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Correlation consistent basis sets for explicitly correlated wavefunctions: Pseudopotential-based basis sets for the post-*d* main group elements Ga–Rn

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New correlation consistent basis sets, cc-pV*n*Z-PP-F12 (n = D, T, Q), for all the post-*d* main group elements Ga–Rn have been optimized for use in explicitly correlated F12 calculations. The new sets, which include not only orbital basis sets but also the matching auxiliary sets required for density fitting both conventional and F12 integrals, are designed for correlation of valence *sp*, as well as the outer-core *d* electrons. The basis sets are constructed for use with the previously published small-core relativistic pseudopotentials of the Stuttgart-Cologne variety. Benchmark explicitly correlated coupled-cluster singles and doubles with perturbative triples [CCSD(T)-F12b] calculations of the spectroscopic properties of numerous diatomic molecules involving 4*p*, 5*p*, and 6*p* elements have been carried out and compared to the analogous conventional CCSD(T) results. In general the F12 results obtained with a *n*-zeta F12 basis set were comparable to conventional aug-cc-pV*x*Z-PP or aug-cc-pwCV*x*Z-PP basis set calculations obtained with $x = n + 1$ or even $x = n + 2$. The new sets used in CCSD(T)-F12b calculations are particularly efficient at accurately recovering the large correlation effects of the outer-core *d* electrons. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4893989]

I. INTRODUCTION

One of the major sources of error in correlated electronic structure calculations is due to incompleteness of the 1-particle basis set used to describe the atomic or molecular orbitals.[1–3] Since the introduction of the correlation consistent family of basis sets,[4] this error has been effectively addressed by any number of extrapolation strategies to an estimated complete basis set (CBS) for a given correlation method (see, e.g., Refs. 5–7). For high accuracy, however, large basis sets of quadruple-zeta or preferably higher must be used. Over the last several years, the use of so-called F12 explicitly correlated methods, which arose from the R12 method of Kutzelnigg and co-workers,[8] has become much more widespread.[9–12] These methods greatly improve the convergence with respect to basis set by including one or more nonlinear correlation factors, e.g., $e^{-\gamma r_{12}}$, into the wavefunction. The F12 ansatz has now been implemented into a number of commonly used correlation methods, including MP2, coupled-cluster singles and doubles (CCSD),[9–12] complete active space 2nd-order perturbation theory (CASPT2),[13] and internally contracted multireference configuration interaction (MRCI).[14] While standard basis sets can be effectively used in F12 approaches, it has been found to be advantageous to optimize Gaussian basis sets directly for use in F12 calculations.[15,16] This has led to the series of cc-pV*n*Z-F12 basis sets (n = D, T, Q), which are currently available for all the elements from H through Ar.[15–17] In the present work, new F12-based correlation consistent basis sets, denoted cc-pV*n*Z-PP-F12, have been developed for all the post-*d* main group elements Ga–Rn. These sets are derived from the standard aug-cc-pV*n*Z-PP and aug-cc-pwCV*n*Z-PP sets,[18–21] which were constructed for use with small-core relativistic pseudopotentials of the Stuttgart-Cologne variety,[19,20,22,23] and also complement the standard all-electron correlation consistent basis sets, valence and core-valence, for these elements.[24–26] To accompany the new orbital basis sets of this work, new auxiliary basis sets have also been determined that are needed for density fitting of the standard 2-electron integrals (MP2FIT), as well as for the resolution of the identity of the many-electron F12 integrals (OPTRI). Preliminary versions of these sets have already been used in extensive coupled cluster benchmark calculations of several diatomic molecules containing the post-3*d* elements Ga–Kr, where they exhibited excellent convergence behavior to the basis set limit compared to standard basis sets in conventional calculations.[27]

General methodology can be found in Sec. II, while details of the basis set development of this work can be found in Sec. III. Benchmark calculations designed to ascertain the accuracy and efficiency of the new sets are reported and discussed in Sec. IV.

II. GENERAL COMPUTATIONAL DETAILS

The MOLPRO suite of *ab initio* programs[28] was used throughout this work together with restricted open-shell Hartree-Fock orbitals and pure spherical harmonic angular momentum basis functions. All of the basis sets of this work are paired with small core, multiconfigurational Dirac-Hartree-Fock-adjusted pseudopotentials of the

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Stuttgart-Cologne variety[19,20,22,23] (replacing 10 electrons for Ga–Kr, 28 electrons for In–Xe, and 60 electrons for Tl–Rn), which were previously employed in the cc-pV*n*Z-PP family of basis sets for these elements.[18–20]

III. BASIS SET DEVELOPMENT

A. Atomic orbital basis sets, cc-pV*n*Z-PP-F12

The development of the F12 atomic orbital (AO) basis sets of this work closely follows the authors' previous work in this area.[15–17] All exponent optimizations were carried out at the MP2-F12 level of theory with the 3C ansatz[29] on the ground states of the neutral atoms. A geminal exponent γ of 1.4 a_0^{-1} was used throughout. The auxiliary basis sets (ABSs) utilized in the AO exponent optimizations corresponded to the def2-QZVPP/JKFIT[30] set for density fitting (DF) of the exchange terms with large, uncontracted even-tempered sets (18*s*17*p*15*d*12*f*10*g*8*h*7*i*) for both the density fitting of the conventional 2-electron integrals and the resolution of the identity (RI) for the many-electron F12 integrals within the complementary auxiliary basis set (CABS) approach.[31] These latter sets can be found in the supplementary material.[32]

In the previously developed cc-pV*n*Z-F12 correlation consistent basis sets,[16,17] the *sp* parts of the basis sets were taken from the conventional aug-cc-pV(n+1)Z basis sets[4,33,34] in order to ensure that the basis set convergence of the HF energy was on par with that of the correlation energy in explicitly correlated calculations. This approach was also followed in the present work by utilizing the (contractions and correlating) *s* and *p* functions of the aug-cc-pV(n+1)Z-PP sets[18–20] and the [1*d*] contracted HF *d*-type function from the cc-pV(n+1)Z-PP sets for use in the new cc-pV*n*Z-PP-F12 basis sets (n = D, T, Q). To these base sets, groups of correlating functions optimized at the MP2-F12/3C level of theory[29] were then added. These latter functions included the usual F12 groupings of valence (*msp* electrons) correlating functions (defined as even-tempered expansions), i.e., 2*d* for DZ, 3*d*2*f* for TZ, and 4*d*3*f*2*g* for QZ. In the present case an additional 1*d*1*f* set was also included that was optimized for MP2-F12 correlation energy of the (m−1)*d* electrons (m will denote the principal quantum number in this work to avoid confusion with the basis set cardinal number n). These latter functions were optimized concurrently with the valence correlating functions in an iterative scheme until there was no significant change in the energies. The motivation for these additional tight functions was twofold, (i) they address the known deficiency of the conventional cc-pV*n*Z-PP basis sets in lacking sufficiently tight *f*-type functions for inner-shell polarization[21,35] (similar in spirit to the "tight-*d* effect" in the 2nd row elements[36]) and (ii) they provide a minimal set of functions needed to describe the correlation of (m−1)*d* electrons. So while the new sets are still predominately valence correlating basis sets, they are also capable of accurately recovering outer-core correlation effects in a very economical and reliable way. This will be shown in detail below through numerous diatomic benchmark calculations. The compositions of the final contracted basis sets are shown in Table I.

Figures 1–3 show the basis set convergence of the MP2 correlation energy both in conventional and MP2-F12/3C calculations for the rare gas atoms Kr, Xe, and Rn. In Figure 1 the frozen-core correlation energies (valence *sp* electrons correlated) from conventional MP2 with aug-cc-pV*n*Z-PP and aug-cc-pwCV*n*Z-PP basis sets are compared to MP2-F12/cc-pV*n*Z-PP-F12 calculations. The F12 calculations utilized the new auxiliary basis sets described below. Estimated CBS limits are shown based on conventional MP2 n^{-3} extrapolations[6,37] of the large aug-cc-pwCV*n*Z-PP basis sets with n = 4 (Q), and 5. As expected, the F12 correlation energies are dramatically closer to the CBS limit compared to the conventional results. Even at the DZ level, the F12 results are comparable or even closer to the CBS limits than the conventional 5Z values. The convergence with basis is seen to be monotonic in all cases. Figures 2 and 3 show the basis set convergence of the core-valence and core-core correlation energies, respectively, where the core is defined as the (m−1)*d* electrons. Even with just the small 1*d*1*f* set of core correlating functions contained in the new basis sets, the F12 calculations recovered a significant amount of core correlation energy. In fact the cc-pV*n*Z-PP-F12 correlation energies are lower than the conventional aug-cc-pwCV(n+1)Z-PP values. The convergence is observed to be generally monotonic for Xe and Rn, but the F12 core correlation energies for Kr show only poor convergence towards the estimated CBS limits, with the cc-pVQZ-F12 results being similar or only slightly lower than the conventional aug-cc-pwCV5Z-PP values. Similar behavior is observed for other members of this row and is presumably due to the inability of the small 1*d*1*f* set of core correlating functions to provide accurate correlation energies for electrons in the compact 3*d* orbital, even with the inclusion of the F12 correlation factor. However, as

TABLE I. Composition of the basis sets developed in this work for the post-*d* elements. The ratio of functions (MP2FIT:OBS and OPTRI:OBS) assumes spherical angular momenta.

Element	Basis designation	OBS	MP2FIT	Ratio	OPTRI	Ratio
4*p*	cc-pVDZ-PP-F12	[6*s*5*p*4*d*1*f*]	(12*s*11*p*10*d*8*f*8*g*3*h*)	5.3	(6*s*8*p*6*d*7*f*5*g*4*h*1*i*)	4.4
	cc-pVTZ-PP-F12	[7*s*6*p*5*d*3*f*]	(13*s*12*p*11*d*9*f*9*g*5*h*)	4.3	(6*s*8*p*6*d*6*f*6*g*5*h*2*i*)	3.3
	cc-pVQZ-PP-F12	[8*s*7*p*6*d*4*f*2*g*]	(14*s*13*p*12*d*10*f*10*g*6*h*3*i*)	3.6	(6*s*6*p*5*d*6*f*6*g*4*h*2*i*)	2.0
5*p*	cc-pVDZ-PP-F12	[6*s*5*p*4*d*1*f*]	(12*s*11*p*11*d*9*f*8*g*3*h*)	5.6	(7*s*6*p*6*d*6*f*5*g*3*h*1*i*)	3.9
	cc-pVTZ-PP-F12	[7*s*7*p*5*d*3*f*]	(13*s*12*p*12*d*10*f*9*g*5*h*)	4.3	(7*s*7*p*6*d*5*f*5*g*4*h*2*i*)	2.8
	cc-pVQZ-PP-F12	[8*s*8*p*6*d*4*f*2*g*]	(14*s*13*p*13*d*11*f*10*g*7*h*3*i*)	3.7	(7*s*5*p*6*d*6*f*5*g*4*h*2*i*)	1.9
6*p*	cc-pVDZ-PP-F12	[6*s*5*p*4*d*1*f*]	(12*s*11*p*11*d*9*f*8*g*3*h*)	5.6	(7*s*6*p*6*d*6*f*5*g*3*h*1*i*)	3.9
	cc-pVTZ-PP-F12	[7*s*7*p*5*d*3*f*]	(13*s*12*p*12*d*10*f*9*g*5*h*)	4.3	(6*s*6*p*6*d*5*f*5*g*3*h*2*i*)	2.6
	cc-pVQZ-PP-F12	[8*s*8*p*6*d*4*f*2*g*]	(14*s*13*p*13*d*11*f*10*g*7*h*3*i*)	3.7	(7*s*5*p*5*d*6*f*5*g*4*h*2*i*)	1.9

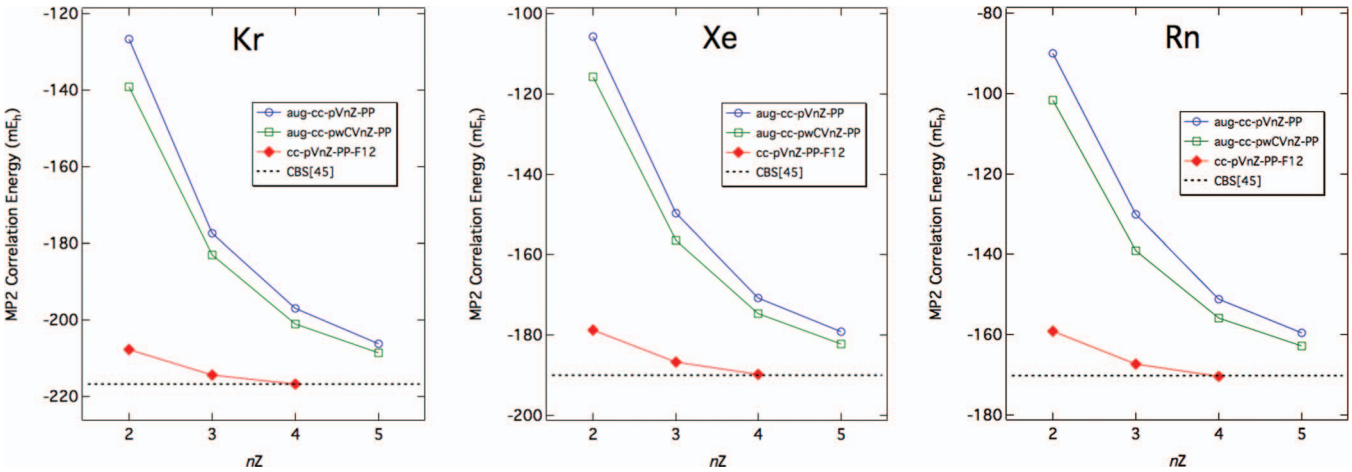

FIG. 1. Convergence of frozen-core MP2 correlation energies from conventional (aug-cc-pVnZ-PP and aug-cc-pwCVnZ-PP basis sets) and explicitly correlated MP2-F12/3C (new cc-pVnZ-PP-F12 basis sets, $\gamma = 1.4$) calculations. The estimated CBS limits are shown by the horizontal dotted lines, which were obtained by n^{-3} extrapolation of conventional aug-cc-pwCVnZ-PP correlation energies with $n = 4, 5$.

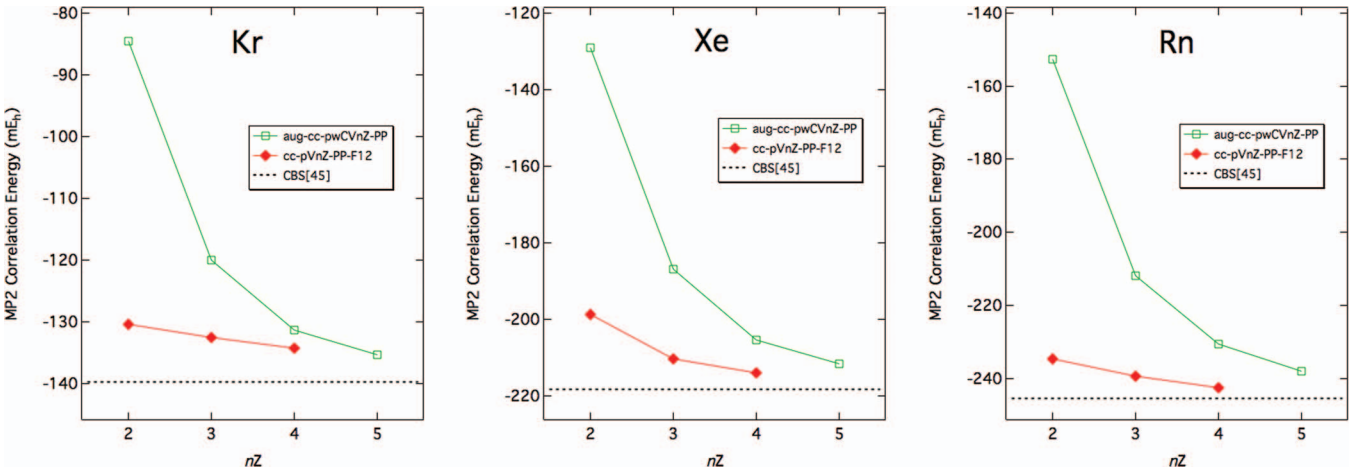

FIG. 2. Convergence of the MP2 $(m-1)d$ electron core-valence correlation contributions using conventional (aug-cc-pwCVnZ-PP basis sets) and explicitly correlated MP2-F12/3C (new cc-pVnZ-PP-F12 basis sets, $\gamma = 1.4$). The estimated CBS limits are shown by the horizontal dotted lines, which were obtained by n^{-3} extrapolation of conventional aug-cc-pwCVnZ-PP correlation energies with $n = 4, 5$.

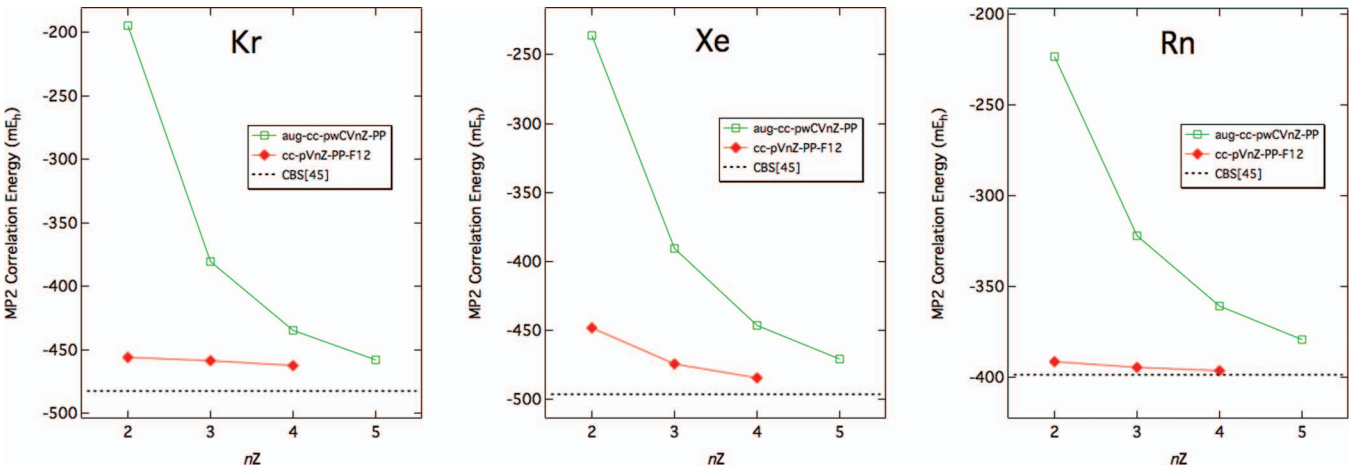

FIG. 3. Convergence of the MP2 $(m-1)d$ electron core-core correlation contributions using conventional (aug-cc-pwCVnZ-PP basis sets) and explicitly correlated MP2-F12/3C (new cc-pVnZ-PP-F12 basis sets, $\gamma = 1.4$). The estimated CBS limits are shown by the horizontal dotted lines, which were obtained by n^{-3} extrapolation of conventional aug-cc-pwCVnZ-PP correlation energies with $n = 4, 5$.

shown below in molecular benchmark calculations, this does not seem to degrade the accuracy of the calculated core correlation *effects* on energetic and spectroscopic properties.

B. Density fitting auxiliary basis sets, MP2FIT

Auxiliary basis sets for the density fitting (suffixed MP2FIT) of the conventional two-electron integrals were developed using similar design and optimization strategies as previously employed for a large number of DF-MP2 ABSs (Refs. 38–40, and references therein). In the present case they are specifically matched to the cc-pV*n*Z-PP-F12 orbital sets described above, and optimization of the uncontracted exponents proceeded via the minimization of the functional[38]

$$\delta_{\mathrm{DF}} = -\frac{1}{4}\sum_{aibj}\frac{(\langle ab||ij\rangle_{\mathrm{DF}} - \langle ab||ij\rangle)^2}{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j},$$

where the two-electron repulsion integrals are denoted $\langle ab||ij\rangle = (ai|bj) - (aj|bi)$, ε_x are Hartree-Fock orbital energies, i and j are occupied orbitals, and a and b are virtual orbitals. All of these optimizations used the analytical auxiliary basis set gradients within the RICC2 module[41,42] of the TURBOMOLE program.[43] All atoms were in their respective ground electronic states and the $(m-1)d$ electrons were included in the correlation treatment and evaluation of δ_{DF}. The $(m-1)sp$ electrons were treated with the frozen core approximation and excluded from the functional.

The pioneering work of Weigend *et al.*[38] in the optimization of ABSs for conventional frozen-core DF-MP2 established guidelines that the number of basis functions in the ABS should be no greater than four times the number of functions in the orbital set, and that the error in the correlation energy due to density fitting should be less than 100 μE_h per atom in molecular calculations. As the energetic error is not directly related to δ_{DF}, for optimization purposes this was transformed to $\delta_{\mathrm{DF}}/|E^{\mathrm{corr}}_{\mathrm{MP2}}| < 10^{-6}$. An additional rule-of-thumb has also been established; the error due to density fitting in molecules should be three or four orders of magnitude smaller than the error due to basis set incompleteness (BSIE) in the orbital basis.[40,44] As the F12 methods greatly reduce the BSIE, one should be wary that the density fitting errors remain negligible. Thus in the present investigation the DF error is assessed at the MP2/DF-MP2 level but compared against the BSIE at the MP2-F12 level.

The compositions of the resulting ABSs are presented in Table I, along with the compositions of the respective orbital basis sets. It can been seen that at the DZ and TZ levels, reaching the desired level of accuracy required more functions than the "four times the functions in orbital basis set (OBS)" guide, but this is a necessity for the DF errors to remain negligible in the F12 framework. ABSs of this size do not cause any efficiency concerns in F12 calculations, as initial testing demonstrates that the bottleneck remains the evaluation of the new many-electron integrals that arise in explicitly correlated methods (the latter are calculated using the RI basis set described in Sec. III C). Statistics of the error caused by density fitting are presented on a per correlated electron basis as the mean unsigned error (MUE), standard deviation (σ), and maximum absolute error (MAX) in the quantity $\delta_{DF}/|E^{corr}_{MP2}|$ for the post-*d* elements in Table S1 of the supplementary material.[32] It can be seen that the errors in the integrals are roughly equivalent for all three basis sets, and that the overall magnitude of the error is very small.

Further validation of the new MP2FIT ABSs has been carried out by comparing the DF error in the correlation energy with the BSIE for a test set of molecules containing post-*d* main group elements. Most of these were taken from Ref. 30 with the addition of As_2, Kr_2, Sb_2, and Bi_2 (all the molecules are listed in Table II). Estimates of the CBS limit have been obtained from (R)MP2-F12/3C(FIX) calculations carried out in MOLPRO with a Schwenke-type extrapolation of the TZ and QZ correlation energies,[45] with the cc-pV*n*Z-F12 basis sets used for lighter elements. The large even-tempered auxiliary basis described in Sec. III A was used for both density fitting and the RI. The coefficient used in the CBS extrapolation was optimized for lighter elements and is employed to create estimates of the BSIE, rather than to obtain rigorous benchmark values for the MP2 CBS limit. Separate CBS limits were produced with the $(m-1)d$ electrons on the post-*d* elements included or excluded from the correlation treatment. All other elements used the standard frozen core definition throughout. The MUE, σ, and MAX of the BSIE for all of the molecules in the test set are presented in Tables S2 and S3 of the supplementary material,[32] where the orbital basis sets have been abbreviated as V*n*Z-F12.

Tests of the error in the MP2 correlation energy due to DF quickly revealed that the magnitude of the error was very sensitive to the ABS used for the lighter elements. Previous recommendations have paired the cc-pVDZ-F12 OBS with aug-cc-pVTZ/MP2FIT, cc-pVTZ-F12 with aug-cc-pVTZ/MP2FIT, and cc-pVQZ-F12 with aug-cc-pVQZ/MP2FIT.[45] Although this DZ recommendation still works well, the other pairings resulted in DF errors that were deemed too large, roughly just two orders of magnitude smaller than the respective BSIE. Increasing the ABSs to aug-cc-pwCVQZ/MP2FIT and aug-cc-pwCV5Z/MP2FIT, for cc-pVTZ-F12 and cc-pVQZ-F12, respectively, reduced the errors by approximately

TABLE II. Test set of molecules containing post-*d* main group elements used to validate the performance of the MP2FIT and OPTRI auxiliary basis sets.

	Molecules
4*p* (Ga-Kr)	GaCl, $GaCl_3$, GaF, GaF_2, GaH_3, GaO, $GeCl_4$, GeF_3, GeF_4, GeH_4, GeO, GeO_2, As_4, As_2, $AsCl_3$, AsH_3, SeH_2, SeO, SeO_2, HBr, $HCBr_3$, Br_2, BrCl, BrO^-, $BrO_2{}^-$, Kr_2
5*p* (In-Xe)	InCl, $InCl_3$, InH, InH_3, InO, SnF_3, SnH_4, SnO, SnO_2, Sb_2, SbF, SbF_3, SbH_3, SbO_2, TeF_3, TeH_2, TeO, TeO_2, I_2, IH, $IO_4{}^-$, $IO_3{}^-$, ICl, XeF_2, XeF_4, $XeOF_4$
6*p* (Tl-Rn)	TlCl, $TlCl_3$, TlH, TlH_3, TlO, PbF_3, PbH_4, PbO, PbO_2, Bi_2, BiF, BiF_3, BiH_3, BiO_2, $PoCl_4$, PoF_2, PoO_2, At_2, AtCl, AtF_3, Rn_2, RnF_2

TABLE III. Density fitting errors (MP2FIT relative to the reference ABS) in the MP2 correlation energy per correlated electron for a test set of molecules containing post-*d* elements. The $(m-1)d$ electrons are frozen (*d*-electron correlation results in parentheses) in the correlation treatment. All values are in μE_h.

ABS		MUE	σ	MAX
VDZ-F12	4*p*	0.38 (0.17)	0.31 (0.11)	1.03 (0.36)
	5*p*	0.33 (0.12)	0.30 (0.07)	1.11 (0.33)
	6*p*	0.41 (0.18)	0.35 (0.16)	1.26 (0.63)
VTZ-F12	4*p*	0.37 (0.16)	0.36 (0.13)	1.26 (0.49)
	5*p*	0.47 (0.17)	0.38 (0.11)	1.30 (0.41)
	6*p*	0.40 (0.23)	0.41 (0.11)	1.22 (0.47)
VQZ-F12	4*p*	0.21 (0.09)	0.13 (0.05)	0.51 (0.20)
	5*p*	0.17 (0.05)	0.14 (0.04)	0.47 (0.15)
	6*p*	0.15 (0.10)	0.14 (0.06)	0.42 (0.20)

a further order of magnitude. The same recommendation has also been made earlier in the review by Hättig *et al.*[9] This also ensured that the DF error of molecules containing both post-*d* and lighter elements was commensurate with those containing only post-*d* elements. This finding indicates that there is scope for MP2FIT ABSs specifically matched to the cc-pV*n*Z-F12 OBS of the lighter elements, and this shall be the topic of a future investigation. The MUE, σ, and MAX DF errors for the test set of molecules are presented in Table III, with the $(m-1)d$ electrons frozen and correlated. The molecules SnF_3, TlO, and PbF_3 were removed from the test set when the $(m-1)d$ electrons were frozen; these systems displayed a significant amount of mixing between the *d* electrons on the post-*d* element and orbitals on the lighter elements, making the designation of a frozen core non-obvious.

A comparison of BSIE with DF errors indicates that the fitting errors are negligible in all cases, despite the large decrease in BSIE due to the explicitly correlated wavefunction. With a VDZ-F12 basis the statistics of the DF error are four orders of magnitude smaller than the BSIE, and this becomes three orders of magnitude with VTZ-F12 and VQZ-F12 (without correlating the *d* electrons). Overall the magnitude of the errors due to density fitting is essentially the same for all three basis set qualities, with some reduction in MAX for larger bases. The errors are also relatively constant whether the $(m-1)d$ electrons are correlated or not, indicating that the errors would be smaller in the *d*'s correlated case on a per correlated electron basis. Reaching these desired levels of accuracy required a relatively large number of functions in the auxiliary basis, but, as mentioned above, this should have negligible consequences in most F12 calculations, especially when more computationally expensive methods [such as coupled-cluster single double triple (CCSD(T))-F12b] are utilized. Of course this may not be the case when local correlation methods are used since these could have a much stronger dependence on the size of the ABS.

C. Complementary auxiliary basis sets, OPTRI

The RI auxiliary basis sets needed for evaluation of the multielectron F12 integrals were optimized for use within the complementary auxiliary basis set (CABS+) approach[31] as implemented in MOLPRO. The resulting OPTRI auxiliary sets are specifically matched to a particular cc-pV*n*Z-PP-F12 orbital basis set since the former only contain the complementary functions, i.e., the full CABS+ basis set is formed by the union of a particular OPTRI set and the OBS. The OPTRI sets are designed to be compact and lead to a linearly independent CABS basis set, i.e., no functions will be deleted in the CABS procedure. This leads to smooth potential energy surfaces and increased numerical stability. As described in Ref. 46, the general procedure is to optimize functions that minimize the value of δRI for the atoms:

$$\delta\mathrm{RI} = \sum_{ij} \frac{\left(V_{ij,ij}^{\mathrm{RI}} - V_{ij,ij}^{\mathrm{RI}_{\mathrm{ref}}}\right)^2}{V_{ij,ij}^{\mathrm{RI}_{\mathrm{ref}}}} + \frac{\left(B_{ij,ij}^{\mathrm{RI}} - B_{ij,ij}^{\mathrm{RI}_{\mathrm{ref}}}\right)^2}{B_{ij,ij}^{\mathrm{RI}_{\mathrm{ref}}}},$$

which involves the diagonal elements of the **V** and **B** matrices arising in MP2-F12 theory.[29] The reference matrices are defined by the reference RI basis sets described above. In order to minimize linear dependencies of the resulting CABS basis sets, the ratio of any two exponents (with the same angular momentum) in the combined CABS basis was constrained to be $\geq$1.5. The 3C ansatz as implemented in MOLPRO was used throughout with a geminal exponent of $1.4\,a_0^{-1}$.

Compared to the previous development of OPTRI sets,[17,46,47] the current work was complicated by having F12 basis sets designed for correlating two different orbital spaces, primarily valence *sp* but also a minimal set for $(m-1)d$. In the present work initial sets of OPTRI exponents were first optimized within the frozen-core approximation (valence *sp* correlation only). Each angular momentum was optimized separately and the *s*, *p*, *d*, and *f* functions employed a reference RI that was truncated at *f*-type functions. The higher angular momentum functions utilized the full reference RI. The resulting sets were then frozen and 0–4 additional functions in each angular momentum were optimized in MP2-F12 calculations that included the valence + $(m-1)d$ electrons. The compositions of the final OPTRI auxiliary sets are given in Table I. Not surprisingly the sizes are much smaller than the MP2FIT sets since the total CABS+ basis set also includes the orbital basis in addition to the functions in the OPTRI set. In general the OPTRI sets also slightly decrease in size as the OBS

TABLE IV. RI errors (OPTRI relative to the reference ABS) per correlated electron in the MP2-F12/3C(FIX) correlation energies for the combined test set of molecules containing post-*d* main group elements. Only the valence electrons are correlated. All values are in μE_h. Excludes GeF_4.

Orbital basis	Error type	MUE	σ	MAX
VDZ-F12	BSIE	1373.9	649.5	3014.4
	RI	4.1	3.9	14.6
VTZ-F12	BSIE	389.2	197.0	1029.0
	RI	2.8	3.4	12.1
VQZ-F12	BSIE	111.2	56.3	294.0
	RI	1.3	1.4	5.2

TABLE V. RI errors (OPTRI relative to the reference ABS) per correlated electron in the MP2-F12/3C(FIX) correlation energies for the combined test set of molecules containing post-*d* main group elements. The valence electrons and $(m-1)d$ electrons are correlated. All values are in μE_h. Excludes GeF4.

Orbital basis	Error type	MUE	σ	MAX
VDZ-F12	BSIE	2882.8	1698.8	9271.7
	RI	21.0	10.1	62.7
VTZ-F12	BSIE	1234.6	714.1	3385.4
	RI	4.9	2.6	11.9
VQZ-F12	BSIE	352.8	204.1	967.3
	RI	3.9	2.3	11.6

becomes more complete. Using the same set of test molecules (shown in Table II) as utilized in the MP2FIT work, the RI errors were also assessed (relative to the reference RI) for the new OPTRI auxiliary sets. These results (per correlated electron) are shown for both valence and valence + $(m-1)d$ electron correlation in Tables IV and V, respectively. In general these errors are about 2 orders of magnitude smaller than the MP2-F12 BSIE. It should be noted that the results shown in these tables excludes results from GeF_4 as those values were anomalously large for reasons yet to be determined ($GeCl_4$, GeF_3, etc., did not show this strange behavior).

D. Choice of geminal exponent, γ

In previous work on the lighter *p*-block elements,[45] values of the geminal exponent γ were recommended based on MP2-F12/3C(FIX) calculations for each orbital basis set, i.e., $0.9\,a_0^{-1}$ (cc-pVDZ-F12), $1.0\,a_0^{-1}$ (cc-pVTZ-F12), and $1.0\,a_0^{-1}$ (cc-pVQZ-F12). These represented a compromise between smaller values generally being energetically favorable for elements in the left half of the *p*-block versus slightly larger values for those in the rightmost half.[16] The sensitivity of the correlation energy with the choice of γ decreases, however, when the size of the OBS increases. When core correlation effects were being considered, a single value of $1.4\,a_0^{-1}$ was found to be adequate for all basis sets. In the present work, recommending a single value of γ for each basis set for all post-*d* elements is particularly challenging, especially when the $(m-1)d$ electrons are correlated. Figure 4 shows the γ dependence of the MP2-F12/3C(FIX) correlation energies for As_2, Sb_2, and Bi_2 near their equilibrium bond distances using the cc-pVTZ-PP-F12 basis set. Results using the cc-pVDZ-PP-F12 set are similar but with overall smaller optimal values of γ. From Fig. 4, when only valence electrons are correlated, the optimal value of γ is about 0.9 for As_2 and progressively gets smaller from Sb_2 to Bi_2, where in the latter case the lowest energy occurs at approximately $\gamma = 0.65$. The differences are even more dramatic when the $(m-1)d$ electrons are correlated. The compact $3d$ orbital leads to a large optimal value of γ for core-core correlation of nearly 2.2, while the analogous values for Sb_2 and Bi_2 are closer to about 1.2. For the inter-shell core-valence contribution to the correlation energy, the optimal values of γ range from about 1.6 (As_2) to 1.0 (Bi_2).

There are a couple of options to attempt to address this problem of how to choose an appropriate geminal exponent, particularly for *d*-electron correlation. It was found in Ref. 27 that more reliable results at the CCSD(T)-F12b level could be obtained by optimizing the amplitudes of the explicitly correlated terms at the MP2-F12 level and then fixing them in the subsequent CCSD-F12b calculation rather than fixing the amplitudes based on the wavefunction cusp conditions[27] (the latter of which is the default in MOLPRO). This approach, however, has not been investigated further in this work. Another strategy is to use more than a single geminal in the F12 calculations, each with a different exponent.[48] This was also investigated previously[27] using preliminary versions of the present

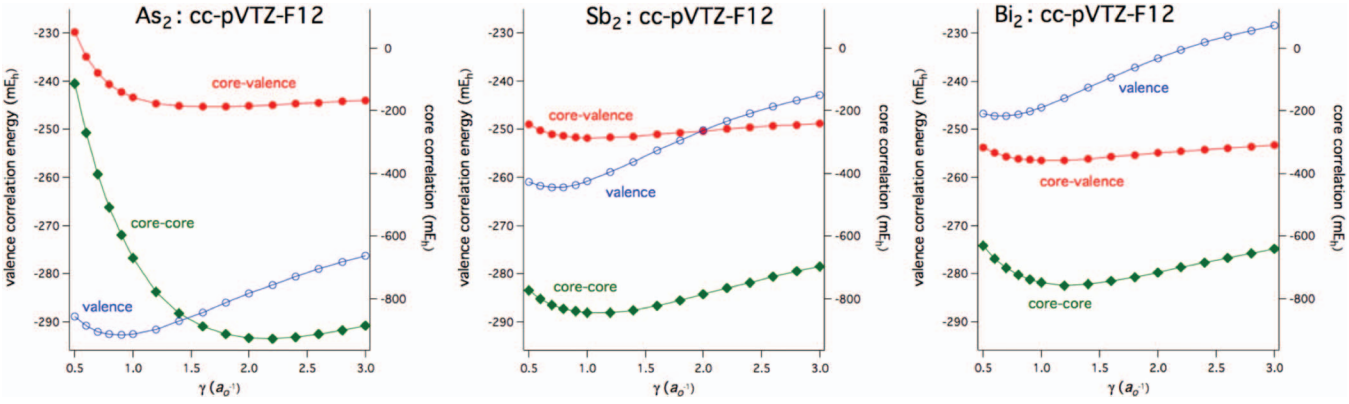

FIG. 4. Dependence of the valence, core-valence, and core-core MP2 correlation energies on the geminal exponent γ in MP2-F12/3C(Fix)/cc-pVTZ-PP-F12 calculations for $r(As_2) = 2.091$ Å, $r(Sb_2) = 2.477$ Å, and $r(Bi_2) = 2.624$ Å.

TABLE VI. Calculated CCSD(T)-F12b frozen-core (valence) and *d*-electron correlation contributions (Δd) for spectroscopic constants of various post-*d* homonuclear diatomics.

		D_e (kcal mol^{-1})		r_e (Å)		ω_e (cm^{-1})	
Molecule	Basis	Valence	Δd	Valence	Δd	Valence	Δd
$X^3\Pi_u$ Ga_2	cc-pVDZ-F12-PP	28.62	+1.46	2.7294	−0.0766	165.5	+7.2
	cc-pVTZ-F12-PP	29.63	+1.47	2.7235	−0.0750	167.3	+7.0
	cc-pVQZ-F12-PP	29.81	+1.54	2.7231	−0.0761	167.4	+6.9
	CBS[Q5][a]	29.90	+1.52	2.7228	−0.0762	167.5	+6.9
$X^3\Pi_u$ In_2	cc-pVDZ-F12-PP	24.95	+1.54	3.0907	−0.0902	113.1	+4.9
	cc-pVTZ-F12-PP	26.03	+1.72	3.0831	−0.0914	114.4	+5.8
	cc-pVQZ-F12-PP	26.19	+2.03	3.0821	−0.0960	114.5	+6.2
	CBS[Q5][a]	26.27	+1.90	3.0819	−0.0948	114.8	+5.9
$X^3\Pi_u$ Tl_2	cc-pVDZ-F12-PP	22.08	+2.38	3.1911	−0.1129	77.5	+5.8
	cc-pVTZ-F12-PP	22.86	+2.61	3.1845	−0.1144	78.0	+6.6
	cc-pVQZ-F12-PP	22.88	+3.17	3.1839	−0.1243	77.9	+7.5
	CBS[Q5][a]	22.94	+3.18	3.1841	−0.1246	78.0	+7.6
$X^1\Sigma_g^+$ As_2	cc-pVDZ-F12-PP	85.77	+2.87	2.1189	−0.0250	428.7	+8.2
	cc-pVTZ-F12-PP	88.08	+2.39	2.1182	−0.0234	429.0	+7.6
	cc-pVQZ-F12-PP	89.19	+2.40	2.1165	−0.0238	430.1	+8.3
	CBS[Q5][a]	90.10	+2.42	2.1155	−0.0251	431.1	+9.3
$X^1\Sigma_g^+$ Sb_2	cc-pVDZ-F12-PP	63.23	+3.60	2.5209	−0.0387	269.8	+7.8
	cc-pVTZ-F12-PP	66.00	+3.32	2.5177	−0.0373	271.6	+7.9
	cc-pVQZ-F12-PP	67.05	+3.24	2.5158	−0.0385	272.2	+8.6
	CBS[Q5][a]	68.11	+3.20	2.5143	−0.0383	273.0	+9.0
$X^1\Sigma_g^+$ Bi_2	cc-pVDZ-F12-PP	52.74	+4.44	2.6804	−0.0471	184.4	+7.6
	cc-pVTZ-F12-PP	55.41	+4.31	2.6757	−0.0449	186.0	+7.7
	cc-pVQZ-F12-PP	56.35	+4.49	2.6731	−0.0472	186.3	+8.9
	CBS[Q5][a]	57.20	+4.40	2.6719	−0.0488	187.0	+9.6
$X^1\Sigma_g^+$ Br_2	cc-pVDZ-F12-PP	51.12	+0.38	2.2903	−0.0121	327.3	+1.7
	cc-pVTZ-F12-PP	51.06	+0.33	2.2914	−0.0110	325.9	+1.7
	cc-pVQZ-F12-PP	51.53	+0.38	2.2894	−0.0113	327.5	+2.3
	CBS[Q5][a]	52.07	+0.46	2.2871	−0.0135	328.0	+3.2
$X^1\Sigma_g^+$ I_2	cc-pVDZ-F12-PP	45.72	+1.33	2.6796	−0.0277	221.1	+3.7
	cc-pVTZ-F12-PP	46.03	+1.18	2.6793	−0.0259	220.5	+3.6
	cc-pVQZ-F12-PP	46.70	+1.10	2.6755	−0.0234	221.7	+3.3
	CBS[Q5][a]	47.41	+1.15	2.6725	−0.0250	222.5	+3.8
$X^1\Sigma_g^+$ At_2	cc-pVDZ-F12-PP	41.09	+2.07	2.8599	−0.0341	158.3	+3.6
	cc-pVTZ-F12-PP	41.81	+1.97	2.8582	−0.0309	158.1	+3.4
	cc-pVQZ-F12-PP	42.29	+1.83	2.8555	−0.0309	158.8	+3.6
	CBS[Q5][a]	42.93	+1.77	2.8530	−0.0329	159.5	+4.1

[a]Conventional CCSD(T) results from Ref. 21 using cc-pwCV*n*Z-PP (n = Q, 5) basis sets.

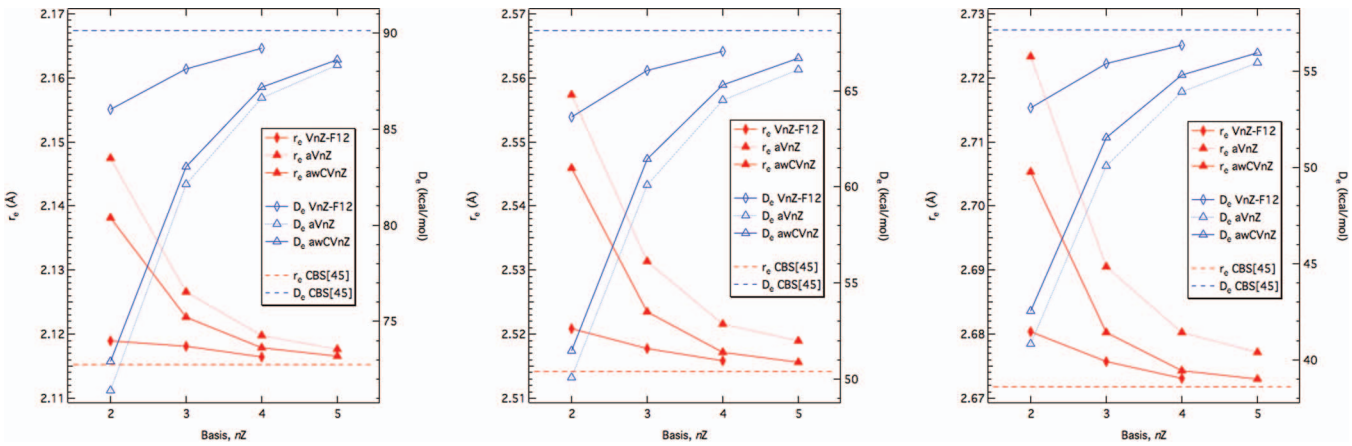

FIG. 5. Calculated frozen-core CCSD(T) values of r_e (Å) and D_e (kcal/mol) for (a) As_2, (b) Sb_2, and (c) Bi_2 as a function of basis set for CCSD(T)-F12b/cc-pV*n*Z-PP-F12 (V*n*Z-F12), CCSD(T)/aug-cc-pV*n*Z-PP (aV*n*Z), and CCSD(T)/aug-cc-pwCV*n*Z-PP (awCV*n*Z). The estimated complete basis set limits, CBS[45], were obtained from conventional CCSD(T) with aug-cc-pwCV*n*Z-PP (n = Q, 5) basis sets.

basis sets for the post-3*d* elements and valence +3*d* correlation. Using two geminals with exponents 0.9 and $1.4\,a_0^{-1}$, noticeable improvements were observed in the *d*-correlation effects on D_e, r_e, and ω_e for the DZ set when compared to the results using a single geminal with exponent $1.4\,a_0^{-1}$. A similar study was carried out in this work, but using pairs of exponents that were a compromise between As, Sb, and Bi: [0.70, 1.20] for DZ, [0.80, 1.25] for TZ, and [0.90, 1.35] for QZ. A comparison of *d*-correlation effects on D_e and r_e using two geminals versus using a single geminal with exponent $1.4\,a_0^{-1}$ was then made for As_2, Sb_2, and Bi_2 (see below for other details of these calculations). At least for these 3 molecules, the only improvement from using 2 geminals was for Δd of D_e at the DZ level, where the resulting values for As_2 and Bi_2 were very similar to both the TZ and QZ results. For the TZ and QZ basis sets the use of 2 geminals had nearly no effect on the calculated *d*-correlation effects. Since the advantages were not so great, single values of γ have been used in the subsequent benchmark calculations of this work, $1.0\,a_0^{-1}$ for valence correlation calculations and $1.4\,a_0^{-1}$ when the $(m-1)d$ electrons were correlated (for calculating Δd a value of $1.4\,a_0^{-1}$ was used for both the valence and *d*-correlation calculations). The excellent results presented and discussed below imply this choice is adequate for most needs.

IV. MOLECULAR BENCHMARK CALCULATIONS

In order to demonstrate the effectiveness of the new basis sets for both valence and $(m-1)d$ electron correlation in molecular systems, CCSD(T) calculations were carried out

TABLE VII. Calculated CCSD(T)-F12b frozen-core (valence) and *d*-electron correlation contributions (Δd) for spectroscopic constants of various post-*d* heteronuclear diatomics.

		D_e (kcal mol^{-1})		r_e (Å)		ω_e (cm^{-1})	
Molecule	Basis[a]	Valence	Δd	Valence	Δd	Valence	Δd
$X^1\Sigma^+$ GaCl	cc-pVDZ-F12-PP	111.44	+0.57	2.2281	−0.0278	363.9	+4.7
	cc-pVTZ-F12-PP	112.09	+0.42	2.2306	−0.0277	361.6	+4.9
	cc-pVQZ-F12-PP	112.75	+0.45	2.2306	−0.0285	361.2	+5.2
	CBS[Q5][b]	113.17	+0.54	2.2301	−0.0299	361.6	+5.7
$X^1\Sigma^+$ InCl	cc-pVDZ-F12-PP	105.62	+1.04	2.4387	−0.0371	313.9	+4.8
	cc-pVTZ-F12-PP	106.40	+0.92	2.4425	−0.0384	311.7	+5.6
	cc-pVQZ-F12-PP	107.11	+0.96	2.4427	−0.0400	311.6	+6.3
	CBS[Q5][b]	107.50	+0.91	2.4420	−0.0410	312.1	+6.2
$X^1\Sigma^+$ TlCl	cc-pVDZ-F12-PP	100.34	+1.77	2.5518	−0.0529	277.5	+4.9
	cc-pVTZ-F12-PP	101.17	+1.67	2.5567	−0.0570	274.9	+7.1
	cc-pVQZ-F12-PP	101.81	+1.63	2.5581	−0.0605	274.8	+8.1
	CBS[Q5][b]	102.15	+1.61	2.5580	−0.0628	275.0	+8.4
$X^1\Sigma^+$ AsN	cc-pVDZ-F12-PP	111.37	+2.13	1.6262	−0.0116	1074.6	+11.3
	cc-pVTZ-F12-PP	113.26	+1.93	1.6261	−0.0113	1074.2	+10.8
	cc-pVQZ-F12-PP	114.05	+1.99	1.6256	−0.0114	1075.7	+11.4
	CBS[Q5][b]	114.69	+2.09	1.6251	−0.0120	1076.4	+12.4
$X^1\Sigma^+$ SbN	cc-pVDZ-F12-PP	81.29	+3.34	1.8485	−0.0204	874.4	+15.2
	cc-pVTZ-F12-PP	83.09	+3.26	1.8484	−0.0207	875.6	+15.4
	cc-pVQZ-F12-PP	83.78	+3.07	1.8477	−0.0207	876.9	+15.5
	CBS[Q5][b]	84.35	+2.95	1.8474	−0.0205	877.4	+15.1
$X^1\Sigma^+$ BiN	cc-pVDZ-F12-PP	65.44	+5.43	1.9559	−0.0359	765.9	+23.3
	cc-pVTZ-F12-PP	67.32	+5.46	1.9550	−0.0366	770.0	+23.5
	cc-pVQZ-F12-PP	67.92	+5.21	1.9544	−0.0361	771.4	+23.4
	CBS[Q5][b]	68.40	+5.02	1.9542	−0.0362	771.7	+23.8
$X^1\Sigma^+$ BrF	cc-pVDZ-F12-PP	62.80	−0.27	1.7589	−0.0038	681.4	+1.2
	cc-pVTZ-F12-PP	62.88	−0.31	1.7606	−0.0030	677.1	+0.3
	cc-pVQZ-F12-PP	63.20	−0.29	1.7597	−0.0032	678.2	+0.9
	CBS[Q5][b]	63.47	−0.34	1.7590	−0.0040	679.3	+1.4
$X^1\Sigma^+$ IF	cc-pVDZ-F12-PP	69.78	−0.04	1.9085	−0.0095	632.3	+2.7
	cc-pVTZ-F12-PP	69.96	−0.17	1.9101	−0.0090	628.4	+1.9
	cc-pVQZ-F12-PP	70.37	−0.30	1.9091	−0.0081	629.2	+1.6
	CBS[Q5][b]	70.60	−0.45	1.9086	−0.0084	629.4	+1.6
$X^1\Sigma^+$ AtF	cc-pVDZ-F12-PP	67.89	+0.78	2.0072	−0.0186	596.2	−3.3
	cc-pVTZ-F12-PP	68.29	+0.64	2.0102	−0.0191	592.4	−3.9
	cc-pVQZ-F12-PP	68.62	+0.39	2.0094	−0.0189	593.4	−3.3
	CBS[Q5][b]	68.82	+0.12	2.0092	−0.0188	594.4	−3.9

[a]The cc-pV*n*Z-F12 sets were used for N, F, and Cl.

[b]Conventional CCSD(T) results from Ref. 21 using cc-pwCV*n*Z-PP (n = Q, 5) basis sets.

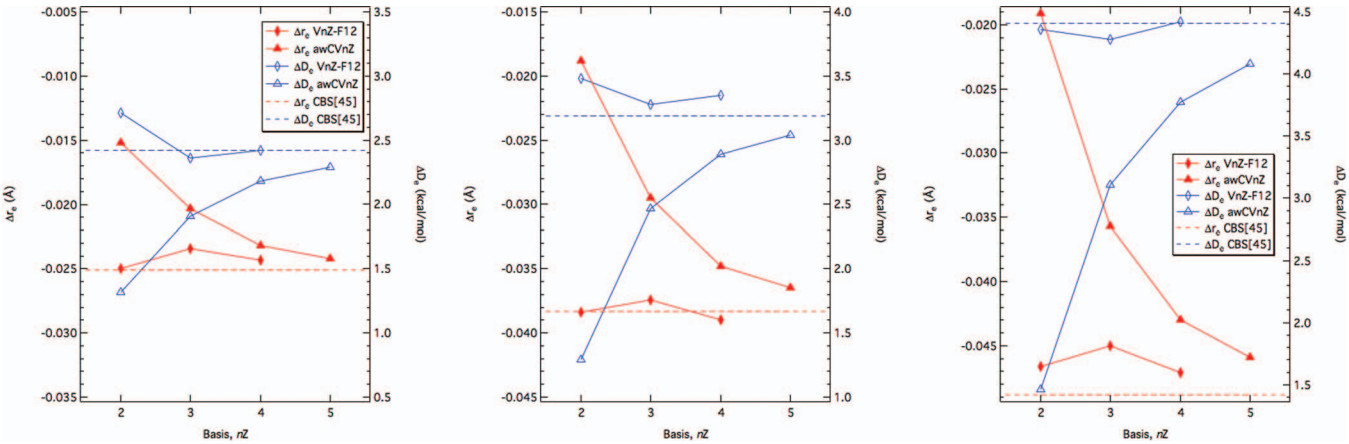

FIG. 6. Calculated CCSD(T) effects of *d* electron correlation for r_e (Δr_e in Å) and D_e (ΔD_e in kcal/mol) for (a) As_2, (b) Sb_2, and (c) Bi_2 as a function of basis set for CCSD(T)-F12b/cc-pV*n*Z-PP-F12 (V*n*Z-F12) and CCSD(T)/aug-cc-pwCV*n*Z-PP (awCV*n*Z). The estimated complete basis set limits, CBS[45], were obtained from conventional CCSD(T) with aug-cc-pwCV*n*Z-PP (n = Q, 5) basis sets.

to determine the spectroscopic constants (D_e, r_e, ω_e) of 9 homonuclear (Table VI and Figure 5) and 9 heteronuclear (Table VII) diatomic molecules distributed among the 4*p*, 5*p*, and 6*p* elements. The choice of molecules was motivated by a previous benchmark study[21] that reported cc-pwCV*n*Z-PP basis sets (n = D-5) for the same elements for use in conventional $(m-1)spd$ core correlation calculations. For the current calculations the CCSD(T)-F12b method was used (with the 3C fixed amplitude ansatz) with the new cc-pV*n*Z-PP-F12, cc-pV*n*Z-PP-F12/MP2FIT, and cc-pV*n*Z-PP-F12/OPTRI basis sets (n = D, T, Q) on the post-*d* elements. The density fitting of the exchange terms for post-*d* elements utilized the def2-QZVPP/JKFIT basis sets. For the lighter elements, cc-pV*n*Z-F12 sets were used for the orbital and OPTRI sets with aug-cc-pV*n*Z-PP and aug-cc-pwCV*n*Z-PP for the MP2FIT context (see above). The auxiliary basis sets for the exchange terms corresponded to cc-pV*n*Z/JKFIT (n = T for DZ and TZ orbital basis sets and n = Q for QZ). Both frozen-core (only *sp* valence electrons correlated) and $msp + (m-1)d$ correlation calculations were carried out. As noted above, in the former case, γ was chosen to be $1.0\,a_0^{-1}$ throughout, while the calculations involving *d*-electron correlation utilized $\gamma = 1.4\,a_0^{-1}$. The $(m-1)d$ correlation contributions to the spectroscopic constants (Δd) were determined using frozen-core calculations with this same value of γ ($1.4\ a_0^{-1}$). For the open-shell species, no symmetry equivalencing of the ROHF orbitals was carried out and the spin-unrestricted[49,50] R/UCCSD(T)-F12b method[51] was used throughout. For the group-13 chlorides, the ROHF orbitals were subjected to a 2 × 2 Boys localization in order to minimize the mixing between the valence 3*s* orbital of Cl with the d_σ core of the post-*d* element (see also Refs. 21 and 27).

Focusing first on the results for the homonuclear diatomic molecules shown in Table VI, the convergence of the frozen-core quantities with basis set is very rapid with the F12b ansatz and the new basis sets. This is also displayed in Fig. 5 for the group 15 diatomics, where the F12b approach with cc-pV*n*Z-PP-F12 basis sets yields dissociation energies and bond lengths comparable to at least $n + 1$ in a conventional treatment. If the comparison is made to the aug-cc-pV*n*Z-PP results, the F12 method yields bond lengths of approximately $n + 2$ quality or better. The convergence with basis set is also very monotonic, which should make the F12 results amenable to basis set extrapolation[45] to recover the small amount of basis set incompleteness error at the QZ level. It can be noted from the conventional CCSD(T)

TABLE VIII. BSSE in the CCSD(T)-F12b valence and *d*-electron correlation contributions for D_e, r_e, and ω_e for group 15 post-*d* nitrides (γ = 1.4).

		D_e (kcal mol^{-1})		r_e (Å)		ω_e (cm^{-1})	
Molecule	Basis[a]	Valence	Δd	Valence	Δd	Valence	Δd
$X^1\Sigma^+$ AsN	cc-pVDZ-F12-PP	+1.32	+0.14	− 0.0014	− 0.0004	+3.9	+0.8
	cc-pVTZ-F12-PP	+0.25	+0.12	− 0.0002	− 0.0003	+0.6	+0.3
	cc-pVQZ-F12-PP	+0.07	+0.17	− 0.0001	− 0.0002	+0.1	+0.7
$X^1\Sigma^+$ SbN	cc-pVDZ-F12-PP	+1.26	+0.50	− 0.0018	− 0.0009	+3.9	+2.1
	cc-pVTZ-F12-PP	+0.27	+0.42	− 0.0004	− 0.0007	+0.7	+1.4
	cc-pVQZ-F12-PP	+0.07	+0.26	− 0.0001	− 0.0004	+0.1	+0.7
$X^1\Sigma^+$ BiN	cc-pVDZ-F12-PP	+0.98	+0.74	− 0.0017	− 0.0015	+3.0	+2.9
	cc-pVTZ-F12-PP	+0.26	+0.59	− 0.0004	− 0.0019	+0.8	+2.7
	cc-pVQZ-F12-PP	+0.07	+0.31	− 0.0001	− 0.0007	+0.2	+1.0

[a]The cc-pV*n*Z-F12 sets were used for N.

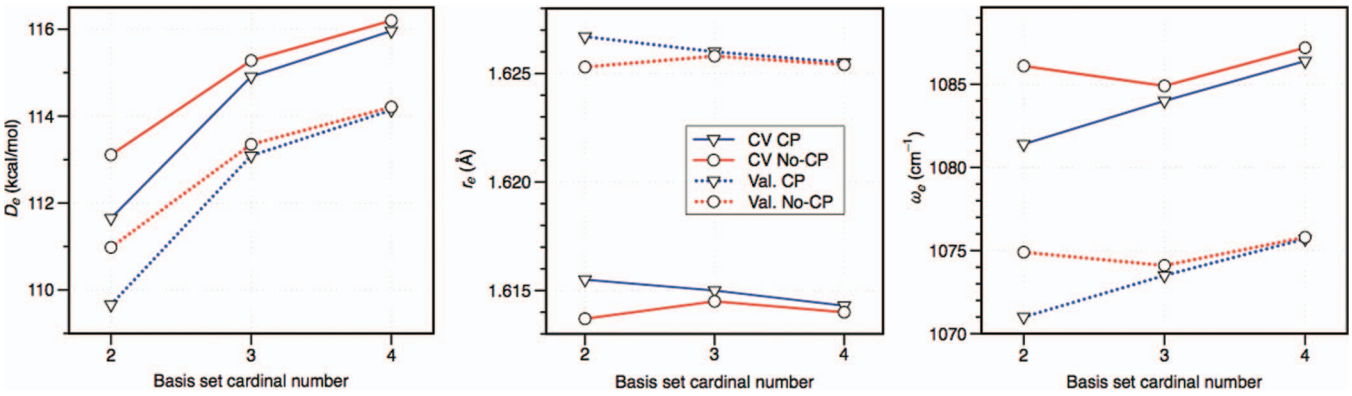

FIG. 7. Calculated CCSD(T)-F12b/cc-pV*n*Z-PP-F12 values of D_e, r_e, and ω_e for the AsN molecule as a function of basis set for both valence (Val.) and valence + *d* electron (CV) correlation. Both counterpoise corrected (CP) and uncorrected (no-CP) values are shown.

results shown in Fig. 5 that the effect of tight high angular momentum functions, as reflected by the difference between the aug-cc-pV*n*Z-PP and aug-cc-pwCV*n*Z-PP results, is certainly not negligible in frozen-core calculations, particularly for the bond lengths of Sb_2 and Bi_2. This underlines the importance of the additional tight 1*d*1*f* functions that have been included throughout the new cc-pV*n*Z-PP-F12 basis sets. In regards to F12 frozen-core results for the heteronuclear diatomics shown in Table VII, as well as the conventional CCSD(T) results from Ref. 21, the convergence trends are very similar to those discussed above for the homonuclear diatomics. In fact for these systems, the $n + 2$ advantage of F12 seems to nearly hold for both D_e and r_e even when compared to the CCSD(T)/cc-pwCV*n*Z-PP results. Taking together all of the diatomic results for valence correlation, the cc-pVQZ-PP-F12 results differ on average (signed) from the conventional CBS limits by just (standard deviations in parentheses) −0.47 (0.29) kcal/mol, +0.0009 (0.0009) Å, and −0.5 (0.3) cm^{-1} for D_e, r_e, and ω_e, respectively. Even at the TZ level the agreement is excellent, −1.04 (0.58) kcal/mol, +0.0020 (0.0020) Å, and −1.2 (0.8) cm^{-1}, respectively.

As already shown in previous work,[21] the effects on D_e and r_e from *d*-electron correlation can be very substantial, but the convergence with respect to basis set in conventional CCSD(T) calculations can unfortunately be very slow. However, as shown in Tables VI and VII, use of CCSD(T)-F12b with the new cc-pV*n*Z-PP-F12 basis sets yields very rapid convergence towards the respective CBS limits. In these cases even DZ quality calculations yield reliable estimates of core correlation effects, to within a few tenths of a kcal/mol for D_e to a few mÅ for the bond length. This can be contrasted with conventional results whereby the *d*-electron correlation effect can often be underestimated (compared to the CBS limit) by a few kcal/mol and a few hundredths of an Å for double- and even triple-zeta core-valence basis sets. As can be seen in Tables VI and VII, as well as in Figure 6, the convergence of these effects with F12, while rapid, is not completely monotonic. Closer inspection shows this can be attributed mainly to basis set superposition error (BSSE), presumably arising from only using a 1*d*1*f* set of functions to recover *d*-electron correlation effects (in addition to the F12 correlation factor of course). This is exemplified in Table VIII for the group-15 nitrides, as well as Figure 7 for AsN, where counterpoise calculations[52] have been carried out. In particular, while the BSSE in valence-only correlated calculations smoothly decreases in all cases as the basis set increases, the BSSE in the core-valence corrections to D_e, r_e, and ω_e predominately only slightly decreases. Comparison to the results shown in Table VII, however, shows that in each case the BSSE values do end up at least an order of magnitude less than the total magnitude of the core-valence correlation effect on each property. On average (signed), however, the cc-pVQZ-PP-F12 results for the effects of *d*-electron correlation are very close to the conventional CBS limits (standard deviations in parentheses): +0.05 (0.10) kcal/mol, +0.0008 (0.0010) Å, and −0.3 (0.5) cm^{-1} for D_e, r_e, and ω_e, respectively. The analogous average signed deviations for cc-pVTZ-PP-F12 are just +0.04 (0.25) kcal/mol, +0.0020 (0.0027) Å, and −0.7 (0.7) cm^{-1}. The statistics for cc-pVDZ-PP-F12 were really not much worse than TZ: +0.13 (0.34) kcal/mol, +0.0017 (0.0037) Å, and −0.8 (1.1) cm^{-1}.

V. CONCLUSIONS

New correlation consistent basis sets for all the post-*d* main group elements Ga-Rn, ranging in size from double- to quadruple-zeta, have been developed for use in explicitly correlated F12 calculations. Orbital basis sets (cc-pV*n*Z-PP-F12) have been developed along with the required auxiliary basis sets, both those for density fitting the conventional 2-electron integrals (MP2FIT) and those for use in the CABS procedure for the F12 many-electron integrals (OPTRI). The sets are designed for use with the same small-core relativistic pseudopotentials as employed in the standard cc-pV*n*Z-PP basis sets. A number of diatomic molecule benchmark calculations were carried out at the CCSD(T)-F12b level of theory with the new basis sets for both *msp* and *msp* + (*m*−1)*d* electron correlation. Compared to previously published conventional CCSD(T) results on the same molecules, the convergence of the F12 results to the estimated CBS limits was much more rapid, both in frozen-core and outer-core *d*-electron correlated calculations. The increased rate of basis set convergence with F12 methods for these elements opens the way to carrying out accurate CCSD(T) calculations of large molecular systems

involving these elements using only relatively small basis sets.

All of the basis sets of the present work are available in the supplementary material,[32] as well as from the downloads section of one of the authors' websites (http://tyr0.chem.wsu.edu/~kipeters/basis.html) and the basis set library of the MOLPRO program (see http://www.molpro.net).

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