Theoretical reference values for the AE6 and BH6 test sets from explicitly correlated coupled-cluster theory

Robin Haunschild · Wim Klopper

Abstract We propose a new computational protocol to obtain highly accurate theoretical reference data. This protocol employs the explicitly correlated coupled-cluster method with iterative single and double excitations as well as perturbative triple excitations, CCSD(T)(F12), using quadruple-ζ basis sets. Higher excitations are accounted for by conventional CCSDT(Q) calculations using double-ζ basis sets, while core/core-valence correlation effects are estimated by conventional CCSD(T) calculations using quadruple-ζ basis sets. Finally, scalar-relativistic effects are accounted for by conventional CCSD(T) calculations using triple-ζ basis sets. In the present article, this protocol is applied to the popular test sets AE6 and BH6. An error analysis shows that the new reference values obtained by our computational protocol have an uncertainty of less than 1 kcal/mol (chemical accuracy). Furthermore, concerning the atomization energies, a cancellation of the basis set incompleteness error in the CCSD(T)(F12) perturbative triples contribution with the corresponding error in the contribution from higher excitations is observed. This error cancellation is diminished by the CCSD(T*)(F12) method. Thus, we recommend the use of the CCSD(T*)(F12) method only for small- and medium-sized basis sets, while the CCSD(T)(F12) approach is preferred for high-accuracy calculations in large basis sets.

1 Introduction

Representative test sets consisting of a few small systems are very important to gauge the accuracy of computational methods. Moreover, small representative test sets are often used to adjust empirical parameters of new approximate methods. The test sets AE6 (six atomization energies) and BH6 (six barrier heights) proposed by Lynch and Truhlar [1] are supposed to be representative sets for the 109 atomization energies and 44 barrier heights of the Database/3 [2] data set. Unfortunately, they involve experimental reference values that have to be corrected for certain contributions (entropic, enthalpic, and zero-point vibrational contributions) that are usually not easily accessible in a new computational method. These corrections add to the uncertainty of the reference values. A very attractive alternative is to obtain highly accurate reference values from computational chemistry. Established protocols yielding very high accuracy are the W4 method [3] from the Wn family of methods [3–6] and the HEAT project [7]. Both involve highly expensive calculations and basis set extrapolations.

The aim of the present study is to propose an alternative computational protocol that comes close to the accuracy of the W4 method but which is computationally less expensive and does not involve basis set extrapolations. This new computational protocol employs explicitly correlated

R. Haunschild (✉) · W. Klopper
Theoretical Chemistry Group, Institute of Physical Chemistry,
Karlsruhe Institute of Technology, KIT Campus South,
Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany
e-mail: haunschild@kit.edu

W. Klopper
e-mail: klopper@kit.edu

coupled-cluster theory including iterative single and double excitations as well as perturbative triple excitations, CCSD(T)(F12) [8–19], augmented with higher-order corrections. The design of our protocol is inspired by prior assessments of the performance of explicitly correlated methods for a variety of systems [20–25]. We present results of our new composite method for the AE6 and BH6 test sets. We note that the highly accurate W4 method has already been applied to the BH6 test set [26] and to five of the six molecules of the AE6 test set [27]. We therefore compare our new results not only to the currently used experimental reference values but also to the values obtained from the W4 method.

Our computational approach allows us to provide relativistic as well as nonrelativistic and frozen-core reference values. We also provide error estimates to gauge the accuracy of the theoretical reference values obtained from our computational protocol. More approximate methods can be compared to these more suitable reference values.

2 Methods

The computational protocol proposed here avoids basis set extrapolations by usage of the explicit treatment of electron correlation by means of the CCSD(T)(F12) method. This yields the CCSD correlation energy very close to the basis set limit and offers a basis set incompleteness correction for the Hartree–Fock energy (CABS singles). We augment the part covered by CCSD(T)(F12) with corrections for higher excitations and core/core-valence correlation. We also propose a method/basis set combination to account for scalar-relativistic effects. If full-relativistic reference values are desired, we suggest to use the experimental fine structure to extract first-order spin-orbit coupling terms.

2.1 Explicitly correlated calculations

Frozen-core CCSD(T)(F12) and core/core-valence correlation energies were calculated with the TURBOMOLE [28] module RICC2 [29] using reference wave functions from the module DSCF [30]. Open-shell species were calculated via unrestricted formalisms. The CCSD(F12) part of the calculations used variant B, ansatz 2, where the strong orthogonality projector

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1\hat{V}_2, \tag{1}$$

$$\hat{O}_\mu = \sum_i |\phi_i(\mu)\rangle\langle\phi_i(\mu)|, \qquad \hat{V}_\mu = \sum_a |\phi_a(\mu)\rangle\langle\phi_a(\mu)|,$$

with occupied orbitals ϕ_i and virtual orbitals ϕ_a

is used, with sp cusp conditions [18] to predetermine the geminal amplitudes and with spin-flipped [19] geminals

that are constructed from a linear combination of six Gaussian functions using recommended exponents [31]. Explicitly correlated calculations employed the cc-pVXZ-F12 series of orbital basis sets [32] with recommended auxiliary basis sets [33] and CABS basis sets [34] from the TURBOMOLE basis set library. The perturbative CABS singles correction (E_{CABS}) was taken into account [15].

2.2 Conventional calculations

Conventional AE-CCSD(T) calculations employing the cc-pwCVQZ and cc-pwCV5Z basis sets [35] in conjunction with recommended RI basis sets [33] were used to estimate the core/core-valence correlation energies. Conventional CCSD(T) calculations for error estimates employing the cc-pVXZ and cc-pV(X + d)Z [36–39] series of basis sets were also performed using the TURBOMOLE program package.

Higher excitation (difference between frozen-core CCSDT(Q) and CCSD(T) calculations) contributions and scalar-relativistic effects (AE-CCSD(T)) were calculated using the programs CFOUR [40] and MRCC [41, 42]. Estimation of higher excitation energies employed the cc-pVDZ and cc-pVTZ basis sets [36] in the case of H, C, and O, while the cc-pV(D + d)Z and cc-pV(T + d)Z basis sets [37] were used in the case of Si and S. The general coupled-cluster code MRCC was used for all CCSDT(Q) calculations. The calculation of scalar-relativistic effects (mass-velocity and Darwin terms) [43, 44] employed the cc-pwCVTZ and cc-pwCVQZ basis sets [35].

3 Results and discussion

3.1 Atomization energies and barrier heights of the AE6 and BH6 test sets

The AE6 test set consists of the atomization energies of the six molecules SiH_4, SiO, S_2, propyne (C_3H_4), glyoxal ($C_2O_2H_2$), and cyclobutane (C_4H_8). The BH6 test set consists of the forward and reverse barrier heights of the three hydrogen transfer reactions $OH + CH_4 \rightarrow CH_3 + H_2O$, $H + OH \rightarrow O + H_2$, and $H + H_2S \rightarrow H_2 + SH$. We use geometries at the QCISD/MG3 level of theory as supplied by Truhlar et al. [45]. We present atomization energies and barrier heights for the AE6 and BH6 test sets from conventional CCSD(T) calculations using the basis sets cc-pVDZ-F12, cc-pVTZ-F12, cc-pVQZ-F12, cc-pV(Q + d)Z, cc-pV(5 + d)Z, cc-pV(6 + d)Z, and CBS-extrapolated CCSD(T) as well as explicitly correlated CCSD(T)(F12) calculations using the basis sets cc-pVDZ-F12, cc-pVTZ-F12, and cc-pVQZ-F12. We use CBS extrapolations only to obtain error estimates for individual

contributions. For the CBS extrapolation of the Hartree–Fock energy [46, 47], we use

$$E^{\mathrm{HF}}(X) = E^{\mathrm{HF}}(\mathrm{CBS}) + Be^{-AX^{1/2}}, \tag{2}$$

fitting $E^{\mathrm{HF}}(\mathrm{CBS})$, A, and B to energies $E^{\mathrm{HF}}(X)$ from calculations with cc-pV$(X + \mathrm{d})$Z basis sets where $X = Q, 5, 6$. The CBS limit correlation energies were estimated by the two-point formula

$$E^{\mathrm{corr.}}(X) = E^{\mathrm{corr.}}(\mathrm{CBS}) + CX^{-3}, \tag{3}$$

fitting $E^{\mathrm{corr.}}(\mathrm{CBS})$ and C to energies $E^{\mathrm{corr.}}(X)$ using cc-pV$(X + \mathrm{d})$Z basis sets where $X = 5, 6$ for CCSD and perturbative (T) correlation energies [48]. Additionally, we also show values for both test sets using the CCSD(T*)(F12) [26] method employing the basis sets cc-pVDZ-F12, cc-pVTZ-F12, and cc-pVQZ-F12. The CCSD(T*)(F12) method scales the perturbative triples of CCSD(T)(F12) with the ratio of the MP2-F12 and MP2 correlation energies,

$$E^{\mathrm{corr.}}_{(\mathrm{T}^*)} = E^{\mathrm{corr.}}_{(\mathrm{T})} \frac{E^{\mathrm{corr.}}_{\mathrm{MP2-F12}}}{E^{\mathrm{corr.}}_{\mathrm{MP2}}}. \tag{4}$$

We also computed corrections for neglected core/core-valence correlation ($\delta_{\mathrm{C/CV}}$),

$$\delta_{\mathrm{C/CV}} = E^{\mathrm{corr.}}_{\mathrm{AE-CCSD(T)/cc-pwCVQZ}} - E^{\mathrm{corr.}}_{\mathrm{FC-CCSD(T)/cc-pwCVQZ}}, \tag{5}$$

higher excitations (δ_{HE}),

$$\delta_{\mathrm{HE}} = E^{\mathrm{corr.}}_{\mathrm{FC-CCSDT(Q)/cc-pV(D+d)Z}} - E^{\mathrm{corr.}}_{\mathrm{FC-CCSD(T)/cc-pV(D+d)Z}}, \tag{6}$$

and scalar-relativistic effects (δ_{MVD}, mass-velocity as well as one- and two-electron Darwin terms), at the AE-CCSD(T)/cc-pwCVTZ level of theory. The latter are used to obtain nonrelativistic experimental reference values while the corrections $\delta_{\mathrm{C/CV}}$ and δ_{HE} are added to the calculated atomization energies and barrier heights. Table 1 compiles the atomization energies of the different quantum chemical methods and experimental reference values for the AE6 test set, while Table 2 presents the barrier heights for the BH6 test set. Here, $\delta_{\mathrm{rel}} = \delta_{\mathrm{SO}} + \delta_{\mathrm{MVD}}$, where δ_{SO} is a correction for spin-orbit effects taken from Ref. [49]. The W4 values were taken from Refs. [26] and [27]. Please note that slightly different geometries were used in Ref. [27]. All three corrections δ_{HE}, $\delta_{\mathrm{C/CV}}$, and δ_{MVD} are of rather small magnitude (about 1 kJ/mol) for all reactions of the BH6 test set and cancel out in parts, but they are much more important for the atomization energies of the AE6 test set. For C_4H_8, δ_{HE}, and $\delta_{\mathrm{C/CV}}$ amount to somewhat more than 20 kJ/mol and for C_3H_4 and $C_2O_2H_2$, they slightly exceed 17 kJ/mol. Explicitly treated electron correlation shows more benefits in the case of atomization energies than for barrier heights.

The atomization energies calculated from FC-CCSD(T) (F12)/cc-pVQZ-F12 + δ_{HE} + $\delta_{\mathrm{C/CV}}$ and FC-CCSD(T*) (F12)/cc-pVQZ-F12 + δ_{HE} + $\delta_{\mathrm{C/CV}}$ are in between the values obtained from FC-CCSD(T)/cc-pV(6 + d)Z

Table 1 Atomization energies for the molecules of the AE6 test set in kJ/mol

	SiH_4	SiO	S_2	C_3H_4	$C_2O_2H_2$	C_4H_8
FC-CCSD(T)/cc-pVDZ-F12 + δ_{HE} + $\delta_{\mathrm{C/CV}}$	1,308.2	758.8	372.9	2,817.1	2,510.3	4,609.4
FC-CCSD(T)/cc-pVTZ-F12 + δ_{HE} + $\delta_{\mathrm{C/CV}}$	1,341.2	788.0	410.8	2,903.8	2,604.7	4,739.0
FC-CCSD(T)/cc-pVQZ-F12 + δ_{HE} + $\delta_{\mathrm{C/CV}}$	1,351.7	801.2	426.3	2,933.1	2,637.7	4,784.1
FC-CCSD(T)(F12)/cc-pVDZ-F12 + δ_{HE} + $\delta_{\mathrm{C/CV}}$	1,352.7	802.4	425.2	2,933.1	2,637.4	4,786.4
FC-CCSD(T)(F12)/cc-pVTZ-F12 + δ_{HE} + $\delta_{\mathrm{C/CV}}$	1,357.2	806.6	431.6	2,947.4	2,653.2	4,807.5
FC-CCSD(T)(F12)/cc-pVQZ-F12 + δ_{HE} + $\delta_{\mathrm{C/CV}}$	1,358.1	809.2	434.7	2,950.9	2,658.2	4,812.1
FC-CCSD(T*)(F12)/cc-pVDZ-F12 + δ_{HE} + $\delta_{\mathrm{C/CV}}$	1,353.8	808.3	432.2	2,940.6	2,649.3	4,796.1
FC-CCSD(T*)(F12)/cc-pVTZ-F12 + δ_{HE} + $\delta_{\mathrm{C/CV}}$	1,357.7	809.3	434.8	2,951.0	2,658.6	4,812.1
FC-CCSD(T*)(F12)/cc-pVQZ-F12 + δ_{HE} + $\delta_{\mathrm{C/CV}}$	1,358.3	810.6	436.4	2,952.7	2,660.9	4,814.4
FC-CCSD(T)/cc-pV(Q + d)Z + δ_{HE} + $\delta_{\mathrm{C/CV}}$	1,351.6	795.5	423.0	2,931.0	2,632.7	4,783.7
FC-CCSD(T)/cc-pV(5 + d)Z + δ_{HE} + $\delta_{\mathrm{C/CV}}$	1,355.6	803.8	430.5	2,943.0	2,647.6	4,800.9
FC-CCSD(T)/cc-pV(6 + d)Z + δ_{HE} + $\delta_{\mathrm{C/CV}}$	1,357.4	807.2	433.8	2,947.8	2,653.8	4,807.8
FC-CCSD(T)/CBS + δ_{HE} + $\delta_{\mathrm{C/CV}}$	1,359.5	811.4	438.1	2,954.3	2,662.2	4,817.1
W4[a]	1,359.6	807.7	436.2	2,952.3	2,657.3	–
Exp.$-\delta_{\mathrm{rel}}$	1,353.7	807.6	431.5	2,952.0	2,655.4	4,812.3
Exp.$-\delta_{\mathrm{SO}}$	1,350.7	806.4	430.1	2,950.0	2,652.6	4,809.0
Exp.	1,348.9	803.7	425.4	2,948.8	2,649.9	4,807.5

[a] The W4 values from Ref. [29] were obtained for slightly different geometries (CCSD(T)/cc-pV(Q + d)Z level of theory), and the impact on the atomization energy is expected to be minor

Table 2 Barrier heights for the reactions of the BH6 test set in kJ/mol

	OH + CH$_3$ → CH$_3$ + H$_2$O		H + OH → O + H$_2$		H + H$_2$S → H$_2$ + SH	
	$E_{\text{fwd}}^{\neq}$	$E_{\text{rev}}^{\neq}$	$E_{\text{fwd}}^{\neq}$	$E_{\text{rev}}^{\neq}$	$E_{\text{fwd}}^{\neq}$	$E_{\text{rev}}^{\neq}$
FC-CCSD(T)/cc-pVDZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$	32.7	79.3	41.8	66.6	17.9	79.6
FC-CCSD(T)/cc-pVTZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$	27.2	78.7	42.5	58.7	15.3	72.8
FC-CCSD(T)/cc-pVQZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$	25.9	80.2	44.0	55.8	15.7	71.9
FC-CCSD(T)(F12)/cc-pVDZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$	28.4	81.8	52.0	67.5	16.9	72.6
FC-CCSD(T)(F12)/cc-pVTZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$	26.3	81.8	47.4	58.1	16.1	71.6
FC-CCSD(T)(F12)/cc-pVQZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$	25.7	81.7	45.3	54.6	16.0	71.4
FC-CCSD(T*)(F12)/cc-pVDZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$	26.6	80.5	51.9	66.2	16.4	71.2
FC-CCSD(T*)(F12)/cc-pVTZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$	25.5	81.2	47.3	57.4	15.9	71.0
FC-CCSD(T*)(F12)/cc-pVQZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$	25.3	81.4	45.3	54.3	15.9	71.1
FC-CCSD(T)/cc-pV(Q + d)Z + δ_{HE} + $\delta_{\text{C/CV}}$	27.3	79.8	44.2	59.4	17.0	75.2
FC-CCSD(T)/cc-pV(5 + d)Z + δ_{HE} + $\delta_{\text{C/CV}}$	26.1	81.1	44.7	57.1	16.7	73.9
FC-CCSD(T)/cc-pV(6 + d)Z + δ_{HE} + $\delta_{\text{C/CV}}$	25.7	81.4	44.8	56.3	16.5	73.3
FC-CCSD(T)/CBS + δ_{HE} + $\delta_{\text{C/CV}}$	25.2	81.4	44.9	55.3	16.3	72.6
W4[a]	25.6	81.0	44.6	54.0	15.8	71.5
Exp.−δ_{rel}	27.3	82.4	44.0	53.8	14.6	69.5
Exp.−δ_{SO}	27.4	82.0	43.7	54.0	14.9	70.1

[a] The W4 values from Ref. [26] were obtained for the geometries of Truhlar et al., but reoptimized symmetrized structures were used when the structure provided by Truhlar et al. was close to a structure with higher symmetry. We assume that this has been the case for the transition state of the reaction OH + CH$_4$ → CH$_3$ + H$_2$O, but not for the other systems

+ δ_{HE} + $\delta_{\text{C/CV}}$ and FC-CCSD(T)/CBS + δ_{HE} + $\delta_{\text{C/CV}}$ and very close to the highly accurate W4 values. Already, the atomization energies from FC-CCSD(T)(F12)/cc-pVDZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$ and FC-CCSD(T*)(F12)/cc-pVDZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$ are closer to the CBS estimates than the values from FC-CCSD(T)/cc-pV(Q + d)Z + δ_{HE} + $\delta_{\text{C/CV}}$ and FC-CCSD(T)/cc-pVQZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$. The atomization energies from FC-CCSD(T*)(F12)/cc-pVXZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$ are surprisingly close to the values from FC-CCSD(T)(F12)/cc-pV(X + 1)Z-F12 + δ_{HE} + $\delta_{\text{C/CV}}$. This suggests that FC-CCSD(T*)(F12)/cc-pVXZ-F12 can be used to approximate FC-CCSD(T)(F12)/cc-pV(X + 1)Z-F12 values when the latter method is computationally too expensive. However, FC-CCSD(T*)(F12)/cc-pVQZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$ overestimates the atomization energies on average compared to the nonrelativistic experimental values (Exp−δ_{rel}) and W4. It is easy to explain why the FC-CCSD(T*)(F12) methods seem to work well for some cases, but not for other systems. The perturbative triples contribution converges faster than the MP2 correlation energy. Hence, Eq. 4 will become less useful in larger basis sets. Any FC-CCSD(T*)(F12) method should only be used with extreme caution and only when none of the more accurate methods is feasible anymore due to system size.

Overall, the atomization energies and barrier heights obtained from FC-CCSD(T)(F12)/cc-pVQZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$ agree best with the currently adopted nonrelativistic

experimental values and the highly accurate W4 values. This makes FC-CCSD(T)(F12)/cc-pVQZ-F12 + $\delta_{\text{C/CV}}$ a very attractive candidate for efficient and highly accurate computations of atomization energies and barrier heights when nondynamical correlation plays a minor role. However, one should expect a larger uncertainty of the experimental values for SiH$_4$ and SiO as they have been obtained using an enthalpy of formation for the silicon atom with a rather large uncertainty of 7.95 kJ/mol [50, 51]. More recent estimates [54] suggest a slightly higher enthalpy of formation (by about 2 kJ/mol) for the silicon atom, which would result in a slightly higher atomization energy of silicon compounds. Also, the experimental reference value of the atomization energy of S$_2$ has been revised to 426.3 kJ/mol (432.4 kJ/mol after subtraction of relativistic effects) [53]. The revised atomization energy of S$_2$ is closer to the values from W4 and FC-CCSD(T)(F12)/cc-pVQZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$ than the previous experimental value.

We did not find revised experimental values for the barrier heights, but we expect them to be slightly less accurate than the values obtained from W4 and FC-CCSD(T)(F12)/cc-pVQZ-F12 + δ_{HE} + $\delta_{\text{C/CV}}$. All experimental hydrogen transfer barrier heights are likely to be somewhat tainted by tunnelling effects. We expect this to be the case for the barriers of the reaction H + H$_2$S → H$_2$ + SH because the experimental reference value is significantly lower than the one from W4 theory for forward

and reverse directions. We expect that the disagreement of the barrier heights of the reaction $OH + CH_4 \rightarrow CH_3 + H_2O$ is most likely due to uncertainties of the experimental values, while experimental values and W4 theory are in good agreement for the barrier heights of the reaction $H + OH \rightarrow O + H_2$. In the present study, we would like to establish a protocol with a similar accuracy as W4, which can also be used to treat larger systems (currently up to ten nonhydrogen atoms). Thus, we recommend FC-CCSD(T)(F12)/cc-pVQZ-F12 $+ \delta_{HE} + \delta_{C/CV}$ as a robust method to calculate atomization energies, barrier heights, and reaction energies. Relativistic reference values are easily derived by addition of δ_{rel}, and frozen-core reference values are available by subtraction of $\delta_{C/CV}$.

3.2 Error estimates

Table 3 presents estimated errors for the FC-CCSD(T)(F12)/cc-pVQZ-F12 $+ \delta_{HE} + \delta_{C/CV}$ level concerning the atomization energies and barrier heights of the AE6 and BH6 test sets. We observe only a very small error in the Hartree–Fock energy, which is much improved by the CABS singles correction of F12 theory. The estimated errors are smaller for barrier heights than for atomization energies. The errors of higher excitations and perturbative triples have opposite signs for atomization energies. This error cancellation is systematic for the atomization energies of the AE6 test set. Thus, we use a slightly different formula for error propagation for atomization energies, as explained in footnote g of Table 3. The error in perturbative triples is greatly reduced by the CCSD(T*)(F12) method. However, the error in higher excitations is not affected by CCSD(T*)(F12), and therefore, the error cancellation between perturbative triples and higher excitations is diminished by the CCSD(T*)(F12) method. This explains why FC-CCSD(T*)(F12)/cc-pVQZ-F12 $+ \delta_{HE} + \delta_{C/CV}$ overestimates atomization energies. This error cancellation does not exist for the barrier heights of the BH6 test set. Instead, errors of core/core-valence treatment and perturbative triples have opposite signs for the barrier heights, and thus, we here observe a cancellation of errors for FC-CCSD(T)(F12) $+ \delta_{HE} + \delta_{C/CV}$. Again, FC-CCSD(T*)(F12)/cc-pVQZ-F12 $+ \delta_{HE} + \delta_{C/CV}$ lessens this error cancellation. Therefore, we recommend to use the CCSD(T*)(F12) method only for small and medium basis set sizes (cc-pVDZ-F12 and cc-pVTZ-F12), while the CCSD(T)(F12) method should be preferred for accurate calculations using cc-pVQZ-F12 and larger basis sets. Effects of excitations higher than perturbative triples for core/core-valence correlation and scalar-relativistic effects

Table 3 Error estimates (in kJ/mol) for the FC-CCSD(T)(F12)/cc-pVQZ-F12 $+ \delta_{HE} + \delta_{C/CV}$ level with respect to the AE6 and BH6 test sets

	ΔHF^a	$\Delta CCSD(F12)^b$	$\Delta pert. T^c$	$\Delta\delta_{HE}^d$	$\Delta\delta_{C/CV}^e$	$\Delta\delta_{MVD}^f$	Total^g
SiH_4	0.18	1.14	0.08	−0.65	−0.06	−0.01	1.32
SiO	0.05	0.94	1.19	−3.47	0.64	−0.10	2.35
S_2	0.25	1.14	2.01	−0.90	−0.10	−0.33	1.65
C_3H_4	0.00	1.72	1.69	−2.57	0.71	−0.13	1.89
$C_2O_2H_2$	−0.12	1.74	2.40	−4.74	0.53	0.16	2.97
C_4H_8	0.02	2.76	2.17	−3.86^h	0.71	−0.10	3.32
$OH + CH_4 \rightarrow CH_3 + H_2O$	0.03	−0.20	−0.38	0.00	0.03	−0.10	0.45
$CH_3 + H_2O \rightarrow OH + CH_4$	0.02	−0.04	−0.21	−0.68	0.03	−0.14	0.73
$H + OH \rightarrow O + H_2$	0.01	−0.16	−0.10	−0.55	0.39	−0.11	0.71
$O + H_2 \rightarrow H + OH$	0.09	−0.26	−0.46	−0.06	0.37	−0.08	0.65
$H + H_2S \rightarrow H_2 + SH$	0.04	−0.12	−0.12	−0.15	0.06	0.03	0.24
$H_2 + SH \rightarrow H + H_2S$	0.04	−0.18	−0.35	0.20	0.07	0.08	0.46

[a] $\Delta HF = E^{HF}(CBS) - (E^{HF}_{cc-pVQZ-F12} + E_{CABS})$, where $E^{HF}(CBS)$ was obtained from Eq. 2 using cc-pV([Q,5,6] + d)Z basis sets

[b] $\Delta CCSD(F12) = E^{CCSD}(CBS) - E^{CCSD}_{cc-pVQZ-F12}$ where $E^{CCSD}(CBS)$ was obtained from Eq. 3 using cc-pV([5,6] + d)Z basis sets

[c] $\Delta pert.T = E^{pert.T}(CBS) - E^{pert.T}_{cc-pVQZ-F12}$ where $E^{pert.T}(CBS)$ was obtained from Eq. 3 using cc-pV([5, 6] + d)Z basis sets

[d] $\Delta\delta_{HE} = \delta_{HE}(CBS) - \delta_{HE}$ where $\delta_{HE}(CBS)$ was obtained from Eqs. 3 and 6 using cc-pV([D,T] + d)Z basis sets

[e] $\Delta\delta_{C/CV} = \delta_{C/CV}(CBS) - \delta_{C/CV}$ where $\delta_{C/CV}(CBS)$ was obtained from Eqs. 3 and 5 using cc-pwCV[Q,5]Z basis sets

[f] $\Delta\delta_{MVD} = \delta_{MVD}(CBS) - \delta_{MVD}$ where $\delta_{MVD}(CBS)$ was obtained from $E^{MVD}(X) = E^{MVD}(CBS) + DX^{-1}$ using cc-pwCV[T,Q]Z basis sets

[g] Error propagation according to: Error $= (\sum_i (error_i)^2)^{1/2}$ where $(error_{HE} + error_{pert.T})^2$ rather than $error_{HE}^2 + error_{pert.T}^2$ was used for atomization energies

[h] Estimated from the average higher excitation error of propyne (C_3H_4) of −0.161 kJ/mol per valence electron because the FC-CCSDT(Q)/cc-pVTZ calculation was too expensive

Table 4 Proposed theoretical reference values for the test sets AE6 and BH6 in kJ/mol with error estimates

	E_{FC}[a]	E_{nrel}[b]	E_{srel}^{c}	E_{rel}[d]
SiH$_4$	1,358.1 ± 1.3	1,358.1 ± 1.3	1,355.1 ± 1.3	1,353.3 ± 1.3
SiO	804.8 ± 2.3	809.2 ± 2.3	808.1 ± 2.3	805.3 ± 2.3
S$_2$	431.9 ± 1.6	434.7 ± 1.6	433.3 ± 1.6	428.7 ± 1.6
Propyne	2,934.9 ± 1.7	2,950.9 ± 1.9	2,948.8 ± 1.9	2,947.7 ± 1.9
Glyoxal	2,646.2 ± 2.9	2,658.2 ± 3.0	2,655.4 ± 3.0	2,652.7 ± 3.0
Cyclobutane	4,792.3 ± 3.2	4,812.1 ± 3.3	4,808.9 ± 3.3	4,807.4 ± 3.3
OH + CH$_4$ → CH$_3$ + H$_2$O	25.6 ± 0.4	25.7 ± 0.4	25.8 ± 0.4	25.4 ± 0.5
CH$_3$ + H$_2$O → OH + CH$_4$	81.3 ± 0.7	81.7 ± 0.7	81.3 ± 0.7	81.3 ± 0.7
H + OH → O + H$_2$	44.8 ± 0.6	45.3 ± 0.7	45.0 ± 0.7	44.6 ± 0.7
O + H$_2$ → H + OH	54.9 ± 0.5	54.6 ± 0.7	54.8 ± 0.7	53.8 ± 0.7
H + H$_2$S → H$_2$ + SH	15.9 ± 0.2	16.0 ± 0.2	15.7 ± 0.2	15.7 ± 0.2
H$_2$ + SH → H + H$_2$S	72.3 ± 0.4	71.4 ± 0.5	72.0 ± 0.5	69.7 ± 0.5

[a] Frozen-core nonrelativistic reference values: FC-CCSD(T)/cc-pVQZ-F12 + δ_{HE}

[b] Nonrelativistic reference values: FC-CCSD(T)/cc-pVQZ-F12 + δ_{HE} + $\delta_{C/CV}$

[c] Scalar-relativistic reference values: FC-CCSD(T)/cc-pVQZ-F12 + δ_{HE} + $\delta_{C/CV}$ + δ_{MVD}

[d] Relativistic reference values: FC-CCSD(T)/cc-pVQZ-F12 + δ_{HE} + $\delta_{C/CV}$ + δ_{MVD} + δ_{SO}

as well as perturbative quadruples for higher excitation contributions are not covered by this error analysis but are expected to be negligible [27, 54]. This expectation is also supported by our comparison to W4 values in Tables 1 and 2.

3.3 Recommended reference values

Table 4 summarizes our theoretical reference values obtained from CCSD(T)(F12)/cc-pVQZ-F12 calculations corrected for higher excitations (iterative triples and perturbative quadruple contributions), core/core-valence correlation, and relativistic effects (both at the CCSD(T) level of theory). They possess a similar accuracy as the values from W4 theory. Reference values suitable for comparison with frozen-core, all-electron, scalar-relativistic, and full-relativistic methods are presented separately. In Table 4, we also supply error estimates for each proposed reference value. The error estimates are derived from the CBS values.

4 Conclusions

In summary, we have proposed a new protocol to predict very accurate atomization energies, barrier heights, and reaction energies without basis set extrapolations. The largest basis set employed is of quadruple-ζ size, while other high-accuracy protocols include basis set sizes up to sextuple-ζ and basis set extrapolations. We have also presented theoretical reference values for the AE6 and BH6 test sets. They are highly accurate as shown by error estimates that were calculated from CBS-extrapolated values

and comparison with values from the highly accurate W4 theory. Our error estimates from error propagation show that the uncertainty of the reference values for atomization energies and barrier heights obtained from our new protocol is well below 1 kcal/mol (chemical accuracy). For barrier heights, our error estimates even suggest a sub-kJ/mol accuracy. Besides being consistently of very high accuracy, the new reference values have other important advantages over the experimental ones: Certain effects (core/core-valence correlation and relativistic effects) can be excluded. Thus, more appropriate reference values for comparison with more approximate methods (frozen-core and/or nonrelativistic methods) are available. We plan to apply the proposed computational protocol to larger test sets where doubt has been casted on currently used reference values.

References

1. Lynch BJ, Truhlar DG (2003) J Phys Chem A 107:8996. erratum: ibid. 108:1460 (2004)
2. Lynch BJ, Truhlar DG (2003) J Phys Chem A 107:3898
3. Karton A, Rabinovich E, Martin JML (2006) J Chem Phys 125:144108
4. Martin JML, de Oliveira G (1999) J Chem Phys 111:1843
5. Parthiban S, Martin JML (2001) J Chem Phys 114:6014
6. Boese AD, Oren M, Atasoylu O, Martin JML, Kállay M, Gauss J (2004) J Chem Phys 120:4129

7. Tajti A, Szalay PG, Császár AG, Kállay M, Gauss J, Valeev EF, Flowers BA, Vázquez J, Stanton JF (2004) J Chem Phys 121:11599
8. Kutzelnigg W (1985) Theor Chim Acta 68:445
9. Kutzelnigg W, Klopper W (1991) J Chem Phys 94:1985
10. Ten-no S (2004) Chem Phys Lett 398:56
11. Fliegl H, Klopper W, Hättig C (2005) J Chem Phys 122:084107
12. Bokhan D, Ten-no S, Noga J (2008) Phys Chem Chem Phys 10:3320
13. Bischoff FA, Wolfsegger S, Tew DP, Klopper W (2009) Mol Phys 107:963
14. Bachorz RA, Bischoff FA, Glöß A, Hättig C, Höfener S, Klopper W, Tew DP (2011) J Comput Chem 32:2492
15. Tew DP, Hättig C, Bachorz RA, Klopper W (2010) In: Čársky P, Paldus J, Pittner J (eds) Recent progress in coupled cluster methods.. Springer, Dordrecht, pp 535–572
16. Klopper W, Manby FR, Ten-no S, Valeev EF (2006) Int Rev Phys Chem 25:427
17. Hättig C, Tew DP, Köhn A (2010) J Chem Phys 132:231102
18. Tew DP, Klopper W, Hättig C (2008) Chem Phys Lett 452:326
19. Tew DP, Klopper W (2010) Mol Phys 108:315
20. Tew DP, Klopper W, Neiss C, Hättig C (2007) Phys Chem Chem Phys 9:1921. erratum: ibid. 10:6325 (2008)
21. Klopper W, Bachorz RA, Hättig C, Tew DP (2010) Theor Chem Acc 126:289
22. Marchetti O, Werner HJ (2008) Phys Chem Chem Phys 10:3400
23. Klopper W, Ruscic B, Tew DP, Bischoff FA, Wolfsegger S (2009) Chem Phys 356:14
24. Marchetti O, Werner HJ (2009) J Phys Chem A 113:11580
25. Werner HJ, Knizia G, Adler TB, Marchetti O (2010) Z Phys Chem 224:493
26. Karton A, Tarnpolsky A, Lamère JF, Schatz GC, Martin JML (2008) J Phys Chem A 112:12686
27. Karton A, Daon S, Martin JML (2011) Chem Phys Lett 510:165
28. TURBOMOLE development version 2010, a development of Universität Karlsruhe (TH) and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com. Accessed 4 April 2011
29. Hättig C, Weigend F (2000) J Chem Phys 113:5154
30. Häser M, Ahlrichs R (1989) J Comput Chem 10:104
31. Tew DP, Klopper W (2005) J Chem Phys 123:074101
32. Peterson KA, Adler TB, Werner HJ (2008) J Chem Phys 128:084102
33. Hättig C (2005) Phys Chem Chem Phys 7:59
34. Yousaf KE, Peterson KA (2008) J Chem Phys 129:184108
35. Peterson KA, Dunning TH Jr (2002) J Chem Phys 117:10548
36. Dunning TH Jr, Peterson KA, Wilson AK (1989) J Chem Phys 90:1007
37. Dunning TH Jr, Peterson KA, Wilson AK (2001) J Chem Phys 114:9244
38. Woon DE, Dunning TH Jr (1993) J Chem Phys 98:1358
39. Wilson AK, van Mourik T, Dunning TH Jr (1997) THEOCHEM 388:339
40. CFOUR, Coupled-Cluster techniques for Computational Chemistry, a quantum-chemical program package by Stanton JF, Gauss J, Harding ME, Szalay PG with contributions from Auer AA, Bartlett RJ, Benedikt U, Berger C, Bernholdt DE, Bomble YJ, Cheng L, Christiansen O, Heckert M, Heun O, Huber C, Jagau TC, Jonsson D, Jusélius J, Klein K, Lauderdale WJ, Matthews DA, Metzroth T, O'Neill DP, Price DR, Prochnow E, Ruud K, Schiffmann F, Schwalbach W, Stopkowicz S, Tajti A, Vázquez J, Wang F, Watts JD and the integral packages MOLECULE (Almlöf J and Taylor PR), PROPS (Taylor PR), ABACUS (Helgaker T, Jensen HJAa, Jørgensen P, and Olsen J), and ECP routines by Mitin AV and van Wüllen C. For the current version, see http://www.cfour.de. Accessed 5 April 2011
41. MRCC (2011) A string-based quantum chemical program suite written by Kállay M. See also Ref. [42] as well as http://www.mrcc.hu. Accessed 5 April 2011
42. Kállay M, Surján PR (2001) J Chem Phys 115:2945
43. Cowan R, Griffin D (1976) J Opt Soc Am 66:1010
44. Klopper W (1997) J Comput Chem 18:20
45. http://t1.chem.umn.edu/misc/database_group/database_therm_bh/ae6bh6.pl. Accessed 5 April 2011
46. Klopper W, Kutzelnigg W (1986) THEOCHEM 135:339
47. Kutzelnigg W (1994) Int J Quant Chem 51:447
48. Helgaker T, Klopper W, Koch H, Noga J (1997) J Chem Phys 109:9639
49. Lynch BJ, Zhao Y, Truhlar DG (2005) JJ Phys Chem A 109:1643
50. Fast PL, Corchado J, Sanchez ML, Truhlar DG (1999) J Phys Chem A 103:3139
51. Curtis LA, Raghavachari K, Redfern PC, Pople JA (1996) J Chem Phys 106:1063
52. Karton A, Martin JML (2007) J Phys Chem A 111:5936
53. Frederix PWJM, Yang CH, Groenenboom GC, Parker DH, Alnama K, Western CM, Orr-Ewing AJ (2009) J Phys Chem A 113:14995
54. Helgaker T, Klopper W, Tew DP (2008) Mol Phys 106:2107