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FEATURE ARTICLE

Accurate computational thermochemistry from explicitly correlated coupled-cluster theory

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Abstract Explicitly correlated coupled-cluster theory has developed into a valuable computational tool for the calculation of electronic energies close to the limit of a complete basis set of atomic orbitals. In particular at the level of coupled-cluster theory with single and double excitations (CCSD), the space of double excitations is quickly extended towards a complete basis when Slater-type geminals are added to the wave function expansion. The purpose of the present article is to demonstrate the accuracy and efficiency that can be obtained in computational thermochemistry by a CCSD model that uses such Slater-type geminals. This model is denoted as CCSD(F12), where the acronym F12 highlights the fact that the Slater-type geminals are functions $f(r_{12})$ of the interelectronic distances r_{12} in the system. The performance of explicitly correlated CCSD(F12) coupled-cluster theory is demonstrated by computing the atomization energies of 73 molecules (containing H, C, N, O, and F) with an estimated root-mean-square deviation from the values compiled in the Active Thermochemical Tables of $\sigma = 0.10$ kJ/mol per valence electron. To reach this accuracy, not only the frozen-core CCSD basis-set limit but also high-order excitations (connected triple and quadruple excitations), core–valence correlation effects, anharmonic vibrational zero-point energies, and scalar and spin–orbit relativistic effects must be taken into account.

Keywords Thermochemistry · Atomization energy · Coupled-cluster theory · Explicitly correlated theory · Basis-set extrapolation

1 Introduction

Explicitly correlated second-order perturbation theory and coupled-cluster methods have recently become available in widely distributed quantum chemistry software such as Molpro [1] and Turbomole [2]. In these explicitly correlated methods, the slow basis-set convergence of standard post-Hartree–Fock methods is dramatically accelerated by using Slater-type geminals to expand the correlated electronic wave function [3–6]. Whereas the standard methods depend solely on orbital products (one-particle functions), the explicitly correlated methods use both orbital products and *two-particle* functions (geminals).

The present article is concerned with the explicitly correlated coupled-cluster method CCSD(F12) [7, 8]. This method is capable of providing highly accurate correlation energies in relatively small basis sets and may be an efficient and economical alternative to coupled-cluster calculations in very large (correlation-consistent) basis sets. When accurate thermochemical data are required, coupled-cluster calculations are usually preformed in very large basis sets, and even then, they are often supplemented with basis-set extrapolations and/or empirical corrections. In the present work, we demonstrate that, by virtue of the CCSD(F12) method, highly accurate results may be obtained at the coupled-cluster singles-and-doubles level

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(CCSD) [9] without falling back on basis-set extrapolations and/or empirical corrections.

Before we focus our attention onto the CCSD(F12) method, however, we shall briefly review the approaches that are currently in use to address the slow basis-set convergence of standard post-Hartree–Fock methods. Using such approaches, it is often possible to obtain highly accurate thermochemical data, that is, with an accuracy comparable to experiment.

In basically all of the highly accurate ab initio methods for computational thermochemistry, the CCSD energy is one of the many components of the respective additivity scheme or multi-level approach (see Sect. 2). In the present work, we shall fix all non-CCSD contributions and compare various methods for computing the CCSD energy. In particular, we shall compare the CCSD(F12) method with the basis-set extrapolation approach. If successful, the CCSD(F12) method could replace the basis-set extrapolations of the CCSD energy that are currently in use in the additivity schemes and multi-level approaches.

2 Accurate methods

Since at least a quarter of a century, computational chemists have been aware of the basis-set problem of quantitatively describing dynamic electron correlation and the need for alternative methods for obtaining those energies close to the limit of a complete basis [10–17]. Semi-empirical *scaling* of correlation energies [18, 19], for example,

$$E_{\mathrm{corr,scaled}} = xE_{\mathrm{corr}}, \quad x > 1, \tag{1}$$

has been applied in order to address the basis-set problem and to obtain much improved results (see also Ref. [20] for recent work on the scaling-all-correlation method, SAC). Another example is the high-level correction (HLC) of the early Gaussian-1 (G1) and Gaussian-2 (G2) methods [21–26]. This HLC consists of simply *adding* a semi-empirical energy correction depending on the number of electrons,

$$\Delta E_{\mathrm{HLC}}/\mathrm{m}E_{\mathrm{h}} = -0.19n_{\alpha} - 5.95n_{\beta}, \tag{2}$$

where n_α and n_β are the number of alpha and beta valence electrons, respectively. The motivation for the HLC was that the poor description of dynamic electron-correlation effects in small and medium-sized basis sets is particularly pronounced when comparing systems in different spin states, for example when calculating the atomization energy of dinitrogen. In this case, the HLC contributes 17.28 mE_h (45 kJ/mol) to the atomization energy. Such a large high-level correction is required, since the basis-set truncation errors are rather different for the different spin states, for example for the high-spin ^{4}S state of N and the closed-shell singlet state of N_2.

Besides semi-empirical scaling of correlation energies and addition of semi-empirical corrections, a third attempt to solve the basis-set problem of dynamic electron correlation is to extrapolate to the basis-set limit. In the complete-basis-set (CBS) methods of Petersson and co-workers [26–34], the extrapolation is based on expressions such as

$${}^{\alpha\beta}e_{ij}^{(2)}(N) = {}^{\alpha\beta}e_{ij}^{(2)}(\infty) + {}^{\alpha\beta}f_{ij}\frac{25}{512}\left(N + {}^{\alpha\beta}\delta_{ij}\right)^{-1}, \tag{3}$$

$${}^{\alpha\alpha}e_{ij}^{(2)}(N) = {}^{\alpha\alpha}e_{ij}^{(2)}(\infty) + {}^{\alpha\alpha}f_{ij}\frac{25}{512}\left(N + {}^{\alpha\alpha}\delta_{ij}\right)^{-5/3}. \tag{4}$$

whereas ${}^{\alpha\beta}f_{ij}$ and ${}^{\alpha\alpha}f_{ij}$ are non-empirical parameters, δ_{ij} and $e_{ij}^{(2)}(\infty)$ are determined by fitting calculated second-order pair energies $e_{ij}^{(2)}(N)$ as a function of the number N of atomic pair natural orbitals (APNO). For details, we refer to the recent literature [35]. Important points to note here are that the basis-set convergence of the $\alpha\beta$ and $\alpha\alpha$ second-order pair energies is different and that the correction obtained at the level of second-order Møller–Plesset perturbation theory (MP2) is multiplied by an "interference factor" smaller than one [27, 28]. This interference factor accounts for the fact that, for a given n-electron system, the basis-truncation error is larger at the MP2 level than at infinite order (full configuration interaction). Indeed, it is shown in Ref. [36] that the interference factor provides a good estimate of the ratio of the CCSD(T) and MP2 basis-set truncation errors of the APNO basis set. (The CCSD(T) model is the CCSD model with noniterative connected triple excitations [37].) Furthermore, the different exponents of -1 and $-5/3$ in Eqs. (3) and (4), respectively, reflect the fact that the basis-set convergence of different spin states behaves differently, and thus, fall in line with the HLC of G1 theory.

More recently, basis-set extrapolation schemes that can more generally be applied to various methods and basis sets have become popular. The two-point Helgaker formula [38]

$$E_{X,X+1} = \frac{(X+1)^3 E_{X+1} - X^3 E_X}{(X+1)^3 - X^3}, \tag{5}$$

for example, is based on the assumption that the basis-set convergence of the correlation energy follows a X^{-3} law with respect to the cardinal number X of the correlation-consistent basis sets [39–46]. Note that Eq. (5) refers to correlation energies only, not to total energies. Helgaker's formula can be applied equally well to MP2 as well as coupled-cluster results obtained in correlation-consistent basis sets (e.g., cc-pVXZ and cc-pV(X + 1)Z). For a given X, Eq. (5) is nothing but a fixed linear combination of two correlation energies from two basis sets,

$$E_{X,X+1} = (1 + c_X)E_{X+1} - c_X E_X, \tag{6}$$

and it is tempting to fit the coefficient c_X to benchmark and/or empirical data, especially for small X [47–49].

Since the number of basis functions grows as X^3 with the cardinal number of the basis set, Eq. (5) is in complete agreement with the CBS extrapolation for $\alpha\beta$ pairs, Eq. (3), which can be viewed as an N^{-1} law for the dependence of the correlation energy on the size of the basis set. Such N^{-1} dependence for the correlation energy computed in cc-pVXZ (X = D, T, Q, 5) correlation-consistent basis sets was already observed in 1995 [50]. In that work, the valence-shell second-order correlation energy of H_2O could accurately be represented as

$$E_{\mathrm{corr}}/\mathrm{m}E_{\mathrm{h}} = -302.7 + 2183\,N^{-1} + 12{,}180\,N^{-2}. \tag{7}$$

The $N^{-5/3}$ dependence for the like-spin pairs translates into a X^{-5} law with respect to the cardinal number. This agrees with the L^{-3} and L^{-5} laws found for the unlike- and like-spin pairs in MP2 theory by Kutzelnigg and Morgan [51], noting that the partial wave expansion (with respect to angular momentum L) and principal expansion (with respect to cardinal number X) are closely related [52]. Indeed, more accurate results are obtained when singlet and triplet coupled pairs are extrapolated using Eq. (5) for the (sum of all) singlet pairs and using

$$E_{X,X+1} = \frac{(X+1)^5 E_{X+1} - X^5 E_X}{(X+1)^5 - X^5}, \tag{8}$$

for the (sum of all) triplet pairs, respectively [53]. Of course, the leading term with respect to the total correlation energy in any case remains $\mathcal{O}(X^{-3})$, but there are cases where the separate extrapolation of singlet and triplet coupled pairs matters, for example for the He–He interatomic potential [54].

Many variants of Helgaker's formula have been reported in the literature, but it is not the purpose of the present article to review all of these slightly different approaches. Rather, we refer to Refs. [47, 55–65] and to the references therein. Note that it also seems possible (and appealing) to formulate extrapolation schemes based on basis-set results from explicitly correlated methods such as MP2-F12 and CCSD-F12 variants, such that even smaller basis sets can be used than at the respective F12 level itself [66, 67]. For early attempts to extrapolate explicitly correlated results, see Refs. [68, 69].

Helgaker's extrapolation formula, being a simple linear combination of two energies, can be used in a straightforward manner to optimize molecular geometries, that is, to determine equilibrium and transition-state structures from linear combinations of gradients and Hessians [48, 70]. Recent examples of such an approach may be found in Refs. [71–73], demonstrating that highly accurate geometries and harmonic vibrational frequencies may be obtained in this manner. Helgaker's extrapolation formula can be applied to MP2 energies as well as CCSD and CCSD(T) energies, in particular since Barnes et al. have shown (for the Ne atom) that the CCSD(T) correlation energy converges as X^{-3} [74]. It is furthermore possible to include the basis-set extrapolation into additivity approaches and multi-level schemes, which may be purely ab initio or semi-empirical. In such schemes, results obtained at various levels of calculations (e.g., CCSD(T) results obtained in a small basis and MP2 results obtained in a large basis) are combined to give an accurate energy. Examples of multi-level schemes include the focal-point analysis of East and Allen [75–79], the multi-coefficient correlation methods (MCCM) of Truhlar and others [20, 80–86], the Weizmann-n methods of Martin et al. [87–92], the HEAT protocol of Tajti, Bomble, and others [93–97], the ATOMIC protocol of Bakowies [65, 98], and the correlation-consistent composite approach (ccCA) of DeYonker et al. [99–106]. Similar but less standardized approaches have been presented by Feller, Dixon, and co-workers [107–115], and the Gaussian-3 [116–119] and Gaussian-4 model chemistries [120–122] have superseded the early G1 and G2 approaches.

Although the basis-set extrapolations and (semi-) empirical corrections are extremely useful in additivity approaches and multi-level schemes, yielding highly accurate atomization energies, heats of formation, reaction barrier heights, and so on, one may wonder whether it may be possible to obtain similarly accurate results without resorting to extrapolations and/or empirical corrections. Indeed, extrapolations and empirical corrections can be avoided by approaching the basis-set limit of the CCSD or CCSD(T) or similar methods by means of explicitly correlated two-particle Slater-type geminals.

Using Slater-type geminals does not mean that the application of the respective method is restricted to very small systems such as few-electron atoms and diatomics. Coupled-cluster calculations using Slater-type geminals are not significantly more time-consuming than standard coupled-cluster calculations (in the same basis). Hence, explicitly correlated coupled-cluster calculations in small or medium-sized basis sets can certainly be applied when standard coupled-cluster calculations in large basis sets can be carried out. Indeed, while yielding equally or more accurate results, explicitly-correlated coupled-cluster calculations in small or medium-sized basis sets are more economical than standard coupled-cluster calculations in large basis sets. Some recent applications of explicitly correlated methods demonstrate their applicability. These include the high-accuracy computation of reaction barriers in enzymes [123], calculations on hydrogenation products of benzene and naphthalene as part of a study of the reactivity of the C_{60} fullerene [124], calculations of the interactions between CO_2 and nitrogen containing organic heterocycles [125], calculations of barrier heights of $CH_4 + CH_3$ reactions [126], calculations of the heats of formation of $HOSO_2$ and $HOSO_4$ [127, 128], a study of the origin of the argon nanocoating shift in the OH stretching fundamental of *n*-propanol [129], a study of the trimerization of pyrazine [130], calculations on astrochemically relevant polyynes [131], and calculations on hydrogen-bonded and π-stacked complexes [132–134].

In the next section, we shall present the theory of explicitly correlated CCSD theory, paying special attention to the CCSD(F12) model. This model will be used in calculations of the atomization energies of the 105 molecules in the test set of Bakowies [62] (we have added H_2). The computational details of these calculations are given in Sect. 4, and the results of the calculations will be presented in Sect. 5.

3 CCSD(F12) theory

In standard coupled-cluster theory with single and double excitations (CCSD), using a spin-orbital formalism, the *n*-electron wave function is written as

$$|\mathrm{CC}\rangle = \exp(\hat{T})|\mathrm{HF}\rangle, \tag{9}$$

where $|\mathrm{HF}\rangle$ is the (unrestricted) Hartree–Fock determinant and $\hat{T} = \hat{T}_1 + \hat{T}_2$, with

$$\hat{T}_1 = \sum_{ai} t_a^i a_a^\dagger a_i, \tag{10}$$

$$\hat{T}_2 = \frac{1}{4}\sum_{abij} t_{ab}^{ij} a_a^\dagger a_i a_b^\dagger a_j. \tag{11}$$

Here, the indices $i, j, k,\ldots$ refer to spin orbitals occupied in $|\mathrm{HF}\rangle$ while the indices $a, b, c,\ldots$ refer to unoccupied (virtual) spin orbitals. The operators $a_a^\dagger a_i$ and $a_a^\dagger a_i a_b^\dagger a_j$ are excitation operators generating singly and doubly substituted determinants, respectively, and t_a^i and t_{ab}^{ij} are the corresponding CCSD singles and doubles amplitudes.

In explicitly correlated CCSD theory, that is, CCSD(F12) theory, the cluster operator $\hat{T}$ is supplemented with an extra excitation operator $\hat{T}_{2'}$, which introduces Slater-type geminals of the form $f(r_{12}) = \exp(-\gamma r_{12})$ into the *n*-electron wave function ($r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between the electrons 1 and 2). Adding two-particle basis functions $f(r_{12})$ to the wave function helps to alleviate the basis-set problem of standard coupled-cluster theory. The extra operator $\hat{T}_{2'}$ reads

$$\hat{T}_{2'} = \frac{1}{8}\sum_{ij\mathbf{kl}} c_{\mathbf{kl}}^{ij} \sum_{xy} \overline{w}_{xy}^{\mathbf{kl}} a_x^\dagger a_i a_y^\dagger a_j, \tag{12}$$

$$\overline{w}_{xy}^{\mathbf{kl}} = \langle|\varphi_x(1)\varphi_y(2)||\hat{w}(12)|\chi_{\mathbf{kl}}(12)\rangle, \tag{13}$$

$$\hat{w}(12) = -\hat{Q}(12)\gamma^{-1}\exp(-\gamma r_{12}). \tag{14}$$

$\hat{Q}(12) = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1\hat{V}_2$ is an appropriate strong-orthogonality projection operator, where $\hat{O}$ and $\hat{V}$ are projection operators onto the spaces of occupied and virual spin orbitals, respectively [135]. The operator $\hat{T}_{2'}$ is referred to as "F12 doubles" excitation operator and the corresponding amplitudes as "F12 amplitudes" or "F12 doubles amplitudes". The formal indices x, y,… refer to virtual spin orbitals that, together with the occupied spin orbitals, form a *complete basis set* (CBS) of spin orbitals. The sum over the bold indices **kl** runs over all occupied spin orbitals φ_m ($\varphi_m\alpha$ and $\overline{\varphi}_m\beta$). For two like-spin orbitals, these bold indices **kl** refer to a pair function (two-electron determinant) of the type $|\varphi_k\alpha(1)\varphi_l\alpha(2)|$ or $|\overline{\varphi}_k\beta(1)\overline{\varphi}_l\beta(2)|$ for alpha or beta orbitals, respectively. For two unlike spins, however, the pair function $\chi_{\mathbf{kl}}(12)$ is a *contracted spin-flipped geminal* [136] defined as

$$\chi_{\mathbf{kl}}(12) = \frac{3}{8}|\varphi_k\alpha(1)\overline{\varphi}_l\beta(2)| + \frac{1}{8}|\overline{\varphi}_l\alpha(1)\varphi_k\beta(2)|, \tag{15}$$

where $\overline{\varphi}_l$ is the spatial part of an occupied beta orbital. The *spin-flipped* second term in Eq. (15) is required to satisfy the electron–electron cusp conditions in open-shell atoms and molecules [136–139].

As is usually done in coupled-cluster theory, the CCSD-F12 equations for the energy and the amplitudes are derived by multiplying the Schrödinger equation

$$\hat{H}|\mathrm{CC}\rangle = E|\mathrm{CC}\rangle \tag{16}$$

from the left with $\exp(-\hat{T})$ and projecting the resulting equation onto the Hartree–Fock reference wave function $\langle\mathrm{HF}|$ and the excitation manifold $\{\langle\mu|\}$. In CCSD(F12) theory, the excitation manifold consists of singles ($\{\langle\mu_1|\}$), doubles ($\{\langle\mu_2|\}$), and F12 doubles ($\{\langle\mu_{2'}|\}$). This yields the CCSD-F12 energy and CCSD-F12 amplitude equations

$$E = \langle\mathrm{HF}\,|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle, \tag{17}$$

$$0 = \langle\mu_1|[\hat{F},\hat{T}_1] + [\hat{F},\hat{T}_{2'}] + \tilde{\Phi} + \left[\tilde{\Phi},\hat{T}_2 + \hat{T}_{2'}\right]|\mathrm{HF}\rangle, \tag{18}$$

$$\begin{aligned} 0 = \langle\mu_2|\left[\tilde{F},\hat{T}_2 + \hat{T}_{2'}\right] + \tilde{\Phi} + \left[\tilde{\Phi},\hat{T}_2 + \hat{T}_{2'}\right] \\ + \frac{1}{2}\left[\left[\tilde{\Phi},\hat{T}_2 + \hat{T}_{2'}\right],\hat{T}_2 + \hat{T}_{2'}\right]|\mathrm{HF}\rangle, \end{aligned} \tag{19}$$

$$\begin{aligned} 0 = \langle\mu_{2'}|\left[\tilde{F},\hat{T}_2 + \hat{T}_{2'}\right] + \tilde{\Phi} + [\tilde{\Phi},\hat{T}_2 + \hat{T}_{2'}] \\ + \frac{1}{2}\left[\left[\tilde{\Phi},\hat{T}_{2'}\right],2\hat{T}_2 + \hat{T}_{2'}\right]|\mathrm{HF}\rangle. \end{aligned} \tag{20}$$

In these equations, $\hat{F}$ is the *n*-electron Fock operator, $\tilde{F} = \exp(-\hat{T}_1)\hat{F}\exp(\hat{T}_1)$ its T1-transformed counterpart, and

$\tilde{\Phi} = \exp(-\hat{T}_1)(\hat{H} - \hat{F})\exp(\hat{T}_1)$ the T1-transformed fluctuation potential.

In the CCSD(F12) model, introduced by Fliegl et al. in 2005 [140], the treatment of the F12 amplitudes is reduced to second order in the fluctuation potential using analogous arguments to those used to simplify the treatment of conventional doubles from CCSD to CC2 [141]. In particular, the Fock operator and the conventional singles and doubles amplitudes and excitation manifolds $\{\langle\mu_1|\}$ and $\{\langle\mu_2|\}$ are taken to be zeroth order. The fluctuation potential, the F12 amplitudes, and the excitation manifold $\{\langle\mu_{2'}|\}$ are taken to be first order. The CCSD(F12) amplitude equations are then obtained by discarding all terms that are higher than second order. This gives

$$0 = \langle\mu_1|[\hat{F}, \hat{T}_1] + [\hat{F}, \hat{T}_{2'}] + \tilde{\Phi} + [\tilde{\Phi}, \hat{T}_2 + \hat{T}_{2'}]|\mathrm{HF}\rangle, \tag{21}$$

$$0 = \langle\mu_2|[\tilde{F}, \hat{T}_2 + \hat{T}_{2'}] + \tilde{\Phi} + [\tilde{\Phi}, \hat{T}_2 + \hat{T}_{2'}] + \frac{1}{2}\big[[\tilde{\Phi}, \hat{T}_2], \hat{T}_2 + 2\hat{T}_{2'}\big]|\mathrm{HF}\rangle, \tag{22}$$

$$0 = \langle\mu_{2'}|[\tilde{F}, \hat{T}_2] + [\hat{F}, \hat{T}_{2'}] + \tilde{\Phi} + [\tilde{\Phi}, \hat{T}_2]|\mathrm{HF}\rangle. \tag{23}$$

The energy expression Eq. (17) is not affected. Note, however, that this energy expression is only used if the F12 amplitudes are *optimized* using the above amplitude equations. If the *fixed-amplitudes* ansatz is used, which is also known as *sp* ansatz or rational-generator approach [142], then the amplitudes are not optimized, and the energy is evaluated using the simplified Lagrange functional [143]

$$E = \langle\mathrm{HF}|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle + \langle\bar{\mathbf{c}}|[\tilde{F}, \hat{T}_2] + [\hat{F}, \hat{T}_{2'}] + \tilde{\Phi} + [\tilde{\Phi}, \hat{T}_2]|\mathrm{HF}\rangle. \tag{24}$$

For the Lagrange multipliers $\bar{\mathbf{c}}$, the (fixed) F12 doubles amplitudes are inserted. Both multipliers and F12 doubles amplitudes refer to spin-flipped geminals. Moreover, using the fixed-amplitudes ansatz of course implies that Eq. (23) needs not be solved.

Compared to the full CCSD-F12 model, Eqs. (18)–(20), all terms quadratic in the F12 amplitudes have been neglected, together with the commutator $\langle\mu_{2'}|[[\hat{F}, \hat{T}_1] + \tilde{\Phi}, \hat{T}_{2'}]|\,\mathrm{HF}\rangle$. The CCSD(F12) simplification leads to a slight loss in accuracy in comparison with the full CCSD-F12 model, but this is a small price to pay for a significant reduction in computational cost and increased numerical stability [144]. Furthermore, since the model is consistent from the point of view of a perturbational analysis, the CCSD(F12) model is appropriate for use in response calculations [145–149].

Beyond the O^2N^4 scaling of conventional CCSD, the F12 terms in the CCSD(F12) iterations scale not worse than O^3N^2X. Depending on the size of the complementary auxiliary basis set (CABS) [135, 150], a CCSD(F12) calculation may take approximately 3–5 times longer than a conventional CCSD calculation in the same orbital basis, and the cost (but not scaling) can be significantly reduced by employing the fixed-amplitudes ansatz.

The CCSD(F12) model including Slater-type geminals, CABS, and ansatz 2B of F12 theory was first implemented in a developmental version of the Dalton program package [7, 8, 151, 152]. This implementation was restricted to closed-shell calculations with restricted Hartree–Fock (RHF) reference. Ten-no has presented an implementation of the CCSD(F12) model using the fixed-amplitudes ansatz and numerical quadratures [153]. In the present work, we report results obtained from an efficient implementation [154–156] of the CCSD(F12) approach in the Turbomole program package using a combination of integral-direct routines and density fitting [154, 155, 157–159]. Furthermore, the CCSD(F12) model is also available by virtue of the automated code generators Smith [160–162] and GeCCo [144, 148, 163] as well as in the DIRCCR12-OS program [164, 165], but in the latter only without the CABS orbitals.

Finally, we note that also other approximations to the full CCSD-F12 model exist. Such approximations are for instance the CCSD-F12x models ($x = a, b$) of Werner and co-workers (available in Molpro) [132, 166–169] and Valeev's CCSD(2)$_{\overline{\mathrm{F12}}}$ model [170–175] (available in MPQC/PSI [176–178]).

4 Computational details

The frozen-core CCSD(F12) calculations [abbreviated as fc-CCSD(F12)] of the present article were performed in the def2-QZVPP basis [179]. For the density-fitting approximation, the aug-cc-pwCV5Z MP2 fitting basis of Hättig was used (aug-cc-pV5Z for H) [180]. The def2-QZVPP Hartree–Fock exchange fitting basis was used as CABS. It was also used for computing matrix elements of the Fock operator (for use in the CCSD(F12) approach) using the RI-JK approximation (resolution-of-identity approximation for Coulomb and exchange) [181]. These (auxiliary) basis sets are exactly the same as in Ref. [182], because the purpose of the present work is to replace the empirically scaled MP2-F12 basis-set truncation errors of that work by ab initio computed F12 corrections obtained at the CCSD(F12) level in the present work. To guarantee a fair comparison, all conditions should be kept unchanged. Hence, the calculation of F12 matrix elements (e.g., approximation 2B, etc.) is also kept equal to that of Ref. [182]. Details are described in Refs. [154] and [155].

All of the molecular geometries used here are identical to those of Ref. [182]. These had been optimized at the all-electron CCSD(T) level [ae-CCSD(T)] in the cc-pCVTZ basis set (cc-pVTZ for H) [39, 43]. The ae-CCSD(T) calculations of the closed-shell molecules had been performed using a restricted Hartree–Fock reference determinant.

The fc-CCSD(F12) calculations were carried out using the Turbomole program [2]. The molecular fc-CCSD(T) calculations in the cc-pCVQZ and cc-pCV5Z basis sets [39, 43] were performed with Molpro [1] or Cfour [183]. The atoms were computed using Cfour [183].

A number of further corrections, reported under "Other" in Table 1, are taken from our earlier work [182]. These corrections include core–valence correlation effects, the difference between fc-CCSD(T) and fc-CCSDT (coupled-cluster theory with singles, doubles, and triples), perturbative corrections for connected quadruple excitations (CCSDT(Q) method [184–186]), scalar relativistic and spin–orbit effects, and anharmonic zero-point vibrational energies. In Ref. [182], the accuracy of all of these corrections and the magnitude of the errors due to missing terms are discussed. If we assume that those errors are statistical in nature, then we may estimate the expected accuracy of our computed atomization energy by Gaussian error propagation. For this, we use the following root-mean-square (RMS) errors per valence electron: 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 diagonal Born–Oppenheimer correction (DBOC). All of these RMS errors were taken from Ref. [182]. The result of the error propagation is

$$\sigma = n_{\text{valence electrons}} \times 0.10 \ \text{kJ/mol}. \tag{25}$$

Thus, this is the accuracy that we may expect from our calculations, assuming that the Hartree–Fock, CCSD, and CCSD(T) contributions have converged with respect to the one-particle basis set.

Accurate, reliable, and internally consistent thermochemical values were taken from the Active Thermochemical Tables (ATcT) [187, 188] for the comparison with experiment. As opposed to the traditional sequential approach, the ATcT derive their results from a Thermochemical Network (TN) using all available knowledge. The ATcT thermochemical values used in the present work were taken from Ref. [182].

5 Results and discussion

We begin with coupled-cluster calculations with singles and doubles (CCSD) in the correlation-consistent core–valence quadruple-zeta basis set (cc-pCVQZ) [43], correlating only the valence electrons (frozen-core approximation, fc-CCSD). The atomic and molecular correlation energies obtained at this level, using an unrestricted Hartree–Fock (UHF) reference for the atoms, are reported in Tables 2 and 3, respectively. These are the energies that will be replaced by much improved fc-CCSD(F12) correlation energies later on.

The atomization energies reported under "CCSD" in Table 1 represent the baseline of our approach, as in Ref. [182]. The 106 molecules of the present study are all closed-shell systems, and restricted Hartree–Fock reference wave functions were used, of course. The CCSD atomization energies in Table 1 were obtained from spin-unrestricted CCSD calculations (UCCSD) on the atoms, based on restricted open-shell Hartree–Fock (ROHF) reference wave functions and semi-canonical orbitals (ROHF-UCCSD level). Hence, atomic CCSD calculations with ROHF references were carried out to define the CCSD atomization energy baseline, whereas atomic CCSD calculations with UHF references were carried out to compute the F12 corrections (*vide infra*).

At the fc-CCSD/cc-pCVQZ level, not only the error in the electron-correlation contribution but also the error in the Hartree–Fock contribution is relatively large (up to a few kJ/mol). To improve the Hartree–Fock part contained in the fc-CCSD/cc-pCVQZ energies, we performed Hartree–Fock calculations in the cc-pCV5Z basis (correlation-consistent core–valence quintuple-zeta), and we report the difference in atomization energies obtained at the Hartree–Fock level in the cc-pCV5Z and cc-pVQZ basis sets as δ_{HF} in Table 1,

$$\delta_{\text{HF}} = E_{\text{HF/cc-pCV5Z}} - E_{\text{HF/cc-pCVQZ}}. \tag{26}$$

RHF calculations were performed for the closed-shell molecules, ROHF calculations for the atoms.

We have added a correction for connected triple excitations from fc-CCSD(T) calculations in cc-pCVQZ and cc-pCV5Z basis sets and subsequent X^{-3} extrapolation (denoted as cc-pCV(Q5)Z level). The corresponding contributions to the atomization energies are reported under "(T)" in Table 1.

To improve the electron correlation part of the fc-CCSD/cc-pCVQZ level, we have performed frozen-core CCSD(F12) calculations in the def2-QZVPP basis. In Ref. [182], similar calculations were performed at the level of second-order perturbation theory (MP2-F12). Here, we report explicitly correlated F12 coupled-cluster results, obtained using spin-flipped geminals as proposed in Ref. [136]. The difference in *electron-correlation contributions* to the atomization energies obtained at the fc-CCSD/cc-pCVQZ and fc-CCSD(F12)/def2-QZVPP levels is reported under "F12" in Table 1,

Table 1 Atomization energies in kJ/mol

Nr[a]	Molecule[b]		CCSD	δ_{HF}	(T)	F12	Other[c]	Total	ATcT	Error
1	CFN	Cyanogen fluoride	1,202.7	0.3	51.5	17.3	−21.0	1,250.8	1,250.3 ± 1.7	0.5
2	CFN	Isocyanogen fluoride	902.4	0.2	55.3	16.2	−17.2	957.0	959.2 ± 2.7	−2.2
3	CF_2	Singlet difluoromethylene	1,028.4	0.6	38.4	14.0	−20.0	1,061.3	1,059.1 ± 0.8	2.2
4	CF_2O	Carbonyl fluoride	1,677.5	−0.1	56.9	22.6	−37.7	1,719.1	1,718.4 ± 0.9	0.7
5	CF_4	Tetrafluoromethane	1,922.1	0.0	55.3	26.9	−51.7	1,952.6	1,947.9 ± 0.6	4.7
6	CHF	Singlet fluoromethylene	855.1	0.8	23.7	9.0	−31.7	857.0		
7	CHFO	Formyl fluoride	1,620.0	0.4	46.4	17.8	−52.9	1,631.7	1,631.4 ± 0.9	0.3
8	CHF_3	Trifluoromethane	1,855.1	0.4	44.8	21.9	−71.1	1,851.2	1,848.7 ± 0.9	2.5
9	CHN	Hydrogen cyanide	1,250.1	0.3	38.5	13.8	−35.1	1,267.6	1,268.3 ± 0.2	−0.7
10	CHN	Hydrogen isocyanide	1,189.6	0.5	36.8	13.3	−35.4	1,204.9	1,207.0 ± 0.6	−2.1
11	CHNO	Cyanic acid	1,627.8	0.5	56.9	21.1	−49.7	1,656.7	1,657.2 ± 1.0	−0.5
12	CHNO	Isocyanic acid	1,725.3	0.7	61.2	21.9	−48.7	1,760.3	1,761.0 ± 0.4	−0.7
13	CHNO	Formonitrile oxide	1,418.5	1.1	74.2	21.0	−41.4	1,473.4	1,474.1 ± 1.2	−0.7
14	CHNO	Isofulminic acid	1,377.6	0.5	59.0	20.3	−48.1	1,409.2	1,410.2 ± 1.0	−1.0
15	CH_2	Singlet methylene	742.1	0.7	8.0	4.6	−41.0	714.3	714.9 ± 0.2	−0.6
16	CH_2F_2	Difluoromethane	1,778.3	0.9	33.5	17.0	−87.3	1,742.3	1,741.7 ± 0.8	0.6
17	CH_2N_2	Cyanamide	1,937.9	1.0	57.6	24.0	−80.1	1,940.5		
18	CH_2N_2	3H-Diazirine	1,754.3	0.9	64.8	23.6	−79.9	1,763.7		
19	CH_2N_2	Diazomethane	1,788.7	1.1	68.0	22.8	−71.5	1,809.1		
20	CH_2O	Formaldehyde	1,515.0	0.7	33.2	13.0	−65.7	1,496.1	1,495.8 ± 0.2	0.3
21	CH_2O	Hydroxymethylene	1,300.8	1.0	30.6	12.4	−67.3	1,277.5	1,277.8 ± 1.1	−0.3
22	CH_2O_2	Dioxirane	1,627.0	0.7	61.7	20.8	−81.6	1,628.6	1,629.6 ± 1.7	−1.0
23	CH_2O_2	Formic acid	2,019.2	0.6	52.7	21.4	−85.0	2,008.9	2,008.4 ± 0.3	0.5
24	CH_2O_3	Performic acid	2,133.8	0.4	78.7	28.1	−91.4	2,149.7		
25	CH_3F	Fluoromethane	1,729.6	1.1	22.3	12.3	−102.0	1,663.3	1,665.1 ± 0.6	−1.8
26	CH_3N	Methanimine	1,778.4	1.3	35.6	15.5	−98.2	1,732.5	1,733.5 ± 1.0	−1.0
27	CH_3NO	Formamide	2,288.1	1.6	53.9	24.2	−111.6	2,256.3		
28	CH_3NO_2	Methyl nitrite	2,379.7	0.8	88.2	30.5	−119.9	2,379.3		
29	CH_3NO_2	Nitromethane	2,385.0	1.5	90.9	31.2	−122.8	2,385.8		
30	CH_4	Methane	1,733.2	0.4	12.1	7.6	−113.6	1,639.8	1,642.2 ± 0.1	−2.4
31	CH_4N_2O	Urea	3,029.4	1.9	72.5	35.4	−158.5	2,980.7		
32	CH_4O	Methanol	2,096.9	1.4	28.9	15.5	−130.9	2,011.8	2,012.7 ± 0.2	−0.9
33	CH_5N	Methylamine	2,378.0	1.7	30.7	17.9	−161.2	2,267.0	2,269.0 ± 0.5	−2.0
34	CO	Carbon monoxide	1,038.8	−0.2	33.6	10.5	−10.1	1,072.6	1,072.1 ± 0.1	0.5
35	CO_2	Carbon dioxide	1,548.6	−0.3	58.1	19.1	−25.8	1,599.7	1,598.2 ± 0.1	1.5
36	C_2F_2	Difluoroacetylene	1,526.3	0.8	57.2	19.8	−29.0	1,575.2	1,577.0 ± 1.7	−1.8
37	C_2F_4	Tetrafluoroethylene	2,350.1	1.2	78.0	32.4	−56.7	2,405.0	2,405.2 ± 1.0	−0.2
38	C_2HF	Fluoroacetylene	1,593.4	0.4	46.3	15.9	−45.5	1,610.5	1,612.3 ± 1.0	−1.8
39	C_2HF_3	Trifluoroethylene	2,345.6	1.2	66.0	27.6	−75.0	2,365.4		
40	C_2H_2	Acetylene	1,637.4	0.6	35.0	12.2	−60.4	1,624.7	1,626.2 ± 0.2	−1.5
41	$C_2H_2F_2$	1,1-Difluoroethylene	2,367.7	0.6	54.3	22.9	−92.0	2,353.7		
42	C_2H_2O	Ketene	2,145.9	0.5	54.6	19.0	−73.4	2,146.6	2,147.3 ± 0.2	−0.7
43	C_2H_2O	Oxirene	1,813.6	2.2	60.4	20.6	−67.7	1,829.1		
44	$C_2H_2O_2$	Glyoxal	2,547.3	0.7	71.9	26.3	−89.0	2,557.3	2,555.3 ± 0.6	2.0
45	C_2H_3F	Fluoroethylene	2,329.1	1.1	42.8	18.1	−108.6	2,282.4	2,278.4 ± 1.7	4.0
46	C_2H_3FO	Acetyl fluoride	2,860.0	0.5	61.5	26.2	−122.5	2,825.7		
47	C_2H_3N	Acetonitrile	2,491.3	0.7	53.1	21.2	−108.2	2,458.2		
48	C_2H_3N	Methyl isocyanide	2,391.4	0.8	51.6	21.1	−109.9	2,354.9		

Table 1 continued

Nr[a]	Molecule[b]		CCSD	δ_{HF}	(T)	F12	Other[c]	Total	ATcT	Error
49	C_2H_4	Ethylene	2,304.3	0.8	31.0	13.3	−124.2	2,225.3	2,225.9 ± 0.2	−0.6
50	C_2H_4O	Acetaldehyde	2,755.0	0.8	48.7	21.0	−137.2	2,688.3	2,688.9 ± 0.4	−0.6
51	C_2H_4O	Oxirane	2,643.5	1.2	49.5	22.3	−143.4	2,573.1	2,573.9 ± 0.5	−0.8
52	$C_2H_4O_2$	Acetic acid	3,254.9	0.7	67.7	29.6	−154.3	3,198.6	3,199.3 ± 1.5	−0.7
53	$C_2H_4O_2$	Methyl formate	3,183.6	0.8	68.7	29.4	−155.8	3,126.7	3,125.2 ± 0.6	1.5
54	C_2H_5F	Fluoroethane	2,951.0	1.0	37.5	20.1	−172.1	2,837.5	2,838.5 ± 1.9	−1.0
55	C_2H_5N	Aziridine	2,925.7	1.3	50.8	24.8	−174.6	2,828.0		
56	C_2H_6	Ethane	2,930.7	0.6	26.7	15.2	−188.6	2,784.7	2,787.2 ± 0.2	−2.5
57	C_2H_6O	Dimethyl ether	3,264.5	1.2	44.4	23.2	−201.4	3,131.8	3,132.4 ± 0.5	−0.6
58	C_2H_6O	Ethanol	3,315.0	1.4	44.3	23.1	−201.7	3,182.2	3,182.8 ± 0.3	−0.6
59	C_2N_2	Cyanogen	1,970.9	0.3	85.9	26.1	−27.5	2,055.6	2,055.8 ± 0.5	−0.2
60	C_3H_3N	Acrylonitrile	3,071.4	0.8	74.8	26.9	−117.1	3,056.9		
61	C_3H_4	Allene	2,858.6	0.9	51.3	19.0	−131.7	2,798.1	2,800.9 ± 0.5	−2.8
62	C_3H_4	Cyclopropene	2,765.9	0.8	51.3	20.5	−134.6	2,703.9	2,705.1 ± 1.0	−1.2
63	C_3H_4	Propyne	2,868.0	0.7	49.9	17.1	−132.1	2,803.5	2,805.6 ± 0.5	−2.1
64	C_3H_6	Cyclopropane	3,490.0	0.7	45.3	22.3	−203.0	3,355.4	3,359.7 ± 0.6	−4.3
65	C_3H_6	Propene	3,520.5	1.0	46.6	21.1	−195.3	3,394.0	3,395.0 ± 0.4	−1.0
66	C_3H_8	Propane	4,136.2	0.8	42.3	22.8	−257.7	3,944.4	3,944.6 ± 0.4	−0.2
67	C_3O_2	Carbon suboxide	2,620.5	−0.1	112.2	30.5	−41.0	2,722.2		
68	C_4H_4	Butatriene	3,415.2	1.1	76.4	24.5	−137.8	3,379.4		
69	C_4H_4	Cyclobutadiene	3,308.7	1.6	77.3	26.4	−142.3	3,271.7		
70	C_4H_4	Tetrahedran	3,200.0	1.0	71.1	29.1	−140.3	3,160.9		
71	C_4H_4	Vinylacetylene	3,454.5	1.0	71.8	25.3	−141.7	3,410.9		
72	C_4N_2	Dicyanoacetylene	3,132.7	0.6	129.6	37.6	−44.8	3,255.6		
73	FH	Hydrogen fluoride	577.0	1.2	9.1	4.6	−26.0	565.9	566.0 ± 0.0	−0.1
74	FHO	Hypofluorous acid	616.2	0.5	34.3	10.7	−36.8	624.9	624.0 ± 0.4	0.9
75	FHO_2	Fluoroperoxide	793.6	0.8	63.2	18.0	−46.5	829.0		
76	FH_2N	Monofluoroamine	1,023.9	1.3	30.8	14.3	−71.4	998.9		
77	FH_3N_2	Fluorohydrazine	1,628.0	2.2	53.7	25.4	−115.0	1,594.4		
78	FNO	Nitrosyl fluoride	806.7	1.0	69.6	18.9	−16.0	880.2		
79	F_2	Difluorine	123.1	0.0	31.9	6.2	−6.3	154.9	154.6 ± 0.2	0.3
80	F_2N_2	Difluorodiazene (cis)	941.9	0.9	81.3	26.5	−29.0	1,021.6		
81	F_2N_2	Difluorodiazene (trans)	938.7	1.1	78.3	26.1	−28.8	1,015.4		
82	F_2O	Difluorine monoxide	317.8	0.6	57.6	13.9	−14.1	375.9	373.3 ± 0.7	2.6
83	F_2O_2	Perfluoroperoxide	505.4	0.7	104.8	21.1	−16.1	615.9	609.7 ± 0.8	6.2
84	F_3N	Trifluoroamine	771.3	1.1	66.8	23.2	−30.4	832.1		
85	HNO	Nitrosylhydride	800.0	1.0	42.3	14.1	−33.4	824.0	823.6 ± 0.1	0.4
86	HNO_2	Nitrous acid (cis)	1,208.8	0.6	70.0	22.3	−49.5	1,252.1	1,251.5 ± 0.4	0.6
87	HNO_2	Nitrous acid (trans)	1,209.1	1.0	70.4	22.2	−49.0	1,253.7	1,253.3 ± 0.1	0.4
88	HNO_2	Nitrous acid, $H–NO_2$	1,170.4	1.4	76.0	22.8	−53.4	1,217.1		
89	HNO_3	Nitric acid	1,491.0	0.7	97.6	30.8	−66.5	1,553.6	1,551.6 ± 0.2	2.0
90	HN_3	Hydrogen azide	1,272.7	1.4	78.1	25.1	−47.2	1,330.1	1,329.7 ± 0.6	0.4
91	H_2N_2	Diazene (cis)	1,151.4	1.5	42.6	17.1	−68.3	1,144.3	1,143.5 ± 0.9	0.8
92	H_2N_2	Diazene (trans)	1,174.0	1.8	41.9	17.2	−69.8	1,165.0	1,165.8 ± 0.7	−0.8
93	H_2N_2	Diazene (iso)	1,072.1	1.8	38.9	17.9	−65.5	1,065.2	1,065.1 ± 0.9	0.1
94	H_2N_2O	Nitrosamide	1,515.2	1.6	68.0	25.8	−79.2	1,531.3		
95	H_2O	Water	948.0	1.9	14.9	7.9	−55.5	917.2	917.8 ± 0.1	−0.6
96	H_2O_2	Hydrogen peroxide	1,070.3	0.9	37.9	14.6	−68.5	1,055.2	1,055.2 ± 0.1	0.0

Table 1 continued

Nr[a]	Molecule[b]		CCSD	δ_{HF}	(T)	F12	Other[c]	Total	ATcT	Error
97	H_3N	Ammonia	1,214.6	1.9	16.5	10.2	−87.3	1,155.8	1,157.3 ± 0.1	−1.5
98	H_3NO	Ammonia oxide	1,336.5	4.1	36.7	19.3	−105.7	1,291.0		
99	H_3NO	Hydroxylamine	1,446.1	1.8	35.8	17.7	−103.3	1,398.1	1,398.7 ± 0.5	−0.6
100	H_4N_2	Hydrazine	1,769.4	2.3	35.6	20.5	−135.1	1,692.7	1,695.6 ± 0.2	−2.9
101	N_2	Dinitrogen	894.5	0.5	39.7	15.0	−9.3	940.3	941.1 ± 0.1	−0.8
102	N_2O	Nitrous oxide	1,023.6	0.5	78.8	22.0	−22.3	1,102.6	1,102.0 ± 0.1	0.6
103	N_2O_3	Dinitrogen trioxide	1,445.7	1.5	146.4	36.8	−36.8	1,593.6	1,591.1 ± 0.2	2.5
104	N_2O_4	Dinitrogen tetraoxide	1,737.9	0.8	180.2	45.6	−53.9	1,910.6	1,908.5 ± 0.2	2.1
105	O_3	Ozone	477.9	0.9	108.3	17.3	−8.0	596.5	596.1 ± 0.1	0.4
106	H_2	Dihydrogen	456.6	0.1	0.0	1.2	−26.1	431.8	432.1 ± 0.0	−0.3

The individual contributions are explained in the text

[a] Same number and same molecule as in Ref. [62] except for dihydrogen

[b] The ae-CCSD(T)/cc-pCVTZ equilibrium geometry was used for each molecule

[c] Further corrections are taken from Ref. [182]. See the text

Table 2 Atomic energies in E_h

Atom		Hartree–Fock[a]	CCSD[b]	CCSD(F12)[c]	CCSD (F12)-*sp*[d]
H	Hydrogen	−0.4999833	…	…	…
C	Carbon	−37.6936272	−0.0913204	−0.0928337	−0.0924916
N	Nitrogen	−54.4043853	−0.1190648	−0.1218208	−0.1213031
O	Oxygene	−74.8186293	−0.1740292	−0.1803760	−0.1794324
F	Fluorine	−99.4158870	−0.2342186	−0.2446494	−0.2431462

[a] Unrestricted Hartree–Fock energy in the def2-QZVPP basis (UHF/def2-QZVPP)

[b] fc-CCSD/cc-pCVQZ correlation energy (UHF reference)

[c] fc-CCSD(F12)/def2-QZVPP correlation energy obtained by optimizing the F12 amplitudes

[d] fc-CCSD(F12)/def2-QZVPP correlation energy obtained with fixed F12 amplitudes

$$\mathrm{F12} = \Delta E_{\text{fc-CCSD(F12)/def2-QZVPP}} - \Delta E_{\text{fc-CCSD/cc-pCVQZ}}. \tag{27}$$

Note that, in order to compute the correction of Eq. (27), we have used UHF reference wave functions both at the fc-CCSD/cc-pCVQZ and at the fc-CCSD(F12)/def2-QZVPP levels for the atoms (Table 2). The F12 corrections can easily be computed from the data shown in Tables 2 and 3.

Table 4 shows the final results of our calculations in terms of a statistical analysis of the 73 atomization energies for which accurate and reliable ATcT values are available. Shown are the statistics for various attempts to approach the basis-set limit of CCSD theory.

If the CCSD(F12) method is used to compute the F12 correction (cf. Table 1), then the mean-absolute deviation (MAD) and RMS error are 1.3 and 1.7 kJ/mol, with a maximum error of 6.2 kJ/mol for F_2O_2. Transferred to errors per valence electron, the corresponding errors are 0.08, 0.10, and −0.3 kJ/mol, respectively (the latter for CH_4). These results were obtained by *optimizing* all F12 doubles amplitudes. When keeping those fixed in the sense of the *sp* ansatz, very similar results are obtained (CCSD(F12)-*sp*). In fact, the CCSD(F12)-*sp* results appear to be slightly more accurate than the CCSD(F12) results from optimized amplitudes. This could be explained by the lack of geminal basis-set superposition error [189] in the CCSD(F12)-*sp* model, but the differences between CCSD(F12)-*sp* and fully optimized CCSD(F12) are really very small. In any case, the computationally inexpensive CCSD(F12)-*sp* method is certainly not inferior to the computationally more involved CCSD(F12) scheme.

Table 4 also shows the results that are obtained by computing the fc-CCSD contribution in the cc-pCVTZ, cc-pCVQZ, and cc-pCV5Z basis sets. The results shown for the cc-pCVQZ basis correspond to our baseline, that is, correspond to the results without adding the F12 correction. Of course, using the smaller cc-pCVTZ instead of the cc-

Table 3 Molecular energies in E_h

Nr	Molecule		Hartree–Fock[a]	CCSD[b]	CCSD(F12)[c]	CCSD(F12)-*sp*[d]
1	CFN	Cyanogen fluoride	−191.7859409	−0.6298489	−0.6511336	−0.6487394
2	CFN	Isocyanogen fluoride	−191.6691801	−0.6321631	−0.6530383	−0.6505171
3	CF_2	Singlet difluoromethylene	−236.7783880	−0.6977454	−0.7254381	−0.7219008
4	CF_2O	Carbonyl fluoride	−311.7674525	−0.9479901	−0.9853070	−0.9808509
5	CF_4	Tetrafluoromethane	−435.8589954	−1.2570985	−1.3105777	−1.3038619
6	CHF	Singlet fluoromethylene	−137.8245587	−0.4358486	−0.4512047	−0.4492713
7	CHFO	Formyl fluoride	−212.8527434	−0.6911326	−0.7162145	−0.7133652
8	CHF_3	Trifluoromethane	−336.9406830	−1.0001895	−1.0413446	−1.0362679
9	CHN	Hydrogen cyanide	−92.9147683	−0.3692335	−0.3787441	−0.3778660
10	CHN	Hydrogen isocyanide	−92.8994262	−0.3615795	−0.3709305	−0.3700631
11	CHNO	Cyanic acid	−167.8038558	−0.6163130	−0.6349840	−0.6331712
12	CHNO	Isocyanic acid	−167.8437312	−0.6135773	−0.6325327	−0.6307573
13	CHNO	Formonitrile oxide	−167.7061838	−0.6344825	−0.6530931	−0.6512398
14	CHNO	Isofulminic acid	−167.7082403	−0.6165174	−0.6348662	−0.6329593
15	CH_2	Singlet methylene	−38.8955654	−0.1718916	−0.1751674	−0.1747524
16	CH_2F_2	Difluoromethane	−238.0195170	−0.7423924	−0.7712539	−0.7677999
17	CH_2N_2	Cyanamide	−147.9784645	−0.5907607	−0.6069247	−0.6055029
18	CH_2N_2	3H-Diazirine	−147.8965217	−0.6025899	−0.6186186	−0.6170941
19	CH_2N_2	Diazomethane	−147.9111183	−0.6012640	−0.6169587	−0.6154712
20	CH_2O	Formaldehyde	−113.9223269	−0.4318370	−0.4446325	−0.4433431
21	CH_2O	Hydroxymethylene	−113.8459372	−0.4266566	−0.4392576	−0.4379207
22	CH_2O_2	Dioxirane	−188.6938909	−0.6950579	−0.7172002	−0.7147406
23	CH_2O_2	Formic acid	−188.8588748	−0.6795607	−0.7019056	−0.6996381
24	CH_2O_3	Performic acid	−263.6371394	−0.9370518	−0.9683271	−0.9648336
25	CH_3F	Fluoromethane	−139.1089372	−0.4846290	−0.5012607	−0.4993826
26	CH_3N	Methanimine	−94.0755272	−0.4098956	−0.4200545	−0.4191580
27	CH_3NO	Formamide	−169.0175302	−0.6543821	−0.6742319	−0.6723790
28	CH_3NO_2	Methyl nitrite	−243.7796349	−0.9190430	−0.9476397	−0.9444309
29	CH_3NO_2	Nitromethane	−243.7792702	−0.9217424	−0.9505772	−0.9474677
30	CH_4	Methane	−40.2167143	−0.2281067	−0.2325258	−0.2321636
31	CH_4N_2O	Urea	−224.1007070	−0.8766883	−0.9035510	−0.9010698
32	CH_4O	Methanol	−115.1008596	−0.4750978	−0.4888444	−0.4875321
33	CH_5N	Methylamine	−95.2621029	−0.4517747	−0.4628470	−0.4619185
34	CO	Carbon monoxide	−112.7896607	−0.3828558	−0.3947093	−0.3934061
35	CO_2	Carbon dioxide	−187.7234566	−0.6354429	−0.6569249	−0.6547489
36	C_2F_2	Difluoroacetylene	−274.5931479	−0.8575500	−0.8889980	−0.8852779
37	C_2F_4	Tetrafluoroethylene	−473.6501181	−1.4140935	−1.4711963	−1.4639979
38	C_2HF	Fluoroacetylene	−175.7282826	−0.5979507	−0.6174457	−0.6153291
39	C_2HF_3	Trifluoroethylene	−374.7582318	−1.1544013	−1.1992258	−1.1937287
40	C_2H_2	Acetylene	−76.8548120	−0.3383643	−0.3460381	−0.3454275
41	$C_2H_2F_2$	1,1-Difluoroethylene	−275.8759899	−0.8949960	−0.9276240	−0.9237989
42	C_2H_2O	Ketene	−151.7971019	−0.5819102	−0.5985064	−0.5969308
43	C_2H_2O	Oxirene	−151.6563755	−0.5966110	−0.6138324	−0.6121818
44	$C_2H_2O_2$	Glyoxal	−226.6959293	−0.8283031	−0.8540529	−0.8513573
45	C_2H_3F	Fluoroethylene	−176.9702808	−0.6362778	−0.6566320	−0.6544179
46	C_2H_3FO	Acetyl fluoride	−251.9190449	−0.8817596	−0.9115303	−0.9082493
47	C_2H_3N	Acetonitrile	−131.9829651	−0.5584833	−0.5723384	−0.5711092
48	C_2H_3N	Methyl isocyanide	−131.9518115	−0.5515363	−0.5653440	−0.5641015

Table 3 continued

Nr	Molecule		Hartree–Fock[a]	CCSD[b]	CCSD(F12)[c]	CCSD(F12)-*sp*[d]
49	C_2H_4	Ethylene	−78.0700161	−0.3771433	−0.3852547	−0.3845993
50	C_2H_4O	Acetaldehyde	−152.9880560	−0.6229960	−0.6403610	−0.6386874
51	C_2H_4O	Oxirane	−152.9393205	−0.6293146	−0.6471978	−0.6455286
52	$C_2H_4O_2$	Acetic acid	−227.9230061	−0.8706774	−0.8976617	−0.8949776
53	$C_2H_4O_2$	Methyl formate	−227.8966830	−0.8698221	−0.8967421	−0.8940148
54	C_2H_5F	Fluoroethane	−178.1665237	−0.6768116	−0.6979121	−0.6956380
55	C_2H_5N	Aziridine	−133.1006195	−0.6063148	−0.6215279	−0.6202814
56	C_2H_6	Ethane	−79.2660250	−0.4195583	−0.4283608	−0.4276515
57	C_2H_6O	Dimethyl ether	−154.1398680	−0.6652526	−0.6834617	−0.6817354
58	C_2H_6O	Ethanol	−154.1567689	−0.6677158	−0.6859051	−0.6842117
59	C_2N_2	Cyanogen	−184.6604828	−0.7058138	−0.7242824	−0.7225057
60	C_3H_3N	Acrylonitrile	−169.8376947	−0.7093997	−0.7269465	−0.7253913
61	C_3H_4	Allene	−115.9140479	−0.5289359	−0.5407194	−0.5397643
62	C_3H_4	Cyclopropene	−115.8735136	−0.5340324	−0.5463928	−0.5454602
63	C_3H_4	Propyne	−115.9165720	−0.5298730	−0.5409346	−0.5399788
64	C_3H_6	Cyclopropane	−117.1098487	−0.5733963	−0.5864299	−0.5854420
65	C_3H_6	Propene	−117.1253074	−0.5697260	−0.5822860	−0.5812676
66	C_3H_8	Propane	−118.3167020	−0.6126413	−0.6258688	−0.6248022
67	C_3O_2	Carbon suboxide	−263.3957087	−0.9409021	−0.9697340	−0.9667730
68	C_4H_4	Butatriene	−153.7567717	−0.6829344	−0.6983209	−0.6970515
69	C_4H_4	Cyclobutadiene	−153.7066105	−0.6926217	−0.7087158	−0.7074191
70	C_4H_4	Tetrahedran	−153.6629430	−0.6945892	−0.7117331	−0.7105287
71	C_4H_4	Vinylacetylene	−153.7746951	−0.6799467	−0.6956276	−0.6943534
72	C_4N_2	Dicyanoacetylene	−260.3687242	−1.0095181	−1.0354089	−1.0329324
73	FH	Hydrogen fluoride	−100.0702079	−0.2998642	−0.3120326	−0.3105938
74	FHO	Hypofluorous acid	−174.8216361	−0.5553165	−0.5761845	−0.5735067
75	FHO_2	Fluoroperoxide	−249.6223266	−0.8144534	−0.8444446	−0.8405331
76	FH_2N	Monofluoroamine	−155.0399487	−0.5233276	−0.5419638	−0.5397621
77	FH_3N_2	Fluorohydrazine	−210.0669913	−0.7496930	−0.7753272	−0.7724586
78	FNO	Nitrosyl fluoride	−228.7289329	−0.7437135	−0.7704641	−0.7671128
79	F_2	Difluorine	−198.7719942	−0.5745206	−0.5977364	−0.5944037
80	F_2N_2	Difluorodiazene (cis)	−307.7248311	−0.9799044	−1.0163829	−1.0116492
81	F_2N_2	Difluorodiazene (trans)	−307.7267848	−0.9767334	−1.0130346	−1.0083849
82	F_2O	Difluorine monoxide	−273.5847390	−0.8282651	−0.8607794	−0.8562276
83	F_2O_2	Perfluoroperoxide	−348.3719753	−1.1047874	−1.1463775	−1.1404612
84	F_3N	Trifluoroamine	−352.7121655	−1.0543870	−1.0972872	−1.0915485
85	HNO	Nitrosylhydride	−129.8482522	−0.4720030	−0.4864883	−0.4848622
86	HNO_2	Nitrous acid (cis)	−204.7409841	−0.7270740	−0.7510152	−0.7482872
87	HNO_2	Nitrous acid (trans)	−204.7400474	−0.7282372	−0.7521424	−0.7494144
88	HNO_2	Nitrous acid, H–NO_2	−204.7205146	−0.7331945	−0.7573292	−0.7546876
89	HNO_3	Nitric acid	−279.5846451	−0.9831883	−1.0167079	−1.0129337
90	HN_3	Hydrogen azide	−163.9160430	−0.6382882	−0.6560986	−0.6543735
91	H_2N_2	Diazene (cis)	−110.0386481	−0.4464120	−0.4584325	−0.4572468
92	H_2N_2	Diazene (trans)	−110.0481885	−0.4456029	−0.4576751	−0.4564932
93	H_2N_2	Diazene (iso)	−110.0197518	−0.4353250	−0.4476507	−0.4464743
94	H_2N_2O	Nitrosamide	−184.9187716	−0.6971540	−0.7188437	−0.7165922
95	H_2O	Water	−76.0666229	−0.2873806	−0.2967401	−0.2958240
96	H_2O_2	Hydrogen peroxide	−150.8506963	−0.5417375	−0.5599848	−0.5579389

Table 3 continued

Nr	Molecule		Hartree–Fock[a]	CCSD[b]	CCSD(F12)[c]	CCSD(F12)-*sp*[d]
97	H_3N	Ammonia	−56.2242363	−0.2620268	−0.2686766	−0.2681197
98	H_3NO	Ammonia oxide	−131.0156706	−0.5099821	−0.5264451	−0.5248618
99	H_3NO	Hydroxylamine	−131.0543726	−0.5122760	−0.5281243	−0.5265267
100	H_4N_2	Hydrazine	−111.2351812	−0.4855615	−0.4988761	−0.4977005
101	N_2	Dinitrogen	−108.9916966	−0.3952522	−0.4064832	−0.4053156
102	N_2O	Nitrous oxide	−183.7645362	−0.6638594	−0.6841022	−0.6819665
103	N_2O_3	Dinitrogen trioxide	−333.3876531	−1.1862777	−1.2248561	−1.2202143
104	N_2O_4	Dinitrogen tetraoxide	−408.2276251	−1.4495527	−1.4978217	−1.4920859
105	O_3	Ozone	−224.3618850	−0.7970088	−0.8226330	−0.8192793
106	H_2	Dihydrogen	−1.1335344	−0.0403568	−0.0408075	−0.0407555

[a] Restricted Hartree–Fock energy in the def2-QZVPP basis (RHF/def2-QZVPP)

[b] fc-CCSD/cc-pCVQZ correlation energy

[c] fc-CCSD(F12)/def2-QZVPP correlation energy obtained by optimizing the F12 amplitudes

[d] fc-CCSD(F12)/def2-QZVPP correlation energy obtained with fixed F12 amplitudes

Table 4 Statistics of the deviations of the computed values from the ATcT reference data (all deviations in kJ/mol)

CCSD approach	δ_{ave}[a]	δ_{mad}[b]	δ_{rms}[c]	95%[d]	δ_{max}[e]	Molecule[f]
Errors per molecule						
CCSD(F12)	−0.1	1.3	1.7	3.4	6.2	F_2O_2
CCSD(F12)-*sp*	−0.5	1.2	1.5	3.0	−4.2	C_3H_6 (cyclopropane)
cc-pCVTZ basis	−45.3	45.3	47.7	95.5	−100.0	N_2O_4
cc-pCVQZ basis	−18.7	18.7	19.9	39.9	−43.5	N_2O_4
cc-pCV5Z basis	−9.0	9.0	9.7	19.4	−20.8	N_2O_4
(TQ) extrapolation	1.2	1.7	2.2	4.4	6.6	C_3H_8 (propane)
(Q5) extrapolation	1.2	1.5	1.9	3.9	7.3	F_2O_2
Errors per valence electron						
CCSD(F12)	−0.03	0.08	0.10	0.21	−0.3	CH_4
CCSD(F12)-*sp*	−0.04	0.08	0.10	0.20	−0.3	CH_4
cc-pCVTZ basis	−2.8	2.8	2.9	5.8	−4.1	N_2H_4
cc-pCVQZ basis	−1.1	1.1	1.2	2.4	−1.7	N_2H_4
cc-pCV5Z basis	−0.55	0.55	0.57	1.1	−0.8	N_2H_4
(TQ) extrapolation	0.09	0.11	0.14	0.28	0.4	C_2H_3F
(Q5) extrapolation	0.07	0.09	0.11	0.22	0.3	C_2H_3F

[a] Mean error

[b] Mean absolute error

[c] Root-mean-square error

[d] 95% confidence limit

[e] Maximum deviation

[f] Molecule with largest error

pCVQZ basis makes the results worse, with MAD and RMS errors of almost 50 kJ/mol. Comparing the cc-pCVQZ results with the CCSD(F12) results, we note that adding the F12 correction reduces the errors by about one order of magnitude.

In contrast to this substantial improvement, increasing the basis from cc-pCVQZ to cc-pCV5Z only reduces the errors by only about a factor of two. The difference between the cc-pCV5Z and cc-pCVQZ results ($E_{CV5Z} - E_{CVQZ}$) is plotted in Fig. 1 as a function of the F12 correction, clearly showing

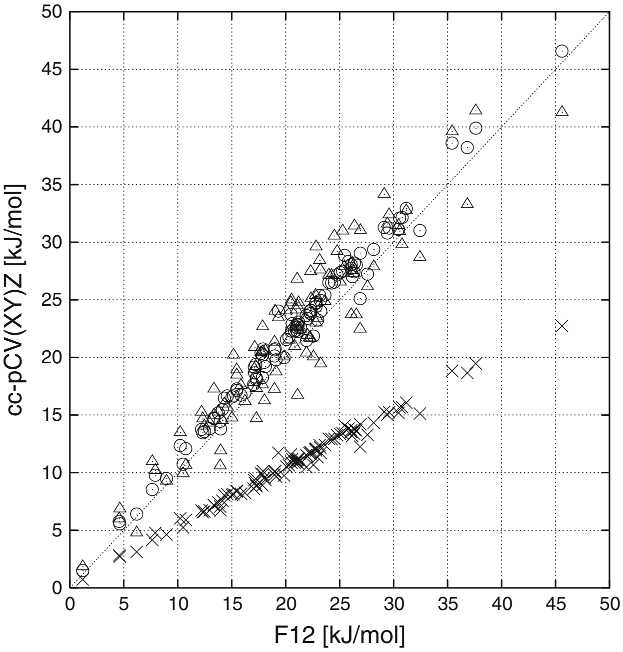

Fig. 1 Basis-set corrections to the fc-CCSD/cc-pCVQZ atomization energies obtained from fc-CCSD/cc-pCV5Z calculations (×) as well as from fc-CCSD/cc-pCV(TQ)Z (Δ) and fc-CCSD/cc-pCV(Q5)Z (O) basis-set extrapolations. The corrections are plotted against the F12 corrections

this factor of two: The $E_{\mathrm{CV5Z}} - E_{\mathrm{CVQZ}}$ differences are about half as large as the F12 corrections (shown as dotted line).

Finally, Table 4 also contains results obtained from Helgaker's extrapolation scheme, both from the cc-pCVTZ/cc-pCVQZ basis-set pair and from the cc-pCVQZ/cc-pCV5Z basis-set pair. Clearly, the extrapolation scheme does an excellent job. The extrapolation from the larger cc-pCVQZ and cc-pCV5Z basis sets yields slightly more accurate results than from the smaller cc-pCVTZ/cc-pCVQZ basis-set pair, but the difference is not substantial. The results of both extrapolations are shown in Fig. 1 as a function of the F12 correction.

The basis-set correction from the cc-pCV(Q5)Z extrapolation agrees well with the F12 correction and is roughly twice as large as the $E_{\mathrm{CV5Z}} - E_{\mathrm{CVQZ}}$ increment. This observation can be rationalized as follows: With $X = 4$ (cc-pCVQZ) and $X + 1 = 5$ (cc-pCV5Z), the X^{-3} extrapolation formula of Helgaker, Eq. (5), becomes

$$E_{\mathrm{CV(Q5)Z}} = \frac{125E_{\mathrm{CV5Z}} - 64E_{\mathrm{CVQZ}}}{61}. \tag{28}$$

Thus, we obtain for the difference $\Delta E_{\mathrm{CV(Q5)Z}} = E_{\mathrm{CV(Q5)Z}} - E_{\mathrm{CVQZ}}$,

$$\Delta E_{\mathrm{CV(Q5)Z}} = \frac{125}{61}(E_{\mathrm{CV5Z}} - E_{\mathrm{CVQZ}}) \approx 2.05\Delta E_{\mathrm{CV5Z}}. \tag{29}$$

Because the (Q5) extrapolated corrections and F12 corrections mutually agree very well, it is clear that the F12 correction must be roughly twice as large as the $E_{\mathrm{CV5Z}} - E_{\mathrm{CVQZ}}$ increment. When looking at this factor more closely, we find that it is slightly smaller than two (1.93). Fitting the ΔE_{CV5Z} data points of Fig. 1 to a line through the origin yields $\Delta E_{\mathrm{CV5Z}} = (0.519 \pm 0.002)\ \Delta E_{\mathrm{F12}}$. In other words,

$$\Delta E_{\mathrm{F12}} \approx 1.93\Delta E_{\mathrm{CV5Z}}. \tag{30}$$

Hence, relative to the CCSD(F12) basis-set incompleteness corrections ΔE_{F12}, the (Q5) extrapolation yields only slightly larger corrections (larger by ca. 6%).

Figure 1 shows that the ΔE_{CV5Z}, $\Delta E_{\mathrm{CV(TQ)Z}}$, and $\Delta E_{\mathrm{CV(Q5)Z}}$ corrections correlate well with the F12 corrections ΔE_{F12}, but that the scatter of the (TQ) extrapolation is larger than that of the more accurate (Q5) extrapolation. Fits of straight lines through the origin yield standard deviations of 0.98 and 2.63 kJ/mol for the (TQ) and (Q5) extrapolations, respectively. Note that all 106 molecules are considered in these fits.

6 Conclusions

We concluded our previous work [182] using empirically scaled MP2-F12 corrections with the words: "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." We have shown in the present work that this is true. No empirical factors are needed to obtain results close the basis-set limit of CCSD theory. The empirical factor of 0.78 chosen in Ref. [182] to scale the MP2-F12 corrections was very reasonable in view of the interference factor of Petersson's CBS theory.

Using the CCSD(F12) coupled-cluster approach to obtain CCSD energies close to the limit of a complete basis, the atomization energies of 73 molecules (containing H, C, N, O, and F) were computed with an estimated RMS deviation (from the values compiled in the Active Thermochemical Tables) of $\sigma = 0.10$ kJ/mol per valence electron. This small remaining error can be traced back to the errors in the various contributions to the atomization energy, und thus, is consistent with assuming that the (frozen-core) CCSD basis-set limit has been reached. Helgaker extrapolations based on cc-pCVTZ and cc-pCVQZ or cc-pCVQZ and cc-pCV5Z correlation energies are almost as accurate (with $\sigma = 0.14$ and 0.11 kJ/mol, respectively) as the CCSD(F12) results, but note that fc-CCSD/cc-pCV5Z calculations are significantly more time consuming than the fc-CCSD(F12)/def2-QZVPP calculations, and that the standard deviation of the (TQ) extrapolation is quite large (almost 3 kJ/mol per molecule). The CCSD(F12) calculations were performed in the def2-QZVPP basis in order to be able to compare the present CCSD(F12)/def2-QZVPP energies with the MP2-F12/def2-QZVPP computed in our earlier work. As shown recently [190], the cc-pVTZ-F12 basis set of Peterson and co-workers [191–193], although smaller in size than the def2-QZVPP basis set, would probably have yielded slightly more accurate atomization energies, and if still more accurate energies would be required, one could use the much larger cc-pVQZ-F12 basis.

Finally, we note that all of our results contain (T) perturbative triples corrections obtained from fc-CCSD(T)/cc-pCV5Z calculations, or more precisely, from (Q5) extrapolations based on fc-CCSD(T)/cc-pCVQZ and fc-CCSD(T)/cc-pCV5Z energies (only extrapolating the triples energy). Although, in the present work, we have succeeded to avoid CCSD calculations in very large basis sets for the singles-and-doubles part, it appears that we still need those large-scale calculations for the (T) part. Hence, we conclude that it seems an important task for the future to address the slow X^{-3} convergence of the triples [92], possibly by means of explicitly correlated connected triple excitations in the spirit of those suggested by Köhn [163].

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References

1. Molpro Version 2009.1 (2009) A package of ab initio programs. See http://www.molpro.net. Accessed 4 Feb 2010
2. Turbomole Version 6.0 (2009) A development of Universität Karlsruhe (TH) and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007. Available from http://www.turbomole.com. Accessed 4 Feb 2010
3. Ten-no S (2004) Chem Phys Lett 398:56
4. Tew DP, Klopper W (2005) J Chem Phys 123:074101
5. Klopper W, Manby FR, Ten-No S, Valeev, EF (2006) Int Rev Phys Chem 25:427
6. Werner HJ, Adler TB, Manby FR (2007) J Chem Phys 126:164102
7. Tew DP, Klopper W, Neiss C, Hättig C (2007) Phys Chem Chem Phys 9:1921
8. Tew DP, Klopper W, Neiss C, Hättig C (2008) Phys Chem Chem Phys 10:6325
9. Purvis GD III, Bartlett RJ (1982) J Chem Phys 76:1910
10. Helgaker T, Jørgensen P, Olsen J (2000) Molecular electronic-structure theory. Wiley, Chichester
11. Bak KL, Jørgensen P, Olsen J, Helgaker T, Klopper W (2000) J Chem Phys 112:9229
12. Dunning TH Jr (2000) J Phys Chem A 104:9062
13. Klopper W, Noga J (2003) ChemPhysChem 4:32
14. Helgaker T, Ruden TA, Jørgensen P, Olsen J, Klopper W (2004) J Phys Org Chem 17:913
15. Tew DP, Klopper W, Helgaker T (2007) J Comp Chem 28:1307
16. Helgaker T, Klopper W, Tew DP (2008) Mol Phys 106:2107
17. Feller D, Peterson KA, Dixon DA (2008) J Chem Phys 129:204105
18. Brown FB, Truhlar DG (1985) Chem Phys Lett 117:307
19. Gordon MS, Truhlar DG (1986) J Am Chem Soc 108:5412
20. Fast PL, Corchado J, Sánchez ML, Truhlar DG (1999) J Phys Chem A 103:3139
21. Pople JA, Head-Gordon M, Fox DJ, Raghavachari K, Curtiss LA (1989) J Chem Phys 90:5622
22. Curtiss LA, Raghavachari K, Trucks GW, Pople JA (1991) J Chem Phys 94:7221
23. Feller D, Peterson KA (1998) J Chem Phys 108:154
24. Feller D, Peterson KA (1999) J Chem Phys 110:8384
25. Fast PL, Sánchez ML, Corchado JC, Truhlar DG (1999) J Chem Phys 110:11679
26. Petersson GA, Malick DK, Wilson WG, Ochterski JW, Montgomery JA Jr, Frisch MJ (1998) J Chem Phys 109:10570
27. Petersson GA, Nyden MR (1981) J Chem Phys 75:3423
28. Nyden MR, Petersson GA (1981) J Chem Phys 75:1843
29. Petersson GA, Al-Laham MA (1991) J Chem Phys 94:6081
30. Petersson GA, Tensfeldt TG, Montgomery JA Jr (1991) J Chem Phys 94:6091
31. Montgomery JA Jr, Ochterski JW, Petersson GA (1994) J Chem Phys 101:5900
32. Ochterski JW, Petersson GA, Montgomery JA Jr (1996) J Chem Phys 104:2598
33. Montgomery JA Jr, Frisch MJ, Ochterski JW, Petersson GA (1999) J Chem Phys 110:2822
34. Montgomery JA Jr, Frisch MJ, Ochterski JW, Petersson GA (2000) Chem Phys Lett 112:6532
35. Wood GPF, Radom L, Peterson GA, Barnes EC, Firsch MJ, Montgomery JA Jr (2006) J Chem Phys 125:094106
36. Klopper W, Bak KL, Jørgensen P, Olsen J, Helgaker T (1999) J Phys B 32:R103
37. Raghavachari K, Trucks GW, Pople JA, Head-Gordon M (1989) Chem Phys Lett 157:479
38. Helgaker T, Klopper W, Koch H, Noga J (1997) J Chem Phys 106:9639
39. Dunning TH Jr (1989) J Chem Phys 90:1007
40. Kendall KA, Dunning TH Jr, Harrison RJ (1992) J Chem Phys 96:6796
41. Woon DE, Dunning TH Jr (1993) J Chem Phys 98:1358
42. Peterson KA,Woon DE, Dunning TH Jr (1994) J Chem Phys 100:7410
43. Woon DE, Dunning TH Jr (1995) J Chem Phys 103:4572
44. Wilson AK, van Mourik T, Dunning TH Jr (1996) J Mol Struct Theochem 388:339
45. Dunning TH Jr, Peterson KA, Wilson AK (2001) J Chem Phys 114:9244
46. Peterson KA, Dunning TH Jr (2002) J Chem Phys 117:10548
47. Truhlar DG (1998) Chem Phys Lett 294:45
48. Chuang YY, Truhlar DG (1999) J Phys Chem A 103:651
49. Halkier A, Helgaker T, Klopper W, Jørgensen P, Császár AG (1999) Chem Phys Lett 310:385
50. Klopper W, Schütz M, Lüthi HP, Leutwyler S (1995) J Chem Phys 103:1085
51. Kutzelnigg W, Morgan JD III (1992) J Chem Phys 96:4484
52. Kutzelnigg W (2008) Phys Chem Chem Phys 10:3460
53. Klopper W (2001) Mol Phys 99:481

54. Klopper W (2001) J Chem Phys 115:761
55. Martin JML (1996) Chem Phys Lett 259:669
56. Varandas AJC (2000) J Chem Phys 113:8880
57. Gdanitz RJ (2000) J Chem Phys 113:5145
58. Lee JS, Park SY (2000) J Chem Phys 112:10746
59. Valeev EF, Allen WD, Hernandez R, Sherrill CD, Schaefer HF III (2003) J Chem Phys 118:8594
60. Schwenke DW (2005) J Chem Phys 122:014107
61. Huh SB, Lee JS (2003) J Chem Phys 118:3035
62. Bakowies D (2007) J Chem Phys 127:084105
63. Bakowies D (2007) J Chem Phys 127:164109
64. Varandas AJC (2007) J Chem Phys 126:244105
65. Bakowies D (2009) J Phys Chem A 113:11517
66. Yamaki D, Koch H, Ten-no S (2007) J Chem Phys 127:144104
67. Hill JG, Peterson KA, Knizia G, Werner HJ (2009) J Chem Phys 131:194105
68. Termath V, Klopper W, Kutzelnigg W (1991) J Chem Phys 94:2002
69. Klopper W (1995) J Chem Phys 102:6168
70. Rodgers JM, Fast PL, Truhlar DG (2000) J Chem Phys 112:3141
71. Heckert M, Kállay M, Gauss J (2005) Mol Phys 103:2109
72. Heckert M, Kállay M, Tew DP, Klopper W, Gauss J (2006) J Chem Phys 125:044108
73. Tew DP, Klopper W, Heckert M, Gauss J (2007) J Phys Chem A 111:11242
74. Barnes EC, Petersson GA, Feller D, Peterson KA (2008) J Chem Phys 129:194115
75. East ALL, Allen WD (1993) J Chem Phys 99:4638
76. Császár AG, Allen WD, Schaefer HF III (1998) J Chem Phys 108:9751
77. Tarczay G, Császár AG, Klopper W, Szalay V, Allen WD, Schaefer III HF (1999) J Chem Phys 110:11971
78. Schuurman MS, Allen WD, von Ragué Schleyer P, Schaefer HF III (2005) J Chem Phys 122:104302
79. Czakó G, Nagy B, Tasi G, Somogyi A, Šimunek J, Noga J, Braams BJ, Bowman JM, Császár AG (2009) Int J Quantum Chem 109:2393
80. Fast PL, Sánchez ML, Truhlar DG (1999) Chem Phys Lett 306:407
81. Fast PL, Corchado JC, Sánchez ML, Truhlar DG (1999) J Phys Chem A 103:5129
82. Lynch BJ, Truhlar DG J Phys Chem A 107:3898
83. Zhao Y, Lynch BJ, Truhlar DG (2004) J Phys Chem A 108:4786
84. Zhao Y, Lynch BJ, Truhlar DG (2005) Phys Chem Chem Phys 7:43
85. Dahlke EE, Orthmeyer MA, Truhlar DG (2008) J Phys Chem B 112:2372
86. Sun YL, Li TH, Chen JL, Hu WP (2009) Chem Phys Lett 475:141
87. Martin JML, de Oliveira O (1999) J Chem Phys 111:1843
88. Boese AD, Oren M, Atasoylu O, Martin JML, Kállay M, Gauss J (2004) J Chem Phys 120:4129
89. Karton A, Rabinovich E, Martin JML, Ruscic B (2006) J Chem Phys 125:144108
90. Karton A, Taylor PR, Martin JML (2007) J Chem Phys 127:064104
91. Karton A, Gruzman D, Martin JML (2009) J Phys Chem A 113:8434
92. Barnes EC, Petersson GA, Montgomery JA Jr, Frisch MJ, Martin JML (2009) J Chem Theory Comput 5:2687
93. Bomble YJ, Vázquez J, Kállay M, Michauk C, Szalay PG, Császár AG, Gauss J, Stanton JF (2006) J Chem Phys 125:064108
94. Tajti A, Szalay PG, Császár AG, Kállay M, Gauss J, Valeev EF, Flowers BA, Vázquez J, tanton JF (2004) J Chem Phys 121:11599
95. Harding ME, Gauss J, Pflüger K, Werner HJ (2007) J Phys Chem A 111:13623
96. Harding ME, Gauss J, Pflüger K, Werner HJ (2008) J Phys Chem A 112:5024
97. Harding ME, Vázquez J, Ruscic B, Wilson AK, Gauss J, Stanton JF (2008) J Chem Phys 128:114111
98. Bakowies D (2009) J Chem Phys 130:144113
99. DeYonker NJ, Cundari TR, Wilson AK (2006) J Chem Phys 124:114104
100. DeYonker NJ, Grimes T, Yockel S, Dinescu A, Mintz B, Cundari TR, Wilson AK (2006) J Chem Phys 125:104111
101. Ho DS, DeYonker NJ, Wilson AK, Cundari TR (2006) J Phys Chem A 110:9767
102. Grimes TV, Wilson AK, DeYonker NJ, Cundari TR (2007) J Chem Phys 127:154117
103. DeYonker NJ, Ho DS, Wilson AK, Cundari TR (2007) J Phys Chem A 111:10776
104. DeYonker NJ, Peterson KA, Steyl G, Wilson AK, Cundari TR (2007) J Phys Chem A 111:11269
105. DeYonker DJ, Mintz B, Cundari TR, Wilson AK (2008) J Chem Theory Comput 4:328
106. GavinWilliams T, Wilson AK (2008) J Sulfur Chem 29:353
107. Feller D, Dixon DA (1998) J Phys Chem A 102:7053
108. Feller D, Dixon DA (1999) J Phys Chem A 103:6413
109. Dixon DA, Feller D, Sandrone G (1999) J Phys Chem A 103:4744
110. Feller D, Dixon DA (2001) J Chem Phys 115:3484
111. Feller D, Dixon DA (2003) J Phys Chem A 107:9641
112. Feller D, Peterson KA, de Jong WA, Dixon DA (2003) J Chem Phys 118:3510
113. Pollack L, Windus TL, de Jong WA, Dixon DA (2005) J Phys Chem A 109:6934
114. Nguyen MT, Matus MH, Lester WA, Dixon DA (2008) J Phys Chem A 112:2082
115. Feller D, Peterson KA (2009) J Chem Phys 131:154306
116. Curtiss LA, Raghavachari K, Redfern PC, Rassolov V, Pople JA (1998) J Chem Phys 109:7764
117. Curtiss LA, Redfern PC, Rassolov V, Kedziora G, Pople JA (2001) J Chem Phys 114:9287
118. Curtiss LA, Raghavachari K (2002) Theor Chem Acc 108:61
119. Curtiss LA (2003) Theor Chem Acc 109:239
120. Curtiss LA, Redfern PC, Raghavachari K (2007) J Chem Phys 126:084108
121. Curtiss LA, Redfern PC, Raghavachari K (2007) J Chem Phys 127:124105
122. Mayhall NJ, Raghavachari K, Redfern PC, Curtiss LA (2009) J Phys Chem A 113:5170
123. Claeyssens F, Harveyn JN, Manby FR, Mata RA, Mulholland AJ, Ranaghan KE, Schütz M, Thiel S, Thiel W, Werner HJ (2006) Angew Chem Int Ed 45:6856
124. Bihlmeier A, Tew DP, Klopper W (2008) J Chem Phys 129:114303
125. Vogiatzis KD, Mavrandonakis A, Klopper W, Froudakis GE (2009) Chem Phys Chem 10:374
126. Klopper W, Bachorz RA, Tew DP, Aguilera-Iparraguirre J, Carissan Y, Hättig C (2009) J Phys Chem A 113:11679
127. Klopper W, Tew DP, González-García N, Olzmann M (2008) J Chem Phys 129:114308
128. González-García N, Klopper W, Olzmann M (2009) Chem Phys Lett 470:59
129. Lee JJ, Höfener S, Klopper W, Wassermann T, Suhm MA (2009) J Phys Chem C 113:10929
130. Jung T, Beckhaus R, Klüner T, Höfener S, Klopper W (2009) J Chem Theory Comput 5:2044
131. Botschwina P, Oswald R, Knizia G, Werner HJ (2009) Z Phys Chem 223:447

132. Marchetti O, Werner HJ (2008) Phys Chem Chem Phys 10:3400
133. Bachorz RA, Bischoff FA, Höfener S, Ottiger P, Leist R, Frey JA, Leutwyler S (2008) Phys Chem Chem Phys 10:2758
134. Lane JR, Kjaergaard HG (2009) J Chem Phys 131:034307
135. Valeev EF (2004) Chem Phys Lett 395:190
136. Tew DP, Klopper W (2010) Mol Phys (in press)
137. Tew DP (2008) J Chem Phys 129:014104
138. Bokhan D, Ten-no S, Noga J (2008) Phys Chem Chem Phys 10:3320
139. Bokhan D, Bernadotte S, Ten-no S (2009) J Chem Phys 131:084105
140. Fliegl H, Klopper W, Hättig C (2005) J Chem Phys 122:084107
141. Christiansen O, Koch H, Jørgensen P (1995) Chem Phys Lett 243:409
142. Ten-no S (2004) J Chem Phys 121:117
143. Tew DP, Klopper W, Hättig C (2008) Chem Phys Lett 452:326
144. Köhn A, Richings GW, Tew DP (2008) J Chem Phys 129:201103
145. Neiss C, Hättig C (2007) J Chem Phys 126:154101
146. Yang J, Hättig C (2009) J Chem Phys 130:124101
147. Yang J, Hättig C (2009) J Chem Phys 131:074102
148. Köhn A (2009) J Chem Phys 130:104104
149. Hanauer M, Köhn A (2009) J Chem Phys 131:124118
150. Klopper W, Samson CCM (2002) J Chem Phys 116:6397
151. Dalton (2005) A molecular electronic-structure program. Release 2.0. See http://www.kjemi.uio.no/software/dalton/dalton.html. Accessed 4 Feb 2010
152. Fliegl H, Hättig C, Klopper W (2006) J Chem Phys 124:044112
153. Bokhan D, Bernadotte S, Ten-no S (2009) Chem Phys Lett 469:214
154. Bischoff FA, Höfener S, Glöß A, Klopper W (2008) Theor Chem Acc 121:11
155. Höfener S, Bischoff FA, Glöß A, Klopper W (2008) Phys Chem Chem Phys 10:3390
156. Bachorz RA (2009) Implementation and application of the explicitly correlated coupled-cluster method in Turbomole. Ph.D Thesis, Universität Karlsruhe (TH), Universitätsverlag Karlsruhe
157. Manby FR (2003) J Chem Phys 119:4607
158. Ten-no S, Manby FR (2003) J Chem Phys 119:5358
159. Werner HJ, Manby FR (2006) J Chem Phys 124:054114
160. Shiozaki T, Kamiya M, Hirata S, Valeev EF (2008) Phys Chem Chem Phys 10:3358
161. Shiozaki T, Kamiya M, Hirata S, Valeev EF (2008) J Chem Phys 129:071101
162. Hirata S (2006) Theor Chem Acc 116:2
163. Köhn A (2009) J Chem Phys 130:131101
164. DIRCCR12-OS (2003) A direct explicitly correlated coupled-cluster program. See http://www.laog.obs.ujf-grenoble.fr/~valiron/ccr12. Accessed 4 Feb 2010
165. Noga J, Kedžuch S, Šimunek J, Ten-no S (2008) J Chem Phys 128:174103
166. Adler TB, Knizia G, Werner HJ (2007) J Chem Phys 127:221106
167. Knizia G, Adler TB, Werner HJ (2009) J Chem Phys 130:054104
168. Rauhut G, Knizia G, Werner HJ (2009) J Chem Phys 130:054105
169. Adler TB, Werner HJ (2009) J Chem Phys 130:241101
170. Valeev EF (2008) Phys Chem Chem Phys 10:106
171. Torheyden M, Valeev EF (2008) Phys Chem Chem Phys 10:3410
172. Valeev EF, Crawford TD (2008) J Chem Phys 128:244113
173. Shiozaki T, Kamiya M, Hirata S, Valeev EF (2009) J Chem Phys 130:054101
174. Shiozaki T, Valeev EF, Hirata S (2009) J Chem Phys 131:044118
175. Torheyden M, Valeev EF (2009) J Chem Phys 131:171103
176. MPQC Version 3.0 (2008) A massively parallel quantum chemistry program, Sandia National Laboratories, Livermore, CA. Available from http://www.mpqc.org. Accessed 4 Feb 2010
177. Crawford TD, Sherrill CD, Valeev EF, Fermann JT, King RA, Leininger ML, Brown ST, Janssen CL, Seidl ET, Kenny JP, Allen WD (2007) J Comp Chem 28:1610
178. Jansen CL, Kenny JP, Nielsen IMB, Krishnan M, Gurumoorthi V, Valeev EF, Windus WL (2006) J Phys Conf Ser 46:220
179. Weigend F, Ahlrichs R (2005) Phys Chem Chem Phys 7:3297
180. Hättig C (2005) Phys Chem Chem Phys 7:59
181. Weigend (2007) J Comp Chem 29:167
182. Klopper W, Ruscic B, Tew DP, Bischoff FA, Wolfsegger S (2009) Chem Phys 356:14
183. Cfour (2009) Coupled-cluster techniques for computational chemistry, a quantum-chemical program package, with contributions from the integral packages molecule (Almlöf J, Taylor PR), Props (Taylor, PR), Abacus (Helgaker T, Jensen HJAa, Jørgensen P, Olsen J), and effective-core-potential routines by Mitin AV and van Wüllen C. For the current version, see http://www.cfour.de. Accessed 4 Feb 2010
184. Kállay M, Gauss J (2005) J Chem Phys 123:214105
185. MRCC (2009) A string-based quantum chemical program suite. See http://www.mrcc.hu. Accessed 4 Feb 2010
186. Kállay M, Surján PR (2001) J Chem Phys 115:2945
187. Ruscic B, Pinzon RE, Morton ML, von Laszewski G, Bittner S, Nijsure SG, Amin KA, Minkoff M, Wagner AF (2004) J Phys Chem A 108:9979
188. Ruscic B, Pinzon RE, Morton ML, Srinivasan NK, Su MC, Sutherland JW, Michael JV (2006) J Phys Chem A 110:6592
189. Tew DP, Klopper W (2006) J Chem Phys 125:094302
190. Bischoff FA, Wolfsegger S, Tew DP, Klopper W (2009) Mol Phys 107:963
191. Peterson KA, Adler TB, Werner HJ (2008) J Chem Phys 128:084102
192. Yousaf KE, Peterson KA (2008) J Chem Phys 129:184108
193. Yousaf KE, Peterson KA (2009) Chem Phys Lett 476:303