Optimized complementary auxiliary basis sets for explicitly correlated methods: aug-cc-pVnZ orbital basis sets

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ABSTRACT

Compact auxiliary basis sets matched to the standard aug-cc-pVnZ and aug-cc-pV(n + d)Z orbital basis sets have been developed for use as resolution-of-the-identity (RI) sets in explicitly correlated F12 calculations. The resulting RI errors from using these sets have been benchmarked in calculations of atomization energies and electron affinities for a number of representative small molecules. These errors were always more than an order of magnitude smaller than the residual basis set error for a given choice of orbital basis set.

1. Introduction

Recent advances in explicitly correlated electronic structure theory, most notably MP2-F12 and CCSD(T)-F12 in which non-linear functions of the interelectronic coordinate are included in the wave function [1–10], exhibit dramatic improvements in the basis set convergence of electron correlation energies compared to conventional calculations. One of the principal difficulties in these new methods is the necessity of computing numerous three- and four-electron integrals. This can be largely avoided, however, by invoking the resolution-of-the-identity (RI) approximation, so that these many-electron integrals can be computed as products of no more than two-electron integrals, which can be calculated very efficiently [11]. The use of auxiliary basis sets (ABS) for the RI, as pioneered by Klopper and Samson for the MP2-R12 method [12], permitted the use of much smaller orbital basis sets (OBS) than previous implementations in which the OBS was used for the RI. This allowed for significant computational savings while retaining the accuracy of the method. This, of course, necessitates choosing a suitable auxiliary RI basis set for a given OBS, increasing the complexity of the method to the end user. The goal of the present work is to develop standard RI basis sets for explicitly correlated methods that are matched to the commonly-used correlation consistent-style orbital basis sets.

In the previous work of Valeev [13], it was noted that the RI approximation is most accurate when the ABS explicitly contains the OBS, and the resulting complementary auxiliary basis set (CABS) approach involves constructing the union of a given OBS with the ABS and deleting any linearly dependent functions for use as the RI basis. Recently CABS-based auxiliary basis sets, de-noted OptRI, were reported by our group that were matched to the cc-pVnZ-F12 series (n = D, T, Q) of orbital basis sets [14]. These exhibited small, well-defined RI errors, and since only the functions complementary to the orbital set were optimized, the resulting RI sets were relatively compact with improved numerical stability in molecular calculations. This latter quality was recently found to lead to numerically stable vibrational frequencies in the work of Rauhut et al. [15], especially when larger orbital basis sets were used. In this work, we report the development of analogous OptRI basis sets matched to the widely used aug-cc-pVnZ (H, He, B–Ne) and aug-cc-pV(n + d)Z (Al–Ar) basis sets (n = D, T, Q, 5) of Dunning and co-workers. Since these orbital basis sets include full shells of diffuse functions for the accurate calculation of weak interactions and negative ions (the cc-pVnZ-F12 sets include only diffuse s and p functions), the resulting OptRI auxiliary basis sets of this work have also been benchmarked in calculations of atomic and molecular electron affinities, as well as the binding energies of rare gas dimers. As in our previous OptRI work the atomization energies of numerous strongly bound molecules are also considered in the evaluation of the RI errors.

2. Methodology

The auxiliary basis sets of the present work were developed in a nearly identical manner to those previously reported for the cc-pVnZ-F12 orbital basis sets [14]. Analogous to the cc-pVnZ-F12/OptRI auxiliary basis sets, the present sets are designed for use in explicitly correlated calculations utilizing the CABS+ method of Valeev [13], but specifically in conjunction with the aug-cc-pVnZ and aug-cc-pV(n + d)Z orbital basis sets [16–19], the latter denoted collectively in this work as AVnZ. The uncontracted Gaussian functions that form the AVnZ/OptRI auxiliary sets were optimized by minimizing the functional

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$$\delta\mathrm{RI} = \sum_{ij} \frac{(V_{ij,ij}^{RI} - V_{ij,ij}^{RI_{ref}})^2}{V_{ij,ij}^{RI_{ref}}} + \frac{(B_{ij,ij}^{RI} - B_{ij,ij}^{RI_{ref}})^2}{B_{ij,ij}^{RI_{ref}}}, \qquad (1)$$

which involves the diagonal elements of the **V** and **B** matrices arising in MP2-F12 theory [10,12]. The reference values appearing in Eq. (1), i.e., $V_{ij,ij}^{RI_{ref}}$ and $B_{ij,ij}^{RI_{ref}}$, are calculated using a large reference RI basis set as described below. Only the valence electrons were correlated and the 3C ansatz [10,20] as implemented in the MOLPRO suite of *ab initio* programs [21] was utilized throughout. The optimal geminal exponents β, as previously determined in Ref. [22] (1.1 for AVDZ, 1.2 for AVTZ and 1.4 for AVQZ and AV5Z) were used. The reference RI basis set was the same as used in Ref. [14], consisting of the uncontracted $18s13p$ (B–Ne) and $20s15p$ (Al–Ar) primitive sets of Partridge [23,24] combined with the *dfghi* functions from the AV6Z basis sets [25,26]. Furthermore, a set of s and p diffuse functions, as well as 2 (3) tight d and 1 (2) tight f functions, were added for B–Ne (Al–Ar) in an even-tempered manner. The reference ABS for hydrogen consisted of the uncontracted aug-cc-pV6Z basis set without the h-type functions. A single tight p function was then added to this set. The choices of density fitting basis sets, CABS thresholds, and other details were identical to the previous cc-pVnZ-F12/OptRI work [14].

3. Results and discussion

3.1. Number and type of functions in the ABS

As can be seen in Table 1, the AVnZ/OptRI auxiliary basis sets are relatively small, mainly since they are explicitly based on the CABS approach and optimally utilize the underlying orbital basis sets. This is especially evident for the QZ and 5Z sets as compared to the MP2FIT basis sets of Hättig and co-workers [27,28]. While neither were originally designed for this purpose, both the JKFIT sets of Weigend [29] and the MP2FIT sets have been commonly-used in explicitly correlated calculations as RI auxiliary sets. One noticeable difference between AVDZ/OptRI and AVDZ/MP2FIT is the presence of a g-type function in the former. (The VDZ/JKFIT set has not been reported, hence its absence from Table 1.) As discussed below, this was found to signficantly decrease the RI error with this orbital basis set. The cc-pVDZ-F12/OptRI sets also include a g-type function for B–Ne and Al–Ar. A comparison with the sizes of the previously reported cc-pVnZ-F12/OptRI basis sets [14] is worth making here, since the AVnZ/OptRI basis sets are, in general, slightly larger. In the construction of the cc-pVnZ-F12 orbital basis sets [22], not only were the Hartree–Fock s and p functions taken from the aug-cc-pV(n + 1)Z basis sets, but the contraction scheme was modified slightly to yield an additional tight p function. This extra function was found to be of significant importance in explicitly correlated calculations in Ref. [22], and its omission from the

AVnZ/OptRI basis sets had a noticeable impact on the RI error in this work. As such, all the AVnZ/OptRI basis sets contain five p functions, compared to four in the case of the cc-pVnZ-F12/OptRI basis sets. Furthermore, for each orbital set apart from AVTZ, it was necessary to augment the auxiliary basis set with a tight s function for the second row elements and, for AV5Z, a tight d function as well. In contrast, the existence of diffuse functions of high angular momentum in the AVnZ orbital basis sets did not lead to a need to add additional diffuse auxiliary basis functions, although an exception to this trend was the Ne dimer. This case is discussed in detail below.

3.2. Correlation energies, atomization energies, and electron affinities

A number of benchmark calculations have been carried out to calibrate the RI errors (relative to calculations with the reference RI auxiliary basis) of the new OptRI auxiliary sets. These included the atomization energies of a total of 49 small molecules: Al_2, AlH, AlN, AlP, B_2, BH_3, BN, C_2, C_2H_4, CH_2 ($^1A_1$), CH_4, Cl_2, CO, CO_2, CS_2, F_2, H_2, H_2CO, H_2CS, H_2O, H_2O_2, H_2S, H_2S_2, HCl, HCN, HF, N_2, N_2H_2, NH_3, O_2, P_2, PH_3, PF_3, PN, S_2, Si_2, SiH_2 ($^1A_1$), SiH_4, SiO, SO, SO_2, SiS, CN, OH, SH, PO, He_2, Ne_2, Ar_2, most of which were used in the previous cc-pVnZ-F12/OptRI work. In addition, a number of atomic and molecular electron affinities were also calculated: C_2, CH_2, CN, OH, PO, SH, SiH_2, SO_2, B, C, O, F, Al, Si, P, S, Cl, since the aug-cc-pVnZ orbital basis sets are generally recommended over cc-pVnZ-F12 in these cases. In order to put the auxiliary basis set errors into perspective, the complete basis set (CBS) limits have also been calculated for each property by extrapolating AV5Z and AV6Z conventional MP2 correlation energies with the usual n^{-3} two-point CBS formula [30,31]. To be consistent with the earlier OptRI benchmarks, the molecular geometries of the neutral species have all been optimized at the CCSD(T)/cc-pCVQZ level of theory [32–34] (all electrons correlated except the 1s pair in 2nd row atoms), while for the anions and rare gas dimers the aug-cc-pCVQZ basis set was used.

Approximate RI basis set errors in the total MP2 correlation energies are given per correlated electron in Table 2, where the new OptRI results are compared to the analogous JKFIT and MP2FIT values. Compared to the basis set error intrinsic to each orbital basis set,

Table 1
Number and type of functions included in the auxiliary basis sets used in this work.

Basis set	H, He	B–Ne	Al–Ar	Ref.
AVDZ/OptRI	$3s3p2d$	$4s5p4d3f1g$	$5s5p4d3f1g$	This work
AVTZ/OptRI	$3s3p2d1f$	$4s5p4d3f2g$	$4s5p4d3f2g$	This work
AVQZ/OptRI	$4s4p3d2f2g$	$4s5p4d3f2g1h$	$5s5p4d3f2g1h$	This work
AV5Z/OptRI	$4s4p3d3f2g1h$	$4s5p4d3f3g2h1i$	$5s5p5d3f3g2h1i$	This work
Reference	$11s7p5d4f3g$	$19s14p8d6f4g3h2i$	$21s16p9d7f4g3h2i$	This work
VTZ/JKFIT	$4s3p2d1f$	$10s7p5d2f1g$	$13s11p9d3f1g$	[29]
VQZ/JKFIT	$4s3p2d2f1g$	$10s7p5d3f2g1h$	$13s11p9d4f2g1h$	[29]
V5Z/JKFIT	$4s3p4d2f1g$	$10s7p5d4f3g2h1i$	$13s11p9d4f3g2h1i$	[29]
AVDZ/MP2FIT	$4s3p2d$	$8s6p5d3f$	$10s8p6d4f$	[28]
AVTZ/MP2FIT	$5s4p3d2f$	$9s7p6d4f2g$	$11s9p8d6f3g$	[28]
AVQZ/MP2FIT	$6s5p4d3f2g$	$9s8p7d6f4g2h$	$12s10p9d7f4g2h$	[28]
AV5Z/MP2FIT	$7s6p5d4f3g2h$	$11s9p8d7f5g4h2i$	$13s12p10d8f6g4h2i$	[27]

Table 2
RI errors per correlated electron (relative to the reference ABS) in the MP2-F12/3C correlation energies with different ABSs for 49 molecules and their associated atoms. All values are in μE_h (MAD is the mean absolute deviation, σ is the standard deviation, and MAX is the maximum absolute deviation).

Orbital basis	Auxiliary basis	MAD	σ	MAX
aug-cc-pVDZ	Reference[a]	(721)	(286)	(1431)
	AVDZ/OptRI	6.5	8.7	25.5
	AVDZ/OptRI($spdf$)	17.6	23.4	81.5
	VTZ/JKFIT	19.7	23.3	86.7
	AVDZ/MP2FIT	19.2	23.9	62.5
aug-cc-pVTZ	Reference[a]	(273)	(132)	(693)
	AVTZ/OptRI	1.9	2.3	6.5
	VTZ/JKFIT	4.6	6.7	20.9
	AVTZ/MP2FIT	2.6	2.2	9.0
aug-cc-pVQZ	Reference[a]	(89)	(67)	(347)
	AVQZ/OptRI	0.8	0.8	3.2
	VQZ/JKFIT	0.8	0.5	2.6
	AVQZ/MP2FIT	0.7	0.5	2.0
aug-cc-pV5Z	Reference[a]	(18)	(32)	(152)
	AV5Z/OptRI	0.4	0.4	2.0
	V5Z/JKFIT	0.2	0.3	1.5
	AV5Z/MP2FIT	0.2	0.3	1.4

[a] Basis set truncation errors per correlated electron for this combination of orbital basis set and the reference ABS are shown in parentheses. The CBS limits were defined by extrapolation of the conventional MP2 correlation energies with aug-cc-pV5Z and aug-cc-pV6Z basis sets. See the text.

Table 3
RI errors (relative to the reference ABS) in the correlation contributions to the MP2-F12/3C atomization energies obtained with different ABSs for the 49 molecule test set. All values are in kcal/mol. (MAD is the mean absolute deviation, σ is the standard deviation, and MAX is the maximum absolute deviation).

Orbital basis	Auxiliary basis	MAD	σ	MAX
aug-cc-pVDZ	Reference[a]	(0.82)	(1.12)	(4.67)
	AVDZ/OptRI	0.06	0.08	0.32
	AVDZ/OptRI(*spdf*)	0.16	0.21	0.77
	VTZ/JKFIT	0.08	0.10	0.50
	AVDZ/MP2FIT	0.20	0.21	0.87
aug-cc-pVTZ	Reference[a]	(0.36)	(0.38)	(1.48)
	AVTZ/OptRI	0.01	0.02	0.06
	VTZ/JKFIT	0.03	0.04	0.17
	AVTZ/MP2FIT	0.01	0.02	0.06
aug-cc-pVQZ	Reference[a]	(0.27)	(0.23)	(0.90)
	AVQZ/OptRI	0.004	0.005	0.015
	VQZ/JKFIT	0.002	0.004	0.018
	AVQZ/MP2FIT	0.001	0.001	0.004
aug-cc-pV5Z	Reference[a]	(0.18)	(0.13)	(0.50)
	AV5Z/OptRI	0.002	0.002	0.007
	V5Z/JKFIT	0.001	0.001	0.006
	AV5Z/MP2FIT	0.000	0.000	0.001

[a] Basis set truncation errors (correlation contribution only) for this combination of orbital basis set and the reference ABS are shown in parentheses. The CBS limits were defined by extrapolation of conventional MP2 correlation energies with aug-cc-pV5Z and aug-cc-pV6Z basis sets. See the text.

the RI errors are at least an order of magnitude smaller in all cases. The OptRI results compare very favorably to the RI errors associated with the generally larger JKFIT and MP2FIT auxiliary sets. Also shown in Table 2 are the effects of removing the single *g*-type function present in the AVDZ/OptRI ABS, denoted AVDZ/OptRI (*spdf*). In this case the average and maximum RI errors per correlated electron more than double compared to the full set and are then very similar to those obtained with the AVDZ/MP2FIT basis set, which also does not have any *g* functions at this level. With the AVTZ through AV5Z orbital basis sets, all of the RI errors obtained with OptRI are on the order of just a few μE_h and the maximum errors are about two orders of magnitude smaller than the residual basis set incompleteness errors. It should also be stressed at this point that, as expected, use of the previously reported cc-pVnZ-F12/OptRI auxiliary sets with the AVnZ orbital basis sets lead to errors more an order of magnitude larger than AVnZ/OptRI, since they are no longer complementary to the OBS.

Similar trends are also observed in the RI errors associated with the calculated atomization energies shown in Table 3. These RI errors are also shown as normal distributions in Fig. 1. At the AVDZ level, the *g*-type function in OptRI again plays an important role, decreasing the RI error by more than a factor of two compared to an OptRI with only *spdf* functions. The latter yields errors similar to AVDZ/MP2FIT. With the OptRI sets the maximum RI errors decrease from 0.32 kcal/mol with AVDZ to 0.06 for AVTZ, 0.015 for AVQZ, and 0.007 kcal/mol for AV5Z. In each case these errors are much less than an order of magnitude smaller than the residual basis set errors with these orbital basis sets. An important exception to this behavior, however, was the weakly-bound Ne dimer. At the double-ζ level the RI error in the dissociation energy was 0.16 kcal/mol – not the largest of the test set, but slightly more
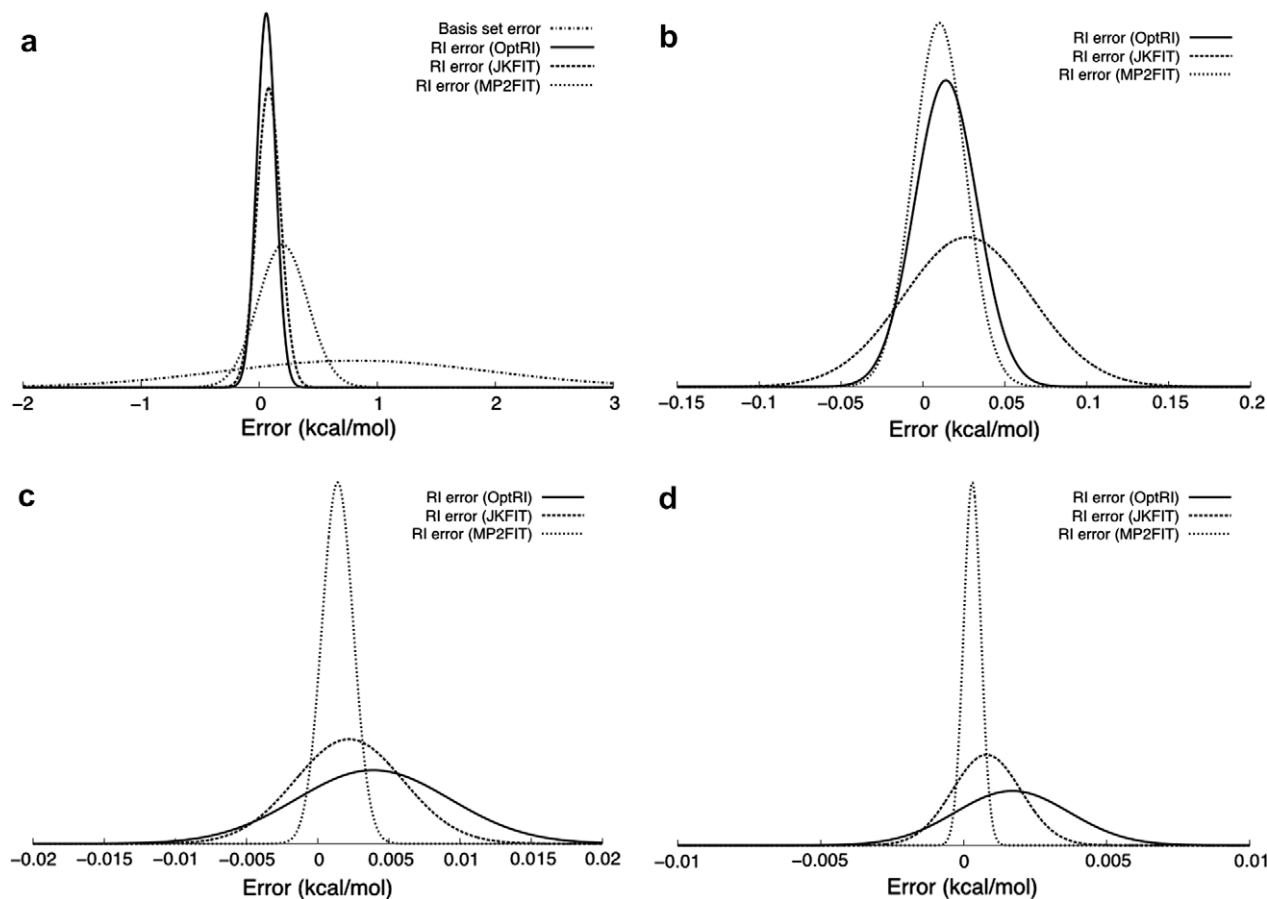

Fig. 1. Basis set and RI errors in the MP2-F12/3C correlation contributions to the atomization energies of a test set of 49 molecules (see the text) using the (a) AVDZ, (b) AVTZ, (c) AVQZ, and (d) AV5Z orbital basis sets. The basis set error distribution is only shown for the AVDZ set since in the other cases it was more than an order of magnitude larger than the average RI errors and was not visible on this scale. RI errors with both the optimized auxiliary basis sets of this work (OptRI), as well as the JKFIT and MP2FIT basis sets of Weigend [12] and Hättig and co-workers, [27,28] respectively, are shown. See also Table 3. The normal distributions are defined by $y(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left\{-\frac{1}{2}\left[\frac{(x-\bar{x})}{\sigma}\right]^2\right\}$.

than half the size of the binding energy itself (correlation contribution only). With the AVTZ basis set the RI error in the correlation energy contribution was also large, 0.07 kcal/mol, which can be compared with 0.001 kcal/mol for He_2 and 0.01 kcal/mol for Ar_2. As such, the atomization energy converges very slowly with respect to the maximum angular momentum in the orbital basis set when the OptRI ABS is used for the Ne dimer. Unlike the results of Tew and Klopper [35] for this species, however, the larger RI errors in this case are not due to partially offsetting errors on both the atom and the dimer. At the AVDZ/OptRI level the RI error in the atom was just 65 μE_h, while that of the dimer was 470 μE_h. After some experimentation it was found that the deficiency in this case was the lack of sufficiently diffuse functions in the OptRI set. Simply adding a single diffuse d and f function to the OptRI AVDZ and AVTZ sets decreased the RI errors to just 0.04 and 0.01 kcal/mol, respectively, and exclusively arose from improvements in the description of the dimer. Adding diffuse d and f functions to the AVDZ and AVTZ OptRI sets for all of the other elements did not, however, have any effect on the RI errors reported in Tables 2–4. Hence adding a few additional diffuse functions to the present OptRI sets are only strongly recommended when the interaction is dominated by very weak interactions.

Perusal of Tables 2–4, as well as Fig. 1c and d, seems to indicate that at the AVQZ and AV5Z levels the OptRI auxiliary sets are not quite as accurate as the analogous MP2FIT ones, although of course calculations with the former do benefit from increased numerical stability since they are complementary to the underlying OBS. The resulting errors, however, are actually very similar to the accuracy of the reference RI basis itself. The convergence of the latter was investigated at the AV5Z level by augmenting the s and p functions of the AV5Z/OptRI set with a large number of higher angular momentum functions that filled the gaps between all the existing functions in the AV5Z orbital basis exponents and also extended these to both more diffuse and tighter exponents in an even-tempered fashion. The resulting reference complementary set of functions: $7p6d5f4g3h$ for H–He, $7d6f5g4h3i$ for B–Ne, and $8d6f5g4h3i$ for Al–Ar, are expected to generate a relatively complete CABS basis for use as the RI. Subsequent calculation of correlation energies and atomization energies with this larger basis as the RI exhibited differences on the order of a few μE_h and thousandths

of a kcal/mol, respectively, compared to the original reference RI. When the OptRI and MP2FIT results are compared to this more accurate RI, OptRI is observed to be slightly more accurate than MP2FIT. Of course, in any event the remaining RI errors are near negligible in either case.

The resulting RI errors for the electron affinities of a few small molecules and atoms are shown in Table 4 (utilizing the original reference RI basis of Table 1). The errors associated with OptRI are analogous to those calculated for the atomization energies and correlation energies. In particular, the addition of diffuse functions to the OptRI sets does not seem to be required for accurate electron affinities, and the OptRI ABSs yield more accurate results than either JKFIT or MP2FIT at the DZ and TZ levels.

4. Conclusions

Compact RI auxiliary basis sets have been optimized to be used in explicitly correlated MP2-F12 or CCSD(T)-F12 calculations with the standard sequences of aug-cc-pVnZ and aug-cc-pV($n + d$)Z orbital basis sets. The resulting OptRI sets have been developed in a CABS framework, which results in only a relatively few number of functions being required since the underlying OBS is fully exploited. The final auxiliary sets were benchmarked in the calculation of atomization energies and electron affinities of a number of small molecules. The errors associated with the use of a number of RI sets were compared to those obtained from an extensive reference ABS. In each case the OptRI sets resulted in RI errors more than an order of magnitude smaller than the basis set error intrinsic to the underlying orbital basis. This is a stringent requirement since with F12 methods the latter is already very small with AVDZ orbital basis sets. As in our previous cc-pVnZ-F12/OptRI work, the present auxiliary sets yield essentially the same accuracies when used in other MP2-F12 methods besides 3C, e.g., the fixed amplitude ansatz, as well in CCSD-F12 calculations. All of the sets of the present work, including diffuse-augmented versions for the rare gas elements, are available for download from the author's website, as well as from the MOLPRO program website.

Table 4
RI errors (relative to the reference ABS) in the correlation contributions to the MP2-F12/3C electron affinities obtained with different ABSs for an 8 mol/8 atom test set. All values are in kcal/mol (MAD is the mean absolute deviation, σ is the standard deviation, and MAX is the maximum absolute deviation).

Orbital basis	Auxiliary basis	MAD	σ	MAX
aug-cc-pVDZ	Reference[a]	(0.73)	(0.40)	(1.65)
	AVDZ/OptRI	0.016	0.021	0.070
	AVDZ/OptRI($spdf$)	0.044	0.035	0.128
	VTZ/JKFIT	0.017	0.025	0.066
	AVDZ/MP2FIT	0.034	0.040	0.128
aug-cc-pVTZ	Reference[a]	(0.19)	(0.10)	(0.36)
	AVTZ/OptRI	0.005	0.003	0.009
	VTZ/JKFIT	0.005	0.007	0.022
	AVTZ/MP2FIT	0.005	0.005	0.015
aug-cc-pVQZ	Reference[a]	(0.06)	(0.06)	(0.13)
	AVQZ/OptRI	0.002	0.002	0.005
	VQZ/JKFIT	0.002	0.001	0.005
	AVQZ/MP2FIT	0.001	0.001	0.002
aug-cc-pV5Z	Reference[a]	(0.05)	(0.05)	(0.15)
	AV5Z/OptRI	0.001	0.001	0.003
	V5Z/JKFIT	0.000	0.000	0.001
	AV5Z/MP2FIT	0.000	0.000	0.000

[a] Basis set truncation errors (correlation contribution only) for this combination of orbital basis set and the reference ABS are shown in parentheses. The CBS limits were defined by extrapolation of conventional MP2 correlation energies with aug-cc-pV5Z and aug-cc-pV6Z basis sets. See the text.

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