min} = \min_i \Delta_i$$

maximum absolute deviation

$$\text{max abs error} = \max_i |\Delta_i|$$

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

Table 4. Statistical Error Measures for the Reaction Energies (kJ/mol)^{a,c}

method	μ	σ	mae	rmsd	max	min	max abs error	range
ref/QZ-F12/TZ-F12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
eq 4	-0.09	0.22	0.16	0.24	0.38	-0.68	0.68	1.06
scaled(T)/CCSD(T)(F12*)/cc-pVTZ-F12	-0.07	0.29	0.21	0.29	0.48	-0.92	0.92	1.40
CCSD(T)(F12*)+ Δ MP2/cc-pVQZ-F12/cc-pVTZ-F12	-0.07	0.30	0.22	0.31	0.52	-0.86	0.86	1.38
CCSD(T)(F12*)/cc-pVTZ-F12	-0.16	0.34	0.28	0.38	0.66	-1.40	1.40	2.06
CCSD(T)+ Δ MP2,1.3/cc-pVTZ-F12/TZVPP	0.39	0.59	0.57	0.70	1.46	-0.89	1.46	2.36
CCSD(T)+ Δ MP2/cc-pVTZ-F12/TZVPP	0.52	0.65	0.69	0.83	1.91	-1.01	1.91	2.92
CCSD(T)+ Δ MP2/cc-pVQZ-F12/TZVPP	0.61	0.71	0.77	0.93	1.99	-1.08	1.99	3.07
CCSD(T)+ Δ MP2/aug-cc-pVTZ/TZVPP	0.27	0.74	0.60	0.78	1.84	-1.63	1.84	3.47
CCSD(T)(F12*)/aug-cc-pVTZ	-0.54	0.80	0.67	0.96	1.79	-4.39	4.39	6.18
CCSD(T)+ Δ MP2/cc-pVTZ-F12/cc-pVTZ	0.34	0.92	0.78	0.97	2.17	-1.93	2.17	4.10
CCSD(T)+ Δ MP2/cc-pVTZ-F12/def2-TZVP	0.46	0.93	0.73	1.03	3.22	-1.75	3.22	4.97
CCSD(T)+ Δ MP2,1.1/cc-pVDZ-F12/TZVPP	0.18	0.95	0.74	0.96	2.19	-2.25	2.25	4.44
CCSD(T)(F12*)+ Δ MP2/cc-pVTZ-F12/cc-pVDZ-F12	-0.34	1.00	0.72	1.05	2.19	-3.10	3.10	5.28
CCSD(T)(F12*)+ Δ MP2/cc-pVQZ-F12/cc-pVDZ-F12	-0.25	1.06	0.76	1.08	2.05	-3.26	3.26	5.31
CCSD(T)+ Δ MP2/cc-pVDZ-F12/TZVPP	0.59	1.09	0.90	1.23	4.00	-1.45	4.00	5.45
CCSD(T)+ Δ MP2/cc-pVDZ-F12/def2-TZVP	0.54	1.26	0.96	1.36	4.97	-2.08	4.97	7.05
CCSD(T)(F12*)/cc-pVDZ-F12	-0.24	1.46	1.05	1.47	3.48	-3.21	3.48	6.69
CCSD(T)(F12)/cc-pVDZ-F12	-0.26	1.46	1.06	1.47	3.53	-3.22	3.53	6.75
CCSD(T)+ Δ MP2/cc-pVTZ-F12/aug-cc-pVDZ	0.63	1.48	1.20	1.60	4.18	-2.61	4.18	6.79
CCSD(T)+ Δ /cc-pVDZ-F12/aug-cc-pVDZ	0.71	1.80	1.47	1.92	6.27	-2.91	6.27	9.18
CCSD(T)+ Δ MP2/aug-cc-pVTZ/cc-pVDZ	0.47	1.84	1.41	1.88	3.89	-5.87	5.87	9.77
CCSD(T)+ Δ MP2/cc-pVTZ-F12/cc-pVDZ	0.71	1.95	1.57	2.06	4.15	-5.90	5.90	10.05
CCSD(T)+ Δ /cc-pVDZ-F12/cc-pVDZ	0.79	2.18	1.73	2.29	6.23	-6.42	6.42	12.66
CCSD(T)+ Δ MP2/cc-pVDZ-F12/TZVP	0.55	2.18	1.65	2.23	5.74	-4.34	5.74	10.08
DLPNO-CC+ Δ MP2/cc-pVTZ-F12/SVP	1.16	2.19	1.94	2.46	5.76	-4.95	5.76	10.72
CCSD(T)+ Δ MP2/aug-cc-pVDZ/TZVPP	-0.56	2.19	1.67	2.24	4.52	-7.82	7.82	12.35
CCSD(T)+ Δ MP2/cc-pVQZ-F12/TZVP	0.97	2.23	1.83	2.41	5.95	-5.28	5.95	11.23
CCSD(T)+ Δ MP2/cc-pVTZ-F12/TZVP	0.88	2.23	1.78	2.38	6.01	-5.21	6.01	11.22
CCSD(T)+ Δ MP2/cc-pVTZ-F12/def2-SVP	0.97	2.27	1.89	2.44	7.28	-5.44	7.28	12.72
CCSD(T)+ Δ /cc-pVDZ-F12/TZVP	0.96	2.29	1.84	2.46	6.67	-5.50	6.67	12.16
CCSD(T)+ Δ /cc-pVDZ-F12/def2-SVP	1.05	2.30	1.95	2.51	6.95	-5.72	6.95	12.67
CCSD(T)(F12*)/aug-cc-pVDZ	-1.92	2.32	2.30	3.00	4.02	-11.26	11.26	15.28
DLPNO-CC+ Δ MP2/cc-pVTZ-F12/QZVPP	0.65	2.47	1.86	2.53	5.91	-8.55	8.55	14.46
CCSD(T)+ Δ MP2/aug-cc-pVDZ/cc-pVDZ	-0.37	2.52	1.92	2.52	4.47	-5.19	5.19	9.66
DLPNO-CC+ Δ MP2/cc-pVQZ-F12/QZVPP	0.74	2.52	1.93	2.61	5.77	-8.79	8.79	14.56
DLPNO-CC+ Δ MP2/cc-pVTZ-F12/TZVPP	1.18	2.56	2.16	2.79	7.09	-7.21	7.21	14.30
DLPNO-CC+ Δ MP2/cc-pVQZ-F12/TZVPP	1.27	2.62	2.22	2.89	7.02	-7.45	7.45	14.47
CCSD(T)+ Δ MP2/aug-cc-pVDZ/SV(P)	0.32	2.73	1.97	2.72	6.38	-6.90	6.90	13.28
CCSD(T)+ Δ MP2/aug-cc-pVTZ/SV(P)	1.16	2.81	2.21	3.01	11.37	-4.77	11.37	16.14
CCSD(T)+ Δ MP2/cc-pVTZ-F12/SV(P)	1.40	2.99	2.38	3.28	13.71	-5.12	13.71	18.82
CCSD(T)+ Δ /cc-pVDZ-F12/SV(P)	1.48	3.01	2.50	3.33	13.38	-5.40	13.38	18.78
CCSD(T)+ Δ MP2/cc-pVDZ/CBS(23)	1.60	3.23	2.50	3.58	12.79	-5.94	12.79	18.74
CCSD(T)/CBS(23)	1.07	3.26	2.15	3.40	10.76	-6.76	10.76	17.52
CCSD(T)+ Δ MP2/aug-cc-pVDZ/TZVP	-0.20	3.27	2.49	3.25	8.07	-5.99	8.07	14.06
DLPNO-CCSD(T)/QZVPP	-0.20	3.90	2.66	3.87	7.21	-14.60	14.60	21.81
CCSD(F12*)/cc-pVDZ-F12	-1.88	5.80	4.41	6.04	10.58	-18.41	18.41	28.99
CCSD(F12*)/aug-cc-pVTZ	-2.20	5.90	4.65	6.24	9.57	-21.59	21.59	31.16
CCSD(F12*)/cc-pVTZ-F12	-1.94	5.91	4.60	6.16	10.44	-19.08	19.08	29.52
B2GP-PLYP/def2-TZVPP	0.98	6.54	4.93	6.55	16.14	-19.68	19.68	35.82
CCSD(T)/def2-TZVP	4.39	7.78	6.29	8.86	25.68	-14.81	25.68	40.49
CCSD(T)/TZVPP	3.17	8.88	4.81	9.35	46.99	-9.25	46.99	56.24
DLPNO-CCSD(T)/TZVPP	2.89	9.42	5.47	9.76	45.29	-13.06	45.29	58.35
B2PLYP/def2-TZVPP	5.30	9.56	8.33	10.85	29.64	-32.07	32.07	61.71
PW6B95-D3/def2-TZVPP	1.97	9.83	7.19	9.93	29.46	-21.52	29.46	50.99
PW6B95-D3(bj)/def2-TZVPP	2.66	10.04	7.60	10.29	29.71	-20.72	29.71	50.43
CCSD(T)/cc-pVTZ	4.04	10.65	6.31	11.30	47.48	-10.07	47.48	57.55
PW6B95/def2-TZVPP	4.41	10.93	9.08	11.69	29.51	-27.20	29.51	56.71
MP2/cc-pVTZ	-1.72	10.94	7.92	10.97	20.70	-40.00	40.00	60.70
MP2/def2-TZVP	-1.50	12.48	9.19	12.44	28.56	-39.67	39.67	68.23
MP2/TZVPP ^c	-2.77	12.53	9.05	12.72	21.52	-42.65	42.65	64.17

Table 4. continued

method	μ	σ	mae	rmsd	max	min	max abs error	range
MP2/TZVPP ^d	-3.72	12.62	9.23	13.04	22.62	-45.49	45.49	68.10
MP2/CBS(23)	-4.54	12.92	10.07	13.57	21.20	-44.71	44.71	65.91
B3LYP-D3/def2-QZVPP	6.53	13.70	11.17	15.05	35.52	-45.28	45.28	80.80
B3LYP-D3/def2-TZVPP	6.79	14.36	11.74	15.76	36.06	-44.00	44.00	80.06
MP2-F12,1.1/aug-cc-pVDZ	-6.50	14.39	11.11	15.66	26.46	-55.78	55.78	82.24
PBE0/def2-TZVPP	-2.00	14.67	11.20	14.67	32.19	-35.75	35.75	67.94
MP2/QZVPP	-6.27	14.73	11.45	15.88	24.02	-56.20	56.20	80.22
MP2-F12,1.2/aug-cc-pVTZ	-5.67	15.24	11.59	16.12	23.77	-56.45	56.45	80.22
MP2-F12/B/cc-pVTZ-F12	-5.43	15.30	11.49	16.09	22.18	-56.53	56.53	78.71
MP2-F12/B/cc-pVDZ-F12	-5.35	15.32	11.39	16.09	21.82	-56.66	56.66	78.48
PBE0-D3/def2-TZVPP	-5.22	15.75	12.47	16.44	32.17	-40.43	40.43	72.60
PBE0-D3(bj)/def2-TZVPP	-5.12	15.94	12.49	16.59	32.52	-41.64	41.64	74.16
MP2/TZVP	1.25	17.34	10.59	17.22	73.31	-43.45	73.31	116.76
B3LYP/def2-QZVPP	11.75	18.55	16.61	21.80	58.29	-66.85	66.85	125.14
B3LYP/def2-TZVPP	12.01	18.70	17.07	22.07	56.36	-65.57	65.57	121.93
TPSSH-D3/def2-TZVPP	7.01	18.81	14.52	19.90	58.16	-35.71	58.16	93.88
TPSSH/def2-TZVPP	11.22	19.72	17.46	22.52	57.01	-33.63	57.01	90.64
TPSSH-D3(bj)/def2-TZVPP	5.78	19.90	14.84	20.54	57.62	-40.88	57.62	98.50
CCSD(T)/TZVP	7.56	19.99	11.26	21.18	107.19	-13.78	107.19	120.97
MP2/def2-SVP	-3.71	20.30	14.20	20.44	73.06	-44.17	73.06	117.23
MP2/aug-cc-pVDZ	-5.65	20.60	13.79	21.17	82.48	-64.64	82.48	147.13
CCSD(T)/aug-cc-pVDZ	0.41	20.82	10.57	20.62	113.45	-28.41	113.45	141.87
MP2/cc-pVDZ	2.12	22.69	12.85	22.57	95.94	-38.93	95.94	134.87
CCSD(T)/SVP	2.69	24.25	14.11	24.16	98.46	-42.16	98.46	140.62
DLPNO-CCSD(T)/SVP	2.73	24.43	14.41	24.35	98.44	-40.16	98.44	138.60
MP2/SV(P)	3.48	27.99	20.57	27.93	77.07	-74.26	77.07	151.33
CCSD(T)/cc-pVDZ	8.26	28.18	16.71	29.09	124.43	-42.88	124.43	167.31
CCSD(T)/SV(P)	10.30	32.78	22.20	34.05	102.35	-80.25	102.35	182.60

^aErrors computed relative to eq 5. The composite methods using MP2-F12 show a relatively good accuracy with respect to the reference. The energies of eq 1 are referred as CCSD(T)+ Δ MP2/CBS/SB. If -F12 basis sets are used, we applied MP2-F12 to compute the CBS value. The data is sorted according to an increasing σ . ^bExtrapolation from the cc-pVDZ and cc-pVTZ basis set; cf. eqs 2 and 3. ^cCalculated with TURBOMOLE (default options). ^dCalculated with ORCA (default options). The result is qualitatively equivalent to TURBOMOLE.

3. RESULTS

In this work we use the test set optimized in ref 84. to analyze the performance of different strategies to obtain reaction energies close to the CCSD(T) basis set limit with respect to accuracy and computational effort. We analyze the accuracy of the different computational schemes with respect to the reference in eq 5. The CCSD(T)(F12*)/cc-pVTZ-F12 level of theory provides already high accuracy⁵² and the cc-pVTZ-F12 basis set is the best we could afford on our hardware at the coupled cluster level. However, we use eq 5 to correct for the basis set effects in the Hartree–Fock, the MP2, and the triples in the smaller triple- ζ basis set. This is in a focal point sense^{14–16} accurate to the CCSD-level including a good estimate for the perturbative triples contribution. In Table 1 we collected the CCSD(T)(F12*) data obtained in our previous work⁸⁴ and the new reference values using eq 5. Please note that the reaction energies are very similar indicating the high accuracy obtainable by the CCSD(T)(F12*) method from Hättig et al.⁵²

3.1. Hartree–Fock Contribution to the Reaction Energies. Table 2 presents the statistical measures for the errors in the Hartree–Fock reaction energies using different basis sets. The reaction energies at the HF/cc-pVQZ-F12+CABS-singles^{95,96,109} level of theory were chosen as a reference. The reaction energies as well as the corresponding errors are given in the Supporting Information. Considering the small cc-pVDZ, cc-pVTZ, and aug-cc-pVDZ basis sets, the basis

set errors are huge as expected. These values are included to illustrate the errors when using too small basis sets. Usually it is desired to achieve chemical accuracy of 4.18 kJ/mol. In this work we define chemical accuracy by means of the 99.7% confidence interval of a Gaussian distributed error, i.e. the error interval of $\mu \pm 3\sigma$ kJ/mol has to be within the interval ± 2.09 kJ/mol. Based on this consideration, we find the condition for chemical accuracy: $|\mu \pm 3\sigma| < 2.09$ kJ/mol. Therefore, it is necessary to use at least the cc-pVDZ-F12 basis set and the CABS-singles correction, if one attempts to obtain chemical accuracy. The quality of this calculation is similar to the cc-pVTZ-F12 calculation without CABS-singles. Considering the CABS-singles correction for the cc-pVTZ-F12 basis set one obtains results of cc-pVQZ-F12 quality. Based on the test set it is evident, that the CABS-singles correction improves the HF-reaction energies by one ζ -level. Finally we note that the CBS(34) and the HF/cc-pVQZ-F12+CABS-singles results agree very well. Therefore, it is evident that the HF/cc-pVQZ-F12+CABS-singles is a suitable reference to analyze the results.

3.2. Error Estimate for the Reference. Considering the basis set convergence of CCSD(T)(F12*) for reaction energies in ref 52, it is found that the error in the cc-pVXZ-F12 basis sets is reduced by a factor of 4, when increasing the cardinal number X . Using the DZ-TZ-difference and scaling it by 1/4, we find a standard deviation of 0.15 kJ/mol and a mean of -0.4 kJ/mol. As a second estimate for the error in the triples contribution we use the difference of the CCSD(T)(F12*)/cc-pVTZ-F12 and

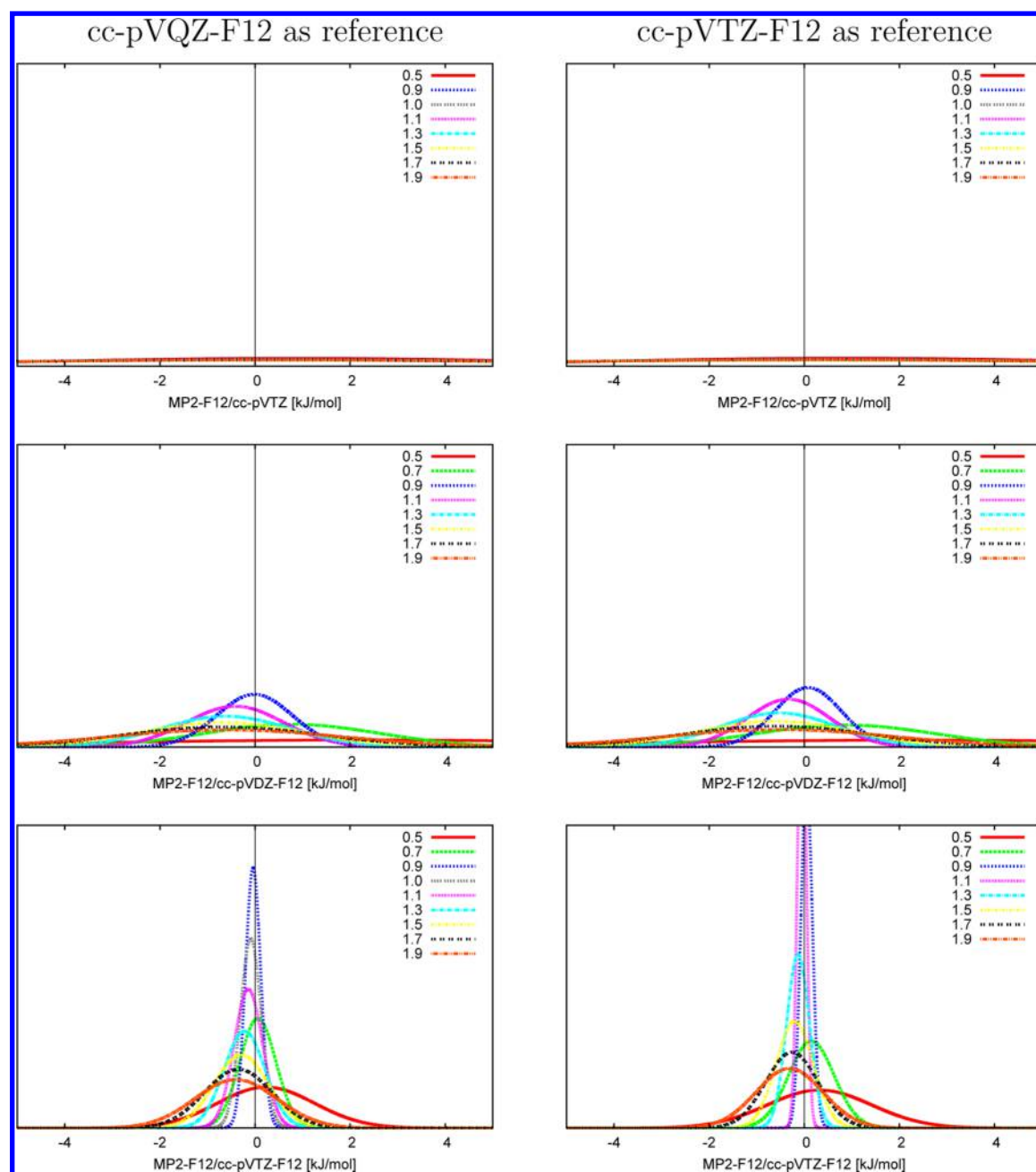


Figure 1. γ -Dependence on the accuracy of MP2-F12 using different basis sets. The errors relative to the MP2-F12/cc-pVQZ-F12 reaction energies using the recommended γ of $1.1a_0^{-1}$ are on the left-hand side. On the right-hand side the errors are computed relative to the MP2-F12/cc-pVTZ-F12 energy, using the recommended γ of $1.0a_0^{-1}$. Since the shape of the Gaussians on the left and on the right is very similar, the cc-pVTZ-F12 calculations are suitable reference values. The Gaussians on the left are broader, because they include the basis set difference from TZ to QZ.

the aug-cc-pVTZ energies. In this case we find a standard deviation of 0.20 kJ/mol and a mean of -0.12 kJ/mol. As a third estimate for the error we used the constant scaling-factor for the triples (1.0527).⁸² Comparing the unscaled with the scaled triples contributions we find a standard deviation of 0.33 kJ/mol and a mean error of -0.07 kJ/mol for the triples contribution in the CCSD(T)(F12*)/cc-pVTZ-F12 calculations.

In order to investigate the effect of this uncertainty on the accuracy of the statistical measures we computed the statistical measures for the standard deviation $\sigma(\sigma)$ and $\mu(\sigma)$ as well as for the mean $\sigma(\mu)$ and $\mu(\mu)$. The data was based on reference energies from eq 5 and 10 000 different sets with Gaussian

distributed random numbers. Using the considerations above and adding a tolerance, the standard deviation for the random numbers was set to 0.4 kJ/mol and the mean to -0.4 kJ/mol. The results are collected in Table 3.

As a second source for the uncertainties in CCSD(T) calculations we use the standard deviation and the mean from the book of Helgaker et al.¹¹⁰ ($\mu = -0.7$ kJ/mol; $\sigma = 3.1$ kJ/mol) which were obtained by a comparison to experimental reaction enthalpies. In the third data set, we insert the errors obtained from the variation of the parameter γ using a double ζ -F12 basis set (vide infra). Considering the entries based on this data, we see, that the choice of γ affects the total accuracy. Therefore, one should carefully look at the results and consider

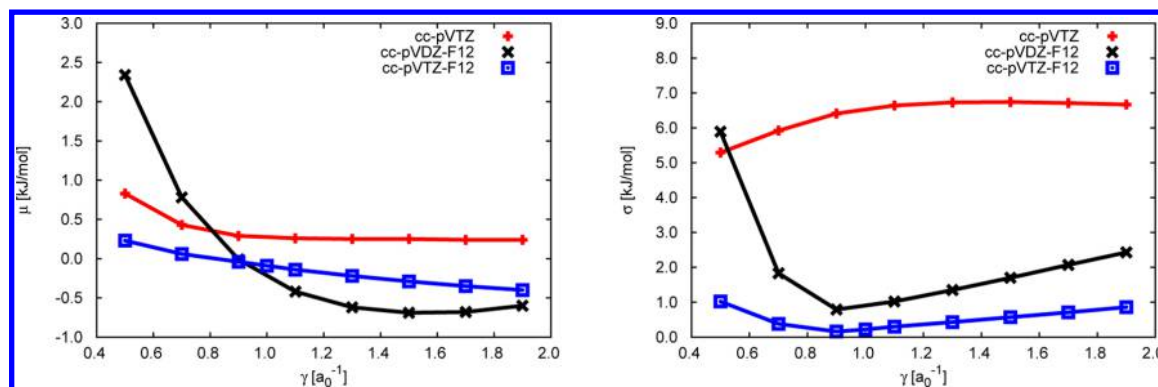


Figure 2. γ -Dependence on the accuracy of MP2-F12 using different basis sets. The errors are relative to the MP2-F12/cc-pVQZ-F12 reaction energies using the recommended γ of $1.1a_0^{-1}$. The standard deviation is rather large in the cc-pVTZ basis set. In this case the HF contribution is responsible for a large part of the error ($\sigma = 4$ kJ/mol see Table 2).

the accuracy required by the application, when using small (efficient) basis sets in the F12-part.

Considering the results of Table 3, it is evident, that the standard deviation is a suitable measure for the validation of the reference. If the standard deviation of the approximate method is significantly larger than the one of the reference, there is no reason to worry—in this case the reference will be suitable. If the standard deviations of both are too close, it is likely that a large part of the error is due to the uncertainty of the reference. When considering the ranking of different methods using the standard deviation, one should keep in mind that the error in the reference is limiting the significance, i.e. at least methods within the range of one standard deviation should be regarded as equally accurate. Furthermore, one should keep in mind that at some point the intrinsic accuracy of the method is the limiting factor and, therefore, a further increase of the basis set does not provide higher accuracy. Considering the last block of Table 3 it is clear that the errors due to the variation of γ are visible for cc-pVDZ-F12, but they are smaller than the intrinsic accuracy of the CCSD(T)/CBS (second block). Therefore, one should not overemphasize this error.

3.3. CCSD(T) Reaction Energies. When using quantum chemical methods to investigate chemical reactions it is very important to know the general accuracy of the computational model. It is well-known that CCSD(T) is a benchmark method which provides very high accuracy when combined with an appropriate basis set (for single reference systems). Since the system of interest is in most cases too large to be computed in a large basis set, it is important to have a detailed knowledge of the accuracy provided by a small basis set calculation. One should also keep in mind that a CCSD(T) or a MP2 calculation using a too small basis set cannot be regarded as benchmark for a DFT calculation, if the standard deviation is larger for the wave function method than the σ of the DFT method, due to the too small basis set. In Table 4 we collected the statistical data for the reaction energies. We choose the reaction energies of eq 5 as a benchmark, since these values should be close to the CCSD(T) basis set limit. Considering the CCSD(T)-(F12*)/cc-pVTZ-F12 energies we find a standard deviation of only 0.34 kJ/mol which is a significantly higher accuracy than the intrinsic accuracy of the CCSD(T) method itself (3.1 kJ/mol). Therefore, we conclude that CCSD(T)(F12*) provides high accuracy for the reactions in our test set. This observation is in agreement with previous findings of Hättig et al.⁵² In the Supporting Information we give all reaction energies explicitly as well as the errors relative to the eq 5. We also included the

errors relative to CCSD(T)(F12*)/cc-pVTZ-F12, since this method should also be accurate.

The results in Table 4 are sorted according to an increasing σ . Since σ is an appropriate measure for the accuracy of the method and a small value of σ corresponds to high accuracy, the methods are listed with decreasing accuracy. Please note that σ is also a suitable measure for the minimum and maximum errors since it is connected to the probability of an error of a given size. When assuming a Gaussian distribution of the errors the 99.7% confidence interval is $\mu \pm 3\sigma$. Using this value is much better than max, min, or range, since these measures represent a single or in case of the range two values of the test set, whereas the standard deviation is computed from the whole test set. When considering the results in Table 4, it is quite notable that many of the composite schemes are at the top, indicating the high accuracy obtainable with eq 1, when using the CCSD(T)(F12*)/cc-pVTZ-F12 calculation as reference.

Considering the accuracy of a small basis set calculation for MP2 or CCSD(T) the values of σ are very large indicating very low accuracy. Please note that the standard deviation of MP2 and CCSD(T) in the applied double- ζ basis sets is above 20 kJ/mol. This standard deviation is higher than the one of modern DFT methods. For instance the σ of B3LYP-D3 is only 14 kJ/mol, which is on average more accurate than MP2 or CCSD(T) in a too small basis set. Therefore, a MP2 or a CCSD(T) calculation in a double- ζ basis set cannot be used to benchmark DFT.

Considering the PW6B95-D3/def2-TZVPP results, we find a remarkable accuracy with a standard deviation of only 9.83 kJ/mol, which is comparable to the result of a CCSD(T) calculation in a triple- ζ basis set (σ :def2-TZVP = 7.78, cc-pVTZ = 10.65, TZVP = 19.99 kJ/mol). Even better accuracy can be obtained by the B2GP-PLYP/def2-TZVPP method of Martin et al.¹⁰³ with a σ of only 6.54 kJ/mol. Therefore, it is clear, that B2GP-PLYP/def2-TZVPP has an excellent accuracy to computational cost ratio and is a good choice, if coupled cluster is infeasible. For larger systems the PW6B95-D3/def2-TZVPP is a very good choice, since it is computationally less demanding than the double hybrid B2GP-PLYP.

If a MP2-F12 based Δ MP2-increment is used to compensate for the error of the basis set, the accuracy improves significantly. When using a double- ζ basis set in the CCSD(T) part, one can obtain a σ of 1.48–3.01 kJ/mol, which is already quite good. If higher accuracy is desired, one has to increase the basis set to triple- ζ -quality at the coupled cluster level. In this case one can

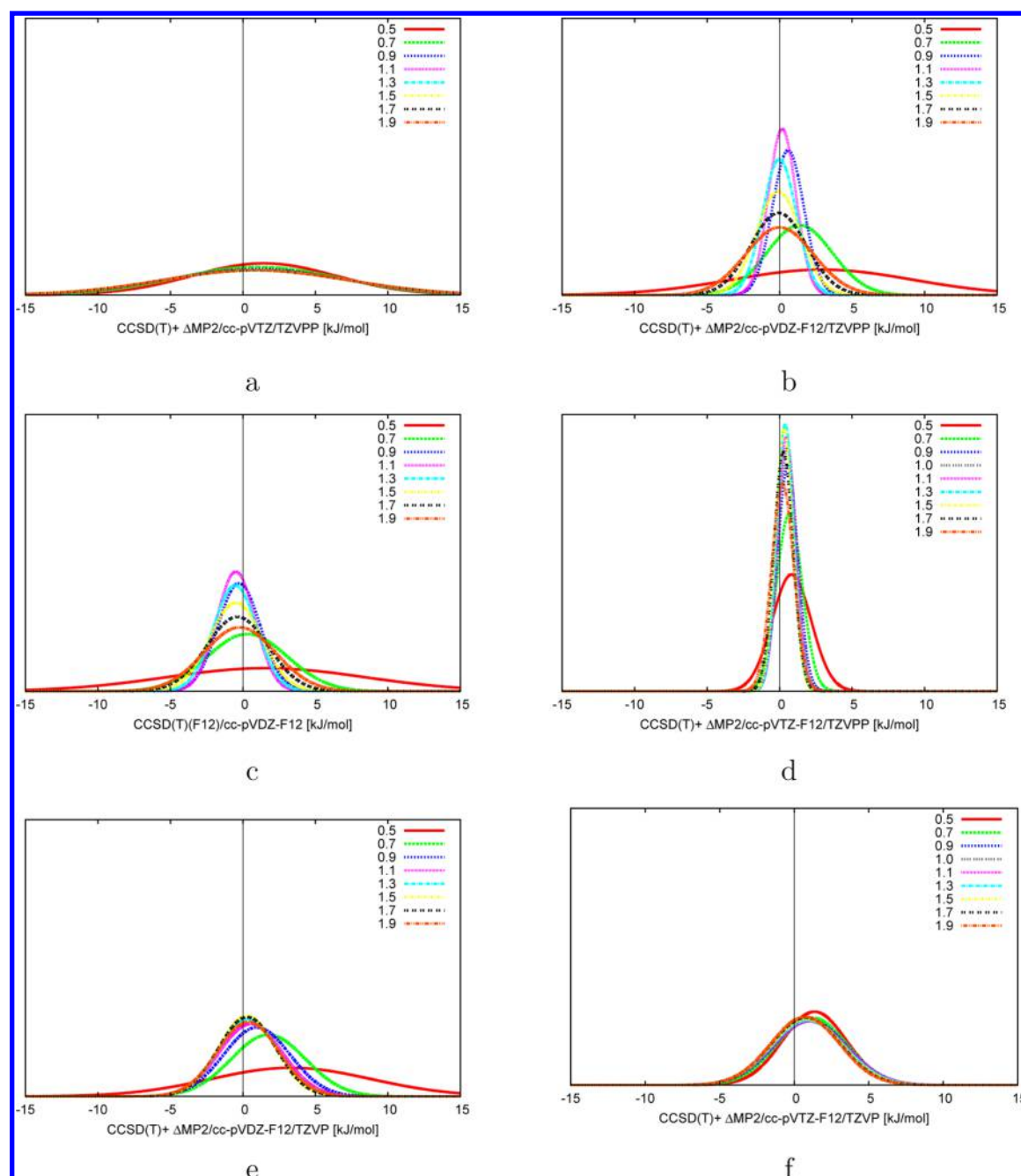


Figure 3. γ -Dependence of the accuracy for different computational schemes including explicitly correlated CCSD(T). In the composite schemes MP2-F12 is used to approach the CBS-limit. The energies of eq 1 are referred as CCSD(T)+ Δ MP2/CBS/SB. If -F12 basis sets are used, we applied MP2-F12 to compute the CBS value. γ is given in a_0^{-1} .

obtain very high accuracy, as σ is only 0.65 kJ/mol for the CCSD(T)+ Δ MP2/cc-pVTZ-F12/TZVPP method. Using the cc-pVQZ-F12 basis set to compute the MP2 increment, the result is slightly worse ($\sigma = 0.71$ kJ/mol). One should not over interpret this finding, since the reference energy carries an error, which is most likely larger than the small increase in the standard deviation. Furthermore, the variation of the parameter γ leads to changes of this size, cf. the standard deviation of CCSD(T)+ Δ MP2/cc-pVTZ-F12/TZVPP with $\gamma = 1.3a_0^{-1}$ is 0.59 kJ/mol. From the point of accuracy we can conclude that the MP2 basis set increment significantly improves the accuracy of a coupled cluster calculation in medium sized basis sets. The total accuracy is comparable to an explicitly correlated

CCSD(T) calculation. When using the two-point extrapolation technique at the Hartree–Fock and the coupled cluster level eqs 2 and 3, the accuracy is significantly improved compared to the normal coupled cluster energy calculation. However, the composite scheme using eq 1 provides higher accuracy. Considering the CCSD(T)+ Δ MP2/CBS(23)/cc-pVDZ method, we find once again that it is more accurate to compute the MP2 basis set increment from F12 theory and to include the CABS-singles in the HF contribution.

3.4. Variation of γ . When using explicitly correlated electronic structure methods it is very important to use an appropriate basis set. A very good choice of the basis set is to use one of the optimized F12-basis sets as proposed by

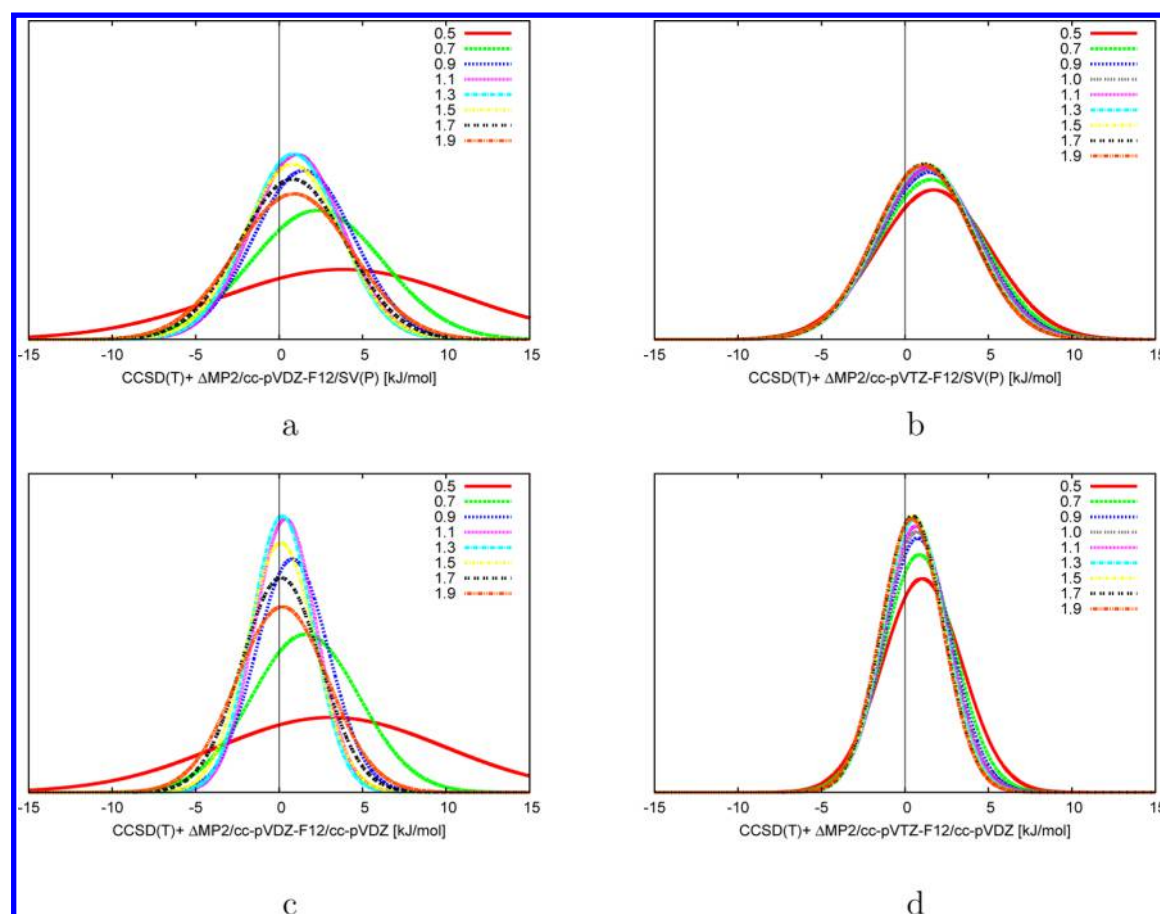


Figure 4. γ -Dependence of the accuracy of CCSD(T)+ Δ MP2/CBS/SB using different basis set combinations. γ is given in a_0^{-1} . The results become more robust with respect to changes in γ , when using the larger cc-pVTZ-F12 basis set.

Peterson.^{80,81} For these basis sets the optimal value of the parameter γ is different. Furthermore, the correlation range is different for core and valence electrons, and one needs different values of γ for these types of electrons in the same calculation, if core–valence correlation is required for an application. Since the accuracy of the results depends on the value of γ ,^{78–80} one should carefully check how a nonoptimal choice affects the results of the calculation. For instance, the increase of γ from the optimal value to $1.4a_0^{-1}$ may increase the error by a factor of 5, when considering the absolute energy in a given basis set.¹⁰⁸ In a recent work Hill and Peterson report that the choice of γ is of crucial importance when correlating d-electrons.¹¹¹

In the context of the ccCA-method it is very attractive to use explicitly correlated MP2 to estimate the basis set limit of MP2. In the timing analysis Mahler and Wilson show, that the computation of the MP2 energy in the quadruple- ζ basis set needs 61% of the overall computer time.¹⁰ Therefore, they propose to use MP2-F12 as a component for the MP2-CBS in the ccCA-method.

On the basis of these considerations, it is evident, that the explicit correlation technique is of very high importance for computational chemistry applications. We analyze the effect of the different γ on the reaction energies in this work by statistical measures. Using this data, a computational chemist will be able to estimate the error in a given application, if he is forced to use a nonoptimal γ .

3.4.1. MP2. The dependence of the accuracy on the parameter γ is shown in Figure 1 for MP2-F12 using different basis sets. On the left-hand side the errors are calculated with

respect to the MP2-F12/cc-pVQZ-F12 values. On the right-hand side the errors are computed with respect to the cc-pVTZ-F12 values. It is notable that the Gaussians in the last plot at the right-hand side are more sharply peaked than the corresponding ones on the left. The reason for this is that the variation of γ is performed with the same basis set as the reference, which leads to higher accuracy. Therefore, one should be careful with such investigations in general, since they will only measure a single contribution of the total error. The complete basis set limit as the reference point is a much better choice, but usually too demanding, as in the case of coupled cluster.

Comparing the right and the left-hand side of Figure 1 we see that the shape of the Gaussian functions is very similar. Therefore, we conclude that the cc-pVTZ-F12 values are a suitable reference. The biggest difference is found, when comparing the last two plots in Figure 1, since the basis set effect is the largest in this case. In the interval from $\gamma = 0.9a_0^{-1}$ to $1.5a_0^{-1}$, the largest difference of the standard deviation for the cc-pVTZ-F12 and the cc-pVQZ-F12 calculations is 0.2 kJ/mol. Therefore, the basis set effect in the reference is estimated to 0.2 kJ/mol for the standard deviation.

Figure 2 shows the γ -dependence of the mean error (left) and the standard deviation (right) for the 51 reaction energies of the test set. The γ -dependence of μ is relatively small for the applied triple- ζ basis sets. In the double- ζ -F12 basis set the γ -dependence is somewhat larger for small values of γ (0.5 – $0.7a_0^{-1}$). For larger values the absolute value of the mean error is less than 0.7 kJ/mol. When considering the standard

Table 5. Timing and Accuracy of Different Coupled Cluster Schemes^a

model	time [h]	rel. time	ave. nbf	μ kJ/mol	σ kJ/mol
B3LYP-D3/def2-TZVPP	3.7	1.0	291	6.79	14.36
B3LYP/def2-TZVPP	3.7	1.0	291	12.01	18.70
TPSSH-D3/def2-TZVPP	4.0	1.1	291	7.01	18.81
PW6B95-D3/def2-TZVPP	4.2	1.1	291	1.97	9.83
CCSD(T)/SV(P)	7.0	1.9	95	10.30	32.78
B2GP-PLYP/def2-TZVPP	9.8	2.7	289	0.98	6.54
CCSD(T)/def2-SVP	15.2	4.1	120	2.69	24.25
CCSD(T)/cc-pVDZ	16.6	4.5	120	8.26	28.18
CCSD(T)+ Δ MP2/cc-pVDZ-F12/SV(P)	23.5	6.4	95/244	1.48	3.01
CCSD(T)+ Δ MP2/cc-pVDZ-F12/def2-SVP	31.8	8.6	120/244	1.05	2.30
CCSD(T)+ Δ MP2/cc-pVDZ-F12/cc-pVDZ	33.1	9.0	120/244	0.79	2.18
B3LYP-D3/def2-QZVPP	35.5	9.7	570	13.70	11.17
B3LYP/def2-QZVPP	35.5	9.7	570	11.75	18.55
CCSD(T)/TZVP	43.7	11.9	156	7.56	19.99
CCSD(T)+ Δ MP2/cc-pVDZ-F12/TZVP	60.2	16.4	156/244	0.59	1.09
CCSD(T)+ Δ MP2/cc-pVTZ-F12/SV(P)	82.5	22.4	95/447	1.40	2.99
CCSD(T)+ Δ MP2/cc-pVTZ-F12/def2-SVP	90.7	24.7	120/447	0.97	2.27
CCSD(T)+ Δ MP2/cc-pVTZ-F12/cc-pVDZ	92.0	25.0	120/447	0.71	1.95
CCSD(T)+ Δ MP2/cc-pVTZ-F12/TZVP	119.2	32.4	156/447	0.88	2.23
CCSD(T)/aug-cc-pVDZ	134.8	36.7	204	0.41	20.82
CCSD(T)+ Δ MP2/cc-pVDZ-F12/aug-cc-pVDZ	151.3	41.2	204/244	0.71	1.80
CCSD(T)/def2-TZVP	173.0	47.1	223	4.39	7.78
CCSD(T)(F12*)/aug-cc-pVDZ	184.3	50.1	205	-1.92	2.32
CCSD(T)+ Δ MP2/cc-pVDZ-F12/def2-TZVP	189.5	51.6	223/244	0.54	1.26
CCSD(T)+ Δ MP2/cc-pVTZ-F12/aug-cc-pVDZ	210.3	57.2	204/447	0.63	1.48
CCSD(T)+ Δ MP2/cc-pVTZ-F12/def2-TZVP	248.5	67.6	223/447	0.46	0.93
CCSD(T)(F12*)/cc-pVDZ-F12	317.9	86.5	244	-0.24	1.46
CCSD(T)/cc-pVTZ	410.0	111.5	285	4.04	10.65
CCSD(T)/CBS(23)	426.6	116.0	120/285	1.07	3.26
CCSD(T)/TZVPP	450.4	122.5	290	3.17	8.88
CCSD(T)+ Δ MP2/cc-pVDZ-F12/TZVPP	466.9	127.0	290/244	0.59	1.09
CCSD(T)+ Δ MP2/cc-pVTZ-F12/cc-pVTZ	485.4	132.0	285/447	0.34	0.92
CCSD(T)+ Δ MP2/cc-pVTZ-F12/TZVPP	525.9	143.0	290/447	0.52	0.65
CCSD(T)(F12*)/cc-pVTZ-F12	3145.2	855.5	447	-0.16	0.34
CCSD(T)(F12*)/aug-cc-pVTZ	3300.3	897.7	450	-0.54	0.80

^aThe timing is based on the sum of the CPU-times of all molecules in the test set except 2,3-methylpentane. This molecule was excluded, because the CCSD(T)(F12*)/aug-cc-pVTZ calculation could not be performed on our standard cluster nodes. The energies of eq 1 are referred to as CCSD(T)+ Δ MP2/CBS/SB. If -F12 basis sets are used, we applied MP2-F12 to compute the CBS value. Please note that the data is only valid for single reference systems.

deviation we find the γ -dependence below 1 kJ/mol, if a triple- ζ basis set is used and below 2 kJ/mol for the cc-pVDZ-F12 basis set, when choosing γ between 0.9 and $1.5a_0^{-1}$. Therefore, we conclude that high accuracy can be obtained in these basis sets, if the exponent of the correlation factor is chosen properly.

Since the standard deviation is relatively independent of the choice of γ in the cc-pVTZ-F12 basis set, we recommend to use this larger basis set in critical cases.

3.4.2. Coupled Cluster. In Figure 3 we present the influence of γ on the accuracy in different models to obtain accurate CCSD(T)/CBS values. The shape of the Gaussian shows the accuracy of the calculations. A broad distribution shows low accuracy and a sharp distribution with a maximum close to 0 kJ/mol indicates high accuracy. In Figure 3a we have a set of relatively broad Gaussians. Since all functions are nearly on top of each other, the choice of γ has no effect on the total accuracy. The reason for this is that the cc-pVTZ basis set is not optimal to represent the MP2-F12-CBS. In this basis set the HF-part using the CABS-singles correction has already a significant error $\sigma = 4$ kJ/mol. When using optimal F12-basis sets, the shape

becomes more sharp as in b and d. Here the effect of γ becomes clearly visible. If the value is too small the results are affected. When using $\gamma = 0.9a_0^{-1}$, the accuracy becomes good. Choosing γ in the range of $\gamma = 0.9a_0^{-1}$ to $1.5a_0^{-1}$ the shape of the Gaussians is similar and therefore the accuracy too. This can be seen in Figure 3b–d. On the basis of this we conclude that the choice of γ is not critical in the typical correlation ranges from $\gamma = 0.9a_0^{-1}$ to $1.5a_0^{-1}$. For atoms which are not in our test set we suggest to use the optimal γ of that atom, if the value is between 0.9 and $1.5a_0^{-1}$ and a global γ is required by the implementation of the quantum chemistry code in use.

An advantage of the composite methods with an MP2-F12 increment to reach the CBS-limit is that one can increase the basis set at the MP2-F12 level separately from coupled cluster. Therefore, it is possible to reduce the γ -dependence of the results without increasing the computational effort too much (consider b and d). This strategy can be useful in critical cases if an explicitly correlated coupled cluster calculation in the large basis set is infeasible and the effect of a particular choice of γ on the accuracy is unclear. In Figure 4 we present the γ -

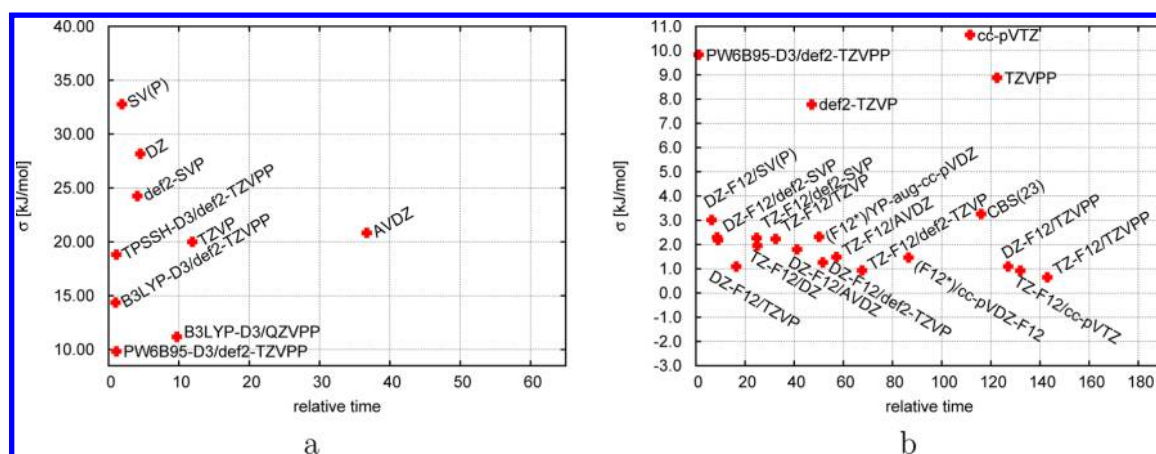


Figure 5. Graphical representation of the data in Table 5. The timing of the B3LYP-D3/def2-TZVPP calculation was normalized to 1. All values refer to the CCSD(T) method, if only a single basis set is given. (F12*) refers to the CCSD(T)(F12*) method, and if 2 basis sets are given the data points refer to the composite CCSD(T)+ΔMP2/CBS/SB method. If F12 basis sets are used, we applied MP2-F12 to compute the CBS value. Since in part a the B3LYP-D3 is below the CCSD(T) data in the small basis set, the DFT calculation is more accurate. In part b one can see the accuracy of different electronic structure methods compared to the computational cost of these methods for a set of medium sized molecules.

dependence of eq 1 for the DZ-F12 and TZ-F12 basis set in combination with CCSD(T) contributions in small basis sets. The Gaussians were plotted at the same scale and are therefore directly comparable. The results are slightly more accurate when using cc-pVDZ for the coupled cluster contribution. Considering the γ -dependence for the MP2 contribution it is clearly visible that the results with the cc-pVTZ-F12 basis set are more robust to changes in γ , as the Gaussian in the right-hand plot are on top of each other. A big advantage of the composite methods is the fact, that MP2-F12 is computationally much less demanding than coupled cluster and one can increase the size of the basis set at much lower cost compared to coupled cluster. On the basis of these findings we conclude that eq 1 is a computational efficient alternative to more rigorous schemes at moderate loss of accuracy.

4. TIMING ANALYSIS

Since the computational resources are usually limited, it is very important to know how much computer time has to be spent, to reach a certain accuracy. In order to perform such an

analysis, we summed the CPU-times of a model for all molecules in the test set (except 2,3-methylpentane). These timings are hardware dependent and have to be interpreted carefully. On the other hand the sum of the CPU-times should be a suitable measure to compare the different computational models in this study. All computations were performed on a cluster of Intel Xeon E3-1270 3.4 GHz Quad-core CPU, 8 GB RAM, and a single hard disk of 1 TB.

In Table 5 we provide the timing and the accuracy for a set of attractive models. The models are sorted with respect to their CPU-times. Since some of the models need more CPU-time at lower accuracy, these strategies are computationally not useful. In Figure 5 we compare the timing and the accuracy of the coupled cluster methods to B3LYP-D3/def2-TZVPP. It is found that one needs at least a triple- ζ basis set with proper polarization functions to be more accurate than B3LYP-D3. The PW6B95-D3^{112,113} functional is of similar accuracy as CCSD(T) with a triple- ζ basis set. As one can see on the time axis the coupled cluster calculations are significantly more expensive, with a relatively small gain in accuracy. When using eq 1 the accuracy is significantly increased, even when using relatively small basis sets at the coupled cluster level.

In Figure 6 we summarized the results of Table 5, and we provide a scheme to systematically increase the accuracy in the most efficient way. The most efficient scheme is on the left side of Figure 6 and has the largest statistical errors. When moving to the right the statistical error decreases with increasing computational demands.

In general it is a good idea to keep the basis set at the coupled cluster level as small as possible. Due to the scaling of the CCSD(T) method the relative timings of the different schemes will change for different systems, but the ranking will not (compare the number of basis functions in Table 5). With this knowledge one can estimate the computational effort of the next level of accuracy. When using a double- ζ basis set at the coupled cluster level the standard deviation is between 1.80 and 3.01 kJ/mol. Using a triple- ζ basis set, the accuracy is around 1 kJ/mol. When using the def2-TZVP and the TZVPP basis sets one can obtain a rather high level of accuracy combined with high efficiency.

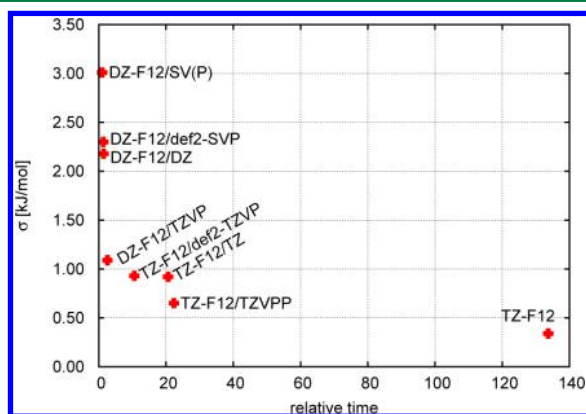


Figure 6. Accuracy of a computation is increased from the left to the right. The CPU-time of CCSD(T)+ΔMP2/cc-pVDZ-F12/SV(P) is normalized to 1. The energies of eq 1 are referred to as CCSD(T)+ΔMP2/CBS/SB. The MP2-F12 method is used to compute the CBS value. TZ-F12 refers to the CCSD(T)(F12*)/cc-pVTZ-F12 energy.

5. CONCLUSION

In this work we analyzed the accuracy and the efficiency of different schemes to obtain the complete basis set limit for CCSD(T) reaction energies. We provide new CCSD(T)/CBS benchmark energies for our previously established test set with 51 reaction energies. On the basis of a standard deviation of only 0.34 kJ/mol it is evident that CCSD(T)(F12*)/cc-pVTZ-F12 provides the CCSD(T)/CBS reaction energies of the test set with high accuracy. It was found that composite schemes using an MP2 increment to reach the basis set limit provide high accuracy combined with high efficiency. In these composite schemes the MP2-F12/cc-pVTZ-F12 method is suitable to compute the MP2 contribution at the basis set limit. We propose to use the def2-TZVP or the TZVPP basis sets at the coupled cluster level in combination with the cc-pVTZ-F12 basis set at the MP2 level to compute reaction energies close to the basis set limit, if high accuracy methods like CCSD(T)-(F12*) or S6-extrapolations are no longer feasible due to their high computational effort. The standard deviation of CCSD(T)+ Δ MP2/cc-pVTZ-F12/def2-TZVP and CCSD(T)+ Δ MP2/cc-pVTZ-F12/TZVPP is found to be only 0.93 and 0.65 kJ/mol. Furthermore, we found, that the choice of the exponent in the correlation factor (γ) changes the results, also in the range of $0.9\text{--}1.5a_0^{-1}$, when using the cc-pVDZ-F12 basis set. When using a triple- ζ -F12 basis set the results are stable with respect to the choice of γ (in the range of $0.9\text{--}1.5a_0^{-1}$). An interesting alternative to high accuracy methods are coupled cluster calculations with double- ζ basis sets using MP2 to compensate for the basis set error. In such calculations one can achieve a medium accuracy with a standard deviation of 1.80–3.01 kJ/mol. The computational effort is only by a factor of 6–9 more expensive than DFT-calculations. This will change when increasing the size of the systems, since the scaling of coupled cluster is much steeper than that of DFT. On the other hand a reduction of the one particle basis set at the coupled cluster level is a way to reduce the computational effort significantly, while keeping a reasonable accuracy.

The method analyzed in this work is also applicable with local coupled cluster methods where the scaling problem of coupled cluster methods is solved. Therefore, it is evident, that the MP2-F12 basis set increment is an interesting part for an efficient high accuracy treatment of large molecules. Based on the statistical data of this work a computational chemist can estimate the computational effort and the accuracy of the different model schemes. Furthermore, one can decide which basis set combination should be used to achieve a given accuracy, while keeping the computational effort as low as possible.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00087.

Supporting tables 1–397 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: joachim.friedrich@chemie.tu-chemnitz.de.

Notes

The author declares no competing financial interest.

■ ACKNOWLEDGMENTS

I thank the Fonds der Chemischen Industrie for financial support due to the Material Cost Allowances program. Tony Anacker, Benjamin Fiedler, and Ivan Tchernook are gratefully acknowledged for reading the manuscript.

■ REFERENCES

- (1) Tajti, A.; Szalay, P.; Csaszar, A.; Kallay, M.; Gauss, J.; Valeev, E.; Flowers, B.; Vazquez, J.; Stanton, J. *J. Chem. Phys.* **2004**, *121*, 11599–11613.
- (2) Harding, M. E.; Vazquez, J.; Ruscic, B.; Wilson, A. K.; Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **2008**, *128*, 114111.
- (3) Martin, J. M. L.; de Oliveira, G. *J. Chem. Phys.* **1999**, *111*, 1843–1856.
- (4) Boese, A.; Oren, M.; Atasoylu, O.; Martin, J.; Kallay, M.; Gauss, J. *J. Chem. Phys.* **2004**, *120*, 4129–4141.
- (5) Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*, 144108.
- (6) Karton, A.; Martin, J. M. L. *J. Chem. Phys.* **2012**, *136*, 124114.
- (7) De Yonker, N. J.; Grimes, T.; Yockel, S.; Dinescu, A. A.; Mintz, B.; Wilson, A. K.; Cundari, T. R. *J. Chem. Phys.* **2006**, *124*, 114104.
- (8) De Yonker, N. J.; Mintz, B.; Cundari, T. R.; Wilson, A. K. *J. Chem. Theory Comput.* **2008**, *4*, 328.
- (9) Nedđ, S. A.; De Yonker, N. J.; Wilson, A. K.; Piecuch, P.; Gordon, M. S. *J. Chem. Phys.* **2012**, *136*, 144109.
- (10) Mahler, A.; Wilson, A. K. *J. Chem. Theory Comput.* **2013**, *9*, 1402.
- (11) Dixon, D. A.; Feller, D.; Sandrone, G. *J. Phys. Chem. A* **1999**, *103*, 4744.
- (12) Feller, D.; Peterson, K. A.; de Jong, W. A.; Dixon, D. A. *J. Chem. Phys.* **2003**, *118*, 3510.
- (13) Feller, D.; Peterson, K. A.; Dixon, D. A. *J. Chem. Phys.* **2008**, *129*, 204105.
- (14) East, A. L. L.; Allen, W. D. *J. Chem. Phys.* **1993**, *99*, 4638.
- (15) Kenny, P.; Allen, W. D.; Schaefer, H. F., III. *J. Chem. Phys.* **2003**, *118*, 7353.
- (16) Schuurman, M. S.; Muir, S. R.; Allen, W. D.; Schaefer, H. F., III. *J. Chem. Phys.* **2004**, *120*, 11586–11599.
- (17) Fast, P. L.; Corchado, J. C.; Sanchez, M. L.; Truhlar, D. G. *J. Phys. Chem. A* **1999**, *103*, 5129.
- (18) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2003**, *107*, 3898.
- (19) Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 1643.
- (20) Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1996**, *104*, 6286–6297.
- (21) Schütz, M. *J. Chem. Phys.* **2000**, *113*, 9986–10001.
- (22) Flocke, N.; Bartlett, R. J. *J. Chem. Phys.* **2004**, *121*, 10935–6003.
- (23) Fedorov, D. G.; Kitaura, K. *J. Chem. Phys.* **2005**, *123*, 134103.
- (24) Subotnik, J. E.; Sodt, A.; Head-Gordon, M. *J. Chem. Phys.* **2006**, *125*, 074116.
- (25) Auer, A.; Nooijen, M. *J. Chem. Phys.* **2006**, *125*, 024104.
- (26) Hermann, A.; Schwerdtfeger, P. *Phys. Rev. Lett.* **2008**, *101*, 183005.
- (27) Kobayashi, M.; Nakai, H. *J. Chem. Phys.* **2009**, *131*, 114108.
- (28) Gordon, M. S.; Mullin, J. M.; Pruitt, S. R.; Roskop, L. B.; Slipchenko, L. V.; Boatz, J. A. *J. Phys. Chem. B* **2009**, *113*, 9646–9663.
- (29) Li, W.; Piecuch, P. *J. Phys. Chem. A* **2010**, *114*, 6721–6727.
- (30) Schwerdtfeger, P.; Assadollahzadeh, B.; Hermann, A. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *82*, 205111.
- (31) Ziolkowski, M.; Jansík, B.; Kjærgaard, T.; Jørgensen, P. *J. Chem. Phys.* **2010**, *133*, 014107.
- (32) Mata, R. A.; Stoll, H. *J. Chem. Phys.* **2011**, *134*, 034122.
- (33) Hoyvik, I.-M.; Kristensen, K.; Jansík, B.; Jørgensen, P. *J. Chem. Phys.* **2012**, *136*, 014105.
- (34) Bates, D. M.; Smith, J. R.; Janowski, T.; Tschumper, G. S. *J. Chem. Phys.* **2011**, *135*, 044123.
- (35) Gordon, M. S.; Fedorov, D. G.; Pruitt, S. R.; Slipchenko, L. V. *Chem. Rev.* **2012**, *112*, 632–672.

- (36) Qi, H. W.; Leverentz, H. R.; Truhlar, D. G. *J. Phys. Chem. A* **2013**, *117*, 4486–4499.
- (37) Neese, F.; Wennmohs, F.; Hansen, A. *J. Chem. Phys.* **2009**, *130*, 114108.
- (38) Neese, F.; Hansen, A.; Liakos, D. G. *J. Chem. Phys.* **2009**, *131*, 064103.
- (39) Liakos, D. G.; Hansen, A.; Neese, F. *J. Chem. Theory Comput.* **2011**, *7*, 76–87.
- (40) Hansen, A.; Liakos, D. G.; Neese, F. *J. Chem. Phys.* **2011**, *135*, 214102.
- (41) Riplinger, C.; Neese, F. *J. Chem. Phys.* **2013**, *138*, 034106.
- (42) Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. *J. Chem. Phys.* **2013**, *139*, 134101.
- (43) Liakos, D. G.; Hansen, A.; Neese, F. *J. Chem. Theory Comput.* **2011**, *7*, 76–87.
- (44) Sparta, M.; Neese, F. *Chem. Soc. Rev.* **2014**, *43*, 5032–5041.
- (45) Rolik, Z.; Kallay, M. *J. Chem. Phys.* **2011**, *135*, 104111.
- (46) Stoll, H. *Chem. Phys. Lett.* **1992**, *191*, 548–552.
- (47) Friedrich, J.; Hanrath, M.; Dolg, M. *J. Chem. Phys.* **2007**, *126*, 154110.
- (48) Friedrich, J.; Dolg, M. *J. Chem. Theory Comput.* **2009**, *5*, 287–294.
- (49) Zhang, J.; Dolg, M. *J. Chem. Theory Comput.* **2013**, *9*, 2992–3003.
- (50) Tew, D. P.; Klopper, W.; Neiss, C.; Hättig, C. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1921.
- (51) Fliegl, H.; Klopper, W. M.; Hättig, C. *J. Chem. Phys.* **2005**, *122*, 084107.
- (52) Hättig, C.; Tew, D. P.; Köhn, A. *J. Chem. Phys.* **2010**, *132*, 231102.
- (53) Hättig, C.; Klopper, W.; Köhn, A.; Tew, D. P. *Chem. Rev.* **2012**, *112*, 4–74.
- (54) Zhang, J.; Dolg, M. *J. Chem. Phys.* **2014**, *140*, 044114.
- (55) Friedrich, J.; Tew, D. P.; Klopper, W.; Dolg, M. *J. Chem. Phys.* **2010**, *132*, 164114.
- (56) Adler, T. B.; Werner, H.-J. *J. Chem. Phys.* **2011**, *135*, 144117.
- (57) Friedrich, J.; Walczak, K. *J. Chem. Theory Comput.* **2013**, *9*, 408–417.
- (58) Vogiatzis, K. D.; Klopper, W. *Mol. Phys.* **2013**, *111*, 2299–2305.
- (59) Vogiatzis, K. D.; Haunschild, R.; Klopper, W. *Theor. Chem. Acc.* **2014**, *133*, 1446.
- (60) Tsuzuki, S.; Uchimaru, T.; Mikami, M.; Tanabe, K.; Sako, T.; Kuwajima, S. *Chem. Phys. Lett.* **1996**, *255*, 347.
- (61) Jurecka, P.; Sponer, J.; Cerny, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985–1993.
- (62) Liakos, D. G.; Neese, F. *J. Phys. Chem. A* **2012**, *116*, 4801–4816.
- (63) Brauer, B.; Kesharwani, M. K.; Martin, J. M. L. *J. Chem. Theory Comput.* **2014**, *10*, 3791–3799.
- (64) Hobza, P.; Sponer, J. *J. Am. Chem. Soc.* **2002**, *124*, 11802.
- (65) Papajak, E.; Truhlar, D. G. *J. Chem. Phys.* **2012**, *137*, 064110.
- (66) Marshall, M. S.; Burns, L. A.; Sherrill, C. D. *J. Chem. Phys.* **2011**, *135*, 194102.
- (67) Dunning, T. H., Jr.; Peterson, K. A. *J. Chem. Phys.* **2000**, *113*, 7799.
- (68) Császár, A. G.; Allen, W. D.; Schaefer, H. F., III *J. Chem. Phys.* **1998**, *108*, 9751.
- (69) Császár, A. G.; Leininger, M. L.; Szalay, V. J. *J. Chem. Phys.* **2003**, *118*, 10631.
- (70) Balabin, R. M. *J. Chem. Phys.* **2009**, *131*, 154307.
- (71) Balabin, R. M. *Chem. Phys. Lett.* **2009**, *479*, 195–200.
- (72) Balabin, R. M. *Comput. Theor. Chem.* **2011**, *965*, 15–21.
- (73) Früchtel, H. A.; Harrison, R. J.; Dyall, K. G. *Int. J. Quantum Chem.* **1997**, *64*, 63.
- (74) Weigend, F. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4285–4291.
- (75) Werner, H. J.; Manby, F. R.; Knowles, P. J. *J. Chem. Phys.* **2003**, *118*, 8149.
- (76) Ten-no, S. *J. Chem. Phys.* **2004**, *121*, 117–129.
- (77) Bachorz, R. A.; Bischoff, F. A.; Glöß, A.; Hättig, C.; Höfener, S.; Klopper, W.; Tew, D. P. *J. Comput. Chem.* **2011**, *32*, 2492–2513.
- (78) Tew, D. P.; Klopper, W. *J. Chem. Phys.* **2005**, *123*, 074101.
- (79) Tew, D. P.; Klopper, W. *J. Chem. Phys.* **2006**, *125*, 094302.
- (80) Peterson, K.; Adler, T.; Werner, H.-J. *J. Chem. Phys.* **2008**, *128*, 084102.
- (81) Hill, J. G.; Mazumder, S.; Peterson, K. *J. Chem. Phys.* **2010**, *132*, 054108.
- (82) Peterson, K.; Kesharwani, M. K.; Martin, J. M. L. *Mol. Phys.* **2015**, *113*, 1551–1558.
- (83) Ivanov, A. S.; Frenking, G.; Boldyrev, A. I. *J. Phys. Chem. A* **2014**, *118*, 7375.
- (84) Friedrich, J.; Hänchen, J. *J. Chem. Theory Comput.* **2013**, *9*, 5381–5394.
- (85) Höfener, S.; Klopper, W. *Mol. Phys.* **2010**, *108*, 1783–1796.
- (86) TURBOMOLE development version, 2009. For further information, see <http://www.turbomole.com>.
- (87) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165–169.
- (88) Ten-no, S. *Chem. Phys. Lett.* **2004**, *398*, 56–61.
- (89) Yousaf, K. E.; Peterson, K. *J. Chem. Phys.* **2008**, *129*, 184108.
- (90) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (91) Weigend, F.; Köhn, A.; Hättig, C. *J. Chem. Phys.* **2002**, *116*, 3175–3183.
- (92) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244.
- (93) Hättig, C. *Phys. Chem. Chem. Phys.* **2005**, *7*, 59–66.
- (94) Yousaf, K. E.; Peterson, K. *Chem. Phys. Lett.* **2009**, *476*, 303.
- (95) Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2008**, *128*, 154103.
- (96) Knizia, G.; Adler, T. B.; Werner, H.-J. *J. Chem. Phys.* **2009**, *130*, 054104.
- (97) Klopper, W.; Samson, C. C. M. *J. Chem. Phys.* **2002**, *116*, 6397–6410.
- (98) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098–3100.
- (99) Vosko, S. H.; Wilk, M.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
- (100) Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 8822–8824.
- (101) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571–2577.
- (102) Grimme, S. *J. Chem. Phys.* **2006**, *124*, 034108.
- (103) Karton, A.; Tarnopolsky, A.; Schatz, G. C.; Martin, J. M. L.; Lamere, J.-F. *J. Phys. Chem. A* **2008**, *112*, 12868–12886.
- (104) Neese, F.; Wennmohs, F. ORCA 3.0.3, an ab initio quantum chemical program package, 2013.
- (105) Zhong, S. J.; Barnes, E. C.; Petersson, G. A. *J. Chem. Phys.* **2008**, *129*, 184116.
- (106) Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243–252.
- (107) Köhn, A. *J. Chem. Phys.* **2010**, *133*, 174118.
- (108) Hill, J. G.; Peterson, K. A.; Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2009**, *131*, 194105.
- (109) Köhn, A.; Tew, D. P. *J. Chem. Phys.* **2010**, *132*, 024101.
- (110) Helgaker, T.; Jørgensen, P.; Olsen, J. *Molecular Electronic Structure Theory*; Wiley, 2004.
- (111) Hill, J. G.; Peterson, K. A. *J. Chem. Phys.* **2014**, *141*, 094106.
- (112) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 5656–5667.
- (113) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456–1465.