Atomization energies from coupled-cluster calculations augmented with explicitly-correlated perturbation theory

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ABSTRACT

The atomization energies of the 105 molecules in the test set of Bakowies [D. Bakowies, J. Chem. Phys. 127 (2007) 084105] have been computed with an estimated standard deviation (from the values compiled in the Active Thermochemical Tables) of ±0.1 kJ/mol per valence electron in the molecule. Equilibrium geometries and harmonic vibrational frequencies were calculated at the all-electron CCSD(T)/cc-pCVTZ level, that is, at the level of coupled-cluster theory with singles, doubles and non-iterative triples in a correlation-consistent polarized core–valence triple-zeta basis. Single-point energy calculations were performed at the all-electron CCSD(T) level in a correlation-consistent polarized core–valence quadruple-zeta basis (cc-pCVQZ), and several corrections were added: (i) a correction for the basis-set truncation error, obtained from second-order perturbation theory using Slater-type geminals (MP2-F12 theory), (ii) a correction for the effect of anharmonicity on the zero-point vibrational energy, (iii) a relativistic correction, (iv) a correction for the difference between the full CCSDT model (coupled-cluster theory with singles, doubles and triples) and the CCSD(T) approximation, and (v) a correction for connected quadruple excitations obtained from CCSDT(Q) calculations. The correction for the basis-set truncation error was obtained from MP2-F12 calculations by scaling the MP2 basis-set truncation error by an empirically optimized "interference factor" of $f_{int} = 0.78$. The reference values from the Active Thermochemical Tables for 73 molecules in the test set, the equilibrium geometries, the harmonic vibrational frequencies, and all of the energy corrections represent valuable data for performance assessments of additivity schemes that will be developed in the future, in which the basis-set truncation error will be calculated at the level of coupled-cluster theory using Slater-type geminals (CC-F12 theory). Such a scheme will be free of empirical corrections and scaling factors.

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1. Introduction

The purpose of the present article is to provide a set of benchmark data in anticipation of rigorous assessments of various explicitly-correlated coupled-cluster R12 and F12 methods (CC-R12 and CC-F12).

These CC-R12 and CC-F12 methods have been developed since the publication of the pioneering work by Kutzelnigg on the He atom in 1985 [1], in which the conventional He-atom configuration-interaction expansion in terms of orbital products was augmented with one extra two-electron function that was linear in the interelectronic distance r_{12}. Furthermore, in this 1985 paper, it was proposed to use basis functions of the form

$$|\chi_{mn}\rangle = \widehat{Q}_{12} f(r_{12}) |mn\rangle \qquad (1)$$

in correlated calculations on many-electron atoms and molecules, where $|mn\rangle$ is an antisymmetrized product of two spin orbitals that are occupied in the Hartree–Fock reference wave function, where $\widehat{Q}_{12} = (1 - \widehat{O}_1)(1 - \widehat{O}_2)$, with $\widehat{O} = \sum_m |m\rangle\langle m|$, is a projection operator taking care of strong orthogonality [1–4], and where $f(r_{12}) = r_{12}$. (It has recently become common practice to speak of R12 methods when $f(r_{12}) = r_{12}$ and of F12 methods when a particular function of r_{12} is used.) For many-electron systems, first R12 results were published at the level of Møller–Plesset perturbation theory (MP2) in Ref. [2] and the general theory for all matrix elements needed in configuration-interaction with singles and doubles (CISD), as well as second- and third-order Møller–Plesset perturbation (MP3) theories, was published in Ref. [3]. First R12 results obtained at the configuration-interaction with doubles (CID) and MP3 levels were published in Ref. [5].

A few years later, Noga et al. developed the CC-R12 methods [6]. In a landmark paper, Noga and Kutzelnigg presented a comprehensive diagrammatic derivation of the CC-R12 equations in the so-called "standard approximation B" at the levels of coupled-cluster

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theory with singles, doubles, and triples (CCSDT) as well as at the level of fourth-order Møller–Plesset (MP4) perturbation theory [7]. Fifth-order non-iterative corrections were also discussed.

An integral-direct CC-R12 program denoted DIRCCR12-OS was developed soon thereafter [8,9], both for closed- and open-shell species [10]. Recent examples of the performance of the DIRCCR12-OS program can be found in Refs. [11–13].

In the years 2002–2004, two important developments triggered renewed interest in the R12 methods. In 2002, Klopper and Samson introduced an auxiliary basis set for the resolution-of-the-indentity (RI) approximation that is used to avoid the calculation of three- and more-electron integrals [14]. In the aforementioned standard approximation (SA), the same basis set was used for the orbital expansion *and* the RI insertion, which simplified the equations dramatically [7], but which required a very large basis set of atomic orbitals to achieve reliable results, as can be seen in Refs. [11–13]. This problem was alleviated by the introduction of the auxiliary basis set.

In 2004, Ten-no proposed to use Slater-type geminals (STGs) of the form $f(r_{12}) = \exp(-\gamma r_{12})$ in place of the linear r_{12} terms [15]. The use of STGs was a significant improvement on the linear r_{12} terms in particular in calculations with small basis sets, which had become possible by using an auxiliary basis set for the RI approximation.

Since 2004, a number of approximate CC-F12 methods have been developed using an auxiliary basis set and STGs.

Fliegl et al. have introduced an approximation to the CCSD-F12 method with singles, doubles, and STGs, which was denoted CCSD(F12) [16]. The corresponding model CCSD(T)(F12) includes a correction for non-iterative connected triple excitations [17]. Tew et al. showed that this CCSD(T)(F12) approach can provide quintuple-ζ quality CCSD(T) correlation energies in just a triple-ζ basis set, not only when optimizing all STG amplitudes [18] but also when keeping these amplitudes fixed [19] at their values dictated by the electron–electron cusp conditions (for a recent discussion of the cusp conditions, cf. Ref. [20]), as first done by Ten-no at the MP2-F12 level [21,22].

Adler et al. have introduced a much simpler approximation to the CCSD-F12 model [23], and in a series of papers, Valeev and co-workers [24–26] have developed the approximate model $CCSD(2)_{\overline{R12}}$, which treats the R12- or F12-dependent terms through Löwdin perturbation theory. Also the fixed-amplitudes approach and corrections for connected triple excitations have been included in the $CCSD(2)_{\overline{R12}}$ model.

Based on an automated implementation by means of computerized symbolic algebra, Shiozaki et al. have implemented a full CCSD-F12 method that relies neither on the SA, nor on truncations or other approximations such at the generalized (GBC) and extended (EBC) Brillouin conditions [27,28]. Instead, these autors use multiple RI insertions. In contrast to this, Bokhan and co-workers have implemented a fixed-amplitude CCSD(T)-F12 method on the basis of the SA, without auxiliary basis [29].

The present work aims at providing benchmark data for future work on performance assessments of the CCSD-F12 method and its approximations.

In the next section, we shall briefly introduce the additivity scheme that is used to calculate the atomization energies of a test set of 106 molecules. This is the same test set that was investigated by Bakowies [30]. It contains 105 closed-shell molecules, plus dihydrogen. The latter was added because it often occurs in assessments of reaction enthalpies.

It is important to note that the additivity scheme given below is not meant as a new "model chemistry" or "composite" or "multicoefficient" method. Rather, the purpose of the present work is to provide accurate equilibrium geometries and a number of energy corrections such that, when added to CCSD-F12 energies, it should

be possible to obtain calculated atomization energies to within a standard deviation of ≈ 0.1 kJ/mol per valence electron from the ATcT reference values (cf. Section 3.1).

Various additivity schemes and model chemistries already exist in the literature (a recent brief review can be found in Ref. [31]). Among these are the Gaussian-*n* ($n = 2,3,4$) theories of Curtiss et al. [32–34], the correlation-consistent composite approach (ccCA) of DeYonker et al. [35,36], the complete basis set (CBS) methods of Petersson and co-workers [37,38], the focal-point analysis (FPA) approach of Allen and co-workers [39,40], the multicoefficient correlation methods (MCCMs) of Fast et al. [41–43], the HEAT protocol of Tajti et al. [44], Bomble et al. [45] and Harding et al. [46], and the Weizmann-*n* ($n = 1$–4) theories of Martin and co-workers [47–50]. Many of these model chemistries contain extrapolations, empirical corrections, and empirical scaling factors. Also Feller, Dixon and co-workers (cf. Refs. [51–56] and references therein) have developed an approach to calculate molecular thermodynamic properties based on fc-CCSD(T) coupled-cluster theory using correlation-consistent basis sets, extrapolations to the basis-set limit, and inclusion of a number of corrections such as core–valence interactions, scalar and spin–orbit relativistic effects and zero-point vibrational energies (ZPVEs).

As already said, the additivity scheme given below, which in its present form contains an empirical scaling factor, should not be misunderstood as a new black-box tool with broad applicability in computational thermochemistry. Rather, the hope is expressed that an accurate and reliable additivity scheme can be designed in the future based on the CCSD(T)(F12)/def2-QZVPP level, for example, free of extrapolations, empirical corrections, and empirical scaling factors. Such a scheme will be studied in future work, using the data compiled in the present work.

The present article is organized as follows: In Section 2, we give a brief overview of the additivity scheme used. More detailed information on the calculation of the individual contributions to the additivity scheme is given in Section 3. Results are presented in Section 4, including a discussion of the remaining sources of error in Section 4.2. Our conclusions are collected in Section 5.

2. Overview of the additivity scheme

In the following, we shall give a brief overview of the additivity scheme used before we turn to the full computational details presented in Section 3.

We shall denote total electronic energies as E and electron-correlation contributions as δE. For example,

$$E_{\text{fc-CCSD(T)/cc-pVTZ}} = E_{\text{Hartree–Fock/cc-pVTZ}} + \delta E_{\text{fc-CCSD(T)/cc-pVTZ}}. \tag{2}$$

The total electronic energy is obtained by adding various corrections to the fc-CCSD(T)/cc-pCVQZ//ae-CCSD(T)/cc-pCVTZ energy,

$$\begin{aligned}E_{\text{total}} = {}&E_{\text{fc-CCSD(T)/cc-pCVQZ}} + \Delta E_{\text{CV}} + \Delta E_{\text{ZPVE}} + \Delta E_{\text{Anh}} + \Delta E_{\text{F12}}\\&+ \Delta E_{\text{MVD}} + \Delta E_{\text{SO}} + \Delta E_{\text{T}} + \Delta E_{\text{(Q)}}.\end{aligned} \tag{3}$$

All of these corrections except ΔE_{Anh} were computed at the ae-CCSD(T)/cc-pCVTZ equilibrium geometry of the molecule in question (cf. Section 3.3). ΔE_{CV} is a correction for core–valence correlation effects, which was obtained as the difference between the ae-CCSD(T)/cc-pCVQZ and fc-CCSD(T)/cc-pCVQZ energies. ΔE_{ZPVE} is the harmonic zero-point vibrational energy calculated at the ae-CCSD(T)/cc-pCVTZ level. ΔE_{Anh} is a correction to the harmonic ZPVE due to anharmonic effects, calculated at the fc-MP2/cc-pVDZ level. ΔE_{F12} is a correction for the basis-set truncation error. It was calculated as follows:

$$\delta E_{\text{F12}} = f_{\text{int}}\left(\delta E_{\text{fc-MP2-F12}} - \delta E_{\text{fc-MP2/cc-pCVQZ}}\right), \tag{4}$$

$$\Delta E_{\text{F12}} = E_{\text{Hartree–Fock/def2-QZVPP}} - E_{\text{Hartree–Fock/cc-pCVQZ}} + \delta E_{\text{F12}}, \tag{5}$$

where f_{int} is an empirical "interference" factor [57–60]. In the course of the present work, an optimization of this factor by minimizing the mean deviation from the ATcT reference values yielded $f_{int} = 0.78$, but we also report the statistical analysis of the calculated atomization energies obtained with $f_{int} = 0.0$ and $f_{int} = 1.0$. Concerning Eq. (5), we note that the Hartree–Fock energy in the def2-QZVPP basis was always lower than in the cc-pCVQZ basis.

ΔE_{MVD} is a correction for scalar-relativistic effects (one-electron Darwin and mass–velocity terms) calculated at the ae-CCSD(T)/cc-pCVTZ level [61,62]. For the atoms C, O, and F, the spin–orbit corrections to the total electronic energy amount to $\Delta E_{SO} = -0.35399, -0.93278$, and -1.61153 kJ/mol, respectively [63].

Finally, a full correction for connected triple excitations and a perturbative correction for connected quadruple excitations were computed as

$$\Delta E_T = E_{CCSDT/cc\text{-}pVTZ} - E_{CCSD(T)/cc\text{-}pVTZ}, \tag{6}$$

$$\Delta E_{(Q)} = E_{CCSDT(Q)/cc\text{-}pVDZ} - E_{CCSDT/cc\text{-}pVDZ}. \tag{7}$$

Note that ΔE_T does *not* refer to the total contribution of connected triples excitations but only to the difference between the CCSDT and CCSD(T) models.

3. Computational details

3.1. Active Thermochemical Tables

Accurate, reliable, and internally consistent thermochemical values were taken from the Active Thermochemical Tables (ATcT) [64–67]. As opposed to the traditional sequential approach, the ATcT derive their results from a thermochemical network (TN) using all available knowledge. The thermochemical values used in the present work have been obtained from the latest version of the Core (Argonne) Thermochemical Network, C(A)TN, which is currently under development [68] and describes ca. 900 species interconnected by ca. 10,000 experimental and theoretical determinations.

3.2. Computer programs

All coupled-cluster and second-order Møller–Plesset (MP2) calculations were carried out with the Mainz–Austin–Budapest 2005 version of the ACES II program [69] and with the MRCC program [70,71]. The coupled-cluster calculations performed with ACES II were carried out at the level of coupled-cluster theory with singles and doubles (CCSD, cf. Refs. [72,73]) including a non-iterative correction for connected triple excitations (CCSD(T), cf. Refs. [74–78]). Kállay's MRCC program was used for coupled-cluster calculations with singles, doubles, and triples including a non-iterative correction for connected quadruple excitations (CCSDT(Q), cf. Refs. [79,80]).

Explicitly-correlated calculations [81,82] were carried out at the level of second-order perturbation theory (MP2-F12) with the TURBOMOLE program [83].

3.3. Geometries and zero-point vibrational energies

All molecular equilibrium geometries were optimized at the all-electron CCSD(T) level [ae-CCSD(T)] in the correlation-consistent polarized core–valence triple-zeta basis set (cc-pCVTZ) of Dunning [84] and Woon and Dunning [85]. Using the cc-pCVTZ basis implies that this basis is used for C, N, O, and F in conjunction with a correlation-consistent polarized valence triple-zeta basis set (cc-pVTZ) for H [84]. Harmonic vibrational frequencies and harmonic ZPVEs were computed at the same level, that is, at the ae-CCSD(T)/cc-pCVTZ level.

The ae-CCSD(T) calculations of the closed-shell molecules were performed using a restricted Hartree–Fock (RHF) reference determinant.

3.4. Anharmonic corrections

MP2 calculations were carried out to obtain anharmonic corrections to the ZPVEs. The cubic force field and those parts of the quartic force field that are required for the determination of anharmonic effects were obtained by means of numerical differentiation of analytical Hessians about the fc-MP2/cc-pVDZ equilibrium structure, as implemented in the Mainz–Austin–Budapest 2005 version of the ACES II program [69,86]. The MP2 calculations of the closed-shell molecules were done using an RHF reference, in the frozen-core approximation, and in the correlation-consistent polarized valence double-zeta (cc-pVDZ) basis set of Dunning [84]. Thus, harmonic ZPVEs were obtained at the ae-CCSD(T)/cc-pCVTZ level and anharmonic corrections to these were obtained at the fc-MP2/cc-pVDZ level.

3.5. Coupled-cluster single-point energies

The CCSD(T) single-point energy calculations of the closed-shell molecules were performed using an RHF reference determinant. The corresponding calculations of the atoms C, N, O, and F were done using a restricted open-shell Hartree–Fock (ROHF) reference as implemented in ACES II, employing semi-canonical orbitals [78].

The single-point energy CCSD(T) calculations were performed in the correlation-consistent polarized core–valence quadruple-zeta (cc-pCVQZ) basis set (cc-pVQZ for H), both in an all-electron treatment [ae-CCSD(T)/cc-pCVQZ] and in a frozen-core treatment [fc-CCSD(T)/cc-pCVQZ]. The difference between these two calculations is referred to as core–valence (CV) contribution.

The single-point energy CCSDT and CCSDT(Q) calculations were performed in the correlation-consistent polarized triple-zeta (cc-pVTZ) and double-zeta (cc-pVDZ) basis sets [84], respectively, in the frozen-core approximation. The corresponding calculations of the atoms C, N, O, and F were done using an unrestricted Hartree–Fock (UHF) reference as implemented in MRCC. The (Q) contribution was obtained as the difference between the fc-CCSDT(Q)/cc-pVDZ and fc-CCSDT/cc-pVDZ energies, using RHF and UHF reference determinants for the molecules and atoms, respectively. Similarly, the full-triples-minus-(T)-triples correction was obtained as the difference between the fc-CCSDT/cc-pVTZ and fc-CCSD(T)/cc-pVTZ energies.

3.6. Explicitly-correlated perturbation theory

The MP2-F12 calculations were carried out using a Slater-type geminal with exponent $\gamma = 1.4\ a_0^{-1}$, represented by a linear combination of six Gaussians with exponents and coefficients taken from Ref. [87].

The implementation of the MP2-F12 method in the RICC2 module [88,89] of TURBOMOLE is described in detail in Refs. [90,91]. The robust density-fitting technique of Manby was used to avoid the computation of four-index integrals [92], and a complementary auxiliary basis set (CABS) [93] was used for the resolution-of-the-indentity (RI) approximation of explicitly-correlated theory. The approach 2B of explicitly-correlated theory [90,91] was used and the amplitudes were optimized in an orbital-invariant manner [94]. The matrix representation of the core Hamiltonian, $\hat{T} + \hat{V}$, was used for the commutator approximation that avoids the two-electron integrals over the operator $[\hat{T}, f(r_{12})]$ [90,95]. For the open-shell MP2-F12 calculations of the atoms, an ROHF reference function and semi-canonical orbitals were used. The core orbitals

(1s for C, N, O, and F) were not included in the MP2-F12 approach (fc-MP2-F12).

The fc-MP2-F12 calculations were performed in the def2-QZVPP basis [96]. For the density-fitting approximation, the aug-cc-pwCV5Z MP2 fitting basis of Hättig was used (aug-cc-pV5Z for H) [97]. The def2-QZVPP Hartree–Fock exchange fitting basis was used in two different manners. On the one hand, it was used as CABS, and on the other hand, it was used for computing matrix elements of the Fock operator using the RI-*JK* approximation [98].

3.7. Relativistic corrections

Darwin and mass–velocity energy corrections [99] were computed analytically [78,100] as first-order molecular properties at the ae-CCSD(T)/cc-pCVTZ level, using RHF and ROHF reference wave functions for the molecules and atoms, respectively.

4. Results and discussion

4.1. Final results

The computed atomization energies are reported in Table 1 and are compared with the ATcT values where available. The deviation of the computed atomization energies from the ATcT values are given in the second-last column. In Table 1, the reported CCSD(T) values refer to the fc-CCSD(T)/cc-pCVQZ//ae-CCSD(T)/cc-pCVTZ level, which is the baseline of the additivity scheme. The values presented in the other columns are the corrections described in Eq. (3).

In the last column of Table 1, the D1 diagnostic of Jansen and Nielsen is given [101], which is an indicator for the multireference character of the molecule's electronic ground state. Since all of the calculations performed in the present work are of the single-reference type, we expected larger deviations for the molecules with large D1 values than for those with small D1 values. To investigate this, we plot in Fig. 1 the deviations of the computed atomization energies from the ATcT values as a function of the molecule's D1 value (from 0 to 0.06). If the F12 correction is omitted, there are large deviations when D1 is large, but there are also large errors for relatively small D1 values (e.g., for cyclopropane, where the error amounts to −29.6 kJ/mol while D1 is only 0.015). Hence, for the molecules under study and in contrast to our expectations, the error is not dominated by the high-level excitations (beyond the CCSDT(Q) model) of coupled-cluster theory, which become more important with increasing multireference character. After adding the F12 correction from MP2-F12 theory (but without scaling with the interference factor f_{int}), we observe a very weak trend of increasing error with increasing D1 diagnostic, but after scaling with the empirical factor of $f_{int} = 0.78$, the remaining deviations appear to be independent of D1. Hence, the final deviations between the calculated atomization energies and the ATcT reference values are independent of D1 up to values of $D1 = 0.06$. The deviations for N_2O_3 and N_2O_4 (with D1 > 0.07, not shown in Fig. 1) are quite large, however. For $f_{int} = 0$, the deviations are −42 and −52 kJ/mol, and for $f_{int} = 1$, they are 13 and 14 kJ/mol, respectively.

The errors reported in Table 1 are statistically analyzed in Table 2. For $f_{int} = 0.78$, we observe that the mean deviation between calculation and ATcT amounts to −0.12 kJ/mol, with a mean absolute deviation of 0.9 kJ/mol and a root-mean-square (RMS) deviation of 1.2 kJ/mol. Table 2 also reports these errors for calculations without F12 corrections from MP2-F12 theory ($f_{int} = 0.0$) as well as for calculations with F12 correction from MP2-F12 theory but without empirical scaling ($f_{int} = 1.0$). In both cases, the errors are substantially larger. In the cases $f_{int} = 0.0$ and $f_{int} = 1.0$, the errors are about 20 and 5–6 times larger, respectively, than for $f_{int} = 0.78$. This

means that already adding the unscaled F12 contribution represents an improvement over the fully uncorrected results, reducing the error by roughly a factor of 3–4. However, a satisfactory agreement between computed and ATcT values is only obtained for $f_{int} = 0.78$.

In Section 4.2, we shall analyze the uncertainties of the individual contributions of the additivity scheme together with the possible errors due to neglected terms. As we shall see, these uncertainties and errors are of about the same order of magnitude and add up (in terms of a Gaussian error propagation) to the observed deviation between the calculated atomization energies and the ATcT reference values. In Section 4.2, we shall focus on the RMS errors *per valence electron* when we discuss the errors of the individual contributions. We do this for two reasons. Firstly, as Harding et al. [46] have pointed out, it is a necessary consequence of size extensivity that the characteristic relative error in atomization energies will remain constant while the absolute error will grow linearly with the size of the system. We have chosen to take the number of electrons in the valence shells (1 for H, 4 for C, 5 for N, 6 for O, 7 for F) as a measure of the size of the system. Secondly, for the propagated estimate of the error to be a legitimate estimate of a standard deviation σ, all of the components also must be a σ or best estimates thereof (e.g., RMS or experience-based-95%-confidence-interval/2, but nothing based on mean absolute errors).

Figs. 2 and 3 show that not only the deviations per molecule (Fig. 2) but also the deviations per valence electron (Fig. 3) appear to form normal distributions (Gaussian distributions). In these figures, the points represent the number of molecules with an error within the corresponding interval (e.g., 16 molecules have a total deviation between −1.5 and −0.5 kJ/mol), and the bell curves are simple non-linear fits to these points.

4.2. Error estimation of individual contributions

4.2.1. Hartree–Fock contributions

Concerning the Hartree–Fock level, our additivity scheme is based on Hartree–Fock calculations in the def2-QZVPP basis [cf. Eq. (5)]. This basis yields Hartree–Fock contributions to the atomization energies closer to the limit of a complete basis than the cc-pCVQZ basis, but the basis-set truncation error is still not negligible. To estimate this error, we have computed the Hartree–Fock contribution in the cc-pCV5Z basis for the 18 molecules shown in Table 3. For these molecules, the RMS deviation between the def2-QZVPP and cc-pCV5Z contributions to the atomization energies amounts to 1.0 kJ/mol per molecule or 0.08 kJ/mol per valence electron. We adopt this RMS error of 0.08 kJ/mol per valence electron for our overall error analysis (cf. Section 4.2.7).

4.2.2. Core–valence contributions

In Table 3, the core–valence contributions to the atomization energies are presented for a selection of 18 molecules, obtained at the CCSD(T) level in the cc-pCVQZ and cc-pCV5Z basis sets as well as from a two-point X^{-3} extrapolation [102] based on the cc-pCVQZ and cc-pCV5Z results, which is denoted cc-pCV(Q5)Z. For the final results presented in Table 1, the CCSD(T)/cc-pCVQZ data were used, and the accuracy of these data can be estimated from the difference between the cc-pCVQZ and cc-pCV(Q5)Z core–valence contributions. The mean absolute and RMS deviations for these 18 molecules amount to 0.36 and 0.46 kJ/mol, respectively. Expressed in terms of error per valence electron, the mean absolute and RMS deviations are 0.033 and 0.042 kJ/mol.

In Ref. [49], Karton et al. report core–valence contributions for the 14 molecules H_2O, C_2H_2, CH_4, CO_2, CO, F_2, FH, N_2, H_3N, N_2O, O_3, C_2H_4, CH_2O (formaldehyde), and HNO, as obtained in W4 theory, that is, at the extrapolated CCSD(T)/aug-cc-pwCV(TQ)Z level.

Table 1
Atomization energies in kJ/mol[a].

Nr.[b]	Molecule[c]		CCSD(T)	CV	ZPVE	Anh.	F12	MVD	SO	T	(Q)	Total	ATcT	Error	D1[d]
1	CFN	Cyanogen fluoride	1252.9	6.9	−26.0	0.1	19.1	−1.8	−2.0	−3.1	4.9	1250.9	1250.3 ± 1.7	0.6	0.027
2	CFN	Isocyanogen fluoride	956.1	5.2	−21.1	0.1	18.0	−1.6	−2.0	−2.4	4.7	957.0	959.2 ± 2.7	−2.2	0.035
3	CF$_2$	Singlet difluoromethylene	1065.6	1.9	−18.6	0.1	14.5	−1.5	−3.6	−1.1	2.6	1060.0	1059.1 ± 0.8	0.9	0.045
4	CF$_2$O	Carbonyl fluoride	1732.6	5.9	−37.5	0.2	22.3	−3.0	−4.5	−3.1	4.3	1717.2	1718.4 ± 0.9	−1.2	0.041
5	CF$_4$	Tetrafluoromethane	1975.6	4.6	−46.1	0.0	25.6	−3.9	−6.8	−3.2	3.6	1949.5	1947.9 ± 0.6	1.6	0.027
6	CHF	Singlet fluoromethylene	878.1	1.8	−32.6	0.6	10.6	−1.0	−2.0	0.0	1.5	857.0			0.038
7	CHFO	Formyl fluoride	1664.8	5.5	−55.2	0.5	19.0	−2.1	−2.9	−2.2	3.5	1631.0	1631.4 ± 0.9	−0.4	0.038
8	CHF$_3$	Trifluoromethane	1898.2	4.5	−67.8	0.0	22.1	−3.1	−5.2	−2.3	2.8	1849.2	1848.7 ± 0.9	0.5	0.026
9	CHN	Hydrogen cyanide	1287.5	6.6	−41.9	0.3	16.1	−0.9	−0.4	−2.5	3.7	1268.5	1268.3 ± 0.2	0.2	0.027
10	CHN	Hydrogen isocyanide	1225.3	5.8	−40.8	0.3	15.7	−1.1	−0.4	−1.6	2.4	1205.7	1207.0 ± 0.6	−1.3	0.029
11	CHNO	Cyanic acid	1683.1	8.2	−56.3	0.3	23.8	−2.2	−1.3	−3.7	5.2	1657.1	1657.2 ± 1.0	−0.1	0.029
12	CHNO	Isocyanic acid	1784.7	8.6	−55.8	0.2	24.5	−2.3	−1.3	−3.0	4.9	1760.4	1761.0 ± 0.4	−0.6	0.043
13	CHNO	Formonitrile oxide	1490.7	8.9	−50.1	0.1	24.6	−2.4	−1.3	−4.7	8.1	1473.9	1474.1 ± 1.2	−0.2	0.051
14	CHNO	Isofulminic acid	1434.6	6.6	−53.2	0.4	22.9	−2.1	−1.3	−3.1	4.7	1409.4	1410.2 ± 1.0	−0.8	0.033
15	CH$_2$	Singlet methylene	749.7	1.6	−43.8	0.6	6.7	−0.4	−0.4	0.9	0.3	715.4	714.9 ± 0.2	0.5	0.009
16	CH$_2$F$_2$	Difluoromethane	1810.3	4.5	−87.3	1.0	18.5	−2.4	−3.6	−1.5	2.0	1741.5	1741.7 ± 0.8	−0.2	0.024
17	CH$_2$N$_2$	Cyanamide	1993.6	9.8	−89.7	1.0	28.0	−2.2	−0.4	−3.5	4.8	1941.5			0.030
18	CH$_2$N$_2$	3H-Diazirine	1817.0	7.1	−87.4	1.2	27.2	−1.7	−0.4	−4.5	5.8	1764.3			0.028
19	CH$_2$N$_2$	Diazomethane	1854.6	9.3	−82.8	1.4	26.8	−2.1	−0.4	−3.5	6.5	1809.9			0.038
20	CH$_2$O	Formaldehyde	1547.1	5.2	−70.2	1.0	15.2	−1.4	−1.3	−1.5	2.5	1496.6	1495.8 ± 0.2	0.8	0.034
21	CH$_2$O	Hydroxymethylene	1330.3	3.5	−70.5	1.0	15.0	−1.4	−1.3	−0.7	2.0	1277.9	1277.8 ± 1.1	0.1	0.038
22	CH$_2$O$_2$	Dioxirane	1686.3	4.8	−85.8	1.1	23.2	−1.8	−2.2	−3.8	6.0	1627.9	1629.6 ± 1.7	−1.7	0.027
23	CH$_2$O$_2$	Formic acid	2070.1	6.7	−89.4	1.2	23.7	−2.6	−2.2	−2.7	4.0	2008.7	2008.4 ± 0.3	0.3	0.041
24	CH$_2$O$_3$	Performic acid	2209.6	6.7	−96.2	1.2	30.7	−2.9	−3.2	−3.8	6.8	2148.9			0.042
25	CH$_3$F	Fluoromethane	1750.8	4.7	−103.9	0.5	14.6	−1.6	−2.0	−0.8	1.2	1663.4	1665.1 ± 0.6	−1.7	0.019
26	CH$_3$N	Methanimine	1812.7	6.4	−104.9	1.4	19.0	−1.5	−0.4	−1.6	2.2	1733.6	1733.5 ± 1.0	0.1	0.027
27	CH$_3$NO	Formamide	2339.9	8.7	−119.5	2.1	28.3	−2.8	−1.3	−2.4	3.6	2256.6			0.040
28	CH$_3$NO$_2$	Methyl nitrite	2464.8	6.8	−127.7	1.8	34.0	−2.6	−2.2	−3.7	7.8	2379.0			0.052
29	CH$_3$NO$_2$	Nitromethane	2472.8	8.3	−131.4	2.2	35.3	−3.2	−2.2	−4.5	8.1	2385.3			0.054
30	CH$_4$	Methane	1744.9	5.0	−117.9	0.3	9.5	−0.8	−0.4	−0.2	0.3	1640.9	1642.2 ± 0.1	−1.3	0.011
31	CH$_4$N$_2$O	Urea	3098.9	11.6	−168.7	3.0	40.7	−3.9	−1.3	−3.6	4.5	2981.0			0.041
32	CH$_4$O	Methanol	2124.4	5.8	−135.5	1.8	18.8	−2.0	−1.3	−1.3	1.6	2012.4	2012.7 ± 0.2	−0.3	0.017
33	CH$_5$N	Methylamine	2407.3	7.2	−169.0	2.6	22.3	−1.9	−0.4	−1.1	1.4	2268.4	2269.0 ± 0.5	−0.6	0.014
34	CO	Carbon monoxide	1071.6	3.8	−12.9	0.0	11.0	−0.7	−1.3	−1.6	2.7	1072.5	1072.1 ± 0.1	0.4	0.035
35	CO$_2$	Carbon dioxide	1605.2	7.0	−30.4	0.1	19.7	−2.1	−2.2	−3.3	5.1	1599.1	1598.2 ± 0.1	0.9	0.042
36	C$_2$F$_2$	Difluoroacetylene	1582.1	11.4	−34.6	0.2	21.6	−3.2	−3.9	−3.5	4.7	1574.8	1577.0 ± 1.7	−2.2	0.027
37	C$_2$F$_4$	Tetrafluoroethylene	2425.5	10.7	−57.3	0.5	33.3	−4.7	−7.2	−4.0	5.3	2402.2	2405.2 ± 1.0	−3.0	0.037
38	C$_2$HF	Fluoroacetylene	1638.5	10.4	−52.5	0.4	17.6	−2.2	−2.3	−3.0	3.6	1610.7	1612.3 ± 1.0	−1.6	0.024
39	C$_2$HF$_3$	Trifluoroethylene	2409.4	10.3	−77.6	0.7	29.2	−3.9	−5.5	−3.2	4.3	2363.5			0.034
40	C$_2$H$_2$	Acetylene	1671.4	9.6	−69.4	0.9	14.6	−1.2	−0.7	−2.3	2.6	1625.5	1626.2 ± 0.2	−0.7	0.025
41	C$_2$H$_2$F$_2$	1,1-Difluoroethylene	2420.2	10.0	−96.8	1.1	24.4	−3.0	−3.9	−2.7	3.4	2352.7			0.029
42	C$_2$H$_2$O	Ketene	2198.9	10.8	−82.8	0.9	21.1	−2.0	−1.6	−2.5	3.9	2146.7	2147.3 ± 0.2	−0.6	0.039
43	C$_2$H$_2$O	Oxirene	1871.9	9.5	−75.7	1.0	24.8	−2.0	−1.6	−3.7	4.8	1828.8			0.026
44	C$_2$H$_2$O$_2$	Glyoxal	2616.9	10.5	−97.3	1.3	29.2	−2.8	−2.6	−3.7	5.7	2557.1	2555.3 ± 0.6	1.8	0.040
45	C$_2$H$_3$F	Fluoroethylene	2370.4	9.6	−115.7	1.4	20.7	−2.2	−2.3	−1.9	2.5	2282.5	2278.4 ± 1.7	4.1	0.024
46	C$_2$H$_3$FO	Acetyl fluoride	2919.4	10.6	−129.3	1.6	28.2	−3.0	−3.3	−3.1	4.0	2825.1			0.039
47	C$_2$H$_3$N	Acetonitrile	2542.8	11.6	−118.9	0.6	24.5	−1.8	−0.7	−3.4	4.3	2459.2			0.027
48	C$_2$H$_3$N	Methyl isocyanide	2441.3	10.5	−118.8	0.6	24.2	−1.9	−0.7	−2.8	3.2	2355.7			0.028
49	C$_2$H$_4$	Ethylene	2334.3	9.3	−133.7	2.1	16.2	−1.4	−0.7	−1.4	1.5	2226.3	2225.9 ± 0.2	0.4	0.025
50	C$_2$H$_4$O	Acetaldehyde	2802.0	10.2	−146.1	1.8	24.0	−2.2	−1.6	−2.3	3.1	2688.9	2688.9 ± 0.4	0.0	0.036
51	C$_2$H$_4$O	Oxirane	2691.0	9.9	−151.5	2.2	25.4	−2.4	−1.6	−3.0	3.1	2573.0	2573.9 ± 0.5	−0.9	0.023
52	C$_2$H$_4$O$_2$	Acetic acid	3320.2	11.7	−163.0	2.1	32.7	−3.4	−2.6	−3.7	4.5	3198.5	3199.3 ± 1.5	−0.8	0.042
53	C$_2$H$_4$O$_2$	Methyl formate	3249.9	11.0	−163.9	2.1	32.4	−3.4	−2.6	−3.8	4.7	3126.5	3125.2 ± 0.6	1.3	0.043
54	C$_2$H$_5$F	Fluoroethane	2987.0	9.5	−179.5	2.5	23.0	−2.4	−2.3	−1.6	1.7	2838.0	2838.5 ± 1.9	−0.5	0.021

55	C_2H_5N	Aziridine	2974.5	11.4	−185.3	2.8	28.8	−2.5	−0.7	−3.0	2.8	2828.7			0.018
56	C_2H_6	Ethane	2956.5	9.6	−196.6	0.9	18.0	−1.6	−0.7	−1.0	0.9	2786.0	2787.2 ± 0.2	−1.2	0.012
57	C_2H_6O	Dimethyl ether	3307.2	10.1	−210.4	3.3	26.8	−2.8	−1.6	−2.2	2.2	3132.6	3132.4 ± 0.5	0.2	0.021
58	C_2H_6O	Ethanol	3357.5	10.6	−210.9	2.9	27.2	−2.7	−1.6	−2.2	2.2	3183.0	3182.8 ± 0.3	0.2	0.018
59	C_2N_2	Cyanogen	2054.5	13.4	−41.2	0.2	29.5	−2.0	−0.7	−6.3	9.1	2056.5	2055.8 ± 0.5	0.7	0.029
60	C_3H_3N	Acrylonitrile	3144.0	16.1	−132.3	1.5	30.8	−2.4	−1.1	−4.9	6.0	3057.7			0.031
61	C_3H_4	Allene	2908.3	14.3	−144.3	1.0	22.4	−2.0	−1.1	−2.6	2.9	2798.9	2800.9 ± 0.5	−2.0	0.023
62	C_3H_4	Cyclopropene	2815.6	14.2	−147.0	2.0	23.4	−2.2	−1.1	−3.6	3.1	2704.3	2705.1 ± 1.0	−0.8	0.024
63	C_3H_4	Propyne	2916.5	14.8	−145.6	1.7	19.7	−2.0	−1.1	−3.3	3.4	2804.1	2805.6 ± 0.5	−1.5	0.025
64	C_3H_6	Cyclopropane	3533.8	14.7	−214.5	1.1	25.3	−2.4	−1.1	−2.8	2.1	3356.1	3359.7 ± 0.6	−3.6	0.015
65	C_3H_6	Propene	3565.7	14.2	−209.2	3.0	24.8	−2.2	−1.1	−2.3	2.3	3395.1	3395.0 ± 0.4	0.1	0.024
66	C_3H_8	Propane	4177.0	14.3	−272.1	4.0	26.6	−2.4	−1.1	−2.0	1.6	3945.9	3944.6 ± 0.4	1.3	0.013
67	C_3O_2	Carbon suboxide	2730.2	16.9	−55.8	0.4	32.1	−3.3	−2.9	−6.6	10.4	2721.3			0.053
68	C_4H_4	Butatriene	3489.4	19.1	−156.4	2.3	28.5	−2.6	−1.4	−3.9	5.1	3380.1			0.031
69	C_4H_4	Cyclobutadiene	3383.7	17.5	−159.0	2.0	30.9	−2.7	−1.4	−4.3	5.6	3272.3			0.031
70	C_4H_4	Tetrahedrane	3268.6	20.0	−156.2	2.6	32.1	−3.3	−1.4	−6.4	4.3	3160.4			0.015
71	C_4H_4	Vinylacetylene	3524.1	19.1	−158.9	1.9	29.2	−2.6	−1.4	−4.8	5.0	3411.6			0.029
72	C_4N_2	Dicyanoacetylene	3258.9	23.5	−67.4	0.5	42.0	−3.3	−1.4	−10.3	13.4	3256.1			0.030
73	FH	Hydrogen fluoride	585.1	0.8	−25.0	0.3	6.6	−0.8	−1.6	−0.4	0.8	565.9	566.0 ± 0.0	−0.1	0.013
74	FHO	Hypofluorous acid	648.8	0.6	−36.5	0.4	12.4	−1.0	−2.5	−1.2	3.3	624.3	624.0 ± 0.4	0.3	0.029
75	FHO_2	Fluoroperoxide	853.8	0.7	−47.4	0.6	20.1	−1.3	−3.5	−2.2	6.6	827.4			0.039
76	FH_2N	Monofluoroamine	1052.9	1.9	−72.7	1.2	17.4	−1.4	−1.6	−0.8	2.1	999.0			0.026
77	FH_3N_2	Fluorohydrazine	1678.7	4.4	−119.2	2.1	30.4	−2.5	−1.6	−1.7	3.5	1594.1			0.034
78	FNO	Nitrosyl fluoride	873.6	1.3	−19.2	0.1	21.2	−1.1	−2.5	−1.6	7.0	878.7			0.050
79	F_2	Difluorine	153.7	−0.3	−5.5	0.0	6.4	−0.2	−3.2	−1.0	3.9	153.8	154.6 ± 0.2	−0.8	0.024
80	F_2N_2	Difluorodiazene (cis)	1019.9	2.2	−31.0	0.3	28.8	−1.7	−3.2	−2.8	7.2	1019.7			0.040
81	F_2N_2	Difluorodiazene (trans)	1013.8	2.3	−30.2	0.3	28.5	−1.8	−3.2	−2.8	6.8	1013.5			0.036
82	F_2O	Difluorine monoxide	372.8	−0.4	−13.7	0.1	14.7	−0.6	−4.2	−1.5	6.2	373.5	373.3 ± 0.7	0.2	0.032
83	F_2O_2	Perfluoroperoxide	605.6	−0.4	−21.5	−0.2	22.8	−0.8	−5.1	−1.7	13.6	612.3	609.7 ± 0.8	2.6	0.048
84	F_3N	Trifluoroamine	835.0	0.1	−27.7	0.2	24.3	−1.7	−4.8	−1.7	5.2	828.9			0.033
85	HNO	Nitrosylhydride	840.7	1.9	−36.4	0.7	17.0	−1.2	−0.9	−1.7	4.2	824.3	823.6 ± 0.1	0.7	0.035
86	HNO_2	Nitrous acid (cis)	1276.2	2.5	−53.2	0.7	24.9	−1.8	−1.9	−2.5	6.7	1251.7	1251.5 ± 0.4	0.2	0.047
87	HNO_2	Nitrous acid (trans)	1276.9	2.6	−53.2	0.7	25.1	−1.8	−1.9	−2.2	6.9	1253.0	1253.3 ± 0.1	−0.3	0.045
88	HNO_2	Nitrous acid, H–NO2	1243.6	3.7	−57.7	0.5	26.1	−2.4	−1.9	−3.2	7.5	1216.4			0.052
89	HNO_3	Nitric acid	1585.1	4.4	−69.8	0.7	33.3	−3.2	−2.8	−5.0	9.2	1552.0	1551.6 ± 0.2	0.4	0.053
90	HN_3	Hydrogen azide	1348.5	6.3	−55.9	0.3	29.5	−2.1	0.0	−4.3	8.5	1330.8	1329.7 ± 0.6	1.1	0.043
91	H_2N_2	Diazene (cis)	1192.4	3.2	−72.8	1.1	21.2	−1.3	0.0	−1.8	3.3	1145.4	1143.5 ± 0.9	1.9	0.028
92	H_2N_2	Diazene (trans)	1214.2	3.3	−74.4	1.1	21.8	−1.4	0.0	−1.8	3.3	1166.1	1165.8 ± 0.7	0.3	0.028
93	H_2N_2	Diazene (iso)	1109.1	3.8	−70.9	1.6	22.5	−1.6	0.0	−1.0	2.5	1066.1	1065.1 ± 0.9	1.0	0.038
94	H_2N_2O	Nitrosamide	1580.4	5.0	−85.9	1.6	30.2	−2.4	−0.9	−2.4	5.8	1531.4			0.048
95	H_2O	Water	961.9	1.6	−56.5	0.9	11.3	−1.1	−0.9	−0.6	1.1	917.6	917.8 ± 0.1	−0.2	0.014
96	H_2O_2	Hydrogen peroxide	1106.2	1.7	−69.8	1.3	17.3	−1.6	−1.9	−1.6	3.4	1055.0	1055.2 ± 0.1	−0.2	0.019
97	H_3N	Ammonia	1230.0	2.7	−90.7	1.3	14.2	−1.1	0.0	−0.3	0.8	1156.9	1157.3 ± 0.1	−0.4	0.011
98	H_3NO	Ammonia oxide	1370.3	3.1	−107.9	0.9	25.8	−1.9	−0.9	−1.3	2.3	1290.5			0.022
99	H_3NO	Hydroxylamine	1480.0	3.1	−106.4	1.8	22.0	−2.0	−0.9	−1.3	2.5	1398.7	1398.7 ± 0.5	0.0	0.017
100	H_4N_2	Hydrazine	1803.1	4.8	−141.2	2.7	26.0	−2.2	0.0	−1.2	2.0	1694.0	1695.6 ± 0.2	−1.6	0.013
101	N_2	Dinitrogen	933.0	3.4	−14.1	0.1	17.2	−0.6	0.0	−2.4	4.3	940.8	941.1 ± 0.1	−0.3	0.026
102	N_2O	Nitrous oxide	1100.3	5.0	−28.7	0.1	24.8	−1.9	−0.9	−5.0	9.2	1102.8	1102.0 ± 0.1	0.8	0.046
103	N_2O_3	Dinitrogen trioxide	1587.7	4.5	−44.8	0.3	41.5	−2.9	−2.8	−6.7	15.6	1592.4	1591.1 ± 0.2	1.3	0.071
104	N_2O_4	Dinitrogen tetraoxide	1912.7	6.6	−61.1	0.3	49.2	−4.3	−3.7	−9.4	17.8	1908.0	1908.5 ± 0.2	−0.5	0.072
105	O_3	Ozone	583.1	0.2	−17.6	−0.1	19.8	−1.1	−2.8	−4.2	17.6	594.9	596.1 ± 0.1	−1.2	0.057
106	H_2	Dihydrogen	456.6	0.0	−26.4	0.3	2.2	0.0	0.0	0.0	0.0	432.7	432.1 ± 0.0	0.6	0.005

[a] The individual contributions are explained in the text, see Section 2.
[b] Same number and same molecule as in Ref. [30] except for dihydrogen.
[c] The ae-CCSD(T)/cc-pCVTZ equilibrium geometry was used for each molecule.
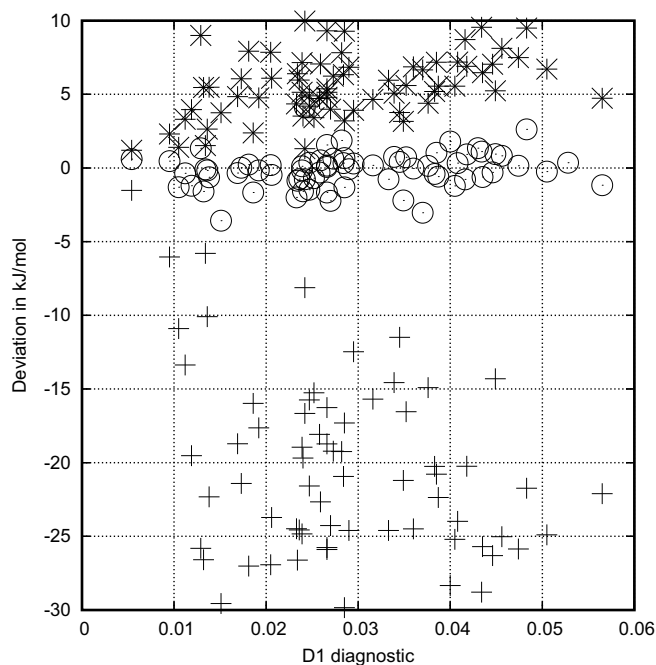[d] D1 diagnostic of Jansen and Nielsen [101] at the fc-MP2/def2-QZVPP level.

Fig. 1. Deviation of the calculated atomization energy (in kJ/mol) from the ATcT reference value, as a function of the D1 diagnostic. Results are shown for the additivity scheme using either unscaled (∗) or scaled (○) F12 contributions. The deviations are also shown for the additivity scheme *without* F12 correction (+).
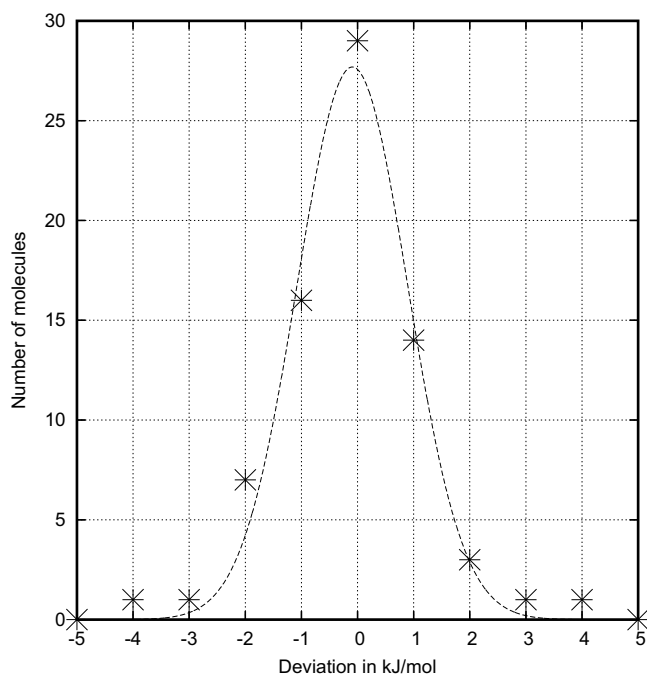

Fig. 2. Distribution of the errors per molecule of 73 molecules (in kJ/mol). Molecules are counted with errors in the same 1 kJ/mol wide interval.

Our CCSD(T)/cc-pCVQZ data agree to within 0.36 kJ/mol (RMS error) with the W4 values. Expressed in terms of error per valence electron, the RMS deviation between our values and the W4 values amounts to 0.032 kJ/mol.

We adopt an RMS error of 0.04 kJ/mol per valence electron for the core–valence contribution.

4.2.3. Zero-point vibrational energies

For the same 14 molecules that were discussed in the previous section, Karton et al. [49] report the accurate ZPVE used in W4 theory. For these molecules, our anharmonic zero-point vibrational energies agree with those given in Ref. [49] to within a mean absolute deviation of 0.27 kJ/mol (the RMS deviation amounts to 0.47 kJ/mol). On a per-valence-electron basis, the mean absolute and RMS deviations are 0.028 and 0.055 kJ/mol, respectively.

Harding et al. [46] report ZPVEs for the molecules N_2, H_2, F_2, CO, C_2H_2, CO_2, H_2O_2, H_2O, CHN (cyanic acid), FH, HNO, and H_3N. Our values deviate from these ZPVEs with an RMS error of 0.24 kJ/mol (0.023 kJ/mol RMS per valence electron).

We also note that, in our calculation of the anharmonic ZPVE, we have neglected the constant G_0 term in the expression [45]

$$E_{ZPVE} = G_0 + \sum_i \frac{\omega_i}{2} + \frac{1}{4} \sum_{i \leqslant j} x_{ij}. \tag{8}$$

In Ref. [44], it was found that neglecting the constant G_0 term leads to errors of the order to a few tenths of a kJ/mol in the enthalpies of formation (at 0 K) of molecules/radicals such as C_2H_2, CH_2, HCO, and HO_2.

In view of the agreement with the HEAT (Ref. [46]) and W4 (Ref. [49]) data, and in view of the missing G_0 contribution, we expect that the zero-point vibrational energies reported in Table 1 are accurate to within ±0.06 kJ/mol per valence electron (RMS error).

Table 2
Statistics of the deviations of the computed values from the ATcT reference data (all deviations in kJ/mol).

F12 scaling	N[a]	δ_{ave}[b]	δ_{mad}[c]	δ_{rms}[d]	95%[e]	δ_{max}[f]	Molecule[g]
Errors per molecule							
$f_{int} = 0.0$	73	−21.7	21.7	23.1	46.3	−52.4	N_2O_4
$f_{int} = 0.78$	73	−0.12	0.90	1.22	2.44	4.1	C_2H_3F
$f_{int} = 1.0$	73	5.98	5.98	6.52	13.0	14.1	N_2O_4
Errors per valence electron[h]							
$f_{int} = 0.0$	73	−1.33	1.33	1.36	2.72	−1.9	H_4N_2
$f_{int} = 0.78$	73	−0.01	0.06	0.08	0.16	0.2	C_2H_3F
$f_{int} = 1.0$	73	0.37	0.37	0.38	0.77	0.7	H_2N_2 (cis-diazene)

[a] Number of molecules in assessment.
[b] Mean error.
[c] Mean absolute error.
[d] Root-mean-square error.
[e] 95% confidence limit.
[f] Maximum deviation.
[g] Molecule with largest error.
[h] Statistics of the error per valence electron. For each molecule, the deviation is divided by the number of valence electrons.
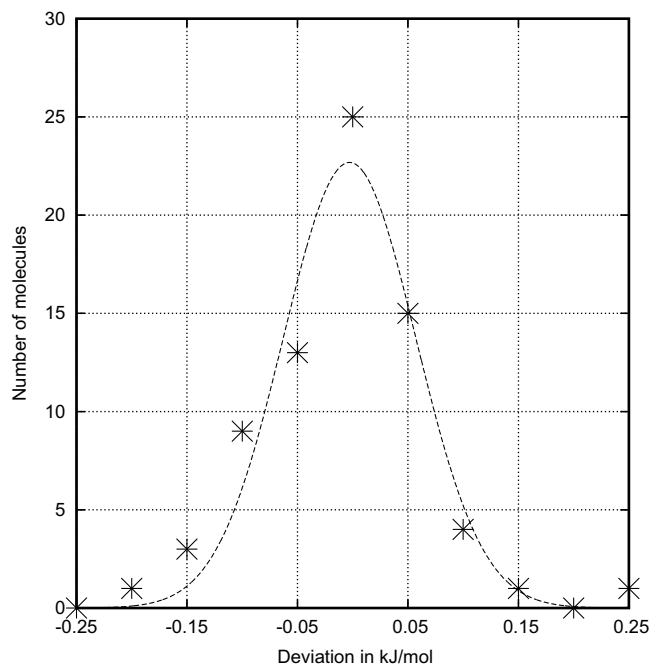
Fig. 3. Distribution of the errors per valence electron of 73 molecules (in kJ/mol). Molecules are counted with errors in the same 0.05 kJ/mol wide interval.

Table 3
Basis-set convergence of the core–valence contribution (kJ/mol) as obtained at the CCSD(T) level.

Nr.[a]	Molecule[b]		cc-pCVQZ	cc-pCV5Z	cc-pV(Q5)Z
1	CFN	Cyanogen fluoride	6.92	7.26	7.61
9	CHN	Hydrogen cyanide	6.59	6.95	7.32
10	CHN	Hydrogen isocyanide	5.78	6.06	6.35
15	CH$_2$	Singlet methylene	1.59	1.65	1.71
20	CH$_2$O	Formaldehyde	5.21	5.43	5.65
30	CH$_4$	Methane	4.99	5.19	5.40
34	CO	Carbon monoxide	3.76	3.96	4.17
35	CO$_2$	Carbon dioxide	7.00	7.33	7.68
40	C$_2$H$_2$	Acetylene	9.60	10.10	10.62
73	FH	Hydrogen fluoride	0.77	0.77	0.77
74	FHO	Hypofluorous acid	0.64	0.62	0.60
79	F$_2$	Difluorine	−0.29	−0.32	−0.35
92	H$_2$N$_2$	Diazene (trans)	3.34	3.44	3.56
95	H$_2$O	Water	1.61	1.63	1.66
97	H$_3$N	Ammonia	2.71	2.80	2.88
101	N$_2$	Dinitrogen	3.38	3.55	3.74
102	N$_2$O	Nitrous oxide	5.03	5.21	5.41
105	O$_3$	Ozone	0.24	0.17	0.09

[a] Same number and same molecule as in Ref. [30].
[b] The ae-CCSD(T)/cc-pCVTZ equilibrium geometry was used for each molecule.

4.2.4. Relativistic corrections

For the same 14 molecules that were discussed in Section 4.2.2, the scalar-relativistic corrections (MVD) given in Table 1 agree with their W4 counterparts of Ref. [49] to within a mean absolute deviation of 0.026 kJ/mol (the RMS deviation amounts to 0.037 kJ/mol or 0.0025 kJ/mol per valence electron). In W4 theory, the scalar-relativistic corrections are obtained at the second-order Douglas–Kroll–Hess CCSD(T)/DK-aug-cc-pV(Q+d)Z level. We feel that the two-electron Darwin term as well as higher-order terms such as the Breit interaction and second-order spin–orbit coupling can safely be neglected for the light molecules studied in the present work, and that both our values and the W4 values are accurate to within ±0.003 kJ/mol (RMS) per valence electron. Atomic spin–orbit coupling terms were taken from the experimental fine structure and their uncertainty is insignificant [63]. We adopt an RMS error uncertainty of 0.003 kJ/mol per valence electron for the relativistic corrections.

4.2.5. Full triples and perturbative quadruples

Table 4 shows post-CCSD(T) contributions to the atomization energies of a selected set of 18 molecules, obtained using the cc-pVDZ and cc-pVTZ basis sets at the fc-CCSDT(Q) level. In Table 4, the results shown for X = (DT) refer to the results obtained from the two-point extrapolation procedure of Helgaker et al. [102] using the cc-pVXZ contributions with X = D and T, which is the level of calculation used in W4 theory [49]. Indeed, the CCSDT–CCSD(T) contributions for the molecules N$_2$ (−3.26 kJ/mol), F$_2$ (−1.50 kJ/mol), CO (−2.35 kJ/mol), FH (−0.57 kJ/mol), and H$_2$O (−0.85 kJ/mol) completely agree with the data presented in Ref. [50]. Karton and co-workers not only report CCSDT–CCSD(T) contributions at the (DT) level but also at the extrapolated (TQ) and (Q5) levels, and it seems that the (DT) extrapolation yields useful estimates. The mean and RMS deviations between the (DT) and (Q5) extrapolated data for the 16 molecules studied in Ref. [50] amount to 0.09 and 0.2 kJ/mol, respectively. This accuracy is quite remarkable in view of the large differences between the cc-pVDZ and cc-pVTZ results (Table 4).

Although the (DT) extrapolated data for the CCSDT–CCSD(T) contributions computed by Karton et al. appear to be astonishingly accurate, we nevertheless feel that the difference between the cc-pVDZ and cc-pVTZ basis sets is too large to use them as a basis for a trustworthy extrapolation. Therefore, we have decided to use the plain fc-CCSDT/cc-pVTZ energies. For the same 14 molecules that were discussed in Section 4.2.2, the fc-CCSDT–fc-CCSD(T) contributions in the cc-pVTZ basis deviate from the W4 data (i.e., the (DT) extrapolated values) by 0.7 kJ/mol on average, with the cc-pVTZ data always underestimating the magnitude of the corresponding W4 corrections. The RMS deviation amounts to 0.8 kJ/mol. Hence, we expect that our CCSDT–CCSD(T) contributions may be a few tenths of a kJ/mol up to 1.5 kJ/mol too small in magnitude. Fortunately, this error is partly cancelled by the CCSDT(Q) contribution.

Concerning the CCSDT(Q) contributions for connected quadruple excitations, Karton et al. note that the (DT) extrapolation does more harm than good [49]. Therefore, these authors prefer to use the fc-CCSDT(Q)/cc-pVTZ results scaled by an empirical factor of 1.1. Thus, in W4 theory, the sum of the contributions denoted T and (Q) in Table 1 is computed as

$$\Delta E_{T+(Q)}(W4) = E_{\text{fc-CCSDT/cc-pV(DT)Z}} - E_{\text{fc-CCSD(T)/cc-pV(DT)Z}} + 1.1 \\ \times \left(E_{\text{fc-CCSDT(Q)/cc-pVTZ}} - E_{\text{fc-CCSDT/cc-pVTZ}} \right). \tag{9}$$

In the present work, however, we compute this sum as

$$\Delta E_{T+(Q)}(\text{present work}) = E_{\text{fc-CCSDT/cc-pVTZ}} - E_{\text{fc-CCSD(T)/cc-pVTZ}} \\ + E_{\text{fc-CCSDT(Q)/cc-pVDZ}} \\ - E_{\text{fc-CCSDT/cc-pVDZ}}. \tag{10}$$

For the 18 molecules of Table 4, the difference between Eqs. (9) and (10) can be computed from the data reported. For these molecules, the mean deviation between Eqs. (9) and (10) amounts to 0.1 kJ/mol, with mean absolute and RMS deviations of 0.40 and 0.60 kJ/mol, respectively. Measured per valence electron, the mean, mean absolute, and RMS deviations amount to 0.015, 0.033, and 0.044 kJ/mol.

We therefore feel that Eq. (10) is sufficiently accurate for our present purposes, partly because there is some fortuitous error compensation between the T and (Q) terms. We adopt an RMS error of 0.05 kJ/mol per valence electron for the combined full-triples-and-perturbative-quadruples contribution.

Table 4
Basis-set convergence of the CCSDT–CCSD(T) and CCSDT(Q)–CCSDT contributions (kJ/mol), obtained in cc-pVXZ basis sets with X = D, T, and (DT).

Nr.[a]	Molecule[b]		ΔE_T			$\Delta E_{(Q)}$			$\Delta E_T + \Delta E_{(Q)}$		
			D	T	(DT)	D	T	(DT)	D	T	(DT)
1	CFN	Cyanogen fluoride	−0.72	−3.14	−4.16	4.91	5.02	5.06	4.19	1.88	0.90
9	CHN	Hydrogen cyanide	−0.64	−2.48	−3.26	3.67	4.03	4.18	3.03	1.55	0.92
10	CHN	Hydrogen isocyanide	0.13	−1.64	−2.39	2.42	2.78	2.93	2.55	1.14	0.55
15	CH$_2$	Singlet methylene	1.06	0.91	0.84	0.35	0.41	0.44	1.41	1.32	1.28
20	CH$_2$O	Formaldehyde	0.11	−1.54	−2.23	2.50	2.46	2.44	2.61	0.92	0.21
30	CH$_4$	Methane	0.21	−0.19	−0.36	0.33	0.30	0.29	0.54	0.11	−0.07
34	CO	Carbon monoxide	0.10	−1.62	−2.35	2.66	2.74	2.77	2.76	1.12	0.42
35	CO$_2$	Carbon dioxide	−0.76	−3.30	−4.37	5.10	4.91	4.83	4.34	1.60	0.45
40	C$_2$H$_2$	Acetylene	−0.60	−2.31	−3.02	2.59	2.99	3.16	1.99	0.69	0.14
73	FH	Hydrogen fluoride	0.04	−0.39	−0.57	0.79	0.46	0.32	0.83	0.07	−0.25
74	FHO	Hypofluorous acid	0.26	−1.16	−1.76	3.30	3.12	3.05	3.56	1.96	1.29
79	F$_2$	Difluorine	0.31	−0.96	−1.50	3.89	3.82	3.79	4.20	2.86	2.29
92	H$_2$N$_2$	Diazene (trans)	0.07	−1.79	−2.58	3.27	3.55	3.66	3.35	1.75	1.08
95	H$_2$O	Water	0.13	−0.56	−0.85	1.10	0.80	0.68	1.23	0.24	−0.17
97	H$_3$N	Ammonia	0.37	−0.28	−0.56	0.79	0.69	0.65	1.16	0.41	0.09
101	N$_2$	Dinitrogen	−0.49	−2.44	−3.26	4.31	4.57	4.67	3.81	2.13	1.41
102	N$_2$O	Nitrous oxide	−2.04	−5.04	−6.30	9.23	9.47	9.58	7.19	4.43	3.28
105	O$_3$	Ozone	−0.59	−4.21	−5.74	17.63	18.72	19.18	17.04	14.51	13.44

[a] Same number and same molecule as in Ref. [30].
[b] The ae-CCSD(T)/cc-pCVTZ equilibrium geometry was used for each molecule.
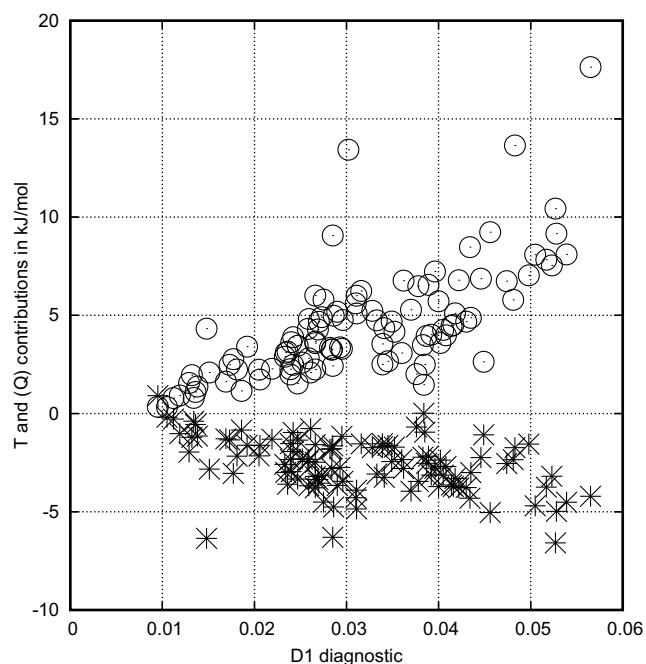
Fig. 4. $\Delta E_T = E_{CCSDT/cc-pVTZ} - E_{CCSD(T)/cc-pVTZ}$ (∗) and $\Delta E_{(Q)} = E_{CCSDT(Q)/cc-pVDZ} - E_{CCSDT/cc-pVDZ}$ (○) contributions (in kJ/mol) as a function of the D1 diagnostic.

We furthermore note that the T, (Q), and higher excitation terms are likely to become more important for molecules with distinct multireference character. Indeed, Fig. 4 shows that the E_T and $E_{(Q)}$ terms tend to increase in magnitude with increasing D1 diagnostic [101]. In other words, the errors discussed here may not be applicable to molecules with very large D1 diagnostics, for which a single-reference correlation treatment is inadequate.

4.2.6. Neglected contributions

In our additivity scheme, a number of contributions have so far not been taken into account. Among these are valence-shell electron-correlation effects beyond the CCSDT(Q) level, core–valence correlation effects beyond the CCSD(T) level, and non-Born–Oppenheimer effects such as the diagonal Born–Oppenheimer correction (DBOC). What errors can be expected due to neglecting these terms? In Ref. [50], Karton et al. find that in the cc-pVQZ basis, the frozen-core CCSDTQ–CCSDT(Q) contribution amounts to −0.69, −0.41, −0.06, and −0.09 kJ/mol for the molecules N$_2$, CO, FH, and H$_2$O, respectively. In the cc-pVDZ basis, the valence–shell correlation contribution due to connected quintuple excitations amounts to 0.48, 0.13, 0.01, and 0.03 kJ/mol, respectively, for the same four molecules. In view of the opposite signs of the CCSDTQ–CCSDT(Q) and connected quintuples contributions, we expect that neglecting these two terms will not give rise to errors significantly larger than ±0.02 kJ/mol per valence electron (RMS error).

Also, core–valence correlation effects beyond the CCSD(T) level are expected to be small (estimated at about 0.03 kJ/mol per valence electron RMS). For the molecules N$_2$, F$_2$, CO, FH, H$_2$O, and C$_2$H$_2$, Karton et al. [50] report CCSDT(Q)–CCSD(T) core–valence contributions of 0.14, 0.08, 0.16, 0.02, 0.03, and 0.13 kJ/mol.

The DBOC may also contribute a few tenths of a kJ/mol to the atomization energy of our molecules, in particular to those with X–H bonds (X = C, N, O, F). For a molecule such as *trans*-butadien, for example, a DBOC of the order of 0.45 kJ/mol was computed by Gauss and co-workers at the coupled-cluster level [103]. Using perturbation theory, values of 0.6 and 1.1 kJ/mol were obtained for benzene and naphthalene [104]. Hence, corrections of the order of 0.1 kJ/mol per X–H bond seem quite reasonable, which implies errors of up to a few tenths of a kJ/mol for the 106 molecules of our test set due to neglecting the DBOC. In Ref. [46], Harding et al. have calculated the DBOC of 26 molecules. In their work, neglecting these contributions would have led to an RMS error of 0.14 kJ/mol per molecule, or 0.02 kJ/mol per valence electron. We adopt this latter RMS error as an estimate of our error due to neglecting the DBOC.

4.2.7. Total statistical uncertainty

If we assume that the errors discussed above are statistical in nature, then we may compute the expected accuracy of our computed atomization energy by Gaussian error propagation. For this, we use the following RMS errors per valence electron: ±0.08 kJ/mol for the Hartree–Fock contribution, ±0.04 kJ/mol for the core–valence contribution, ±0.06 kJ/mol for the zero-point vibrational energy, ±0.003 kJ/mol for the relativistic correction, ±0.05 kJ/mol for

full triples and perturbative quadruples, ±0.02 kJ/mol for valence-shell post-CCSDT(Q) effects, ±0.03 kJ/mol for core–valence post-CCSD(T) effects, and ±0.02 kJ/mol for the DBOC. The result of the error propagation may be expressed as

$$\sigma = n_{\text{valence electrons}} \times 0.13 \text{ kJ/mol}, \tag{11}$$

where $n_{\text{valence electrons}}$ is the number of electrons in the valence shell. For molecules such as methane, ethane, and propane, Eq. (11) yields total uncertainties of σ = 1.0, 1.8, and 2.6 kJ/mol, respectively. For diatomics such as N_2 and CO, the uncertainty amounts to σ = 1.3 kJ/mol. We feel that these are very reasonable estimates of the accuracy of our additivity scheme. Only six of the 105 molecules of the Bakowies test set (H_2 is a somewhat special case) for which reference ATcT values are available, show a deviation from these values larger than the uncertainty given by Eq. (11). None of the molecules except H_2 show a deviation larger than 2σ, which can be interpreted as an estimate of the 95%-confidence limit.

5. Conclusions

The atomization energies of the 105 molecules in the test set of Bakowies [30] have been computed with an estimated standard deviation from the ATcT values of ±0.1 kJ/mol per electron in the valence shell of the molecule. This accuracy has been achieved by adding an empirically scaled MP2-F12 correction for the basis-set truncation error of the cc-pCVQZ basis, in which the ae-CCSD(T) calculations were carried out. Without adding such a correction, the standard deviation would have been as large as 1.3 kJ/mol per valence electron. Hence, the errors were reduced by more than an order of magnitude by the F12 corrections.

In the present work, we have introduced an empirical scaling factor of f_{int} = 0.78 to account for the interference effect in the basis-set truncation error, that is, for the fact that at the level of second-order perturbation theory, the basis-set truncation error is significantly larger (ca. 25%) than at the full configuration-interaction level. However, even without resorting to such an interference factor, that is, by adding 100% of the MP2-F12 correction, the errors in the computed atomization energies would have been reduced already by a factor of 3–4.

In future work, we shall investigate the performance of various coupled-cluster CC-F12 methods to see how these methods could be used to replace the scaled MP2-F12 corrections in the present additivity scheme. When using CC-F12 methods, no empirical factors will be needed, and an additivity scheme using F12 methods and no empirical factors is a very appealing prospect—from the point of view of both theory and efficiency.

Concerning the latter, we notice that our scheme, which includes the ΔE_{F12} correction for the basis-set truncation error, is more efficient than the schemes that are based on CCSD(T) calculations in very large basis sets such as aug-cc-pCVQZ and aug-cc-pCV5Z followed by extrapolation (e.g., in the HEAT345 approach [46]). To demonstrate this, let us take fluoroperoxide (FHO$_2$) as an example. On our hardware, the fc-CCSD(T) calculations of this molecule in the cc-pCVQZ and aug-cc-pCVQZ basis sets took 4 and 23 h, respectively, on a single processor. The corresponding calculation in the aug-cc-pCV5Z basis has not been carried out but we estimate that the computation time for this calculation would have amounted to about 180 hours. The Hartree–Fock and MP2-F12 calculations (correlation energy only) in the def2-QZVPP basis each took only 6 min while the corresponding fc-CCSD(F12)/def2-QZVPP calculation took 5 h. In other words, by using explicitly-correlated theory, the computation time needed for the fc-CCSD(T) part of the composite scheme can be reduced by a factor of 35–45, from about 180 to 4 or 5 h, for fluoroperoxide. Nevertheless, considerable computation time is still required for the fc-

CCSDT/cc-pVTZ and fc-CCSDT(Q)/cc-pVDZ calculations, and for the ae-CCSD(T)/cc-pCVTZ calculation of the harmonic vibrational frequencies. For fluoroperoxide, these calculations took 28, 13 and 40 h, respectively. Of course, as soon as very large basis sets are no longer needed at the CCSD(T) level by virtue of using explicitly-correlated theory, other contributions will become the computationally most demanding steps in the additivity scheme.

Acknowledgements

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