Quintuple-ζ quality coupled-cluster correlation energies with triple-ζ basis sets

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The explicitly-correlated coupled-cluster method CCSD(T)(R12) is extended to include F12 geminal basis functions that decay exponentially with the interelectronic distance and reproduce the form of the average Coulomb hole more accurately than linear-r_{12}. Equations derived using the Ansatz 2 strong orthogonality projector are presented. The convergence of the correlation energy with orbital basis set for the new CCSD(T)(F12) method is studied and found to be rapid, 98% of the basis set limit correlation energy is typically recovered using triple-ζ orbital basis sets. The performance for reaction enthalpies is assessed *via* a test set of 15 reactions involving 23 molecules. The title statement is found to hold equally true for total and relative correlation energies.

I. Introduction

Efficient methods for computing accurate correlation energies are central to theoretical chemistry. The convergence of the hierarchy of coupled-cluster methods towards the full CI limit is well established and is rapid for electronic states dominated by a single reference determinant.[1–5] Conversely, the convergence with respect to the orbital basis is extremely slow. At best, the deviation from the basis set limit is proportional to $(L + 1)^{-3}$, L denoting the largest angular momentum quantum number represented in the orbital basis.[6–8] For CCSD(T) with correlation consistent basis sets the error only reduces as n^{-1} with the number of functions n.[9] In R12 methods[10–13] the correlated wave function is expanded using both the usual virtual orbitals and additional geminals, pair functions of the form

$$\hat{Q}_{12}\, r_{12}\phi_i(1)\phi_j(2). \qquad (1)$$

ϕ_i and ϕ_j are occupied Hartree–Fock orbitals and r_{12} is the interelectronic distance. The $\hat{Q}_{12}$ projection operator ensures that the excitations corresponding to replacing two Hartree–Fock orbitals with the geminal function are outside the space spanned by conventional double replacements. These R12 basis functions rectify the principal deficiency of the orbital basis, they efficiently reproduce the wave function form near the electronic cusps.[14,15] Subsequently, the convergence to the basis set limit of a coupled-cluster method is rapid, the error is proportional to $(L + 1)^{-7}$.[16,17]

At the second order Møller–Plesset perturbation (MP2) level of theory it has been conclusively demonstrated by several research groups that the geminal functions introduced by Ten-no,[18]

$$\hat{Q}_{12}\, \exp(-\gamma r_{12})\phi_i(1)\phi_j(2), \qquad (2)$$

recover an even greater proportion of the correlation energy than those in eqn (1).[19,20] This has been termed the F12 variant of the R12 theory of Kutzelnigg,[21] which forms the foundation for the expeditious evaluation of the numerous, difficult many-electron integrals that arise. MP2 correlation energies computed with the MP2-F12 method using only an aug-cc-pVTZ orbital basis are superior to those computed using an aug-cc-pV5Z basis in the conventional manner. The scaling of computational effort for coupled-cluster R12 methods with system size is similar to their conventional counterparts. Obtaining high accuracy results with small basis sets has obvious potential benefits, we have therefore extended our F12 implementation to CCSD(T) calculations. We observed that the impressive gain in accuracy when replacing (1) with (2) is lost if $\hat{Q}_{12}$ is too restrictive. The formal space of double excitations can be partitioned into three subspaces: both replacements within the finite basis, both replacements outside the finite basis, and mixed replacements. For F12 calculations $\hat{Q}_{12}$ should be chosen such that only the conventional doubles are outprojected, which is denoted Ansatz 2 in R12 theory. $\hat{Q}_{12}$ for the simpler Ansatz 1 additionally projects out the mixed replacements. The purpose of this article is to report our extension of the CCSD(T)(R12) method to Ansatz 2 and the inclusion of the geminal functions in eqn (2). In section IV we study the basis set convergence of five small molecules in detail and in section V we evaluate the performance of CCSD(T)(F12) for computing reaction enthalpies using a set of fifteen reactions, previously used to assess the Ansatz 1 CCSD(T)(R12) method. We demonstrate that quintuple-ζ CCSD(T) correlation energies are obtained by using a triple-ζ quality orbital basis.

II. CCSD(T)(F12)

The equations for the inclusion of R12 geminal basis functions in the evaluation of coupled-cluster energies have been derived

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by Noga *et al.*[12,13] The difficult integrals are avoided by successive insertions of an approximate resolution of the identity (RI). In this original theory the orbital basis was used for the RI completeness insertions. Consequently Ansatz 1 and 2 led to the same working equations and special, large basis sets were required for meaningful CC-R12 calculations. The necessary modifications to the theory when using an auxiliary basis set for the RI approximation have been formulated by Fliegl *et al.* for the CC2-R12 equations.[22] These authors present expressions and results for both Ansatz 1 and 2, concluding that Ansatz 2 is superior. The CC2 method is closely related to CCSD, differing only in the doubles amplitude equations. These are obtained from the CCSD expressions by removing the terms higher than first order in the fluctuation potential.[23]

Fliegl *et al.* have also advocated a simplified CCSD-R12 method, CCSD(R12).[24] By analogy with the CC2 model, they discard terms that involve the R12 doubles amplitudes and are higher than first order in the fluctuation potential. CCSD(R12) is an improvement over CCSD-R12 because the omitted terms are expensive, small and numerically inaccurate (their evaluation requires repeated use of the RI approximation). We choose to pursue the CCSD(R12) approach in this work. The CCSD(R12) wave function is

$$|\mathrm{CCSD}\rangle = \exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_{2'})|\mathrm{HF}\rangle. \tag{3}$$

The singles, doubles and R12 doubles cluster operators for closed shell systems are defined by the following amplitudes and excitation operators

$$\hat{T}_1 = \sum_{ai} t_i^a E_{ai}, \tag{4}$$

$$\hat{T}_2 = \tfrac{1}{2}\sum_{aibj} t_{ij}^{ab} E_{ai}E_{bj}, \tag{5}$$

$$\hat{T}_{2'} = \tfrac{1}{2}\sum_{kilj} c_{ij}^{kl} \sum_{\alpha\beta} w_{kl}^{\alpha\beta} E_{\alpha i}E_{\beta j}. \tag{6}$$

We adhere as closely as possible to the notation used in ref. 25, where a detailed discussion of the excitation operators E_{ai} may be found. The indices i, j, indicate occupied orbitals and a, b, refer to virtual orbitals. A formally complete one-electron basis has been introduced to express the R12 double excitations in the occupation vector formalism: $\{\phi\} = \{\phi_i\} \oplus \{\phi_\alpha\} = \{\phi_i\} \oplus \{\phi_\alpha\} \oplus \{\phi_{\alpha_\perp}\}$. The coefficients for the representation of the geminal function $\hat{Q}_{12}r_{12}|\phi_k\phi_l\rangle$ by the basis vectors $|\phi_\alpha\phi_\beta\rangle$ are the matrix elements

$$w_{kl}^{\alpha\beta} = \langle\phi_\alpha\phi_\beta|\,\hat{Q}_{12}\,r_{12}|\phi_k\phi_l\rangle. \tag{7}$$

The CCSD(R12) equations for determining the amplitudes and the energy are conveniently expressed in terms of the Fock operator $\hat{f}$ and the $\hat{T}_1$-transformed fluctuation potential $\tilde{\hat{\Phi}} = \exp(-\hat{T}_1)\hat{\Phi}\exp(\hat{T}_1)$

$$E = E_{\mathrm{HF}} + \langle\mathrm{HF}|\hat{\Phi}(\tfrac{1}{2}\hat{T}_1^2 + \hat{T}_2 + \hat{T}_{2'})|\mathrm{HF}\rangle, \tag{8}$$

$$0 = \langle\mu_1|[\hat{f}, \hat{T}_1] + \tilde{\hat{\Phi}} + [\tilde{\hat{\Phi}}, \hat{T}_2 + \hat{T}_{2'}]|\mathrm{HF}\rangle, \tag{9}$$

$$0 = \langle\mu_2|[\hat{f}, \hat{T}_2 + \hat{T}_{2'}] + \tilde{\hat{\Phi}} + [\tilde{\hat{\Phi}}, \hat{T}_2 + \hat{T}_{2'}] + \tfrac{1}{2}[[\tilde{\hat{\Phi}}, \hat{T}_2], \hat{T}_2 + 2\,\hat{T}_{2'}]|\mathrm{HF}\rangle, \tag{10}$$

$$0 = \langle\mu_{2'}|[\hat{f}, \hat{T}_2 + \hat{T}_{2'}] + \tilde{\hat{\Phi}} + [\tilde{\hat{\Phi}}, \hat{T}_2]|\mathrm{HF}\rangle. \tag{11}$$

Comparison with the CC2-R12 equations of ref. 22 reveals that only three new R12 terms arise, $\langle\mu_2|[\tilde{\hat{\Phi}}, \hat{T}_{2'}]|\mathrm{HF}\rangle$, $\langle\mu_2|[[\tilde{\hat{\Phi}}, \hat{T}_2], \hat{T}_{2'}]|\mathrm{HF}\rangle$ and $\langle\mu_{2'}|[\tilde{\hat{\Phi}}, \hat{T}_2]|\mathrm{HF}\rangle$. The explicit formulae for evaluating these contributions for Ansatz 2 are collected in Table 1. To derive these formulae we have assumed that the generalised Brillouin condition is fulfilled ($f_\alpha^i = f_i^a = 0$) and we have used the following definition of $\hat{Q}_{12}$.[26,27]

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

$$\hat{O}_1 = \sum_i |\phi_i(1)\rangle\langle\phi_i(1)|, \tag{13}$$

$$\hat{V}_1 = \sum_a |\phi_a(1)\rangle\langle\phi_a(1)|. \tag{14}$$

We use the complementary auxiliary basis set approach of Valeev[27] for the RI approximation and the strategy for its application is described in the appendix of ref. 22. The corresponding expressions for Ansatz 1 will be presented in the context of CCSD(R12) response theory in a forthcoming article.[28] Detailed discussions of the remaining contributions to eqns (8)–(11) and the approximations used for their evaluation are contained in ref. 17, 22 and 27. The orbital-only amplitudes for the perturbative triples correction to the CCSD-R12 energy satisfy the equation

$$0 = \langle\mu_3|[\hat{f}, \hat{T}_3] + [\hat{\Phi}, \hat{T}_2 + \hat{T}_{2'}]|\mathrm{HF}\rangle. \tag{15}$$

The connected triples amplitudes for excitations involving mixed orbital and geminal replacements are not considered. Maintaining a consistent treatment of the R12 doubles in the Ansatz 2 CCSD(T)(R12) method, we neglect the R12 contribution to the second order triples amplitudes[24] and evaluate the perturbative triples energy correction using the conventional singles and doubles amplitudes in the usual way.[29]

It only remains to comment on the replacement of the R12 geminal functions with those of eqn (2). The only changes to the formulae in Table 1 are the integrals involving the geminal basis functions r_{rs}^{pq} and s_{rs}^{pq} where the correlation factor r_{12} is substituted for the exponential function $\exp(-\gamma r_{12})$. The minor modifications involved in the evaluation of the commutator of the correlation factor with the kinetic energy, which enters the equations at the MP2 level, has been described elsewhere.[30] The evaluation of the matrix elements over the exponential of r_{12} is possible, but somewhat involved.[18] In our current implementation in the DALTON program[31] the exponential is approximated as a linear combination of six Gaussians, whose elements are easily evaluated and are related to the Boys function.[20,30] The coefficients for the fit are given in ref. 20.

Using the same orbital basis, CCSD(F12) calculations are more expensive than orbital-only CCSD calculations. New two-electron integrals are required and additional terms must be evaluated for the amplitude expressions. For a system with n occupied orbitals, the R12 integral evaluation and

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Table 1 The additional terms required for CCSD(R12) with Ansatz 2 that are absent from the CC2-R12 amplitude equations

$$\langle\mu_2|[[\tilde{\hat{\Phi}},\hat{T}_{2'}]|\mathrm{HF}\rangle + \langle\mu_2|[\tilde{\hat{\Phi}},\hat{T}_2],\hat{T}_{2'}]|\mathrm{HF}\rangle$$

$$\Omega^A_{aibj} = \sum_{mn} c^{mn}_{ij}(V^\dagger)^{mn}_{\tilde{a}\tilde{b}} \qquad \Omega^B_{aibj} = \sum_{kl} t^{ab}_{kl} \sum_{mn} c^{mn}_{ij}(V^\dagger)^{mn}_{kl}$$

$$\Omega^C_{aibj} = -\left(\tfrac{1}{2}+\hat{P}_{ij}\right)\sum_{p'k}\bar{t}^{p'b}_{jk}\left(g^{\tilde{i}p'}_{k\tilde{a}} - \sum_{dl} t^{ad}_{li}\, g^{p'd}_{lk}\right)$$

$$\Omega^D_{aibj} = \tfrac{1}{2}\sum_{p'k}(2\bar{t}^{bp'}_{jk} - \bar{t}^{p'b}_{jk})(L^{p'\tilde{i}}_{k\tilde{a}} + \sum_{dl}(2t^{ad}_{il} - t^{da}_{il})L^{p'd}_{kl}$$

$$\Omega^E_{aibj} = \sum_{p'}\bar{t}^{ap'}_{ij}\left(\sum_k (L^{p'\tilde{k}}_{\tilde{b}k} - L^{p'k}_{bk}) - \sum_{dlm}(2t^{db}_{lm} - t^{bd}_{lm})g^{dp'}_{lm}\right)$$

$$- \sum_c t^{ac}_{ij}\sum_{p'lm}\bar{t}^{p'b}_{lm}L^{p'c}_{lm} - \sum_k t^{ab}_{ik}\sum_{lmn}(2c^{mn}_{lj} - c^{nm}_{lj})(V^\dagger)^{mn}_{lk}$$

$$\langle\mu_{2'}|[\tilde{\hat{\Phi}},\hat{T}_2]|\mathrm{HF}\rangle$$

$$\Omega^B_{kilj} = \sum_{cd} t^{cd}_{ij}\tilde{V}^{cd}_{kl} \qquad \Omega^C_{kilj} = -\sum_{p'b} r^{p'b}_{kl}\left(\tfrac{1}{2}+\hat{P}_{ij}\right)\sum_{cm} t^{cb}_{jm} g^{\tilde{i}c}_{mp'}$$

$$\Omega^D_{kilj} = \sum_{p'b} r^{p'b}_{kl}\,\tfrac{1}{2}\sum_{cm}(2t^{bc}_{jm} - t^{cb}_{jm})L^{c\tilde{i}}_{mp'}$$

$$\Omega^E_{kilj} = \sum_{p'b} r^{p'b}_{kl}\sum_c t^{bc}_{jl}\sum_m (L^{c\tilde{m}}_{p'm} - L^{cm}_{p'm})$$

t^{ab}_{ij}, orbital and c^{kl}_{ij}, geminal amplitudes[a]

$$g^{pq}_{rs} = \langle\phi_r(1)\phi_s(2)|r_{12}^{-1}|\phi_p(1)\phi_q(2)\rangle$$

$$r^{pq}_{rs} = \langle\phi_r(1)\phi_s(2)|r_{12}|\phi_p(1)\phi_q(2)\rangle$$

$$s^{pq}_{rs} = \langle\phi_r(1)\phi_s(2)|r_{12}r_{12}^{-1}|\phi_p(1)\phi_q(2)\rangle$$

$$\bar{t}^{bp'}_{ij} = \sum_{kl} c^{kl}_{ij} r^{bp'}_{kl} \qquad L^{pq}_{rs} = 2g^{pq}_{rs} - g^{qp}_{rs}$$

$$V^{rs}_{kl} = s^{rs}_{kl} + \sum_{mn} r^{mn}_{kl} g^{rs}_{mn} - \sum_{ab} r^{ab}_{kl} g^{rs}_{ab}$$

$$- \hat{P}^{rs}_{kl}\sum_{mp} r^{mp}_{kl} g^{rs}_{mp} - \hat{P}^{rs}_{kl}\sum_{mp'} r^{mp'}_{kl} g^{rs}_{mp'}$$

$$\tilde{V}^{rs}_{kl} = s^{rs}_{kl} + \sum_{mn} r^{\tilde{m}\tilde{n}}_{kl} g^{rs}_{mn} - \sum_{ab} r^{ab}_{kl} g^{rs}_{\tilde{a}\tilde{b}}$$

$$- \hat{P}^{rs}_{kl}\sum_{mp} r^{\tilde{m}p}_{kl} g^{rs}_{mp} - \hat{P}^{rs}_{kl}\sum_{mp'} r^{\tilde{m}p'}_{kl} g^{rs}_{mp'}$$

$$\hat{P}^{ab}_{kl} V^{ab}_{kl} = V^{ab}_{kl} + V^{ba}_{lk} \qquad \hat{P}_{ij} \text{ permutes } i \leftrightarrow j$$

[a] $ij\cdots$ denote occupied and $ab\cdots$ virtual, canonical Hartree–Fock orbitals. $pq\cdots$ indicate the *full* set of canonical orbitals and p' the orthogonal auxiliary orbitals which satisfy $\langle p'|p\rangle = 0$. $\tilde{i}$, $\tilde{a}\cdots$ have been transformed by the $\hat{T}_1$ amplitudes as described in ref. 22 and 25.

transformation requires at most $\mathcal{O}(n^2N^3N')$ floating-point operations, N and N' are the number of orbital and auxiliary basis functions.

To solve the MP2 equations in the zeroth iteration, the matrix $\langle kl|r_{12}\hat{Q}_{12}(\hat{f}_{12} - \varepsilon_i - \varepsilon_j)\hat{Q}_{12}r_{12}|mn\rangle$ must be diagonalised for each orbital pair ij. The formal scaling of R12 methods is thus n^8, but the prefactor is very small and this is of no concern for current computations. The scaling of the CCSD(F12) method is therefore effectively the same as its conventional counterpart. For both geminal and orbital-only CCSD calculations, the total computer time required depends predominantly on the duration of each CCSD iteration. Most R12 contributions to the amplitude equations are less expensive than the conventional terms. The C and D R12 contributions to the conventional doubles vector function are the most demanding, involving $O(n^3N^2N')$ operations. Note that the structure of the R12 terms is analogous to the conventional terms, the doubles amplitudes t^{ab}_{ij} are replaced by contracted R12 amplitudes $\bar{t}^{bp'}_{ij}$ (see Table 1). With an auxiliary basis similar in size to the orbital basis, each CCSD(F12) iteration requires approximately twice the time of an orbital-only calculation. Indeed, progress has been made in R12 methodology to reduce the prefactor associated with the additional contributions through density fitting and improved RI approximations.[32,33]

III. Computational details

It is important to include adequate diffuse functions in the orbital basis for R12 and F12 calculations.[20] All of the calculations presented in this article were performed using the aug-cc-pVXZ or aug-cc-pV(X+d)Z basis sets of Dunning and co-workers,[34–36] with the neglect of core correlation. Since optimised diffuse functions are not available for the cc-pVXZ Li basis sets, we define the exponents of the augmentation functions, for each spherical harmonic, to be one third of the lowest exponent present in the cc-pVXZ basis. In section IV we describe computations using sextuple-ζ quality auxiliary basis sets for the atoms H, Li, C, O and F. These are constructed by extending the s series of the WTBS basis[37,38] by one diffuse function and using the formula $\zeta^l = \zeta^0(l+3)/3$ to generate the exponents ζ^l of a 21s14p7d6f5g4h3i basis. l denotes the angular momentum quantum number of the spherical harmonic and the formula is applied to the s functions with smallest exponents. As auxiliary basis for the H atom we used the uncontracted d-aug-cc-pV6Z set. The reactions described in section V involve somewhat larger systems and also contain sulfur and chlorine. The calculations were performed with the aug-cc-pVXZ orbital basis sets for atoms H, C, N and O, and the aug-cc-pV(X+d)Z orbital basis sets for S and Cl with a Ne frozen core. For the auxiliary basis we used the uncontracted quintuple-ζ basis in every case. All of the explicitly-correlated calculations described in this article were performed with the complementary auxiliary basis set method of Valeev,[27] and with the standard approximation B for computing the geminal matrix elements over the Fock operator.[16]

IV. Basis set convergence

Here we demonstrate that the improved convergence behaviour of MP2-F12 over MP2 and MP2-R12 for Ansatz 2 also

extends to CCSD and CCSD(T) calculations. For illustration, we choose the five molecules H_2O, CO, F_2, Li_2 and LiF. The geometries are optimised at the MP2 level using the aug-cc-pVTZ basis sets with the neglect of core correlation. We perform CCSD(T), CCSD(T)(R12) and CCSD(T)(F12) calculations, using the exponential correlation factor $\exp(-\gamma r_{12})$ with $\gamma = 1.3$, chosen based on MP2-F12 calculations from previous studies.[20,39,40] We examine the convergence of the correlation energy with the size of the orbital basis, increasing the cardinal number from 2 to 5 in the aug-cc-pV*X*Z basis sets of Dunning and co-workers. For the auxiliary basis we use uncontracted sextuple-ζ quality sets, which are sufficient to remove the error due to the approximate RI from our considerations. A description of the large auxiliary basis sets and the aug-cc-pV*X*Z basis for Li is given in section III. The computed MP2, CCSD and CCSD(T) frozen-core correlation energies of our five molecules are presented in Tables 2–6.

A. MP2

The MP2 correlation energies computed using the F12 method and an aug-cc-pVDZ orbital basis are consistently better than the results of conventional MP2 calculations using an aug-cc-pV5Z basis, recovering more than 97% of the basis set limit. Li_2 is exceptional since $\gamma = 1.3$ is far from optimum for this molecule (see below), optimising γ brings it into line with the other molecules. Large orbital basis sets are clearly an unnecessary expense for MP2 correlation energies. (The values in Tables 2–4 differ slightly from those published in ref. 20 due to the larger auxiliary basis sets used in the current work.) The general rapid convergence of the MP2-R12 and MP2-F12 methods to the basis set limit is well documented.[17,18,39–41] Simply replacing the linear-r_{12} geminal functions (1) with Ten-no's geminal functions (2) yields a gain in accuracy equivalent to increasing the orbital basis by between one and two cardinal numbers. The exponential function reproduces the average shape of the Coulomb hole over a wider range of r_{12} than is possible using linear-r_{12}, reducing the demand on the orbital basis.[20] More than 95% of the basis set limit correlation energy is typically obtained using a basis of double-ζ quality.[42] The vast majority of the correlation energy does not depend on the finer details of the Hartree–Fock wave function.[42–46] Caution must, however, be advised when using double-ζ quality basis sets, because the magnitude and sign of the error in the correlation energy due to the unconverged Hartree–Fock reference is not yet fully understood.

B. CCSD

Treating correlation at the MP2 level is often insufficient for the accurate determination of energies and properties. It is then desirable to compute the basis set limit of the CCSD method, which also forms the base for various additivity schemes to include higher order corrections.[47–56] The convergence to the basis set limit is from above for each of our molecules at every level of theory. Although the convergence of the conventional orbital expansion is observed to be faster for CCSD than for MP2, it is nonetheless slow. With an aug-cc-pVTZ basis the correlation energy is too small by as much as 10% (F_2, LiF). For water the absolute error is 0.025 E_h, and it is only reduced to 0.010 E_h when using an aug-cc-pVQZ basis. Energy differences are more important than total energies for chemistry. Taking the CCSD(T)(F12) aug-cc-pV5Z values as a reference, the correlation contribution to the reaction energy of $F_2 + Li_2 \rightarrow 2LiF$ is in error by 14 kJ mol^{-1} when computed using an aug-cc-pVTZ basis, and has the wrong sign. The error is reduced to 5 kJ mol^{-1} and 3 kJ mol^{-1} when the aug-cc-pVQZ and aug-cc-pV5Z basis sets are used. The CCSD correlation energies computed using the CCSD(R12) method converge much more rapidly to the basis set limit. Due to the $(L + 1)^{-7}$ rather than $(L + 1)^{-3}$ dependence of the leading error contributions, the improvement of R12 over the conventional method increases with the cardinal number of the basis used. Conversely, CCSD(R12) energies using a double-ζ quality orbital basis are not a significant improvement over orbital-only results. This is also seen at the MP2 level of theory. CCSD(R12) calculations with an aug-cc-pVTZ basis are, however, more accurate than conventional calculations using an aug-cc-pVQZ basis for all our molecules except Li_2, which has already converged to within 0.25 mE_h of the basis set limit. This statement also applies to the energy differences involved in the above reaction energy. Performing calculations with the geminal functions (2) rather than (1) universally improves the CCSD correlation energies. In every case aug-cc-pVTZ CCSD(F12) calculations recover 99% of the basis set limit correlation energy. With the exception of Li_2 this is more than is achieved through orbital-only aug-cc-pV5Z calculations. The valence-only CCSD correlation energies computed using the CCSD(F12) method with an aug-cc-pV5Z orbital basis represent the best estimate of the basis set limit for these molecules to date, they are more accurate than Q5 two point extrapolations, which give energies of sextuple-ζ quality.[57] They are also expected to be more accurate than 56 two point extrapolations. The observed improvement of CCSD(F12) over orbital-only CCSD is slightly less than that of MP2-F12 over conventional MP2.

Table 2 MP2, CCSD and CCSD(T) correlation energies (−mE_h) of H_2O computed using conventional, R12 and F12 ($\gamma = 1.3$) methods with aug-cc-pV*X*Z orbital basis sets

	MP2			CCSD			Δ*E*(T)			CCSD(T)		
X	Orb	R12	F12	Orb	R12	F12	Orb	R12	F12	Orb	R12	F12
D	219.73	271.05	295.20	227.47	265.87	284.79	5.24	5.06	4.87	232.71	270.94	289.66
T	268.71	291.08	298.61	273.38	289.40	295.02	8.67	8.54	8.44	282.04	297.93	303.46
Q	286.26	297.58	300.04	288.51	295.86	297.49	9.41	9.33	9.31	297.93	305.20	306.80
5	293.25	299.57	300.51	293.62	297.51	298.10	9.69	9.65	9.64	303.32	307.15	307.74

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Table 3 MP2, CCSD and CCSD(T) correlation energies ($-\mathrm{m}E_\mathrm{h}$) of CO computed using conventional, R12 and F12 ($\gamma = 1.3$) methods with aug-cc-pVXZ orbital basis sets

	MP2			CCSD			ΔE(T)			CCSD(T)		
X	Orb	R12	F12	Orb	R12	F12	Orb	R12	F12	Orb	R12	F12
D	301.22	366.53	399.26	307.82	357.92	381.44	12.60	12.29	11.64	320.42	370.21	393.08
T	362.52	391.03	402.56	364.40	384.31	392.60	17.89	17.61	17.42	382.29	401.92	410.01
Q	385.50	400.57	404.29	383.79	393.29	395.62	19.08	18.92	18.86	402.87	412.21	414.48
5	394.91	403.49	404.96	390.59	395.68	396.56	19.55	19.46	19.43	410.14	415.14	415.99

Table 4 MP2, CCSD and CCSD(T) correlation energies ($-\mathrm{m}E_\mathrm{h}$) of F_2 computed using conventional, R12 and F12 ($\gamma = 1.3$) methods with aug-cc-pVXZ orbital basis sets

	MP2			CCSD			ΔE(T)			CCSD(T)		
X	Orb	R12	F12	Orb	R12	F12	Orb	R12	F12	Orb	R12	F12
D	426.63	544.34	599.30	434.04	526.02	568.58	12.60	12.39	11.44	446.64	538.40	580.02
T	534.77	587.50	604.75	537.70	578.40	592.01	19.66	19.30	19.02	557.35	597.69	611.03
Q	574.53	602.17	608.23	573.95	593.36	597.57	21.35	21.13	21.07	595.30	614.49	618.64
5	591.49	606.99	609.52	587.39	597.73	599.43	22.06	21.94	21.91	609.45	619.67	621.35

Table 5 MP2 and CCSD correlation energies ($-\mathrm{m}E_\mathrm{h}$) of Li_2 computed using conventional, R12 and F12 ($\gamma = 1.3$) methods with aug-cc-pVXZ orbital basis sets

	MP2			CCSD		
X	Orb	R12	F12	Orb	R12	F12
D	19.23	20.86	21.95	30.69	31.22	31.15
T	21.16	21.94	22.57	31.53	31.68	31.73
Q	22.13	22.51	22.82	31.82	31.86	31.89
5	22.46	22.80	22.86	31.87	31.90	31.91

Table 6 MP2, CCSD and CCSD(T) correlation energies ($-\mathrm{m}E_\mathrm{h}$) of LiF computed using conventional, R12 and F12 ($\gamma = 1.3$) methods with aug-cc-pVXZ orbital basis sets

	MP2			CCSD			ΔE(T)			CCSD(T)		
X	Orb	R12	F12	Orb	R12	F12	Orb	R12	F12	Orb	R12	F12
D	229.41	289.78	320.49	228.63	275.80	299.62	4.98	4.98	4.79	233.61	280.78	304.41
T	287.54	316.20	325.72	283.76	305.87	313.48	8.95	8.82	8.70	292.71	314.69	322.18
Q	309.35	324.64	327.83	303.76	314.37	316.63	9.81	9.71	9.69	313.57	324.08	326.33
5	318.60	327.34	328.59	310.97	316.70	317.56	10.18	10.11	10.11	321.14	326.81	327.67

It is not yet clear whether this is due to the approximations involved in our CCSD(F12) method, or whether it arises from the differing convergence behaviours of MP2 and CCSD. In particular, the sign and magnitude of the errors introduced by assuming the generalised Brillouin condition and by neglecting high order terms in the amplitude equations are not yet fully understood. However, the consequences are known to be minor for larger basis sets.[19,24] It is perhaps more probable that the difference between the MP2 and CCSD convergence behaviours stems from the singles excitations. R12 methods do not currently correct for the incomplete singles basis, although in principle there is no difficulty in doing so. CCSD(F12) calculations using an aug-cc-pVDZ basis are relatively unimpressive, coinciding with conventional values of intermediate aug-cc-pVTZ and aug-cc-pVQZ quality. The basis set for the description of the single excitations is particularly poor at the double-ζ level, and the Hartree–Fock reference is far from converged. Additionally, the higher order terms, neglected in the CCSD(F12) amplitude equations, become more important for small basis sets where the magnitude of the F12 contribution is considerable. We therefore recommend the use of basis sets of at least triple-ζ quality for CCSD(F12) calculations.

C. CCSD(T)

The rate of convergence to the basis set limit of the triples correction is as slow as that of a conventional CCSD calculation. Since the perturbative triples energy correction is an order of magnitude smaller than the CCSD correlation energy, this is not critical, a deviation of 10% results in small errors in total and relative energies. The R12 contributions to the triples correction are not evaluated in the CCSD(T)(R12) method

Table 7 Method and aug-cc-pVXZ basis set dependence of optimum γ values for Ansatz 2 F12 calculations for X = D, T and Q

	H_2O			CO			F_2			Li_2			LiF		
Method	D	T	Q	D	T	Q	D	T	Q	D	T	Q	D	T	Q
MP2-F12	1.2	1.4	1.4	1.1	1.4	1.4	1.3	1.6	1.5	0.6	0.7	0.8	1.3	1.3	1.4
CCSD(F12)	1.2	1.4	1.4	1.1	1.3	1.4	1.4	1.5	1.5	0.3	0.5	0.8	1.3	1.2	1.4
CCSD(T)(F12)	1.2	1.4	1.4	1.1	1.3	1.4	1.4	1.5	1.5	0.3	0.5	0.8	1.3	1.2	1.4

and the results are almost identical to the orbital-only values. Since the conventional doubles amplitudes are reduced in R12 calculations, the perturbation correction is slightly smaller, but the difference diminishes for larger orbital basis sets. The reduction is slightly larger for F12 than for R12. The resulting loss in accuracy is never a significant contribution to the overall remaining deviation from the basis set limit. For all of the molecules tested, the CCSD(T) correlation energies computed using the CCSD(T)(F12) method with an aug-cc-pVTZ orbital basis are of equivalent or superior accuracy to those computed with an aug-cc-pV5Z basis in the conventional manner. Although the improvement of F12 over orbital-only calculations is slightly less for CCSD(T) than for CCSD, due to the missing geminal contributions to the triples correction, the quality of the resulting correlation energies is nonetheless excellent. The basis set limit CCSD(T) valence-only correlation energies for the molecules H_2O, CO, F_2, Li_2 and LiF at their optimum frozen-core MP2/aug-cc-pVTZ geometries are $-308(1)$ mE_h, $-416(2)$ mE_h, $-621(3)$ mE_h, $-31.91(0.02)$ mE_h and $-328(1)$ mE_h, respectively. The uncertainty is given in parentheses and is estimated by taking the difference between the aug-cc-pVQZ and aug-cc-pV5Z CCSD(T)(F12) values. The remaining deviation from the basis set limit is likely to contain approximately equal contributions from the CCSD correlation energy and the perturbative triples correction. The Hartree–Fock contribution is often the dominant term in reaction energies. The highly accurate CCSD(T) correlation energies that result from CCSD(T)(F12) calculations must be combined with converged Hartree–Fock energies if accurate total and relative energies are required.

D. Optimising the exponent in $\exp(-\gamma r_{12})$

All of the F12 calculations discussed in the previous sections were performed with a fixed exponent $\gamma = 1.3$. In this section we examine the effect of varying γ. It is understood that the optimum γ is related to the size of the average Coulomb hole and depends on the effective nuclear charge experienced by the valence electrons.[20] Our set of five molecules span a wide range of effective nuclear charges and should be a sufficient test for compounds of light elements. For each molecule we perform MP2-F12, CCSD(F12) and CCSD(T)(F12) calculations using $0 \leq \gamma \leq 3$ and orbital basis sets aug-cc-pVXZ with cardinal numbers 2, 3 and 4. The values of γ that give the maximum correlation energy at each level of theory are presented in Table 7. For the triple-ζ quality basis, the distribution of γ_{opt} ranges from 0.5 for Li_2 to 1.5 for F_2, which represent two extremes of valence electron environments. The value of γ_{opt} for LiF is much closer to that of F_2 than Li_2 because it is much more probable to locate an electron near F than Li. For a given molecule, γ_{opt} is more dependent on the quality of the basis set than on the correlation method. Previous MP2 studies have indicated that the geminal basis functions contribute to both short and long range correlation.[20,40] Typically γ_{opt} is lower for small basis sets where there are insufficient diffuse functions. The strong dependence of γ_{opt} for Li_2 on the basis size is symptomatic of poorly chosen augmentation functions. For properly optimised F12 orbital basis sets the range of γ_{opt} for Li_2 is likely to be somewhat reduced and shifted to higher γ values. The detailed γ dependence of the CCSD(T)(F12) correlation energies for F_2, Li_2 and LiF are displayed in Fig. 1–3. We also include curves for Ansatz 1 and indicate the corresponding CCSD(T)(R12) values. The plots for H_2O and CO are very similar to Fig. 3. The essential features of the CCSD(T) correlation energy γ dependence are identical for all five molecules and for both Ansätze. It is also similar to that observed for MP2-F12.[18,20] At $\gamma = 0$ the orbital-only correlation energy is recovered. The gradient is approximately zero at the ordinate because we fit the exponential with a set of Gaussian functions that do not exhibit a cusp. The magnitude of the correlation energy initially grows rapidly with γ, matching the CCSD(T)(R12) value before $\gamma = 0.2$. Thereafter it increases more gradually and the maximum at γ_{opt} is located in a relatively flat region. The γ dependence near the minimum is strongest for the lowest quality orbital basis and is particularly strong for Li_2 in the double-ζ basis, for the reasons previously discussed. For aug-cc-pVTZ calculations there is always a wide region of γ where the Ansatz 2 F12 correlation energies are significantly better than the R12 values. For Ansatz 1, the non-linear geminal functions offer almost no improvement over linear-r_{12}. In Table 8 we report the γ_{opt} CCSD(T)(F12) correlation energies for our five molecules, together with the maximum difference in correlation energy between γ_{opt} and $\gamma = 1.0$ or 1.5. There is clearly only a small gain in correlation energy upon optimising γ, compared to fixing γ at a value between 1.0 and 1.5. If it did become necessary to refine γ, it is reasonable to perform the optimisation at the MP2 level of theory since the results in Table 7 demonstrate that γ_{opt} for CCSD is close to the MP2 value. The perturbative triples correction is only indirectly dependent on the geminal basis function and is insensitive to the exponent γ.

V. Reaction enthalpies

It is important to assess the performance of CCSD(T)(F12) for thermochemistry. A test set of 15 reactions involving 23 compounds of H, C, N, O, S and Cl atoms has been developed by Werner and co-workers [41,58] and Fliegl *et al.*[59] for this purpose. The CCSD(T) aug-cc-pVXZ energies have been

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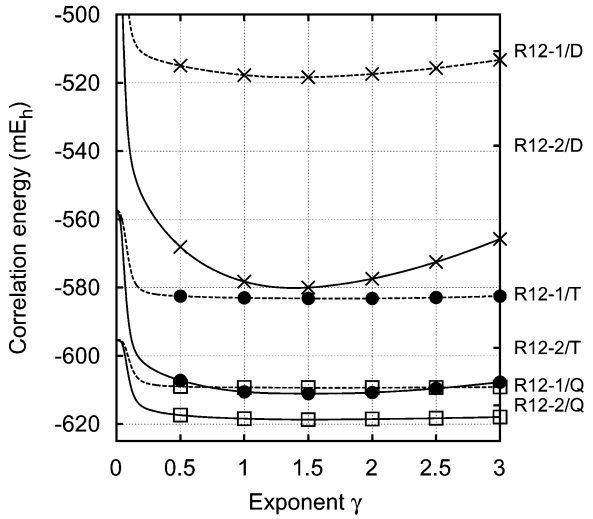


Fig. 1 CCSD(T)(F12) correlation energy of F_2 computed within Ansatz 1 (- - - - -) and Ansatz 2 (——) as a function of the exponent γ using the aug-cc-pVXZ orbital basis sets with X = D (×), T (●) and Q (□). The corresponding CCSD(T)(R12) energies are indicated on the second y axis by R12-1/X and R12-2/X.

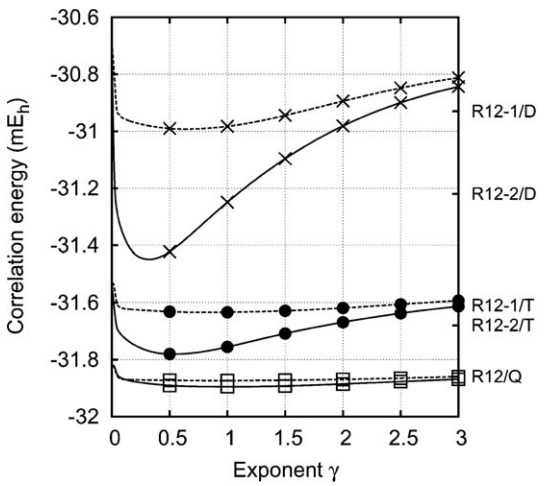


Fig. 2 CCSD(F12) correlation energy of Li_2 computed within Ansatz 1 (- - - - -) and Ansatz 2 (——) as a function of the exponent γ using the aug-cc-pVXZ orbital basis sets with X = D (×), T (●) and Q (□). The corresponding CCSD(R12) energies are indicated on the second y axis by R12-1/X and R12-2/X.

computed, for X = T, Q and 5, at the frozen core MP2/aug-cc-pVTZ geometries. The reference for the basis set limit is taken as the quintuple-ζ Hartree–Fock energies combined

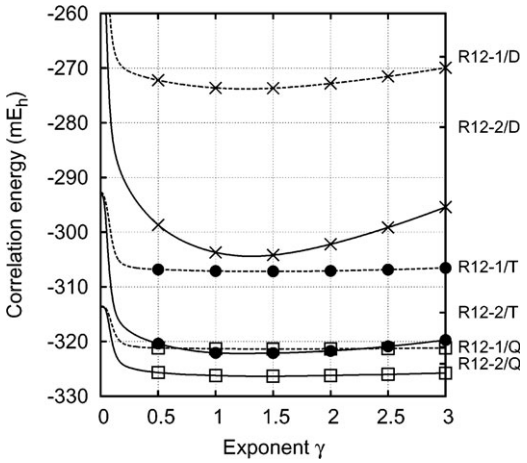


Fig. 3 CCSD(T)(F12) correlation energy of LiF computed within Ansatz 1 (- - - - -) and Ansatz 2 (——) as a function of the exponent γ using the aug-cc-pVXZ orbital basis sets with X = D (×), T (●) and Q (□). The corresponding CCSD(T)(R12) energies are indicated on the second y axis by R12-1/X and R12-2/X.

with the extrapolated Q5 correlation energies, using the extrapolation formula of Helgaker *et al.*[8] The experimental values are taken from the NIST database[60] and the electronic energy differences are extracted by removing zero-point vibration and finite temperature effects computed using density functional theory.[59] The precision of the experimental data is estimated to be 4 kJ mol^{-1}. The details of the orbital basis sets and the auxiliary basis for the F12 calculations are given in section III. The exponent of the geminal basis functions is fixed at γ = 1.3.

The correlation contribution to the 15 reaction enthalpies for the aug-cc-pVXZ CCSD(T) and aug-cc-pVTZ CCSD(T)(F12) methods are compared to the basis set limit in Table 9. The quality of the CCSD(T)(F12) results, computed with an aug-cc-pVTZ basis, is the same as that of aug-cc-pV5Z orbital-only calculations. This is apparent from the error distributions. The mean and standard deviation (S_N) of the CCSD and CCSD(T) correlation energies, relative to the basis set limit, are given in Table 10. We present statistics for both the 23 individual molecular correlation energies, and the correlation contribution to the 15 reaction enthalpies. The corresponding model normal distributions are displayed in Fig. 4 and 5. The excellent performance of the Ansatz 2 F12 coupled-cluster methods, observed for the set of five small molecules, is repeated here. Molecular correlation energies computed using CCSD(F12) with an aug-cc-pVTZ orbital basis are superior to the orbital-only aug-cc-pV5Z values with an average deviation from the basis set limit of only 7 mE_h.

Table 8 CCSD(T)(F12) aug-cc-pVXZ correlation energies (mE_h) for optimised γ. The maximum deviation of the energy between γ_{opt} and γ = 1.0 or γ = 1.5 is given in parentheses

X	H_2O	CO	F_2	Li_2	LiF
D	−289.72 (0.47)	−393.48 (1.32)	−580.10 (1.84)	−31.45 (0.35)	−304.41 (0.70)
T	−303.47 (0.13)	−410.01 (0.18)	−611.10 (0.54)	−31.78 (0.07)	−322.19 (0.11)
Q	−306.80 (0.07)	−414.48 (0.10)	−618.69 (0.29)	−31.89 (0.00)	−326.34 (0.12)

Table 9 CCSD(T) reaction enthalpies computed with aug-cc-pVXZ (X = T, Q, 5) orbital basis sets, Q5 extrapolation and CCSD(T)(F12) with an aug-cc-pVTZ basis in kJ mol^{-1}

	Correlation contribution					ΔH_R		
Reaction	T	Q	5	F12	Q5	5	F12	exp
$CO + NH_3 \rightarrow HCONH_2$	−26.12	−29.72	−30.55	−30.56	−31.43	−41.04	−41.05	−39.00
$H_2C_2O + H_2CO \rightarrow C_2H_4O + CO$	7.07	7.90	7.73	7.54	7.54	−16.79	−16.98	−14.80
$CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S$	69.78	72.91	74.40	73.00	75.96	−47.86	−49.25	−46.60
$CO + Cl_2 \rightarrow COCl_2$	−57.26	−58.88	−58.86	−59.49	−58.85	−115.50	−116.12	−115.40
$NH_3 + 4H_2O_2 \rightarrow HNO_3 + 5H_2O$	20.71	15.44	14.00	11.98	12.50	−745.38	−747.41	−741.20
$C_2H_2 + H_2 \rightarrow C_2H_4$	9.52	9.53	9.84	9.67	10.18	−206.53	−206.70	−202.70
$CO + H_2 \rightarrow H_2CO$	−20.81	−22.57	−22.56	−22.37	−22.56	−21.52	−21.32	−20.80
$H_2O_2 + H_2 \rightarrow 2H_2O$	28.71	26.42	26.22	25.80	26.02	−365.16	−365.59	−363.50
$H_2CO + H_2 \rightarrow CH_3OH$	−2.56	−3.83	−3.70	−3.94	−3.56	−123.23	−123.48	−122.70
$C_2H_6 + H_2 \rightarrow 2CH_4$	12.08	12.38	12.74	12.62	13.12	−76.03	−76.15	−78.00
$C_2H_4 + H_2 \rightarrow C_2H_6$	−2.42	−1.76	−1.66	−2.60	−1.55	−165.55	−166.48	−164.10
$C_2H_2 + H_2O \rightarrow CH_3CHO$	7.39	8.86	8.84	7.64	8.82	−161.15	−162.35	−160.80
$CH_4 + 4H_2O_2 \rightarrow CO_2 + 6H_2O$	113.21	105.42	103.38	101.13	101.23	−1214.97	−1217.22	−1211.30
$SO_2 + H_2O_2 \rightarrow SO_3 + H_2O$	31.45	25.19	22.90	22.37	20.50	−208.25	−208.79	−204.40
$CO + H_2O_2 \rightarrow CO_2 + H_2O$	5.30	1.44	0.38	−0.51	−0.74	−390.75	−391.64	−392.40

Table 10 The mean and standard deviation of the CCSD and CCSD(T) basis set errors, relative to the Q5 extrapolated values, for the correlation contribution to the molecular energies (mE_h) and reaction enthalpies (kJ mol^{-1})

	CCSD				CCSD(T)			
Basis	$\bar{E}_{mol}$	σ	$\Delta\bar{H}_R$	σ	$\bar{E}_{mol}$	σ	$\Delta\bar{H}_R$	σ
T	43.04	24.20	2.91	4.99	45.99	25.91	2.59	4.84
Q	17.69	10.26	0.94	1.99	18.96	11.02	0.77	1.96
5	9.06	5.25	0.48	1.02	9.71	5.64	0.40	1.01
F12	6.98	4.00	0.16	0.95	10.58	6.16	−0.33	1.01

Even though the subsequent perturbative triples contribution is only of triple-ζ quality, the CCSD(T)(F12) correlation energy is on average as close to the basis set limit as one would expect from the conventional method using an aug-cc-pV5Z basis. Due to the careful construction of the orbital basis sets, energy differences are generally more accurate than total energies through error cancellation. The mean error for the conventional CCSD(T) method is 25.5 kJ mol^{-1} for the total correlation energies and only 0.4 kJ mol^{-1} for the correlation contribution to the reaction enthalpies, when an aug-cc-pV5Z basis is used. The same level of error cancellation is also observed for the CCSD(T)(F12) method, using an aug-cc-pVTZ orbital basis. Indeed, the statistics for the reaction enthalpies show that the CCSD(F12) aug-cc-pVTZ errors are smaller on average than the conventional method using an aug-cc-pV5Z basis. When the perturbative triples correction is also computed, the two methods produce the same quality results and are on average less than 0.5 kJ mol^{-1} from the basis set limit, with a standard deviation of only 1 kJ mol^{-1}. The aug-cc-pV5Z CCSD(T) and aug-cc-pVTZ CCSD(T)(F12) total reaction enthalpies are compared to the experimental values in Table 9. The correlation contributions are combined with the quintuple-ζ Hartree–Fock values for both sets of data. The agreement of both methods with experiment is within the bounds of experimental accuracy and the magnitude of the missing theoretical contributions.

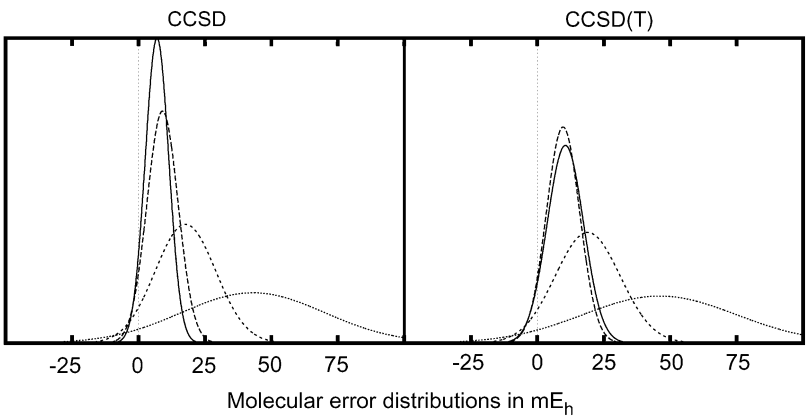


Fig. 4 Basis set error distributions of the CCSD and CCSD(T) correlation energies for 23 molecules using aug-cc-pVXZ, X = T (···), Q (- - -) and 5 (---), and F12 with aug-cc-pVTZ (——).

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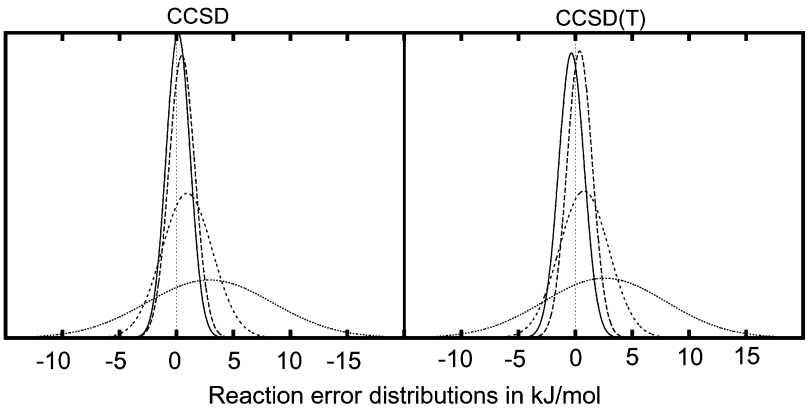


Fig. 5 Basis set error distributions of the CCSD and CCSD(T) correlation energy contributions to 15 reaction enthalpies using aug-cc-pV*X*Z, X = T (···), Q (---) and 5 (--), and F12 with aug-cc-pVTZ (——).

VI. Conclusion

One-particle basis functions are ill adapted to describe the details of short range electron correlation and expensive calculations involving large numbers of orbital basis functions are required for chemical accuracy. It is clear from the large body of work using explicitly-correlated wave functions that it is possible to accurately describe dynamic correlation with relatively few, well chosen basis functions, provided that it is possible to evaluate the Hamiltonian matrix elements.[61–64] Due to the many developments in R12 methodology, the errors introduced by the approximate evaluation of the geminal contributions to the correlation energy can be made insignificant for triple-ζ basis sets or larger. By employing geminal basis functions that depend exponentially on the interelectronic distance, the F12 methods reliably return quintuple-ζ quality MP2, CCSD and CCSD(T) total and relative correlation energies using orbital basis sets of triple-ζ quality. Since the scaling of R12 methods with system size is effectively the same as conventional methods, CCSD(T)(F12) is capable of providing energy differences to chemical accuracy at an affordable cost.

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