

MP2-F12 Basis Set Convergence near the Complete Basis Set Limit: Are *h* Functions Sufficient?

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Cite This: *J. Phys. Chem. A* 2022, 126, 3964–3971



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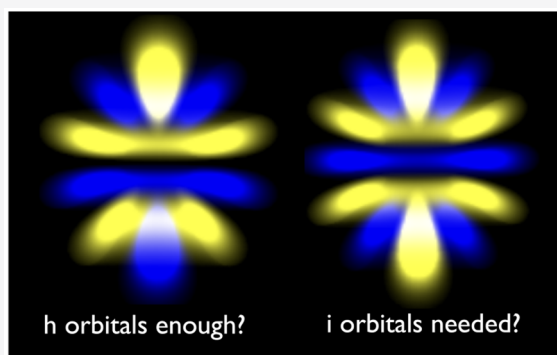


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ABSTRACT: We have investigated the title question for the W4-08 thermochemical benchmark using *l*-saturated truncations of a large reference (REF) basis set, as well as for standard F12-optimized basis sets. With the REF basis set, the root-mean-square (RMS) contribution of *i* functions to the MP2-F12 total atomization energies (TAEs) is about 0.01 kcal/mol, the largest individual contributions being 0.04 kcal/mol for P_2 and P_4 . However, even for these cases, basis set extrapolation from $\{g,h\}$ basis sets adequately addresses the problem. Using basis sets insufficiently saturated in the *spdfgh* angular momenta may lead to exaggerated *i* function contributions. For extrapolation from *spdfg* and *spdfgh* basis sets, basis set convergence appears to be quite close to the theoretical asymptotic $\propto L^{-7}$ behavior. We hence conclude that *h* functions are sufficient even for highly demanding F12 applications. With one-parameter extrapolation, *spdf* and *spdfg* basis sets are adequate, aug-cc-pV{T,Q}Z-F12 yielding a RMSD = 0.03 kcal/mol. A limited exploration of CCSD(F12*) and CCSD-F12b suggests our conclusions are applicable to higher-level F12 methods as well.



INTRODUCTION

Explicitly correlated quantum chemistry methods (see refs 1–3 for reviews) get their name from the inclusion of basis functions that involve explicit interelectronic distances (so-called “geminal” functions, as distinct from “orbital” functions that only involve a single electronic position).

The *de facto* standard at this point are the F12 geminals introduced by Ten-no:⁴

$$F(r_{12}) = \frac{1 - \exp(\gamma r_{12})}{\gamma} \quad (1)$$

which in the limit for small r_{12} corresponds to adding r_{12} , and hence to satisfying the Kato cusp condition.⁵ (For reasons of computational convenience, the Slater function is typically approximated by a linear combination of Gaussians, which actually is reminiscent of the Gaussian geminal approach of Persson and Taylor⁶ a decade earlier.)

Exigencies for the underlying orbital basis set are quite different from those in a pure orbital calculation, as not so much effort needs to be invested in describing correlation near the interelectronic cusp. Hence basis sets specifically optimized for F12 calculations, such as the cc-pVnZ-F12 ($n = D, T, Q, S$) family by Peterson and co-workers,^{7,8} or their anion-friendly aug-cc-pVnZ-F12 variants,⁹ perform much better in an F12 setting than similar-sized basis sets for orbital calculations (such as the correlation consistent family of Dunning and co-workers). Indeed, both their contraction patterns and their exponents are markedly different⁷ from those for the

corresponding orbital-optimized basis sets. In fact, it has been shown¹⁰ that non-F12 basis sets in thermochemical applications lead to erratic, nonmonotonous basis set convergence due to elevated basis set superposition error.

It is well-known that F12 calculations exhibit fairly rapid basis set convergence in terms of the maximum angular momentum L in the basis set: for two-electron model systems, Kutzelnigg and Morgan¹¹ showed $\propto L^{-7}$ for explicitly correlated calculations, compared to L^{-3} for singlet-coupled pair correlation energies in pure orbital calculations.

Hence, few F12 practitioners go beyond $L = 4$ (i.e., *g* functions), that is, beyond cc-pVQZ-F12 or aug-cc-pVQZ-F12 basis sets. In accurate thermochemical applications, one may find (e.g., refs 10 and 12) cc-pV5Z-F12 or aug-cc-pwCV5Z^{13–15} applied, both of which go up to *h* functions. At least one major electronic structure code often used for F12 calculations, MOLPRO,¹⁶ has a hard limit of *i* functions overall, and hence (because of the need for one extra L step in the RI-MP2 auxiliary basis set) in practice the orbital basis set in F12 calculations tops out at *h* functions. Two other codes,

Received: April 11, 2022

Revised: May 25, 2022

Published: June 10, 2022

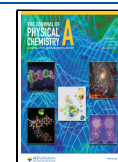


Table 1. RMSD (kcal/mol) for the TAEs of the W4-08 Dataset

truncated REF basis sets						
	REF-d	REF-f	REF-g	REF-h	REF-i	
	Ordinary MP2					
<i>a</i>	13.136	4.965	2.205	1.203		0.789
<i>b</i>	13.137	4.981	2.221	1.219		0.791
	MP2-F12					
<i>a</i>	1.942	0.334	0.062	0.016		0.004
<i>b</i>	1.898	0.329	0.060	0.014		0.006
Extrapolations MP2-F12						
	REF- $\{d,f\}$	REF- $\{f,g\}$	REF- $\{g,h\}$	REF- $\{h,i\}$		
<i>a</i>	0.133	0.027	0.006	REF		REF
<i>b</i>	0.127	0.022	REF	0.006		0.006
F12 optimized correlation consistent						
	VDZ-F12	VTZ-F12	AVTZ-F12	VQZ-F12	AVQZ-F12	VSZ-F12
<i>a</i>	1.437	0.325	0.315	0.084	0.063	0.044
<i>b</i>	1.444	0.328	0.317	0.085	0.065	0.046
core–valence correlation consistent						
	ACV6Z $\{f\}$	ACV6Z $\{g\}$	ACV6Z $\{h\}$	ACV6Z	awCV5Z	ditto, AV6Z(H)
<i>a</i>	0.375	0.082	0.028	0.019	0.030	0.033
<i>b</i>	0.368	0.081	0.028	0.018	0.027	0.031
Valence aug-cc-pV($n + d$)Z						
		AVSZ	AV6Z(h)	AV6Z		
<i>a</i>		0.055	0.041	0.020		
<i>b</i>		0.059	0.051	0.022		

^aRelative to REF- $\{h,i\}$ (largest systems omitted, 90 systems retained). ^bRelative to REF- $\{g,h\}$ limit (all of W4-08, 96 systems).

Turbomole¹⁷ and the most recent versions of ORCA, are capable of going up to at least *i* functions in an F12 context.

i functions are routinely employed in accurate *orbital-only* calculations, usually with basis set extrapolation as in the W4,^{18–20} HEAT,^{21,22} and FPD^{23–25} thermochemical protocols. One study in our group¹² on the W4–17 thermochemical benchmark²⁶ went up to *k* functions.

In the present note, we will investigate basis set convergence at the MP2-F12 level for the total atomization energies (TAEs) in the W4-08 subset²⁷ of W4-17. We will show that, while *i* functions may still make some contributions to the atomization energies of some molecules (particularly, those featuring multiple bonds between second-row elements), this can be adequately addressed through $\propto L^{-7}$ basis set extrapolation, and *de facto* F12 basis set convergence is achieved with *h* functions.

COMPUTATIONAL METHODS

All calculations were carried out using ORCA 5,^{28–30} with density fitting for HF and MP2 disabled through the NoCoSX and NoRI keywords. This leaves only the CABS (complementary auxiliary basis set for F12) as a fitting basis set, thus eliminating the Coulomb-exchange and RI-MP2 fitting basis sets as possible “confounding factors”. For technical reasons, UHF references were used for open-shell species.

The largest *spdfgh* basis set we considered was the reference basis set from Hill et al.³¹ which was also used in refs 8 and 10, for calibrating the VSZ-F12 basis set. The *sp* part of this is the aug-cc-pV6Z (AV6Z for short) basis set from which two (first row) or one (second row) additional primitives were decontracted; the *dfgh* part is made up of large even-tempered sequences. This basis set we denote REF-h. For its CABS, we used the large uncontracted “reference-ri” basis set associated

with it. REF-f and REF-g basis sets were generated by simple truncation of REF-h at *f* and *g* functions, respectively. (The linear dependency threshold for CABS was left at its default value of 10^{-8} throughout. The MP2-F12 ansatz used in ORCA corresponds to version D, which is a slight simplification³² of ansatz C,^{33,34} together with fixed geminal amplitudes^{4,31} determined from the Kato cusp condition. This is basically equivalent to the default of “3C(Fix)” in MOLPRO.¹⁶)

In addition, for a large subset of molecules, we considered an even larger REF-i basis set to which four *i* functions have been added. Here, for the CABS basis set, we added a *k* function with the same exponent to every *i* function.

Aside from VTZ-F12, VQZ-F12, and VSZ-F12 basis sets, we considered aug-cc-pV($n+d$)Z ($n = T, Q, S, 6$; AV n Z+d for short),^{35–38} as well as the core–valence correlation basis sets aug-cc-pwCV n Z ($n = T, Q, S$; awCV n Z for short),¹⁵ and aug-cc-pCV n Z ($n = Q, S, 6$; ACV n Z).¹⁵ (We are only correlating valence electrons here, but it has been shown^{8,10,12} that the additional radial flexibility of core–valence basis sets is beneficial for F12 calculations as well.) For V n Z-F12 ($n = D, T, Q$; V n Z-F12 for short) and AV n Z ($n = T, Q, S$), standard CABS “OptRI” basis sets^{39,40} are available. For AV6Z+d we carried out two sets of calculations; in the first, we repurposed Hättig’s unpublished DF-AV6Z basis set from the Turbomole library (downloaded from the Basis Set Exchange⁴¹) as the CABS; in the second, we employed the reference-RI from ref 31 instead. For the ACV6ZnoI basis set, which is a simple truncation of ACV6Z at *h* functions, we employed reference-RI as the CABS.

As for the geminal exponent, for VTZ-F12 and VQZ-F12 we set $\gamma = 1.0$, and for VSZ-F12 $\gamma = 1.2$, as recommended in the literature for these respective basis sets.^{7,8} For the REF-*n* and ACV n Z, a fixed $\gamma = 1.4$ was used throughout as per common

Table 2. TAE (kcal/mol) as a Function of the Basis Set for Some Representative Molecules

basis	MP2	MP2-F12 truncated REF basis sets					differences			extrapolations			
	AV{5,6}Z + d	REF-d	REF-f	REF-g	REF-h	REF-i	Δh^a	Δi^b	{h,i} - {g,h}	{d,f}	{f,g}	{g,h}	{h,i}
BF ₃	496.38	496.45	496.56	496.53	496.52	496.52	-0.01	0.00	0.00	496.58	496.53	496.52	496.52
AlCl ₃	330.07	326.78	329.82	330.35	330.40	330.40	0.05	0.00	-0.01 ₇	330.39	330.46	330.41 ₄	330.39 ₇
S ₄	260.73	252.68	259.49	260.53	260.66	260.67	0.13	0.01	-0.02	260.77	260.74	260.70	260.68
Si ₂ H ₆	526.53	528.99	526.94	526.49	526.36	526.31	-0.13	-0.04	-0.02	526.56	526.39	526.32	526.30
P ₄	308.18	296.18	306.29	307.91	308.14	308.18	0.23	0.04	-0.01	308.20	308.23	308.21	308.20
P ₂	120.44	116.67	119.42	120.26	120.44	120.48	0.18	0.04	0.00	119.94	120.43	120.50	120.50
Cl ₂	64.49	61.80	64.24	64.52	64.55	64.56	0.03	0.01	0.00	64.70	64.57	64.56	64.56
SO ₃	382.96	383.30	382.82	382.61	382.53	382.51	-0.07	-0.02	-0.01	382.73	382.57	382.51	382.50
C ₂ H ₂	414.26	413.81	414.16	414.25	414.26	414.26	0.01	0.00	0.00	414.22	414.26	414.26	414.26
C ₂ H ₄	566.53	567.32	566.64	566.51	566.48	566.47	-0.03	-0.01	0.00	566.52	566.48	566.47	566.47
C ₂ H ₆	712.78	713.87	712.91	712.74	712.70	N/A	-0.04	N/A	N/A	712.73	712.70	712.69	N/A
CO ₂	415.47	415.17	415.47	415.56	415.57	415.57	0.01	0.00	0.00	415.53	415.57	415.57	415.57
N ₂ O	296.09	295.34	295.99	296.17	296.21	296.22	0.04	0.02	0.01	296.11	296.20	296.22	296.23
SiH ₄	318.13	319.74	318.38	318.08	318.00	317.98	-0.08	-0.02	-0.01	318.13	318.02	317.98	317.97
PH ₃	234.51	236.24	234.75	234.46	234.40	234.38	-0.07	-0.02	-0.01	234.47	234.40	234.38	234.37
CH ₄	417.87	418.47	417.93	417.84	417.82	417.81	-0.02	0.00	0.00	417.83	417.82	417.81	417.81
H ₂ O	237.53	237.98	237.63	237.56	237.56	237.56	-0.01	0.00	0.00	237.56	237.55	237.56	237.56

^a Δh = TAE[REF-h] - TAE[REF-g]. ^b Δi = TAE[REF-i] - TAE[REF-h].

practice for large orbital basis sets. (An elevated gamma restricts the geminal to the closer-in part of the cusp.)

Throughout this paper, we will refer to two-point basis set extrapolation using the braces notation, for example, V{T,Q}Z-F12 refers to extrapolation from VTZ-F12 and VQZ-F12 basis sets. See ref 42 for a discussion on how all two-point extrapolation schemes (e.g., refs 43–46) are interrelated.

RESULTS AND DISCUSSION

Convergence for *l*-Saturated Basis Sets through *l* = 6, REF-i. Performance statistics with truncations of the large REF-i basis set at different angular momenta can be found in Table 1. We were able to obtain TAEs for all 96 species in W4-08 through REF-h, plus REF-i for all species except six: B₂H₆, C₂H₆, CH₃NH₂, CH₂NH₂, CH₃NH, and NCCN (dicyanogen).

As mentioned in the introduction, according to Kutzelnigg and Morgan,¹¹ the *l*-saturated basis set convergence behavior in an R12 calculation, for a closed-shell pair energy, should asymptotically be $\propto L^{-7}$. Is this indeed the case here? One simple test would be to consider the RMS difference between MP2-F12 atomization energies obtained by $A + B \cdot L^{-7}$ extrapolation from the REF-{g,h} basis set pair with those obtained in the same manner from the REF-{h,i} pair. As can be seen in Table 1, the RMS difference between these two columns is just 0.006 kcal/mol. We obtain the same value to three decimal places if we minimize RMSD with respect to the REF-{g,h} extrapolation exponent, for which we find 6.514 as the optimum value. Both observations indicate that for these large *l*-saturated basis sets we are essentially in the $\propto L^{-7}$ regime (note that even for REF-{fg} we already obtain 6.232 as the optimum extrapolation exponent). Incidentally, they also suggest that the MP2-F12/REF-{h,i} values are as close as we can reasonably hope to get to a CBS limit reference. The largest individual differences are for cyclic S₄, 0.020 kcal/mol, and Si₂H₆, -0.020 kcal/mol, followed by 0.017 kcal/mol for AlCl₃, 0.0152 kcal/mol for N₂, and 0.012 kcal/mol for CS₂, SiH₄, and N₂O. Convergence for some representative molecules is summarized in Table 2

Using MP2-F12/REF-{*l*-1,*l*} extrapolation, and minimizing RMSD with respect to the extrapolation exponents, we obtain REF-{d,f} 0.13, REF-{f,g} 0.027, and as already mentioned REF-{g,h} 0.006 kcal/mol; with the respective exponents 4.543, 6.232, and 6.514.

Let us now consider the TAE increments Δh = TAE[MP2-F12/REF-h] - TAE[MP2-F12/REF-g] and Δi = TAE[MP2-F12/REF-i] - TAE[MP2-F12/REF-h]. The RMS Δh = 0.046 kcal/mol, but individual values can reach as high as 0.23 kcal/mol for P₄, 0.18 kcal/mol for P₂, and 0.13 kcal/mol for S₄. Δi is much smaller, 0.011 kcal/mol RMS, but for P₄ and P₂ it reaches 0.042 and 0.039 kcal/mol, respectively. The latter are definitely amounts of interest for high-accuracy electronic structure calculations (as the MP2-F12 basis set incompleteness error is at least a semiquantitative indication of what the corresponding CCSD(T)-F12 error would be). For some perspective, however, the corresponding numbers for *orbital-only* MP2 are RMS(Δh) = 1.01 and RMS(Δi) = 0.43 kcal/mol, with the largest individual values (again for P₄) being 3.30 and 1.57 kcal/mol, respectively, followed by S₄, 2.63 and 1.13 kcal/mol. It is thus clear that MP2-F12 Δi values are 1–1.5 orders of magnitude smaller, and that basis sets convergence has essentially been achieved by the time one gets to REF-h. For the anomalous cases of P₂ and P₄, the unusually slow basis set convergence has been documented in detail by Persson and Taylor⁴⁷ (see also Karton and Martin⁴⁸). And even for those, L^{-7} basis set extrapolation can clearly “fill in the cracks”: the REF-{h,i} - REF-{g,h} difference for P₄ is just 0.011 kcal/mol, while that for P₂ vanishes entirely. We conclude that, at least for REF-*l* *l* saturated basis sets, there appears to be no compelling need to go beyond *h* functions in F12 calculations. This is good news, of course, for users of F12 correlation codes in program suites such as MOLPRO that do not permit going beyond *i* functions in the auxiliary basis sets (i.e., beyond *h* functions in the orbital basis set).

The slower basis set convergence for multiple-second-row species like P₂, P₄, S₃, and AlCl₃ compared to their isovalent first-row counterparts N₂, N₄, O₃, and BF₃, respectively, can be rationalized to some degree in terms of the lower-lying 3d (and, to a lesser degree, 4f orbitals). This is probably best

Table 3. NBO Angular Momentum Populations at the HF/cc-pV(Q+d)Z and CCSD(T)/cc-pV(Q+d)Z Levels for Selected Molecules^a

		HF/aug-cc-pV(Q+d)Z			CCSD(T)/aug-cc-pV(Q+d)Z		
		<i>d</i>	<i>f</i>	<i>g</i>	<i>d</i>	<i>f</i>	<i>g</i>
N ₂	N	0.02493	0.00186	0.00047	0.04513	0.00509	0.00110
P ₂	P	0.05648	0.00407	0.00127	0.11985	0.01390	0.00295
N ₄	N	0.02957	0.00297	0.00177	0.05414	0.00719	0.00322
P ₄	P	0.07726	0.00759	0.00231	0.14830	0.01982	0.00591
F ₂	F	0.00417	0.00036	0.00008	0.03159	0.00442	0.00079
Cl ₂	Cl	0.02517	0.00232	0.00029	0.13406	0.01664	0.00315
ClF	Cl	0.02472	0.00114	0.00009	0.12730	0.01451	0.00250
	F	0.01462	0.00159	0.00014	0.04186	0.00607	0.00105
BF ₃	B	0.01056	0.00148	0.00133	0.02739	0.00487	0.00227
	F	0.01533	0.00089	0.00014	0.04272	0.00457	0.00090
AlF ₃	Al	0.03366	0.00374	0.00131	0.05659	0.00763	0.0020
	F	0.01551	0.00055	0.00005	0.04518	0.00445	0.00092
AlCl ₃	Al	0.04607	0.00326	0.00126	0.07284	0.01325	0.00539
	Cl	0.02818	0.00199	0.00033	0.14337	0.01487	0.00303
O ₃	O _{center}	0.02316	0.00262	0.00139	0.05121	0.00824	0.00280
	O _{arm}	0.00932	0.00077	0.00016	0.03595	0.00464	0.00092
SO ₂	S	0.13859	0.00462	0.00158	0.20438	0.01357	0.00340
	O	0.05272	0.00284	0.00037	0.07735	0.00736	0.00135
S ₃	S _{center}	0.13475	0.00947	0.00350	0.21280	0.02570	0.00712
	S _{arm}	0.03427	0.00290	0.00042	0.12586	0.01544	0.00274
CF ₂	C	0.01101	0.00076	0.00035	0.03559	0.00379	0.00106
	F	0.01858	0.00144	0.0002	0.04511	0.00540	0.00106
CCl ₂	C	0.02856	0.00389	0.00247	0.06138	0.01049	0.00395
	Cl	0.02118	0.00187	0.00032	0.12422	0.01451	0.00294
SO ₃	S	0.20747	0.00753	0.00531	0.26897	0.01818	0.00714
	O	0.04415	0.00249	0.00039	0.06929	0.00673	0.00128
S ₄	S _{bridge}	0.08992	0.00638	0.00186	0.17087	0.02129	0.00515
	S _{apex}	0.03694	0.00354	0.00058	0.13287	0.01680	0.00311
F ⁻		0.0	0.0	0.0	0.03380	0.00428	0.00086
Cl ⁻		0.0	0.0	0.0	0.12942	0.01480	0.00335
HF	F	0.00987	0.00049	0.00006	0.03680	0.00404	0.00078
HCl	Cl	0.01563	0.00089	0.00006	0.12527	0.01291	0.00252

^aPopulations refer to unique atoms (e.g., to one of the four equivalent N atoms in tetrahedral N₄). CCSD(T)/cc-pVQZ geometry for N₄, *r*_{NN} = 1.4551 Å, was taken from ref 49.

illustrated by considering the *d*, *f*, and *g* populations in a natural population analysis (NPA),⁵⁰ presented in Table 3 for selected molecules at the HF/AVQZ+d and CCSD(T)/AVQZ+d levels. One sees a high *d* population already at the HF level for cases like SO₃, which is a paradigmatic example of “inner polarization” in which the oxygen lone pairs back-donate into the empty 3*d* of sulfur (and similarly for other second row elements in high oxidation states; see ref 51 and references therein), which thereby becomes an ‘honorary valence orbital of the second kind’.⁵² It should be noted that this is primarily an SCF-level effect, and hence the increase in 3*d* population upon introducing correlation is quite modest in comparison. For cases like P₂ and P₄, however, this effect is clearly not operative—one does see a significant *d* population even at the HF level, but it is much enhanced by correlation, especially when compared to the isovalent first-row species N₂ and N₄. Moreover, this is not just limited to the *d* orbitals: natural orbital occupations for *f* and *g* shells clearly decay more slowly for the second-row species than for their first-row cognates. Similar observations can be made for Cl₂ vs F₂, S₃ vs O₃, and the like.

cc-pVnZ-F12 and Related Basis Sets. How does the cc-pVnZ-F12 series perform compared to the REF- $\{h,i\}$ basis set

limit estimate? RMSDs are 1.44, 0.33, 0.084, and 0.044 for *n* = D,T,Q,S, respectively. The latter is close to the “no extrapolation required” goal, but there is still some room for improvement in high-accuracy thermochemistry applications, where one would like a 3σ = 0.1 kcal/mol error bar. AVTZ-F12 performs only marginally better (0.31 kcal/mol) than the underlying VTZ-F12, while AVQZ-F12, at 0.063 kcal/mol, does represent a modest gain over VQZ-F12. It was previously shown^{8,12} that the aug-cc-pwCVSZ core–valence basis set (awCVSZ for short) performs remarkably well for F12 calculations, despite not being developed for this purpose at all: the RMSD = 0.030 kcal/mol we find here is consistent with that observation. (Expanding the hydrogen basis set from AVSZ to AV6Z yields the same performance to within statistical noise, RMSD = 0.033 kcal/mol.) The underlying valence-correlation basis set, aug-cc-pVSZ or AVSZ, has a higher RMSD = 0.055 kcal/mol; adding some radial flexibility by instead using AV6Z(h), that is, aug-cc-pV6Z with the highest angular momentum *i* removed, reduces RMSD slightly to 0.041 kcal/mol. This however is cut in half when the *i* functions are restored, RMSD = 0.022 kcal/mol for AV6Z. By comparing the two columns of numbers, we find several molecules where *i* function contributions deceptively seem to

reach 0.1 kcal/mol, such as P_4 , S_4 , and $AlCl_3$, plus another 0.07 kcal/mol for S_3 . However, we have already established with the REF-h and REF-i basis set that the true i contribution is much smaller; it is a well-known basis set convergence phenomenon (see, e.g., the older review of basis sets by Davidson and Feller⁵³) that insufficiently saturating the basis in lower angular momenta can exaggerate the impact of the highest angular momentum (through basis set superposition error). If we instead compare the core–valence versions of these basis sets, the i -increments are substantially reduced, with P_4 and P_2 now remaining as the principal outliers. Finally, if one wants a single “prepackaged” basis set without extrapolation, ACV6Z has the smallest RMSD (0.019 kcal/mol) of them all.

A Comment about Basis Set Extrapolation. We have considered three sets of extrapolation exponents:

1. From the literature, as optimized for the very small training set of Hill et al.³¹ (that paper itself for $V\{D,T\}Z$ -F12 and $V\{T,Q\}Z$ -F12), ref 54 for $V\{Q,S\}Z$ -F12, and ref 55 for $AV\{T,Q\}Z$ -F12.
2. By minimization of RMSD from REF- $\{h,i\}$ total energies for such W4-08 species for which we have REF-i energies.
3. By minimization of RMSD from REF- $\{h,i\}$ TAEs for the same species.

The three sets of extrapolation exponents are compared in Table 4 below, as are the RMSDs for total atomization energies

Table 4. Two-Point Extrapolation Exponents and RMSD from REF- $\{h,i\}$ (kcal/mol) for Different Basis Set Pairs

	$V\{D,T\}Z$ - F12	$V\{T,Q\}Z$ - F12	$AV\{T,Q\}Z$ - F12	$V\{Q,S\}Z$ - F12
Extrapolation Exponents				
lit. ^{31,54,55}	3.0878	4.3548	4.6324	5.0723
W4-08 E_{total}	3.45	5.03	5.64	5.27
W4-08 TAE	3.80	5.11	5.97	4.36
RMSD with These Exponents (kcal/mol)				
lit.	0.178	0.046	0.046	0.034
W4-08 E_{total}	0.123	0.039	0.030	0.034
W4-08 TAE	0.107	0.038	0.029	0.033
regular MP2 for comparison				
	$AV\{D,T\}Z$ +d	$AV\{T,Q\}Z$ +d	$AV\{Q,S\}Z$ +d	$AV\{5,6\}Z$ +d
Extrapolation Exponents				
lit. ^a	2.136	2.531	2.740	2.835
W4-08 TAE	2.571	2.963	2.908	2.910
RMSD with These Exponents (kcal/mol)				
lit. ^a	3.386	1.062	0.272	0.118
W4-08 TAE	1.800	0.458	0.216	0.111

^aExtrapolation exponents from Table 8 of ref 31.

with them. The TAE-optimized exponent $V\{Q,S\}Z$ -F12 appears anomalously small, but this is an artifact of the very flat surface there, which precludes a “clean” optimization. E_{total} gives a somewhat better defined minimum, though even there the surface is quite flat. In terms of RMSD, for $V\{Q,S\}Z$ -F12 all three possible exponents yield the same error. For $AV\{T,Q\}Z$ -F12, both optimized values from the present work yield superior RMSDs to the value from ref 55; for VTZ-F12 the same holds, although the difference here is quite modest. Finally, for the $V\{D,T\}Z$ -F12 pair, the two optimized values from the present work are clearly superior to the one

from Hill et al.³¹ For reasons of numerical stability (notably because it eliminates the anomaly for $V\{Q,S\}Z$ -F12), we favor the set optimized from total energies. The difference in RMSD is negligible; however, this is good news, since ideally one wants to be in a scenario where basis set extrapolation is only a minor component of the final result and is relatively insensitive to details of the extrapolation procedure. Note that, while all basis set pairs considered here are clearly some distance away from the asymptotic L^{-7} regime, the exponents *do* increase in that direction as L gets larger.

For some perspective, we add the RMSDs for regular MP2 with aug-cc-pV(L-1+d)Z and aug-cc-pV(L+d)Z basis sets. It is sobering to see that even $AV\{5,6\}Z$ +d only reaches the accuracy level of $V\{D,T\}Z$ -F12, and that $V\{T,Q\}Z$ -F12 already markedly exceeds it.

What Do These Results Imply for CCSD-F12 and CCSD(T)-F12? At the request of a reviewer, we will address what we may infer for the basis set convergence of higher-level methods like CCSD(T)(F12*) or CCSD(T)-F12b.

First of all, the treatment of parenthetical triples (T) does not benefit in any way from the F12 treatment,⁵⁶ so the convergence of that contribution is effectively the same as in an orbital calculation. The latter has been addressed in great detail in a recent book chapter by one of us:⁵⁷ suffice to say here that basis set convergence of (T) with angular momentum is actually fairly rapid, and that radial flexibility of the basis set is actually more important than angular flexibility.

This leaves us then with CCSD-F12, or rather with the various practical approximations to it such as CCSD-F12b,⁵⁸ $CCSD_{F12}$,^{59,60} and $CCSD(F12^*)$.⁶¹ Of these, $CCSD(F12^*)$ has been shown⁶² to be the most rigorous approximation that still is computationally feasible, while CCSD-F12b is widely used owing to its implementation for both closed-shell and open-shell cases in the MOLPRO¹⁶ program system.

The basis set convergence of differences between different CCSD-F12 approximations has been studied in great detail in ref 12. In a nutshell: if correlation is predominantly dynamic then these differences decay quickly with increasing basis sets, but even moderate amounts of static correlation can cause nontrivial differences (as large as 0.3 kcal/mol) to persist even for *spdfgh* basis sets.

As additional complications, all of the available (to us) implementations of approximate CCSD-F12 methods require DFMP2 and JKFit auxiliary basis sets (further complicating comparisons), and the only $CCSD(F12^*)$ implementation at our disposal with which we were able to get enough calculations in REF- h basis sets to converge, i.e., that in MOLPRO, is limited to closed shell. Hence we resorted to calculating a number of closed-shell reaction energies instead. The relevant basis set increments are reported in Table 5. Auxiliary basis sets were taken from the Supporting Information of ref 31.

The basis set increments given there for g and h layers are obtained directly. For the i layer, the ORCA MP2-F12 values are calculated directly while the MOLPRO values are obtained by $L^{-\alpha}$ extrapolation. (It can be easily shown that an estimate for the next basis set increment after $E(L) - E(L - 1)$ is given by the following formula:)

$$E(L + 1) - E(L) \approx [E(L) - E(L - 1)] \frac{1 - \left(\frac{L}{L+1}\right)^\alpha}{\left(\frac{L}{L-1}\right)^\alpha - 1} \quad (2)$$

Table 5. Comparison of REF-*n* Basis Set Increments (kcal/mol) for a Number of Closed-Shell Reactions at the MP2-F12, CCSD-F12b, and CCSD(F12*) Levels^a

		ORCA		MOLPRO (includes MP2Fit and JKFit)		
		MP2-F12	MP2-F12	CCSD(F12*)	CCSD-F12b	(F12*)-F12b
$P_4 \rightarrow 2P_2$	Δg	0.054	0.066	-0.014	-0.125	0.111
	Δh	0.132	0.108	0.006	-0.042	0.048
	Δi	0.036	0.026(5)	0.001(0)	0.010(2)	-0.009(2)
$2HF \rightarrow F_2 + H_2$	Δg	0.078	0.076	0.089	-0.014	0.103
	Δh	0.011	0.008	0.021	-0.012	0.033
	Δi	0.002	0.002(0)	0.005(1)	0.003(1)	0.002(1)
$CO + H_2O \rightarrow CO_2 + H_2$	Δg	0.127	0.126	0.180	0.317	-0.137
	Δh	0.017	0.014	0.011	0.036	-0.025
	Δi	0.003	0.003(1)	0.003(1)	0.009(2)	-0.006(2)
$N_2 + H_2O \rightarrow N_2O + H_2$	Δg	0.139	0.14	0.173	0.245	-0.072
	Δh	0.022	0.015	0.014	0.022	-0.008
	Δi	0.002	0.004(1)	0.003(1)	0.005(1)	-0.002(0)
$3H_2S \rightarrow S_3 + 3H_2$	Δg	2.026	2.038	1.716	2.013	-0.297
	Δh	0.380	0.373	0.15	0.213	-0.063
	Δi	0.082	0.090(19)	0.036(7)	0.051(11)	-0.015(3)
$H_2S + 2H_2O \rightarrow SO_2 + 3H_2$	Δg	0.354	0.359	0.433	0.626	-0.193
	Δh	0.045	0.038	0.052	0.099	-0.047
	Δi	0.006	0.009(2)	0.012(3)	0.024(5)	-0.012(3)
$2PH_3 \rightarrow P_2 + 3H_2$	Δg	1.420	1.424	0.923	1.056	-0.133
	Δh	0.315	0.31	0.085	0.109	-0.024
	Δi	0.075	0.075(16)	0.021(4)	0.026(5)	-0.005(1)
$4PH_3 \rightarrow P_4 + 6H_2$	Δg	2.786	2.782	1.859	2.236	-0.377
	Δh	0.499	0.511	0.165	0.259	-0.094
	Δi	0.113	0.123(26)	0.040(8)	0.063(13)	-0.023(5)
$3H_2O \rightarrow O_3 + 3H_2$	Δg	0.229	0.233	0.243	0.137	0.106
	Δh	0.039	0.032	0.042	-0.013	0.055
	Δi	0.008	0.008(2)	0.010(2)	0.003(1)	0.007(2)

^aValues that do not include an uncertainty interval in parentheses were calculated directly. Values that do include such an uncertainty interval were estimated as the average between L^{-7} (ideal case) and L^{-5} (pessimistic scenario) extrapolation, with one-half the distance between the two values taken as the uncertainty interval.

For the sake of the estimate, we considered $\alpha = 7$ (the asymptotic convergence rate) as a best-case scenario, and $\alpha = 5$ as a worst-case scenario (for VQZ-F12 and VSZ-F12, we have previously found⁵⁴ the intermediate value $\alpha \approx 6$). The average of both extrapolated values, plus or minus half the difference between them, is taken as our approximate estimate.

As can be seen in Table 5, basis set convergence of especially CCSD(F12*) actually seems, depending on the reaction, comparable to or faster than that of MP2-F12. And for those reactions where Δi is still somewhat significant at the MP2-F12 level, the corresponding estimated CCSD-F12b and especially CCSD(F12*) increments are actually up to 3 times smaller.

We hence conclude that our conclusions about the lack of necessity of *i* functions in MP2-F12 calculations also apply to CCSD-F12b, CCSD(F12*), and other approximations to CCSD-F12.

As an aside, we note that the CCSD(F12*) – CCSD-F12b differences, while nontrivial, are conspicuously smaller than what was observed for cc-pVQZ-F12, cc-pVSZ-F12, and aug-cc-pwCVSZ in ref 12. Clearly, here too, the greater radial flexibility of the REF-*n* basis sets puts them at an advantage, even as they are unwieldy for practical production calculations.

CONCLUSIONS

We may conclude that for basis sets that are adequately saturated in the angular momenta represented, the contribution of *i* functions to total atomization energies is minimal

(about 0.01 kcal/mol RMS): the largest individual contributions we have found here only reach 0.04 kcal/mol (for P_4 and P_2), and even that is adequately captured by L^{-7} extrapolation from REF- $\{g,h\}$, which is closer than 0.01 kcal/mol RMS to the CBS limit. (In this *L* region, basis set convergence behavior for MP2-F12 is found to be quite close to the asymptotic¹¹ L^{-7} .) Comparison of AV6Z with and without *i* functions indicates more significant *i* contributions, owing to insufficient radial saturation. The *h* contribution is more significant, reaching 0.23 kcal/mol for P_4 . REF- $\{g,h\}$ extrapolation is within less than 0.01 kcal/mol RMS of REF- $\{h,i\}$, the largest single difference being 0.02 kcal/mol for S_4 . This means that the REF- $\{g,h\}$ L^{-7} extrapolation is an acceptable proxy for the F12 basis set limit, and that *h* functions are sufficient even for highly demanding F12 applications.

If one-parameter extrapolation with an adjustable exponent is permissible, *spdf* and *spdfg* basis sets are adequate, with aug-cc-pV{T,Q}Z-F12 yielding the RMSD = 0.03 kcal/mol.

Finally, the somewhat slower basis set convergence in the second row—especially when there are multiple adjacent such elements—can be rationalized to some degree in terms of lower-lying *3d* and *4f* orbitals.

A limited investigation for closed-shell reactions indicates that basis set convergence of CCSD(F12*) and CCSD-F12b is comparable to or faster than that of MP2-F12, and that hence our conclusions about the relative insignificance of *i*-function contributions apply to F12 methods more broadly.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.2c02494>.

Spreadsheet with all raw energies and total atomization energies (XLSX)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Work on this paper was supported in part by the Israel Science Foundation (Grant 1969/20) and by the Minerva Foundation (Grant 2020/05). We thank Prof. Amir Karton for helpful discussions. This paper is dedicated to Prof. Peter R. Taylor in honor of his 70th birthday, and of his landmark contributions (e.g., refs 6 and 63–65) to the theory and practice of explicitly correlated quantum chemistry.

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