Communications: Accurate and efficient approximations to explicitly correlated coupled-cluster singles and doubles, CCSD-F12

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We propose a novel explicitly correlated coupled-cluster singles and doubles method CCSD(F12*), which retains the accuracy of CCSD-F12 while the computational costs are only insignificantly larger than those for a conventional CCSD calculation. © *2010 American Institute of Physics*. [doi:10.1063/1.3442368]

The explicitly correlated coupled-cluster singles and doubles CCSD-F12 method returns near basis set limit CCSD energies using only double- or triple-ζ orbital basis sets. However, the additional computational cost of the F12 contributions to the amplitude equations is considerable,[1–3] which renders this method impractical for general applications. Several simplified models have therefore been proposed: CCSD(F12),[4,5] CCSD-F12a,[6,7] CCSD-F12b,[6,7] and CCSD(2)$_{\overline{\text{F12}}}$.[8,9] While CCSD(F12) is almost as accurate as CCSD-F12,[3] the cost is still three to five times that of a CCSD calculation in the same orbital basis. Although the remaining models have essentially the same cost as CCSD, our investigations show that the basis set errors are at least 50% larger than those of CCSD(F12). In this article, we communicate a new model CCSD(F12*), which has a computational cost close to that of conventional CCSD, while retaining the accuracy of CCSD(F12).

The CCSD-F12 method is obtained by augmenting the CCSD cluster operator $\hat{T}=\hat{T}_1+\hat{T}_2$ with double excitations into explicitly correlated pair functions, $\hat{T}_{2'}$ and proceeding as for CCSD, keeping all $\hat{T}_{2'}$ contributions in the resulting equations.[1–3] The energy expression reads

$$E_{\text{CCSD-F12}}=\langle \text{HF}|\hat{\tilde{H}}+[\hat{H},\hat{T}_2+\hat{T}_{2'}]|\text{HF}\rangle \tag{1}$$

and the amplitudes are obtained from a set of nonlinear equations $\mathbf{\Omega}(\hat{T}_1,\hat{T}_2,\hat{T}_{2'})=0$, with the residuals

$$\Omega_a^i=\left\langle \begin{matrix} i \\ a \end{matrix}\right| \hat{\tilde{H}}+[\hat{\tilde{H}},\hat{T}_2+\hat{T}_{2'}]|\text{HF}\rangle, \tag{2}$$

$$\Omega_{ab}^{ij}=\left\langle \begin{matrix} ij \\ ab \end{matrix}\right| \hat{\tilde{H}}+\left[\hat{\tilde{H}}+\frac{1}{2}[\hat{H},\hat{T}_2+\hat{T}_{2'}],\hat{T}_2+\hat{T}_{2'}\right]|\text{HF}\rangle, \tag{3}$$

$$\Omega_{xy}^{ij}=\left\langle \begin{matrix} ij \\ xy \end{matrix}\right| \hat{\tilde{H}}+[\hat{\tilde{H}},\hat{T}_2+\hat{T}_{2'}]+\frac{1}{2}[[\hat{H},2\hat{T}_2+\hat{T}_{2'}],\hat{T}_{2'}]|\text{HF}\rangle. \tag{4}$$

$i,j,\ldots$ denote occupied and $a,b,\ldots$ are unoccupied spin orbitals. $\hat{\tilde{H}}=\exp(-\hat{T}_1)\hat{H}\exp(\hat{T}_1)$. The explicitly correlated part of the cluster operator

$$\hat{T}_{2'}=\sum_{i>j;\alpha>\beta}\sum_{x>y} c_{xy}^{ij} w_{\alpha\beta}^{xy} a_{ij}^{\alpha\beta} \tag{5}$$

comprises of excitations into geminals constructed as $|w_{xy}\rangle=\hat{Q}_{12}\left(\frac{3}{8}+\frac{1}{8}\hat{S}_{xy}\right)f_{12}(r_{12})|xy\rangle$, where $\hat{S}_{xy}$ permutes the spatial components of spin orbitals x and y in the determinant $|xy\rangle$.[10–12] In second quantization the $|w_{xy}\rangle$ are represented by an expansion in unoccupied orbitals of a formally complete one-electron basis (denoted by indices $\alpha,\beta,\ldots$) with expansion coefficients $w_{\alpha\beta}^{xy}=\langle\alpha\beta|w_{xy}\rangle$. The orbitals x,y are chosen to be the active occupied orbitals and $f_{12}(r_{12})=-(1/\gamma)e^{-\gamma r_{12}}$.[13,14] The corresponding projection states are defined as $\left\langle \begin{matrix} ij \\ xy \end{matrix}\right|=\Sigma_{\alpha>\beta}\langle\text{HF}|a_{\alpha\beta}^{ij}w_{\alpha\beta}^{xy}$. Using the complementary auxiliary basis set (CABS) approach,[15] the ansatz 2 strong orthogonality projector $\hat{Q}_{12}$ is approximated as

$$\hat{Q}_{12}\approx 1-\hat{P}_1\hat{P}_2-\hat{O}_1\hat{P}_2'-\hat{P}_1'\hat{O}_2, \tag{6}$$

$$\hat{Q}_{12}\approx \hat{P}_1'\hat{P}_2'+\hat{V}_1\hat{P}_2'+\hat{P}_1'\hat{V}_2. \tag{7}$$

The second expression is used whenever the unit operator results in three-electron integrals so that only one- and two-electron integrals are required. $\hat{O}$, $\hat{V}$, and $\hat{P}'$ project onto the occupied, virtual, and complementary virtual subspaces, respectively, and $\hat{P}=\hat{O}+\hat{V}$.

The CCSD(F12) approximation[4] neglects small but expensive higher-order $\hat{T}_{2'}$ contributions to the CCSD-F12 amplitude equations,

$$\Omega_{ab,(\text{F12})}^{ij}=\left\langle \begin{matrix} ij \\ ab \end{matrix}\right| \hat{\tilde{H}}+[\hat{\tilde{H}},\hat{T}_2+\hat{T}_{2'}]+\frac{1}{2}[[\hat{H},\hat{T}_2+2\hat{T}_{2'}],\hat{T}_2]\times|\text{HF}\rangle, \tag{8}$$

$$\Omega_{xy,(\text{F12})}^{ij}=\left\langle \begin{matrix} ij \\ xy \end{matrix}\right| \hat{\tilde{H}}+[\hat{F}_D,\hat{T}_{2'}]+[\hat{\tilde{H}},\hat{T}_2]|\text{HF}\rangle. \tag{9}$$

$\hat{F}_D=\hat{O}\hat{F}\hat{O}+(1-\hat{O})\hat{F}(1-\hat{O})$ is the zeroth-order Hamiltonian in explicitly correlated Møller–Plesset perturbation theory. Numerical stability and computational efficiency are both en-

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hanced by adopting the rational generator (fixed-amplitude) approach,[10] where the coefficients c_{xy}^{ij} are not optimized but fixed at $c_{xy}^{ij}=\delta_x^i\delta_y^j-\delta_x^j\delta_y^i$ to satisfy the first-order s- and p-wave coalescence conditions. The energy is then calculated from the Lagrangian[16]

$$L_{(\mathrm{F12})}=\langle \mathrm{HF}|\hat{\bar{H}}+[\hat{H},\hat{T}_2+\hat{T}_{2'}]|\mathrm{HF}\rangle+\sum_{i>j}\sum_{x>y}c_{xy}^{ij}\Omega_{xy,(\mathrm{F12})}^{ij}. \quad (10)$$

The multipliers are approximated by the amplitudes. Although considerably cheaper than CCSD-F12, the CCSD(F12) approximation with the fixed-amplitude approach is still two to three times more costly than conventional CCSD. This comes from contractions involving the CA orbitals, required to evaluate coupling terms between $T_{2'}$, $\hat{T}_2$, and $\hat{T}_1$. Our investigations indicate that these terms can be neglected with very little loss in accuracy.

We first propose a novel approximation CCSD[F12], obtained by neglecting all F12 contributions to CCSD(F12) that are fourth order or higher in the energy within the Møller–Plesset perturbation theory. Both $\hat{T}_1$ and $\hat{T}_2$ are treated as first order in the perturbation to avoid any reliance on the Brillouin condition,

$$\Omega_{i,[\mathrm{F12}]}^{a}=\left\langle \begin{matrix} a \\ i \end{matrix}\right|\hat{\bar{H}}+[\hat{\bar{H}},\hat{T}_2]+[\hat{H},\hat{T}_{2'}]|\mathrm{HF}\rangle, \quad (11)$$

$$\Omega_{ab,[\mathrm{F12}]}^{ij}=\left\langle \begin{matrix} ab \\ ij \end{matrix}\right|\hat{\bar{H}}+[\hat{\bar{H}},\hat{T}_2]+\frac{1}{2}[[\hat{H},\hat{T}_2],\hat{T}_2]+[\hat{H},\hat{T}_{2'}]|\mathrm{HF}\rangle, \quad (12)$$

$$\Omega_{xy,[\mathrm{F12}]}^{ij}=\left\langle \begin{matrix} xy \\ ij \end{matrix}\right|\hat{H}+[\hat{F}_D,\hat{T}_{2'}]+[\hat{H},\hat{T}_1+\hat{T}_2]|\mathrm{HF}\rangle. \quad (13)$$

If this approximation is combined with the fixed-amplitude ansatz, all $\hat{T}_{2'}$ contributions to Eqs. (11) and (12) can be evaluated once in advance of the iterative solution of the cluster equations.

This may clearly be seen from the explicit equations, which we present below in the spin-orbital formalism. We begin by defining the following matrix elements:

$$V_{pq}^{xy}=\langle pq|r_{12}^{-1}|w_{xy}\rangle, \quad w_{ab''}^{xy}=\langle ab''|w_{xy}\rangle, \quad (14)$$

where b'' runs over indices in the complementary space spanned by the CABS. From these basic quantities, the following intermediates can be evaluated:

$$\mathcal{V}_p^i=\sum_k\sum_{x>y}c_{xy}^{ik}V_{pk}^{xy}, \quad \mathcal{V}_{pq}^{ij}=\sum_{x>y}c_{xy}^{ij}V_{pq}^{xy}, \quad (15)$$

$$\mathcal{C}_a^i=\sum_{kc''}f_k^{c''}\sum_{x>y}c_{xy}^{ik}w_{ac''}^{xy}, \quad (16)$$

$$\mathcal{C}_{ab}^{ij}=\hat{P}_{(a|b)}\sum_{x>y}c_{xy}^{ij}\sum_{c''}f_a^{c''}w_{c''b}^{xy}, \quad (17)$$

$$\mathcal{U}_a^i=-\sum_{jkc''}g_{jk}^{ic''}\sum_{x>y}c_{xy}^{jk}w_{ac''}^{xy}, \quad (18)$$

$$\mathcal{U}_{ab}^{ij}=\hat{P}_{(a|b)}\hat{P}_{(i|j)}\sum_{kc''}g_{ak}^{ic''}\sum_{x>y}c_{xy}^{jk}w_{bc''}^{xy}, \quad (19)$$

where $\hat{P}_{(a|b)}A_{ab}^{ij}=A_{ab}^{ij}-A_{ba}^{ij}$ and $g_{pq}^{rs}=\langle pq||rs\rangle$ are antisymmetrized electron repulsion integrals. Using these definitions, the CCSD[F12] Lagrangian energy expression is simply

$$L_{[\mathrm{F12}]}=E_{\mathrm{CCSD}}+\Delta E_{\mathrm{MP2\text{-}F12}}^{\mathrm{unc}}+\sum_{ai}(\mathcal{V}_a^i+\mathcal{U}_a^i)t_a^i+\sum_{a>b,i>j}(\mathcal{C}_{ab}^{ij}+\mathcal{V}_{ab}^{ij}+\mathcal{U}_{ab}^{ij})t_{ab}^{ij}, \quad (20)$$

where E_{CCSD} is the usual CCSD energy expression and $\Delta E_{\mathrm{MP2\text{-}F12}}^{\mathrm{unc}}$ is the explicitly correlated part of the MP2-F12 energy expression, excluding the coupling to t_{ab}^{ij}. The coupling terms occur via the Fock operator ($\mathcal{C}$ term) and the two-electron repulsion integrals leading to a ladder-type contribution via the $\mathcal{V}$ intermediate and a ring-type contribution via the $\mathcal{U}$ intermediate. Similar linear coupling terms occur for the residuals

$$\Omega_{a,[\mathrm{F12}]}^{i}=\Omega_{a,\mathrm{CCSD}}^{i}+\mathcal{C}_a^i+\mathcal{V}_a^i+\mathcal{U}_a^i, \quad (21)$$

$$\Omega_{ab,[\mathrm{F12}]}^{ij}=\Omega_{ab,\mathrm{CCSD}}^{ij}+\mathcal{C}_{ab}^{ij}+\mathcal{V}_{ab}^{ij}+\mathcal{U}_{ab}^{ij}, \quad (22)$$

where Ω_{CCSD} is the conventional part. For fixed c_{xy}^{ij}, only the constant part of each residual needs to be modified and there is obviously no additional effort during the iterative solution of the coupled-cluster equations.

Results presented below show that CCSD[F12] is almost as accurate as CCSD(F12), only for systems with strong correlation effects noticeable deviations occur. This can be rectified by including the most important higher-order coupling contributions, i.e., the terms in CCSD(F12) that remain if the projection operator Eq. (6) is replaced by the more restrictive ansatz 1 projector $\hat{Q}_{12}^{(1)}=1-\hat{P}_1\hat{P}_2-\hat{P}_1\hat{P}_2'-\hat{P}_1'\hat{P}_2$,

$$\Omega_{a,(\mathrm{F12}^*)}^{i}=\Omega_{a,[\mathrm{F12}]}^{i}+\left\langle \begin{matrix} i \\ a \end{matrix}\right|[[\hat{H},\hat{T}_1],\hat{Q}_{12}^{(1)}\hat{T}_{2'}]|\mathrm{HF}\rangle, \quad (23)$$

$$=\Omega_{a,[\mathrm{F12}]}^{i}-\sum_k\mathcal{V}_k^{i,(1)}t_a^k, \quad (24)$$

$$\Omega_{ab,(\mathrm{F12}*)}^{ij}=\Omega_{ab,[\mathrm{F12}]}^{ij}+\left\langle \begin{matrix} ij \\ ab \end{matrix}\right|[[\hat{H},\hat{T}_1+\hat{T}_2],\hat{Q}_{12}^{(1)}\hat{T}_{2'}]|\mathrm{HF}\rangle+\left\langle \begin{matrix} ij \\ ab \end{matrix}\right|\frac{1}{2}[[[\hat{H},\hat{T}_1],\hat{T}_1],\hat{Q}_{12}^{(1)}\hat{T}_{2'}]|\mathrm{HF}\rangle, \quad (25)$$

$$=\Omega_{ab,[\mathrm{F12}]}^{ij}+\sum_{kl}\mathcal{V}_{kl}^{ij,(1)}\left(\frac{1}{2}t_{ab}^{kl}+t_a^kt_b^l\right)-\hat{P}_{(a|b)}\sum_k\mathcal{V}_{ak}^{ij,(1)}t_b^k-\hat{P}_{(i|j)}\sum_k\mathcal{V}_k^{j,(1)}t_{ab}^{ik}, \quad (26)$$

and the additional term in Ω_{xy}^{ij} leads to a further energy contribution

$$L_{(\mathrm{F12}^*)}=L_{[\mathrm{F12}]}+\sum_{i>j}\sum_{x>y}c_{xy}^{ij}\left\langle \begin{matrix} ij \\ xy \end{matrix}\right|\hat{Q}_{12}^{(1)}\frac{1}{2}[[\hat{H},\hat{T}_1],\hat{T}_1]|\mathrm{HF}\rangle, \quad (27)$$

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TABLE I. CCSD basis set error statistics for reaction energies and atomization energies computed using CCSD-F12 models and cc-pVXZ-F12 basis sets (kJ/mol per valence electron).

		RE				AE			
Method	X	Mean	σ_N	rms	Max	Mean	σ_N	rms	Max
(F12)	D	−0.10	0.10	0.14	−0.32	−0.61	0.21	0.65	−1.05
	T	−0.01	0.01	0.02	−0.06	−0.08	0.08	0.11	−0.33
	Q	0.00	0.01	0.01	0.01	0.04	0.05	0.06	−0.13
(F12*)	D	−0.10	0.10	0.14	−0.32	−0.60	0.21	0.64	−1.04
	T	−0.01	0.01	0.02	−0.06	−0.08	0.08	0.11	−0.33
	Q	0.00	0.01	0.01	0.01	0.04	0.05	0.06	−0.13
[F12]	D	−0.09	0.11	0.14	−0.30	−0.32	0.23	0.39	−0.76
	T	−0.01	0.02	0.02	−0.05	0.05	0.09	0.10	−0.26
	Q	0.00	0.00	0.00	−0.01	0.10	0.05	0.11	0.17
F12b	D	−0.16	0.20	0.26	−0.53	−0.85	0.38	0.93	−1.54
	T	−0.03	0.05	0.06	−0.12	−0.16	0.12	0.20	−0.40
	Q	0.00	0.01	0.01	−0.03	0.05	0.06	0.07	0.14
F12a	D	−0.14	0.20	0.25	−0.50	−0.37	0.27	0.46	−0.79
	T	−0.02	0.04	0.05	−0.11	0.19	0.09	0.21	0.58
	Q	0.00	0.01	0.01	0.02	0.27	0.06	0.28	0.45
$(2)_{\overline{F12}}$	D	−0.13	0.15	0.20	−0.42	−0.72	0.44	0.85	−1.48
	T	−0.02	0.02	0.03	−0.08	−0.13	0.17	0.21	−0.53
	Q	0.00	0.00	0.00	0.01	0.04	0.08	0.09	−0.19
$(2^*)_{\overline{F12}}$	D	−0.21	0.19	0.28	−0.63	−1.47	0.50	1.55	−2.40
	T	−0.06	0.05	0.08	−0.18	−0.29	0.14	0.32	−0.57
	Q	−0.01	0.01	0.02	−0.03	0.00	0.06	0.06	−0.14

$$= L_{[\mathrm{F12}]} + \frac{1}{2}\sum_{abij} \mathcal{V}_{ab}^{ij,(1)} t_a^i t_b^j. \tag{28}$$

All additional contributions included in CCSD(F12*) can be evaluated from $V_{pq}^{xy,(1)} = \langle pq | r_{12}^{-1} \hat{Q}_{12}^{(1)} | w_{xy} \rangle$. However, for computational convenience we use Eq. (14) with the full projector $\hat{Q}_{12}$, instead. The additional contributions therefore incur no significant costs.

Three other approximations have previously been forwarded in literature. The CCSD-F12a and CCSD-F12b methods[6,7] are defined by

$$\Omega_{a,\mathrm{F12x}}^i = \Omega_{a,\mathrm{CCSD}}^i + \mathcal{V}_a^{i,(0)} - \sum_k \mathcal{V}_k^{i,(0)} t_a^k, \tag{29}$$

$$\Omega_{ab,\mathrm{F12x}}^{ij} = \Omega_{ab,\mathrm{CCSD}}^{ij} + \mathcal{C}_{ab}^{ij} + \mathcal{V}_{ab}^{ij,(0)} - \hat{P}_{(a|b)} \sum_k \mathcal{V}_{ak}^{ij,(0)} t_b^k, \tag{30}$$

$$L_{\mathrm{F12a}} = E_{\mathrm{CCSD}} + \Delta E_{\mathrm{MP2\text{-}F12}}^{\mathrm{unc}} + \sum_{a>b,i>j} \mathcal{C}_{ab}^{ij} t_{ab}^{ij}, \tag{31}$$

$$L_{\mathrm{F12b}} = L_{\mathrm{F12a}} + \sum_{ai} \mathcal{V}_a^{i,(0)} t_a^i + \sum_{a>b,i>j} \mathcal{V}_{ab}^{ij,(0)} t_{ab}^{ij} + \frac{1}{2}\sum_{abij} \mathcal{V}_{ab}^{ij,(0)} t_a^i t_b^j. \tag{32}$$

For the $\mathcal{V}^{(0)}$ intermediates, a modified projector $\hat{Q}_{12}^{(0)} = 1 - \hat{P}_1 \hat{P}_2$ is used. In the CCSD(2)$_{\overline{F12}}$ approximation, the CCSD

TABLE II. rms basis set errors of CCSD(T)-F12/cc-pVXZ-F12 reaction energies and atomization energies for approximate F12 models (kJ/mol per valence electron).

	X	(F12)	(F12*)	[F12]	F12b	F12a	$(2)_{\overline{F12}}$	$(2^*)_{\overline{F12}}$
RE	D	0.19	0.19	0.18	0.30	0.34	0.24	0.33
	T	0.04	0.04	0.03	0.07	0.06	0.04	0.10
	Q	0.01	0.01	0.01	0.01	0.01	0.01	0.02
AE	D	1.07	1.06	0.72	1.31	0.29	1.12	1.85
	T	0.26	0.26	0.11	0.32	0.22	0.28	0.42
	Q	0.05	0.05	0.07	0.05	0.26	0.08	0.06

TABLE III. Asymptotic scaling of the cost. n is the number of correlated electrons and N and X are the number of orbital and CA basis functions, respectively. Typically $N < X < 3N$ and the number of iterations is in the order of 10.

Method	Noniterative	Iterative
CCSD	$\propto nN^4$	$\propto n^2N^4$
CCSD-F12a	$\propto n(N+X)^2N^2$	$\propto n^2N^4$
CCSD-F12b	$\propto n^2N^4$	$\propto n^2N^4$
$\mathrm{CCSD}(2)_{\overline{F12}}$	$\propto n^2N^3(N+X)$	$\propto n^2N^4$
CCSD[F12]	$\propto n^2N^3(N+X)$	$\propto n^2N^4$
CCSD(F12*)	$\propto n^2N^3(N+X)$	$\propto n^2N^4$
CCSD(F12)	$\propto n^2N^3(N+X)$	$\propto n^2N^3(N+X)$

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amplitude equations are solved without F12 contributions and the energy is evaluated using

$$L_{(2)_{\overline{\mathrm{F12}}}} = E_{\mathrm{CCSD}} + \Delta E^{\mathrm{unc}}_{\mathrm{MP2\text{-}F12}} + 2 \sum_{a>b,i>j} (\mathcal{C}^{ij}_{ab} + \mathcal{V}^{ij}_{ab}) t^{ij}_{ab} \quad (33)$$

for a closed-shell or spin-unrestricted Hartree–Fock reference. For restricted open-shell Hartree–Fock references an additional contribution of $2\Sigma_{ai}\mathcal{V}^{i}_{a}t^{i}_{a}$ is included. In fact, Eq. (33) differs slightly from the method proposed by Valeev,[8] which neglects the $\mathcal{C}$ coupling. We refer to the original method as $\mathrm{CCSD}(2^{*})_{\overline{\mathrm{F12}}}$.

We assess the performance of the new and existing CCSD-F12 models through the basis set errors of computed reaction and atomization energies. Our test set comprises of 30 small closed-shell molecules of H, C, N, O, and F, for which the basis set limits of the CCSD total energies are known to be within 0.05 kJ/mol per valence electron,[17] an accuracy of better than 0.01 kJ/mol per valence electron for relative energies. The reaction energies are for the decomposition of 25 of the molecules into H_2, CO, CO_2, N_2, and F_2. All calculations were performed with TURBOMOLE (Ref. 18) using the cc-pVXZ-F12 basis sets,[19] X=D, T, and Q with the recommended exponents for the correlation factor. The optimized CA basis sets were used for the complementary auxiliary orbital space and aug-cc-pwCVYZ MP2 and Coulomb density fitting basis sets, with Y=T, Q, and 5 for orbital basis sets X=D, T, and Q, respectively. A basis set correction for the singles was computed using the (S2) method[17,20] and spin-unrestricted calculations using restricted open-shell Hartree-Fock (ROHF) references were performed for the atoms.

From the standard deviation, mean, root mean squared (rms), and maximum basis set errors for the various CCSD-F12 models reported in Table I, it is immediately clear that the CCSD(F12) and $\mathrm{CCSD(F12^{*})}$ models are of essentially equivalent accuracy. The remaining models are all deficient to varying degrees. While CCSD[F12] is accurate for reaction energies, it is less reliable for atomization energies. The missing higher-order terms, $\mathcal{V}^{i}_{k}$, in particular, lead to overshooting and a slow convergence with basis size for total energies, although this does lead to fortuitous error cancellation for cc-pVDZ-F12 results.

The rms basis set errors for the CCSD-F12x reaction energies are twice those of the CCSD(F12) method. This arises predominantly from the imbalance created by the missing ringlike terms $\mathcal{U}$. In accord with Werner and coworkers, we find that the CCSD-F12a and b models perform equivalently for reaction energies and that F12a overshoots for atomization energies due to the missing ladder-type $\mathcal{V}$ term in the Lagrangian,[6,7] resulting in error compensation for the cc-pVDZ-F12 basis. We find that the perturbative $\mathrm{CCSD}(2)_{\overline{\mathrm{F12}}}$ method is more accurate than the CCSD-F12b model, even though the Lagrangians are very similar, but slightly inferior to CCSD(F12). Neglecting the $\mathcal{C}$ coupling, $\mathrm{CCSD}(2^{*})_{\overline{\mathrm{F12}}}$, significantly deteriorates the accuracy.

For chemical applications it is often essential to include triple excitations to obtain reliable predictions. Although recent progress has been made in extending F12 theory to accelerate the basis set convergence of the perturbative triples correction in CCSD(T),[21] it is current practice to simply compute the (T) energy correction in the usual way, using t^{a}_{i} and t^{ab}_{ij} from the CCSD-F12 calculation. In Table II we report CCSD(T) rms basis set errors for reaction energies and atomization energies, computed in this way using the various CCSD-F12 models. Comparing Tables I and II one sees that the basis set error in the CCSD and (T) contributions are of similar magnitude for all basis sets. Consequently, the loss of accuracy of the CCSD-F12x and $\mathrm{CCSD}(2)_{\overline{\mathrm{F12}}}$ methods over CCSD(F12) results in a significant increase in the corresponding CCSD(T) basis set errors for our test set, particularly for the cc-pVDZ-F12 basis.

The proposed $\mathrm{CCSD(F12^{*})}$ approximation preserves the accuracy of the full CCSD-F12 model, but at a computational cost equivalent to a conventional CCSD calculation, plus a small overhead for the evaluation of some additional intermediates (cf. Table III). The improved accuracy of the $\mathrm{CCSD(F12^{*})}$ model over the existing approximations of similar cost will have an even larger impact once efficient F12 methods for triple excitations have been developed. We also note that the iterative rather than perturbative nature of the $\mathrm{CCSD(F12^{*})}$ and the balanced treatment of single and double excitations makes this method suitable for applications in the framework of response theory.

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