Comment on Quintuple-ζ quality coupled-cluster correlation energies with triple-ζ basis sets by D. P. Tew, W. Klopper, C. Neiss and C. Hättig, *Phys. Chem. Chem. Phys.*, 2007, 9, 1921 [erratum]

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After rectifying a small programming error, CCSD(F12) correlation energies are even better than previously reported, particularly for double-ζ basis sets.

The CCSD(F12) and CCSD(T) values reported in the article by our group[1] in 2007 are incorrect due to a small programming error. Since our values are used as reference data for related F12 methods, it is important that we report the correct values. The conclusion stated in the title of the article, that the CCSD(T)(F12) method yields quintuple-ζ quality coupled-cluster correlation energies with triple-ζ basis sets is in no way diminished by these new results. In fact, the correct correlation energies are a universal improvement upon the erroneous values. Our current implementation is in complete agreement with an independently programmed CCSD(F12) program that uses generalised contraction routines[2] and we are certain that the values reported here are reliable. The performance of the CCSD(T)(F12) method is now also in line with the performance of related CCSD(T)-F12 methods of Valeev,[3] Werner *et al.*[4] and Noga, Ten-no *et al.*[5]

Here we report the correct CCSD(F12) and CCSD(T)(F12) correlation energies for the molecules H_2O, CO, F_2, Li_2 and LiF at their optimum frozen-core MP2/aug-cc-pVTZ geometries. Tables 1–6 replace Tables 2–6 and 8 in the original article (this is shown clearly in the Table captions). We do not present replacements for Fig. 1–3 because, although the energies are shifted, the dependence of the correlation energies on the exponent γ in the F12 correlation factor is essentially the same as before. The detailed conclusions drawn from the previous data are also largely unchanged. The only exceptions are the remarks concerning the disappointing performance of CCSD(F12) with an aug-cc-pVDZ basis, as the performance is now substantially improved. The CCSD(F12) correlation energies using this basis were previously observed to lie between the aug-cc-pVTZ and aug-cc-pVQZ conventional CCSD values. From Tables 1–6 one sees that the quality of the correct CCSD(F12)/aug-cc-pVDZ correlation energies is between that of the conventional aug-cc-pVQZ and aug-cc-pV5Z values. However, the (T) correction computed using the aug-cc-pVDZ basis remains much too small due to
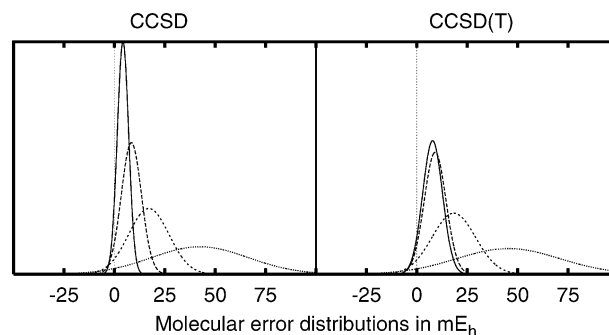
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Fig. 1 (Fig. 4 revised) Basis set error distributions of the CCSD and CCSD(T) correlation energies for 23 molecules using aug-cc-pVXZ, X = T (·······), Q (------) and 5 (– – – –), and F12 with aug-cc-pVTZ (———).

the absence of explicitly correlated contributions. The CCSD(T)(F12)/aug-cc-pVDZ correlation energies are generally of comparable quality, or slightly inferior to conventional CCSD(T)/aug-cc-pVQZ values.

Regarding 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, the previous predictions are unchanged, except for F_2. The values from the new data are −308(1), −416(1), −622(2), −31.91(0.02) and −328(1) mE_h respectively. The uncertainty is given in parentheses and is estimated by taking the
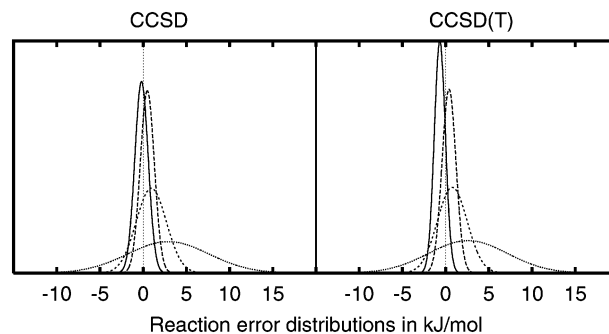

Fig. 2 (Fig. 5 revised) Basis set error distributions of the CCSD and CCSD(T) correlation energy contributions to 15 reaction enthalpies using aug-cc-pVXZ, X = T (·······), Q (------) and 5 (– – – –), and F12 with aug-cc-pVTZ (———).

Table 1 (Table 2 revised) 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-pVXZ orbital basis sets

X	MP2			CCSD			ΔE(T)			CCSD(T)		
	Orb.	R12	F12	Orb.	R12	F12	Orb.	R12	F12	Orb.	R12	F12
D	219.73	271.05	295.20	227.47	270.58	291.09	5.24	5.11	4.96	232.71	275.69	296.05
T	268.71	291.08	298.61	273.38	290.37	296.10	8.67	8.55	8.46	282.04	298.92	304.56
Q	286.26	297.58	300.04	288.51	296.11	297.81	9.41	9.34	9.32	297.93	305.45	307.12
5	293.25	299.57	300.51	293.62	297.55	298.17	9.69	9.65	9.64	303.32	307.20	307.81

Table 2 (Table 3 revised) MP2, CCSD and CCSD(T) correlation energies ($-mE_h$) of CO computed using conventional, R12 and F12 ($\gamma = 1.3$) methods with aug-cc-pVXZ orbital basis sets

X	MP2			CCSD			ΔE(T)			CCSD(T)		
	Orb.	R12	F12	Orb.	R12	F12	Orb.	R12	F12	Orb.	R12	F12
D	301.22	366.53	399.26	307.82	361.23	388.42	12.60	12.25	11.84	320.42	373.48	400.25
T	362.52	391.03	402.56	364.40	385.63	394.10	17.89	17.63	17.45	382.29	403.26	411.55
Q	385.50	400.57	404.29	383.79	393.68	396.14	19.08	18.93	18.87	402.87	412.61	414.01
5	394.91	403.49	404.96	390.59	395.71	396.67	19.55	19.46	19.43	410.14	415.17	416.10

Table 3 (Table 4 revised) MP2, CCSD and CCSD(T) correlation energies ($-mE_h$) of F_2 computed using conventional, R12 and F12 ($\gamma = 1.3$) methods with aug-cc-pVXZ orbital basis sets

X	MP2			CCSD			ΔE(T)			CCSD(T)		
	Orb.	R12	F12	Orb.	R12	F12	Orb.	R12	F12	Orb.	R12	F12
D	426.63	544.34	599.30	434.04	535.38	584.36	12.60	12.26	11.76	446.64	547.65	596.12
T	534.77	587.50	604.75	537.70	580.08	594.08	19.66	19.32	19.10	557.35	599.40	613.18
Q	574.53	602.17	608.23	573.95	593.96	598.46	21.35	21.16	21.09	595.30	615.12	619.55
5	591.49	606.99	609.52	587.39	597.83	599.64	22.06	21.94	21.92	609.45	619.78	621.55

Table 4 (Table 5 revised) MP2 and CCSD correlation energies ($-mE_h$) of Li_2 computed using conventional, R12 and F12 ($\gamma = 1.3$) methods with aug-cc-pVXZ orbital basis sets

X	MP2			CCSD		
	Orb.	R12	F12	Orb.	R12	F12
D	19.23	20.86	21.95	30.69	31.09	31.23
T	21.16	21.94	22.57	31.53	31.71	31.74
Q	22.13	22.51	22.82	31.82	31.86	31.90
5	22.46	22.80	22.86	31.87	31.90	31.91

difference between the aug-cc-pVQZ and aug-cc-pV5Z CCSD(T)(F12) values.

We also report the correct CCSD(T)(F12)/aug-cc-pVTZ values for the 15 reaction energies considered. The values in Tables 7 and 8 replace those in Tables 9 and 10 of the original article. Similarly, Fig. 1 and 2 replace Fig. 4 and 5. Previously, the CCSD(T)(F12) method was assessed relative to an estimate of the basis set limit using the two-point extrapolation formula of Helgaker *et al.*[6] with the aug-cc-pVQZ and aug-cc-pV5Z basis sets (Q5). However, the availability of

Table 5 (Table 6 revised) MP2, CCSD and CCSD(T) correlation energies ($-mE_h$) of LiF computed using conventional, R12 and F12 ($\gamma = 1.3$) methods with aug-cc-pVXZ orbital basis sets

X	MP2			CCSD			ΔE(T)			CCSD(T)		
	Orb.	R12	F12	Orb.	R12	F12	Orb.	R12	F12	Orb.	R12	F12
D	229.41	289.78	320.49	228.63	280.56	307.98	4.98	4.96	4.84	233.61	285.52	312.83
T	287.54	316.20	325.72	283.76	306.57	314.48	8.95	8.82	8.73	292.71	315.39	323.21
Q	309.35	324.64	327.83	303.76	314.63	317.02	9.81	9.72	9.70	313.57	324.34	326.72
5	318.60	327.34	328.59	310.97	316.73	317.64	10.18	10.11	10.11	321.14	326.85	327.75

Table 6 (Table 8 revised) CCSD(T)(F12) aug-cc-pVXZ correlation energies (mE_h) for optimised γ. The maximum deviation of the energy between γ_{opt} and $\gamma = 1.0$ or 1.5 is given in parentheses

X	H_2O	CO	F_2	Li_2	LiF
D	−296.17 (0.66)	−400.59 (1.26)	−596.12 (1.83)	−31.49 (0.34)	−312.83 (0.73)
T	−304.55 (0.10)	−411.55 (0.14)	−613.26 (0.61)	−31.83 (0.11)	−323.20 (0.14)
Q	−307.12 (0.07)	−415.00 (0.09)	−619.60 (0.31)	−31.90 (0.00)	−326.74 (0.14)

Table 7 (Table 9 revised) CCSD(T) reaction enthalpies (ΔH_R) computed with an aug-cc-pV5Z orbital basis, CCSD/(56) + (T)/Q5 extrapolation and CCSD(T)(F12) with an aug-cc-pVTZ basis in kJ mol^{-1}

Reaction	Correlation contribution			ΔH_R		
	5	F12	Extrap.	5	F12	Exp.
$CO + NH_3 \rightarrow HCONH_2$	−30.56	−31.49	−31.60	−41.04	−41.98	−39.00
$H_2C_2O + H_2CO \rightarrow C_2H_4O + CO$	7.73	7.27	7.56	−16.79	−17.24	−14.80
$CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S$	74.40	73.30	74.96	−47.86	−48.96	−46.60
$CO + Cl_2 \rightarrow COCl_2$	−58.86	−60.47	−58.31	−115.50	−117.11	−115.40
$NH_3 + 4H_2O_2 \rightarrow HNO_3 + 5H_2O$	14.00	11.57	12.47	−745.39	−747.82	−741.20
$C_2H_2 + H_2 \rightarrow C_2H_4$	9.84	9.35	10.06	−206.53	−207.03	−202.70
$CO + H_2 \rightarrow H_2CO$	−22.57	−22.71	−22.69	−21.52	−21.67	−20.80
$H_2O_2 + H_2 \rightarrow 2H_2O$	26.22	25.82	26.36	−365.16	−365.56	−363.50
$H_2CO + H_2 \rightarrow CH_3OH$	−3.70	−4.26	−3.55	−123.23	−123.80	−122.70
$C_2H_6 + H_2 \rightarrow 2CH_4$	12.74	13.03	13.09	−76.03	−75.74	−78.00
$C_2H_4 + H_2 \rightarrow C_2H_6$	−1.65	−2.70	−1.60	−165.53	−166.58	−164.10
$C_2H_2 + H_2O \rightarrow CH_3CHO$	8.85	7.25	8.36	−161.14	−162.74	−160.80
$CH_4 + 4H_2O_2 \rightarrow CO_2 + 6H_2O$	103.38	101.29	102.14	−1214.97	−1217.06	−1211.30
$SO_2 + H_2O_2 \rightarrow SO_3 + H_2O$	22.90	20.81	20.75	−208.25	−210.35	−204.40
$CO + H_2O_2 \rightarrow CO_2 + H_2O$	0.37	−0.84	−0.76	−390.75	−391.96	−392.40

Table 8 (Table 10 revised) The mean and standard deviation (σ) of the CCSD and CCSD(T) basis set errors, relative to the CCSD/(56) + (T)/(Q5) extrapolated values, for the correlation contribution to the molecular energies ($\bar{E}_{mol}$ in mE_h) and reaction enthalpies (ΔH_R in kJ mol^{-1})

Basis	CCSD				CCSD(T)			
	$\bar{E}_{mol}$	σ	$\overline{\Delta H_R}$	σ	$\bar{E}_{mol}$	σ	$\overline{\Delta H_R}$	σ
T	42.41	23.94	2.90	4.71	45.36	25.65	2.59	4.56
Q	17.06	9.99	0.94	1.75	18.33	10.76	0.77	1.73
5	8.43	4.99	0.48	0.81	9.08	5.39	0.39	0.80
6	4.88	2.89	0.28	0.47				
F12	4.26	2.83	−0.19	0.77	7.82	4.92	−0.67	0.64

CCSD/aug-cc-pV6Z correlation energies for this set of molecules has made it possible to improve the estimate of the basis set limit.[7] In ref. 7, the CCSD/aug-cc-pV6Z correlation energy for CH$_3$CHO was missing. Here we have computed it to be −637.958738 mE_h. The basis set limit used for the values presented in Tables 7 and 8 is computed by separate extrapolation of the CCSD and (T) contributions, using

Helgaker's two-point formula with 56 and Q5 basis sets respectively. The conclusions concerning the performance of CCSD(T)(F12) for reaction energies are unchanged. Quintuple-ζ quality coupled-cluster correlation energies are obtained with the CCSD(T)(F12) method using triple-ζ basis sets.

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