Systematically convergent basis sets for explicitly correlated wavefunctions: The atoms H, He, B–Ne, and Al–Ar

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Citation: The Journal of Chemical Physics **128**, 084102 (2008); doi: 10.1063/1.2831537
View online: http://dx.doi.org/10.1063/1.2831537
View Table of Contents: http://aip.scitation.org/toc/jcp/128/8
Published by the American Institute of Physics

THE JOURNAL OF CHEMICAL PHYSICS **128**, 084102 (2008)

Systematically convergent basis sets for explicitly correlated wavefunctions: The atoms H, He, B–Ne, and Al–Ar

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(Received 12 November 2007; accepted 11 December 2007; published online 25 February 2008)

Correlation consistent basis sets have been optimized for use with explicitly correlated F12 methods. The new sets, denoted cc-pV*n*Z-F12 (n=D,T,Q), are similar in size and construction to the standard aug-cc-pV*n*Z and aug-cc-pV($n+d$)Z basis sets, but the new sets are shown in the present work to yield much improved convergence toward the complete basis set limit in MP2-F12/3C calculations on several small molecules involving elements of both the first and second row. For molecules containing only first row atoms, the smallest cc-pVDZ-F12 basis set consistently recovers nearly 99% of the MP2 valence correlation energy when combined with the MP2-F12/3C method. The convergence with basis set for molecules containing second row atoms is slower, but the new DZ basis set still recovers 97%–99% of the frozen core MP2 correlation energy. The accuracy of the new basis sets for relative energetics is demonstrated in benchmark calculations on a set of 15 chemical reactions. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2831537]

I. INTRODUCTION

One of the largest uncertainties in standard correlated electronic structure methods is due to the slow convergence of the one-particle basis set, where the correlation energy converges toward the complete basis set (CBS) limit at a rate of only about $\ell_{\max}^{-3}$, where $\ell_{\max}$ is the maximum angular momentum in the basis set. Significant progress has been made over the last several years, however, due to the development and use of sequences of correlation consistent basis sets,[1–5] which allow for an accurate extrapolation to the CBS limit. The main drawback of this approach is that these extrapolations are most accurate only when very large basis sets are used, e.g., at least cc-pVQZ and preferably cc-pV5Z and higher, which can quickly become very computationally demanding. A more efficient route around the basis set problem, which is due in large part to a poor description of the Coulomb cusp and associated correlation hole by products of one-particle functions, is by using an approach where functions of the interelectronic distance are explicitly included in the wavefunction. Until recently, the most successful of these explicitly correlated techniques was the R12 method originally implemented by Kutzelnigg and Klopper at the MP2 level of theory,[6] in which functions linear in r_{12} were included. The expensive three- and four-electron integrals introduced by this method were reduced to products of two-electron integrals using resolutions of the identity (RI),[7,8] which made R12 practical for molecular calculations.[9] One of the early drawbacks of this method, however, was that the atomic orbital basis set was used for the RI, and hence very large basis sets were required and only relatively small systems could be treated. This latter problem was ameliorated by Klopper and Samson by using auxiliary RI basis sets,[7] but the overall basis set convergence was still not significantly faster than conventional methods until large basis sets were used.

There have been many recent and exciting developments in explicit correlation methods,[7,10–33] many of which have also been outlined in a recent review.[32] The relative importance of various approximations has also recently been investigated.[20,25] The key finding was that the choice of correlation factor was the most important consideration, and that nonlinear correlation factors, particularly $e^{-\beta r_{12}}$, were found to give much improved results compared to a function linear in r_{12}.[20–25] Explicitly correlated methods using these general correlation factors have been denoted F12. Recently, new explicitly correlated MP2-F12 methods have been implemented[18,24,25] in which local correlation approximations can be used and many of the required integrals are computed using efficient density fitting approximations.[13] These methods can be applied to much larger molecules than previous MP2-F12 implementations. It has been shown that with basis sets of triple zeta quality, reaction energies can be obtained within 1 kJ/mol of the MP2 basis set limit.[25] This was more accurate than conventional MP2 with basis set extrapolation using correlation consistent quadruple and quintuple zeta basis sets. Similar improvements for the coupled cluster singles and doubles method have recently been reported using the CCSD(T)(F12) method of Klopper and co-workers[11,30] and the CCSD(T)-F12 approximations of Adler *et al.*[33]

Commonly used basis sets for describing electron correlation effects, e.g., standard correlation consistent sets, are not, however, optimal for use with explicitly correlated methods. Since they were optimized in conventional corre-

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lated calculations, these basis sets attempt to describe not only the Hartree–Fock (HF) wavefunction but also correlation effects involving *both* the correlation hole and the longer-range portion of the electronic wavefunction. Particularly in the new F12 methods, the wavefunction in the region of the correlation hole can be accurately described by the nonlinear correlation factor. Thus, the one-particle basis set must then only accurately describe the HF wavefunction and longer-range electron correlation effects. Possibilities then exist for considerable savings. In the present work, new correlation-consistent-type basis sets are developed at the MP2-F12 level of theory for main group elements through the second row (H, He, B–Ne, and Al–Ar). The resulting basis sets, denoted cc-pVnZ-F12, where n=D, T, and Q, exhibit improved convergence of MP2-F12 atomic and molecular correlation energies compared to the standard diffuse-augmented correlation consistent basis sets. Benchmark calculations on numerous molecules containing first and second row atoms are presented, including a number of reaction energies, in order to test the efficacy of the new basis sets in explicitly correlated calculations.

II. GENERAL COMPUTATIONAL DETAILS

All of the calculations of the present work employed the MOLPRO suite of *ab initio* programs[34] and only the pure spherical harmonic components of the $dfghi$ angular momentum functions were utilized. In general, only the valence electrons were correlated (frozen-core approximation), and the optimization of basis set exponents employed numerical gradients using either conjugate gradient or Simplex algorithms.[35] While conventional HF calculations were performed throughout, density fitting was employed in the MP2-F12 calculations. The latter employed the cc-pV5Z/JKFIT auxiliary basis sets of Weigend[36] for the exchange and Fock operators together with the aug-cc-pV5Z/MP2FIT sets of Hättig[37] for the remaining two-electron integrals. The JKFIT basis sets for the rare gas atoms He, Ne, and Ar were not available; therefore, those for Ne and Ar were obtained by simple extrapolation of the O, F and S, Cl basis set exponents, respectively. In the case of He, the aug-cc-pV5Z/MP2FIT set[37] was used for this purpose. The RI auxiliary basis sets required for the multicenter three- and four-electron integrals were analogous to the large sets used previously by Klopper[38] and Klopper and Samson.[7] Specifically for B–Ne and Al–Ar, the uncontracted $(18s13p)$ and $(20s15p)$ sets of Partridge,[39,40] respectively, were combined with the $dfghi$ angular momentum functions of the aug-cc-pV6Z basis sets.[41,42] 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 fashion. In the cases of H and He, uncontracted aug-cc-pV6Z basis sets were utilized without their h-type functions but with the addition of a tight p function (obtained by even tempered extrapolation). The complementary auxiliary basis set approach (CABS)[25,27] was used throughout with a relative threshold $(s_{\min}/s_{\max})$ of 5.0×10^{-9}, where $s_{\min}$ and $s_{\max}$ were the smallest and largest eigenvalues, respectively, of the complementary auxiliary overlap matrix (see Ref. 25). Two different MP2-F12 approximations were used in this work, the rigorous 3C ansatz and 3C(D).[25] The former is used for the preliminary investigations as well as the final benchmark calculations, while the 3C(D) ansatz was used in the optimization of the final basis sets in order to minimize effects due to geminal basis set superposition.

In all cases, the Slater function in the F12 correlation factor was approximated by an expansion of six Gaussians, and the expansion coefficients were fitted as described in Ref. 25. The choice of geminal exponent, β (in a_0^{-1}) varied throughout this work. Initial investigations and the final basis set optimizations used a fixed value of 1.4, which was based on previous work in the literature. Then, β was varied for fixed basis sets to determine the optimal values as a function of the basis. After determining the recommended value for each basis set, these were then employed in subsequent benchmark calculations.

III. BASIS SET DEVELOPMENT

A. Initial investigations of possible *dfghi* correlating functions

Analogous to the construction of standard correlation consistent basis sets,[1,5] the first step in generating a hierarchical basis set series exhibiting systematic convergence to the CBS limit is to first determine the identity and number of correlating functions to include for a given basis set. To this end, Fig. 1 displays the incremental correlation energy lowerings for the Ne atom as optimal exponents of functions of increasing angular momentum are added to the basis set. The results of Fig. 1(a) were determined at the conventional MP2 level of theory, while the data of Fig. 1(b) were obtained by MP2-F12 with the 3C ansatz[17,25] and a geminal Slater exponent of β=1.4. The base set to which the $dfgh\cdots$ functions were added consisted of the $(18s13p)$ primitive set of Partridge contracted to $[8s7p]$, and the optimized exponents ζ_k were constrained to follow an even tempered sequence, i.e., $\zeta_k=\alpha\gamma^{k-1}$. The results of Fig. 1 were calculated in the usual manner: first a single d function was added to the $[8s7p]$ base set and optimized (either by MP2 or MP2-F12/3C), then two to five d-type functions were optimized. One f function was then added to the resulting $[8s7p5d]$ set and optimized, then two f functions, etc. The analogous results for s and p correlating functions are shown as insets in Fig. 1 and were determined similarly by adding functions to $[2s7p5d3f2g]$ and $[8s1p5d3f2g]$ base sets, respectively. The incremental correlation energy lowering of Fig. 1(a) are very reminiscent of the configuration interaction results shown previously for the oxygen atom in the original work of Dunning,[1] and the usual correlation consistent groupings of correlating functions are easily observed, i.e., $1d$ for cc-pVDZ, $2d1f$ for cc-pVTZ, etc. The MP2-F12/3C results of Fig. 1(b), however, are markedly different. In particular, the convergence of the energy with respect to increasing angular momentum is much faster than in conventional MP2, with the incremental correlation energies dropping by about an order of magnitude between the addition of the first functions of d, f, g, and h symmetries. The overall magnitudes of the incremental lowerings are also much smaller compared to the conventional

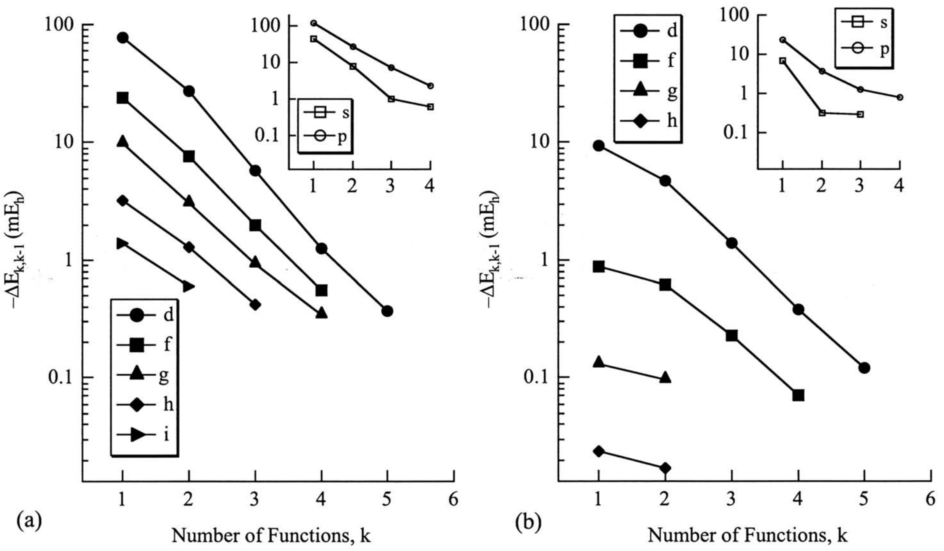

FIG. 1. Incremental contributions of correlating functions to the frozen core correlation energy of the Ne atom, $-\Delta E_{k,k-1}$ (in mE_h), calculated at the (a) MP2 and (b) MP2-F12/3C ($\beta = 1.4 a_0^{-1}$) levels of theory.

MP2 results since the F12 correlation factor alone is now recovering a large fraction of the correlation energy. It should also be pointed out that the incremental contributions due to *p*-type functions are relatively large and somewhat slowly convergent. The contributions of *s*-type functions, however, are much smaller in comparison to conventional MP2. In addition, it can also be observed in Fig. 1(b) that the first two functions of each angular momentum recover very similar amounts of correlation energy, especially for the *f*, *g*, and *h* functions. Obviously, a different set of "correlation consistent" groupings seems to be warranted for F12 methods based on these results for the Ne atom.

In the present case, however, it would be a mistake to decide on a new basis set prescription based only on atomic calculations since in these cases the HF energy is not sensitive to the presence of higher angular momentum functions. In conventional correlated calculations on molecules, e.g., using the cc-pV*n*Z basis sets[1,4,5] as well as the polarization consistent pc-*n* sets of Jensen,[43,44] this has been shown not to be a problem since (a) the basis set error of the correlation energy is a large fraction of the error in the total energy and (b) the optimal HF exponents and their relative energetic importance are very similar to those obtained in correlated calculations. On the other hand, due to the much decreased importance of higher angular momentum functions in explicitly correlated calculations as shown in Fig. 1(b), this might not be expected to hold true for F12-type calculations. In fact, this is dramatically apparent from the incremental HF and MP2-F12 correlation energies calculated for the N_2 molecule and plotted in Fig. 2. These energies were obtained by adding successive polarization/correlating functions to the contracted *s* and *p* portion of the aug-cc-pVQZ basis set and optimizing them for the total MP2-F12/3C energy. These results are also given explicitly in Table I together with the analogous values obtained in conventional MP2 optimizations. As is apparent in Fig. 2 (and Table I), the first function of each angular momentum symmetry makes very strong contributions to the HF wavefunction with less correlation energy recovery at the MP2-F12 level of theory. As is well known, however, the convergence of the HF energy with successive polarization functions is rapid and nearly exponential,[45,46] so the addition of a second polarization/correlating function makes strong contributions to the MP2-F12 correlation energy. These trends can be understood by comparing the optimized MP2 and MP2-F12 even tempered parameters of Table I. In general, both conventional MP2 and HF optimized exponents are much tighter than those required for the MP2-F12 correlation energy, and the resulting exponents obtained in (total energy) MP2-F12 optimizations are thus a compromise between minimizing the HF energy and the MP2-F12 correlation energy.

From the results on the N_2 molecule, as well as those discussed above for the Ne atom, a possible strategy for con-

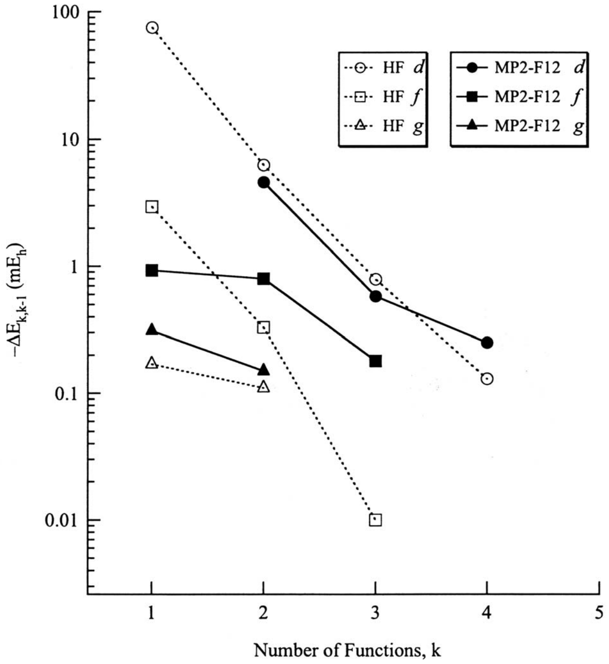

FIG. 2. Incremental contributions of polarization/correlating functions to the HF energy (open symbols) and frozen core MP2-F12/3C ($\beta = 1.4 a_0^{-1}$) correlation energy (closed symbols) for the N_2 molecule, $-\Delta E_{k,k-1}$ (in mE_h). The exponents were optimized for the total MP2-F12/3C energy.

TABLE I. Comparison of the incremental contributions of polarization/correlating functions to the HF energy and correlation energy (in mE_h) together with the optimized even-tempered exponent parameters ($\zeta_k = \alpha\gamma^{k-1}$) for the N_2 molecule (r=1.098 12 Å). The total energy (MP2 or MP2-F12/3C) was used for the exponent optimizations in each case. The base set to which optimized functions were added corresponded to the contracted *sp* part of the aug-cc-pVQZ basis set.

	E(Corr)	ΔE(HF)	ΔE(Corr)	α_{opt}[a]	γ_{opt}
		Conventional MP2			
[5*s*4*p*]+1*d*	−336.79	−75.62	−74.06	1.006	
+2*d*	−356.56	−5.78	−19.77	0.536	3.130
+3*d*	−360.24	−0.64	−3.68	0.425	2.598
+4*d*	−361.36	−0.16	−1.12	0.296	2.263
[5*s*4*p*4*d*]+1*f*	−385.89	−3.17	−24.53	1.302	
+2*f*	−392.37	−0.11	−6.49	0.703	2.708
+3*f*	−393.96	−0.02	−1.58	0.583	2.299
[5*s*4*p*4*d*3*f*]+1*g*	−402.34	−0.26	−8.39	1.576	
+2*g*	−404.98	−0.04	−2.64	0.861	2.549
		MP2-F12/3C ($\beta=1.4a_0^{-1}$)			
[5*s*4*p*]+1*d*	−412.14	−75.09	+2.19[b]	0.868	
+2*d*	−416.74	−6.27	−4.60	0.433	3.242
+3*d*	−417.32	−0.79	−0.58	0.353	2.927
+4*d*	−417.57	−0.13	−0.25	0.194	2.569
[5*s*4*p*4*d*]+1*f*	−418.51	−2.95	−0.93	0.994	
+2*f*	−419.31	−0.33	−0.80	0.511	2.967
+3*f*	−419.49	−0.01	−0.18	0.388	2.206
[5*s*4*p*4*d*3*f*]+1*g*	−419.80	−0.31	−0.31	0.872	
+2*g*	−419.95	−0.15	−0.15	0.561	3.207

[a] The HF optimized α values for the first functions of *d*, *f*, and *g* angular momenta were 0.967, 1.386, and 1.669, respectively, with concomitant incremental HF energy lowerings of −73.83, −3.12, and −0.26 mE_h.

[b] This positive incremental correlation energy contribution is due to the very poor description of the HF wavefunction without *d* functions.

structing correlation consistent basis sets for both atomic and molecular F12 calculations would be to (a) optimize basis sets primarily in molecular calculations and (b) add at least two functions of each new angular momentum symmetry to the basis set in order to describe both the HF and correlation energies. The latter yields a new prescription for F12 optimized basis sets for B–Ne, denoted cc-pV*n*Z-F12: 2*d* for n=D, 3*d*2*f* for n=T, and 4*d*3*f*2*g* for n=Q. It should be noted that this leads to the same number of higher angular momentum functions as the standard aug-cc-pV*n*Z basis sets.[3]

One large question that remains, however, is how the convergence behavior for the second row atoms Al–Ar compares to the first row. Figure 3 plots the incremental correlation energy contributions for the Ar atom, both conventional MP2 [Fig. 3(a)] and MP2-F12/3C [Fig. 3(b)]. These were obtained in a similar fashion as in Fig. 1, but the constraint to even tempered expansions was relaxed for the *d* and *f* functions since the distributions of optimal exponents were significantly different from the even tempered pattern, particularly in the MP2-F12 case. Therefore, in both the MP2 and

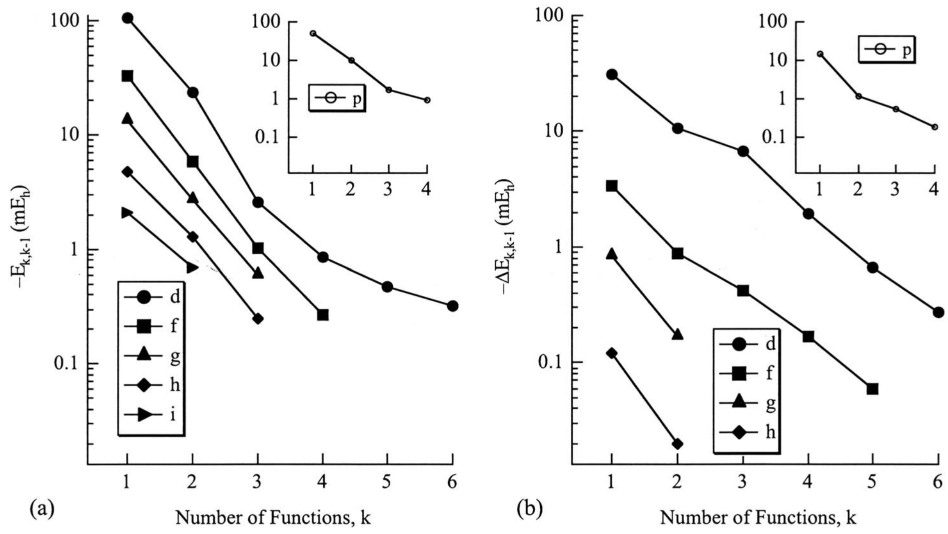

FIG. 3. Incremental contributions of correlating functions to the frozen core correlation energy of the Ar atom, $-\Delta E_{k,k-1}$ (in mE_h), calculated at the (a) MP2 and (b) MP2-F12/3C ($\beta=1.4a_0^{-1}$) levels of theory.

MP2-F12 optimizations for Ar, the (3*d*), (4*d*), and (3*f*) sets of exponents were fully optimized, while the (5*d*) and (4*f*) optimizations were carried out with only the tightest exponent allowed to freely vary (the remainder being constrained to an even tempered sequence). All other cases used the even tempered prescription. This strategy was also used in the final basis sets for the second row elements. Upon comparison to Fig. 1, the magnitudes of the incremental correlation contributions at the conventional MP2 level (see also Ref. 5) are only about 1.5 times larger than those for the Ne atom, while those determined in MP2-F12 calculations are greater compared to Ne by more than a factor of 3. Hence, it is expected that the MP2-F12 basis set convergence will be significantly slower for the second row atoms compared to the first row. Comparison of the optimized exponents between MP2 and MP2-F12 for the Ar atom also shows that while the most diffuse MP2-F12 values are generally more diffuse than the conventional MP2-optimized ones, which is in agreement with the first row, the innermost exponents, particularly the *d* and *f* exponents, are much tighter than those obtained with conventional MP2.

It can also be observed in Fig. 3 that unlike the Ne atom (cf. Fig. 1) the first two functions of each angular momentum do not yield similar incremental correlation contributions. To determine whether this indicated a fundamental difference between the first and second row atoms, perhaps requiring a different cc-pV*nZ*-F12 prescription, MP2-F12/3C calculations were carried out on the P_2 molecule analogous to those discussed above for N_2. The resulting trends observed for P_2 were completely analogous to those of N_2, i.e., the first optimized functions of each angular momentum symmetry primarily lowered the HF energy, while subsequent functions of that symmetry recovered relatively more MP2-F12 correlation energy. Thus, the prescription described above for the first row will be used for the second row with only one major adjustment, an extra *d* function will be added at each zeta level. This extra *d* is completely analogous to the function added in the cc-pV($n+d$)Z basis sets[2] and is now well known to be required at the HF level for molecular calculations involving second row atoms. In the present case, an appropriate function arises naturally in the MP2-F12 optimizations, even for the Ar atom. Hence, for the second row atoms, cc-pVDZ-F12 contains three *d* functions, cc-pVTZ-F12 has a 4*d*2*f* set, and cc-pVQZ-F12 consists of 5*d*3*f*2*g*.

Last, considerations for He and H_2 should be discussed. In both cases, the convergence of the MP2-F12 total energy is extremely rapid, but some of the same considerations discussed above for the first and second row were found to be valid as well. Hence, it was determined that the cc-pVDZ-F12 basis should contain two *p*-type functions in analogy to the 2*d*-type functions included for B–Ne. Since the convergence with higher angular momentum functions is sufficiently rapid, however, the cc-pVTZ-F12 basis sets for H and He consist of just a 3*p*1*d* set while the cc-pVQZ-F12 basis is constructed with 4*p*2*d*1*f*.

B. Choosing Hartree-Fock and *s* and *p* correlating functions

As discussed above, unlike conventional calculations, the basis set errors in the total energies obtained with explicitly correlated methods can be dominated by the HF error for small and moderate sized basis sets. The choice of HF set to use in each cc-pV*n*Z-F12 basis set can also to some extent determine the *s* and *p* functions used for correlation. In the present work, the contracted HF *s* and *p* functions from the cc-pV($n+1$)Z basis sets were used for the new cc-pV*n*Z-F12 basis sets, e.g., the contracted [2*s*1*p*] set from the cc-pVTZ basis sets were used in the cc-pVDZ-F12 basis for the first row atoms. This choice significantly decreases the HF basis set error with very little additional computational cost. In addition, the single diffuse *s* and *p* augmenting functions from the aug-cc-pV($n+1$)Z sets were also included in the cc-pV*n*Z-F12 sets in order to provide an accurate description of lone pairs in molecules such as H_2O or NH_3. While this general prescription was also followed for the He atom, diffuse *s* functions were not included in the H basis sets. Of course, the H atom basis sets could easily be augmented in the rare instance when these functions are deemed important. It should be noted that the inclusion of just *s* and *p* diffuse functions may not be sufficient for a rapid convergence of properties strongly dependent on the long-range part of the wavefunction, e.g., electron affinities or van der Waals binding energies. Further extension of the higher angular momentum functions might then be considered in these cases, perhaps by using an even tempered scheme.

In terms of the choice of *s* and *p* correlating functions, the insets in Figs. 1 and 3 indicate that the convergence of the MP2-F12 correlation energy with *s* functions is very rapid, while that of the *p* functions is somewhat slow and similar to the convergence behavior of the *d*-type functions, especially for the Ne atom. Thus, the *s*-type correlating functions were simply taken from those of the cc-pV($n+1$)Z basis sets, e.g., the two *s*-type correlating functions uncontracted in the cc-pVTZ basis sets were also used in the cc-pVDZ-F12 basis. For the *p*-type correlating functions, it was decided to also use the two *p*-type correlating functions from the cc-pV($n+1$)Z sets but also add an additional tight *p* in each case, e.g., three *p* functions in the cc-pVDZ-F12, a set of four *p* functions in the cc-pVTZ-F12, etc. For the first row atoms, this merely involved uncontracting an additional function from the HF sets, but for the second row, this latter choice was not always optimal. Thus, in the cc-pVDZ-F12 basis sets for the second row atoms, the most diffuse *p* function was uncontracted from the cc-pVTZ HF set and this was combined with two functions that were explicitly optimized for MP2-F12. The cc-pVTZ-F12 basis sets for the second row involved the explicit optimization of just one tight *p* function, while in the QZ case, it was possible to just uncontract the five most diffuse *p* functions from the underlying HF set.

Thus, in terms of the final contracted sizes of the new cc-pV*n*Z-F12 basis sets in comparison to aug-cc-pV*n*Z (H, He, B–Ne) and aug-cc-pV($n+d$)Z (Al–Ar), the sets for H are the same size, those for He include one additional *s*-type

TABLE II. Composition of the new cc-pV*n*Z-F12 basis sets.

	cc-pVDZ-F12	cc-pVTZ-F12	cc-pVQZ-F12
H	$(5s2p)/[3s2p]$	$(6s3p1d)/[4s3p1d]$	$(8s4p2d1f)/[5s4p2d1f]$
He	$(7s2p)/[4s2p]$	$(8s3p1d)/[5s3p1d]$	$(9s4p2d1f)/[6s4p2d1f]$
B–Ne	$(11s6p2d)/[5s5p2d]$	$(13s7p3d2f)/[6s6p3d2f]$	$(15s9p4d3f2g)/[7s7p4d3f2g]$
Al–Ar	$(16s12p3d)/[6s6p3d]$	$(17s13p4d2f)/[7s7p4d2f]$	$(21s13p5d3f2g)/[8s8p5d3f2g]$

function, while those for the first and second rows include one additional *s* and two *p* functions. Thus, a total of just zero, one, and seven extra contracted functions, respectively, for each value of *n*. The composition of the new basis sets are given in Table II.

C. Optimization of final cc-pV*n*Z-F12 basis sets for H, He, B–Ne, and Al–Ar

Basis set optimizations on molecules have been systematically addressed in the development of the polarization consistent basis sets by Jensen and co-workers.[43,44] In the present work, the set of systems chosen for the basis set optimizations are shown in Table III. Due to program limitations at the time this work was initiated, the molecules and atoms were restricted to closed-shell systems, but still span a variety of bonding environments. The geometries of the molecules were optimized at the coupled cluster singles and doubles with perturbative triples [CCSD(T)] level of theory[47,48] using the cc-pCVQZ basis sets.[49,50] Both the valence and outer core electrons (all electrons for B–Ne and $2s2p3s3p$ for Al–Ar) were correlated in these calculations. The resulting geometries for many of the molecules containing only first-row atoms were thus equivalent to those reported previously by Bak *et al.*[51] In the case of the H_2 molecule, however, a stretched bond length $(1.25r_e)$ was utilized in the basis set optimizations.[43] All correlation energies cited in this work for H_2, however, refer to the values at r_e. All geometries used in the present work are available as supplemental material.[52]

In order to minimize geminal basis set superposition errors in the optimization process, the 3C(D) ansatz[25] of MP2-F12 was used throughout, with orbital localization determined using the Pipek-Mezey method.[53] A relatively large value of the geminal exponent β, 1.4, was used in all the optimizations so that the optimized basis functions might predominately describe long range electron correlation. Only valence electrons were correlated.

In initial optimizations involving the molecules of Table III, correlating basis functions were optimized for each molecule separately and the final values of the exponents for a particular element were obtained by averaging these exponents. This procedure, however, did not lead to well behaved basis sets. In the final approach, the correlating basis functions for a given element were optimized for the weighted sum of the total MP2-F12/3C(D) energies of all the molecules utilized for that element, e.g., for nitrogen $E_{\text{opt}}=E(N_2)/2+E(NH_3)+E(N_2H_2)/2$.

TABLE III. Atoms and molecules selected for use in the basis set optimizations.

H_2, He
B: $\{BN, BH_3\}$, C: $\{C_2, CH_2(^1A_1), CH_4, C_2H_4\}$, N: $\{N_2, NH_3, N_2H_2\}$, O: $\{H_2O, H_2O_2, H_2CO\}$,
F: $\{F_2, HF\}$, Ne
Al: {AlP, AlN, AlH}, Si: $\{Si_2, SiS, SiO, SiH_2, SiH_4\}$, P: $\{P_2, PN, PH_3\}$, S: $\{H_2S, H_2S_2, H_2CS\}$,
Cl: $\{Cl_2, HCl\}$, Ar

IV. RESULTS AND DISCUSSION

A. Dependence on geminal exponent β

To this point, the variation of the MP2-F12/3C correlation energies with the geminal exponent β has not been discussed, although it is well known in previous studies[22,23] that the correlation energy can be very sensitive to its choice, particularly for small basis sets. The sensitivity of the MP2-F12/3C correlation energy to the choice of β is shown in Fig. 4, where the basis set errors per correlated electron (in kcal/mol) are shown as a function of β (the basis set limits were taken from Sec. IV B). Results using the cc-pVDZ-F12 basis

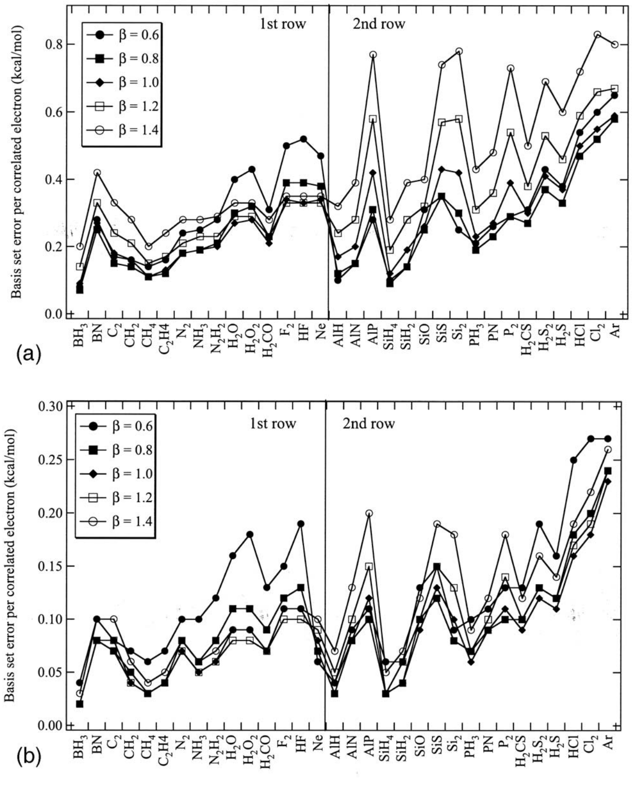

FIG. 4. Basis set errors per correlated electron (in kcal/mol) as a function of the geminal exponent β (in a_0^{-1}) with the MP2-F12/3C method and the (a) cc-pVDZ-F12 and (b) cc-pVTZ-F12 basis sets.

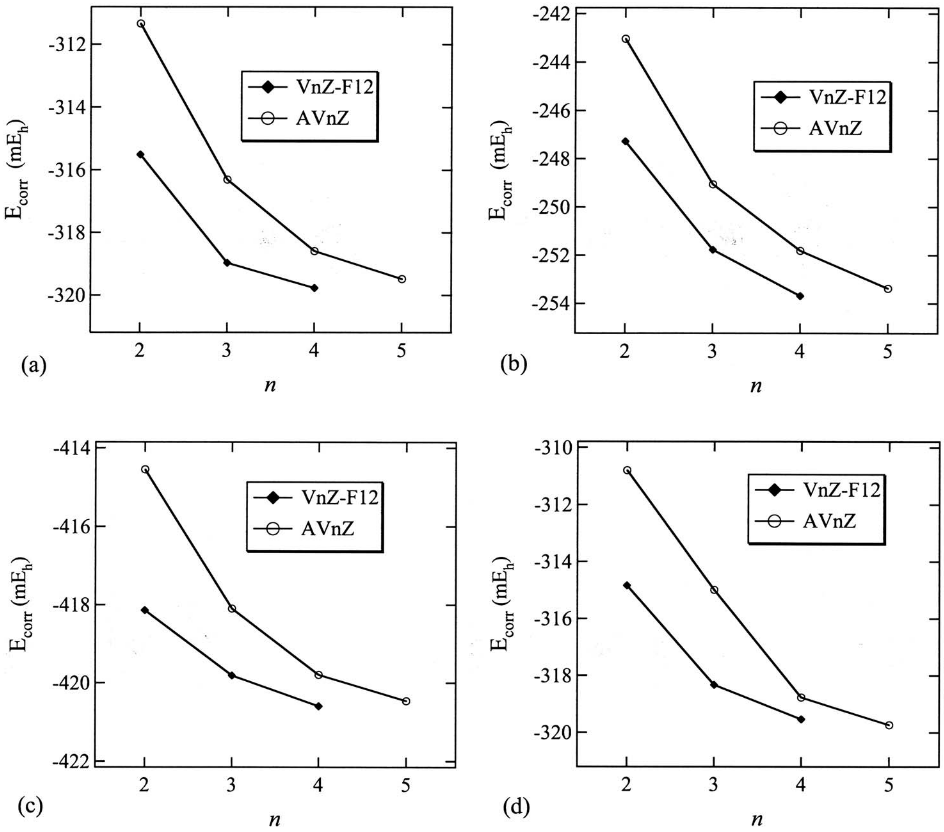

FIG. 5. Basis set dependence of the MP2-F12/3C frozen core correlation energy for (a) Ne, (b) Ar, (c) N_2, and (d) P_2 using sequences of AV*n*Z (n=D−5), and the new V*n*Z-F12 (n=D−Q) basis sets. Fixed, recommended values of the geminal exponent β were used in each case (cf. Tables IV and V).

set are given in Fig. 4(a), while those using the cc-pVTZ-F12 basis are plotted in Fig. 4(b). Obviously, from these figures, the choice of β can be an important consideration in obtaining accurate correlation energies. With the cc-pVDZ-F12 basis set, a relatively small value for β of about 0.9 appears to yield errors below about 0.4 kcal/mol per correlated electron across all the species of Table III. For systems containing second row elements, the use of β values equal or larger than 1.2 yield much larger errors with this basis set. Much of the sensitivity of the correlation energy on the choice of β is removed with use of the cc-pVTZ-F12 basis set as shown in Fig. 4(b). Nearly optimal correlation energies can be obtained with β=1.0. In summary, to avoid the optimization of β in routine calculations, the recommended values appropriate for both first and second row atoms are 0.9, 1.0, and 1.1 for cc-pVDZ-F12, cc-pVTZ-F12, and cc-pVQZ-F12, respectively. The same analysis has been carried out for the aug-cc-pV*n*Z and aug-cc-pV(n+d)Z basis sets, which leads to somewhat larger recommended β values of 1.1 (DZ), 1.2 (TZ), and 1.4 (QZ and 5Z).

B. Convergence of correlation energies

Figures 5(a)–5(d) compare the convergence of the MP2-F12/3C correlation energy as a function of the cardinal number n of the basis set for Ne, Ar, N_2, and P_2 using the new cc-pV*n*Z-F12 (denoted V*n*Z-F12) and standard aug-cc-pV*n*Z (first row) and aug-cc-pV(n+d)Z (second row) basis sets (latter denoted by simply AV*n*Z here and below). The recommended values of the geminal exponent β discussed above were used in each case. Substantially faster convergence is observed with the new basis sets. In particular, the cc-pVTZ-F12 and cc-pVQZ-F12 sets yield MP2-F12 correlation energies nearly equivalent to MP2-F12/AVQZ and MP2-F12/AV5Z results, respectively. For the smallest cc-pVDZ-F12 basis set, MP2-F12/AVTZ quality results are obtained for both N_2 and P_2, while results intermediate between AVDZ and AVTZ are obtained for Ne and Ar. MP2-F12/3C correlation energies as a function of basis set have been calculated for all the atoms and molecules of Table III and are given in Tables IV and V (energies calculated at the optimized β values for each molecule are given in the supplementary material). In all cases, the trends are very similar as those plotted in Fig. 5. It is worth noting that even with just the cc-pVDZ-F12 basis set, the MP2-F12/3C correlation energy of the Ne atom is lower than the conventional MP2 value with a cc-pV7Z basis.[54]

Also shown in Tables IV and V are the estimated CBS limits for each species. These were obtained by extrapolation of the MP2-F12/3C correlation energies using the cc-pVTZ-F12 and cc-pVQZ-F12 basis sets via

$$E(n) = E(\mathrm{CBS}) + A_1/n^4, \tag{1}$$

where A_1 is a fitting parameter and E(CBS) is the estimated CBS limit correlation energy (n=3 and 4 in this case). The choice of n^{-4} in Eq. (1) was dictated by comparing the resulting CBS limits with the accurate benchmark values previously determined by Klopper and Samson[7] for CH_2, N_2, NH_3, H_2O, HF, F_2, and Ne, as well as the finite element results of Flores[55] for Ne and Ar. Explicitly correlated methods should formally converge[6,7] as $\ell_{\max}^{-7}$, but like the standard correlation consistent basis sets the new sets are not saturated

TABLE IV. Frozen core correlation energies (in mE_h) for the systems of first row atoms and molecules of Table III (including H_2 and He) obtained from MP2-F12/3C calculations using the series of basis sets aug-cc-pVnZ (denoted AVnZ) and cc-pVnZ-F12 (denoted VnZ-F12). The β values are in a_0^{-1}.

	AVDZ (β=1.1)	AVTZ (β=1.2)	AVQZ (β=1.4)	AV5Z (β=1.4)	VDZ-F12 (β=0.9)	VTZ-F12 (β=1.0)	VQZ-F12 (β=1.1)	CBS[a]
H_2	−33.81	−34.15	−34.22	−34.24	−34.13	−34.22	−34.24	−34.25
He	−36.94	−37.19	−37.32	−37.36	−37.12	−37.29	−37.34	−37.37
BH_3	−124.06	−125.28	−125.60	−125.70	−124.98	−125.56	−125.68	−125.7
BN	−364.07	−367.94	−369.13	−369.64	−366.71	−369.03	−369.68	−370.0
C_2	−380.27	−383.50	−384.77	−385.31	−383.67	−384.80	−385.43	−385.7
$CH_2(^1A_1)$	−153.23	−155.03	−155.56	−155.76	−154.46	−155.48	−155.74	−155.9
CH_4	−216.28	−218.21	−218.77	−218.93	−217.67	−218.67	−218.89	−219.0
C_2H_4	−368.05	−370.93	−372.00	−372.32	−370.22	−371.84	−372.30	−372.5
N_2	−414.55	−418.10	−419.79	−420.46	−418.14	−419.81	−420.59	−420.9
NH_3	−260.53	−263.11	−264.04	−264.32	−262.11	−263.82	−264.27	−264.5
N_2H_2	−452.84	−457.03	−458.76	−459.33	−456.01	−458.54	−459.32	−459.7
H_2O	−295.00	−298.31	−299.73	−300.18	−296.95	−299.39	−300.13	−300.5
H_2O_2	−559.94	−565.51	−568.14	−569.00	−563.19	−567.61	−568.96	−569.6
H_2CO	−441.25	−445.30	−447.13	−447.75	−444.14	−446.79	−447.70	−448.1
F_2	−599.09	−606.01	−609.43	−610.69	−603.80	−609.38	−610.97	−611.7
HF	−312.70	−316.72	−318.62	−319.25	−315.21	−318.33	−319.23	−319.6
Ne	−311.35	−316.31	−318.59	−319.48	−315.51	−318.97	−319.77	−320.1

[a] Obtained by extrapolation of the cc-pVnZ-F12 (n=T, Q) correlation energies with n^{-4} (see the text).

in each angular momentum for a given n, and hence the actual convergence is slower than the theoretical value. Of course, n^{-4} is much slower than the convergence of the partial wave expansion, and thus this particular choice is entirely empirical, but in all cases the correlation energies resulting from Eq. (1) agreed with previous benchmark values to well within 0.1 mE_h. MP2-F12/3C calculations involving all the molecules containing just first row atoms were also carried out with the large universal R12 basis sets of Noga and co-workers.[56,57] These results agreed with the estimated CBS limits obtained from Eq. (1) to within 0.1 mE_h in all cases. Unfortunately, similar results for comparison are not available for nearly all the systems containing second row elements in Table V. In the case of the Ar atom, however, the MP2-F12/3C CBS limit resulting from extrapolation with Eq. (1) is identical to the finite element result of Flores.[55] The estimated accuracy of the other CBS limits and hence the appropriateness of Eq. (1) for second row atom-containing systems will have to await further benchmark studies.

In regard to the possibility of extrapolating the cc-pVDZ-F12 and cc-pVTZ-F12 results, a n^{-3} form of Eq.

TABLE V. Frozen core correlation energies (in mE_h) for the systems of second row atoms and molecules of Table III obtained from MP2-F12/3C calculations using the series of basis sets aug-cc-pV(n+d)Z (denoted AVnZ) and cc-pVnZ-F12 (denoted VnZ-F12). The β values are in a_0^{-1}.

	AVDZ (β=1.1)	AVTZ (β=1.2)	AVQZ (β=1.4)	AV5Z (β=1.4)	VDZ-F12 (β=0.9)	VTZ-F12 (β=1.0)	VQZ-F12 (β=1.1)	CBS[a]
AlP	−236.44	−240.83	−242.78	−243.53	−239.24	−242.30	−243.34	−243.8
AlN	−284.99	−286.88	−288.28	−288.86	−287.07	−288.16	−288.90	−289.2
AlH	−67.86	−68.98	−69.40	−69.55	−68.72	−69.35	−69.51	−69.6
Si_2	−244.17	−248.80	−250.67	−251.30	−247.00	−250.20	−251.06	−251.5
SiS	−293.27	−299.07	−301.53	−302.61	−297.13	−301.11	−302.48	−303.1
SiO	−378.54	−381.79	−383.77	−384.49	−380.95	−383.49	−384.46	−384.9
SiH_2	−120.51	−122.50	−123.19	−123.41	−121.88	−123.03	−123.31	−123.4
SiH_4	−157.81	−159.79	−160.50	−160.70	−159.43	−160.34	−160.60	−160.7
P_2	−310.80	−314.99	−318.77	−319.74	−314.84	−318.33	−319.54	−320.1
PN	−386.09	−389.82	−391.68	−392.44	−388.97	−391.47	−392.41	−392.9
PH_3	−188.32	−190.75	−192.31	−192.69	−190.29	−192.07	−192.60	−192.9
H_2S	−214.35	−218.76	−220.23	−220.93	−216.93	−219.95	−220.89	−221.3
H_2S_2	−405.30	−413.75	−416.62	−418.06	−410.35	−416.07	−417.92	−418.8
H_2CS	−373.78	−378.97	−380.96	−381.86	−377.05	−380.67	−381.82	−382.4
Cl_2	−439.46	−449.59	−453.66	−455.83	−445.48	−453.14	−455.88	−457.2
HCl	−232.90	−238.25	−240.36	−241.47	−236.10	−240.06	−241.48	−242.1
Ar	−243.04	−249.06	−251.82	−253.39	−247.28	−251.78	−253.70	−254.6

[a] Obtained by extrapolation of the cc-pVnZ-F12 (n=T, Q) correlation energies with n^{-4} (see the text).

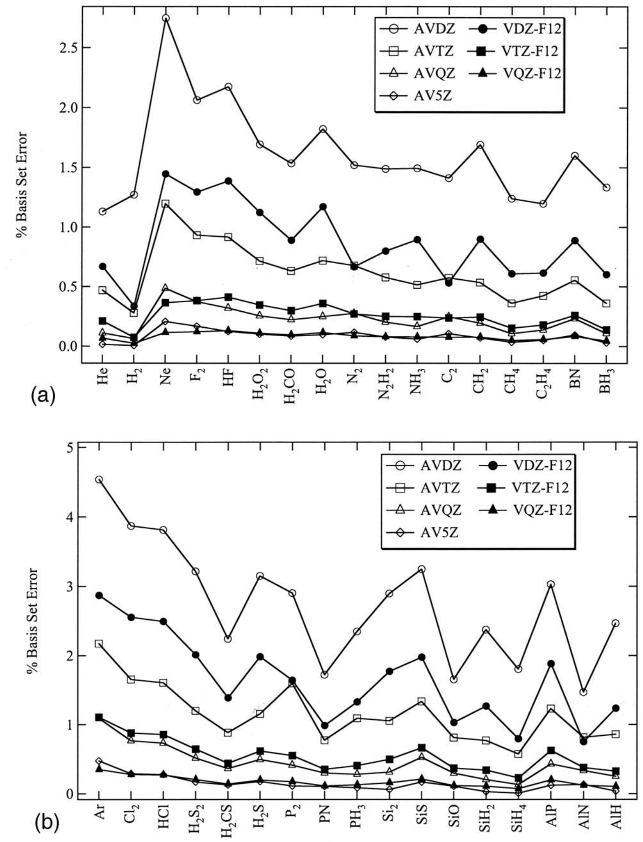

FIG. 6. Basis set errors of the correlation energy as a percentage of the CBS limit using the MP2-F12/3C method (recommended β values used throughout) for the (a) first row atom-containing and (b) second row atom-containing molecules of Table III.

(1) worked well for the systems of Table IV, yielding a signed average deviation compared to the accurate TQ extrapolations of just 0.04 mE_h with a standard deviation of 0.18 mE_h. The largest deviations were just 0.3–0.4 mE_h (Ne, N_2, and C_2). For the atoms and molecules of Table V, this scheme consistently underestimated the TQ CBS extrapolated correlation energies by an average of 0.27 mE_h (standard deviation of 0.29 mE_h). The largest deviations in these cases were observed for Ar (+0.9 mE_h) and Cl_2 (+0.8 mE_h). Certainly, more extensive investigations along these lines are warranted.

Figures 6(a) and 6(b) plot the results of Tables IV and V, respectively, as the percent differences from the TQ extrapolated CBS limits obtained from Eq. (1), i.e., the percent basis set errors in the MP2-F12/3C correlation energies. In the case of the systems containing only first row elements [Fig. 6(a)], the basis set errors with the smallest cc-pVDZ-F12 basis set are generally only about 1%. These increase to 1%–3% for the second row-containing molecules shown in Fig. 6(b). The fluctuations in the errors at the DZ level observed in Fig. 6 result from changes in the molecular environment that evidently cannot be accounted for by a basis set containing just two to three *d*-type functions. Upon increasing the basis set to cc-pVTZ-F12, both the fluctuations and magnitudes of the percentage error strongly decrease. The percent errors drop to just under 0.5% for first row-containing systems and under 1% for those containing second-row elements, although the error for Ar is still slightly above 1%. Use of the cc-pVQZ-F12 basis set yields nearly benchmark quality results throughout. Also shown in Fig. 6 are the analogous results obtained using the AV*n*Z basis sets. The advantage of the new sets is clear for both the magnitude and variation in the percentage basis set errors.

C. Calculation of reaction energies

While it has been demonstrated that accurate correlation energies can be obtained with relatively modest-sized basis sets using MP2-F12 methods, accurate energy differences are of more general interest. As a first test of the accuracy of the new basis sets for energy differences, the reaction energies for several of the reactions of Ref. 18 have been calculated together with some selected reactions involving S and Cl (using the recommended β values discussed above). The reactions used, together with their reference CBS HF and MP2 correlation energy contributions, are given in Table VI. [The individual energies and geometries used are available in the supplementary material (Ref. 52)]. The HF values are calculated with the AV6Z basis set,[41,42] while three sets of MP2/CBS correlation energy contributions to the reaction energies are shown, one obtained by extrapolation of individual molecular MP2-F12/3C correlation energies using the cc-pVTZ-F12 and cc-pVQZ-F12 basis sets with Eq. (1) and the other two from standard n^{-3} extrapolations[58,59] of conventional MP2 correlation energies calculated with the AVQZ, AV5Z, and AV6Z basis sets. In general, the MP2-F12/3C and conventional MP2 CBS limits are very similar, i.e., the correlation contributions based on conventional [Q5] extrapolated energies have a mean absolute deviation (MAD) relative to the extrapolated F12 results of just 0.07 kcal/mol. Comparison of the [56] extrapolated results show slightly better agreement with the accurate F12 limits, with a MAD of 0.04 kcal/mol. However, focusing just on the reactions involving second row elements, the conventional MP2 [56] extrapolations differ from the analogous [Q5] results by nearly 0.3 kcal/mol, which reflects the slower basis set convergence for second row elements even for conventional MP2 calculations. In regard to the CBS limit correlation energies for the *individual* molecules involved in these reactions, significantly larger errors are observed; the MAD values for the conventional [Q5] and [56] extrapolations compared to the F12-based CBS results are 0.67 and 0.31 kcal/mol, respectively.

Figure 7 plots the errors in the MP2-F12/3C reaction energies with respect to their CBS reference values (extrapolated F12 results) when DZ quality basis sets are used, cc-pVDZ-F12 and AVDZ. The results shown in Fig. 7(a) include the errors in the HF reaction energies; hence, large differences are observed between VDZ-F12 and AVDZ. In fact, when the new VDZ-F12 basis sets are used, the errors in the reaction energies for reactions 1–12, i.e., those containing only first row atoms, are all below 1 kcal/mol. The errors increase, however, for those containing second row atoms and particularly for the reactions involving SO_2 and SO_3 since the HF energy is very sensitive to the inclusion of *f*-type functions in these cases, which are not present in the

TABLE VI. Reactions and reference MP2/CBS reaction energies (in kcal/mol) used in the present work.

No.	Reaction	ΔE_r (HF) (AV6Z)	ΔE_r (Correlation only) F12/3C [TQ][a]	MP2 [Q5][b]	MP2 [56][b]
1	$C_2H_2+H_2\rightarrow C_2H_4$	−51.72	+4.86	+4.78	+4.77
2	$C_2H_4+H_2\rightarrow C_2H_6$	−39.16	−1.71	−1.72	−1.74
3	$C_2H_6+H_2\rightarrow 2CH_4$	−21.22	+3.63	+3.59	+3.62
4	$CO+H_2\rightarrow HCHO$	+0.25	−5.89	−5.91	−5.95
5	$H_2CO+H_2\rightarrow CH_3OH$	−28.56	−1.27	−1.32	−1.31
6	$H_2O_2+H_2\rightarrow 2H_2O$	−93.55	+1.90	+1.77	+1.88
7	$C_2H_2+H_2O\rightarrow CH_3CHO$	−40.63	+4.02	+4.09	+3.95
8	$CH_3CHO+H_2\rightarrow C_2H_5OH$	−23.39	−1.89	−1.95	−1.95
9	$CO+NH_3\rightarrow HCONH_2$	−2.51	−9.61	−9.57	−9.65
10	$CO+H_2O\rightarrow CO_2+H_2$	+0.06	−10.40	−10.26	−10.41
11	$HCOOH+NH_3\rightarrow HCONH_2+H_2O$	−0.69	−1.27	−1.30	−1.27
12	$H_2CCO+H_2CO\rightarrow C_2H_4O+CO$	−5.86	+2.58	+2.59	+2.58
13	$SO_2+H_2O_2\rightarrow SO_3+H_2O$	−55.38	−0.92	−0.95	−0.94
14	$CO+Cl_2\rightarrow COCl_2$	−13.51	−19.32	−19.49	−19.27
15	$CS_2+2H_2O\rightarrow CO_2+2H_2S$	−29.23	+24.60	+24.75	+24.46

[a] CBS limits for the correlation contributions obtained by extrapolating MP2-F12/3C correlation energies using the cc-pV*n*Z-F12 (n=T, Q) basis sets with n^{-4} (see the text).

[b] CBS limits for the correlation contributions obtained by extrapolating conventional MP2 correlation energies using the AV*n*Z (n=Q, 5 or n=5, 6) basis sets with n^{-3} (see the text).

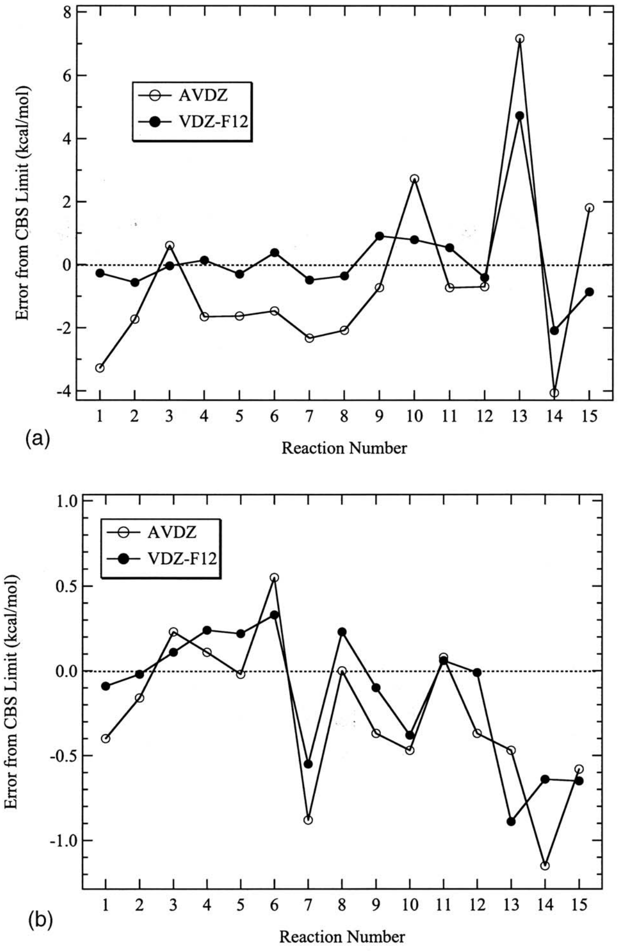

FIG. 7. Basis set errors in the reaction energies of Table VI using DZ basis sets, (a) total energy and (b) correlation contributions, using the MP2-F12/3C ansatz ($\beta=0.9a_0^{-1}$ for VDZ-F12 and $\beta=1.1a_0^{-1}$ for AVDZ).

DZ basis sets. Figure 7(b) plots only the MP2-F12/3C correlation contributions to the reaction energies with the same DZ basis sets. For reactions 1–12, the errors are at or below 0.5 kcal/mol and those for the remaining reactions are below 1 kcal/mol when the new cc-pVDZ-F12 basis sets are used. In fact, the MAD is just 0.30 kcal/mol across all 15 reactions with a standard deviation of 0.27 kcal/mol. The use of the AVDZ set in MP2-F12/3C yields somewhat larger errors, i.e., a MAD of 0.39 kcal/mol with a standard deviation of 0.30 kcal/mol. The close agreement between these two basis sets is somewhat surprising since the MADs per correlated electron for the individual molecules of these reactions are 0.23 kcal/mol for VDZ-F12 and 0.39 kcal/mol for AVDZ.

Figures 8(a) and 8(b) plot the analogous MP2-F12/3C errors in the reaction energies for TZ quality basis sets. Use of the new cc-pVTZ-F12 basis sets yields total reaction energies (including the HF error) all below 0.5 kcal/mol, except for reaction 15 which has an error of about −0.7 kcal/mol. The basis set errors are smaller and more regular than those arising from use of the AVTZ sets. In particular, there are still a rather large HF error for reaction 13 with the latter sets. The errors in the correlation contributions shown in Fig. 8(b) are all below about 0.2 kcal/mol with the cc-pVTZ-F12 basis set. The MADs for the correlation contributions to the reaction energies total 0.08 kcal/mol for VTZ-F12 and 0.17 kcal/mol for AVTZ.

Last, the cc-pVQZ-F12 results for the MP2-F12/3C correlation contributions to the reaction energies are compared to the AVQZ and AV5Z values in Fig. 9. Overall, the new cc-pVQZ-F12 sets lead to very small errors, less than 0.1 kcal/mol, which are on the order of the uncertainty of the CBS extrapolations. In general, these results are more accurate than MP2-F12/AVQZ and in many cases even MP2-F12/AV5Z.

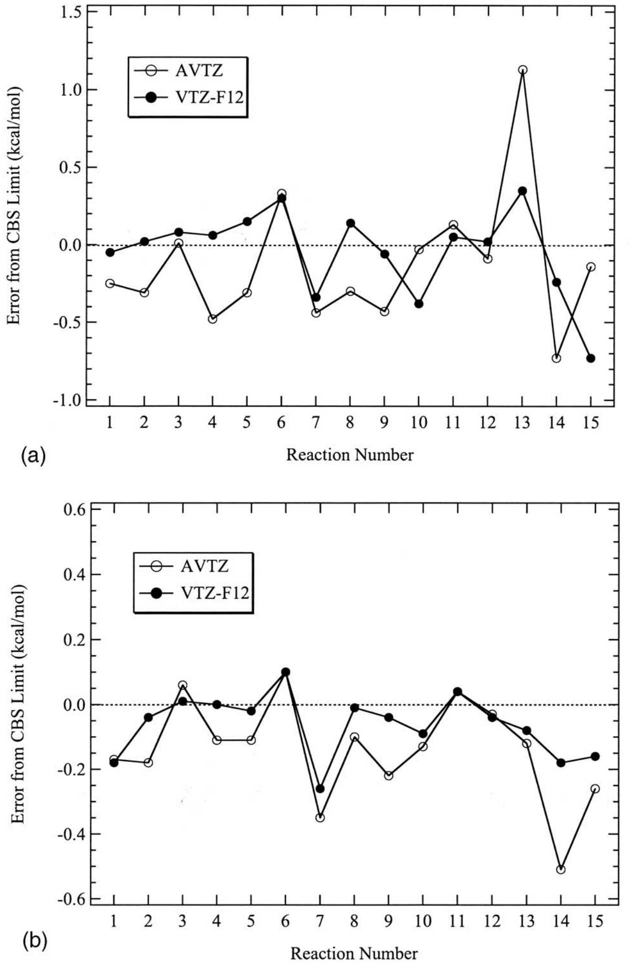

FIG. 8. Basis set errors in the reaction energies of Table VI using TZ basis sets, (a) total energy and (b) correlation contributions, using the MP2-F12/3C ansatz ($\beta=1.0a_0^{-1}$ for VTZ-F12 and $\beta=1.2a_0^{-1}$ for AVTZ).

V. SUMMARY

New basis sets ranging in quality from double to quadruple zeta have been developed for use with explicitly correlated F12 methods. The new sets, denoted cc-pV*n*Z-F12 ($n=$D,T,Q), were developed within a correlation consistent methodology and exhibit regular convergence toward the CBS limit in MP2-F12/3C calculations on several small molecules involving elements of both the first and second rows. Compared to standard aug-cc-pV*n*Z (first row) and aug-cc-pV($n+d$)Z (second row) basis sets, which are of similar size and composition, the new F12 basis sets yield significantly improved HF and MP2-F12/3C energies. In fact, for molecules containing only first row atoms, the smallest cc-pVDZ-F12 basis set consistently recovers nearly 99% of the MP2 valence correlation energy when combined with the MP2-F12/3C method. Benchmark quality results are obtained with the cc-pVQZ-F12 basis set. The convergence with basis set for molecules containing second row atoms is somewhat slower, but the new DZ basis set still recovers 97%–99% of the frozen core MP2 correlation energy, while cc-pVTZ-F12 exhibits basis set errors between 0.5% and 1%.

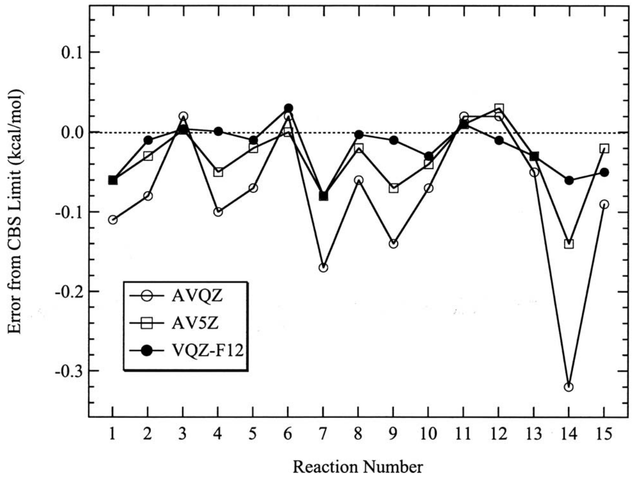

FIG. 9. Basis set errors in the correlation energy contributions to the reaction energies of Table VI using QZ and 5Z basis sets using the MP2-F12/3C ansatz ($\beta=1.1a_0^{-1}$ for VQZ-F12 and $\beta=1.4a_0^{-1}$ for AVQZ and AV5Z).

The accuracy of the new basis sets for relative energetics is demonstrated in benchmark calculations on a set of 15 chemical reactions. In these cases, both cc-pVDZ-F12 and AVDZ yield similar results for the MP2 correlation contributions when using MP2-F12/3C, MAD values between 0.3 and 0.4 kcal/mol with standard deviations of about 0.3 kcal/mol. The maximum errors were found to be 0.9–1.0 kcal/mol. When including the HF contributions to the reaction energies, however, the new sets were significantly more accurate. In the case of cc-pVTZ-F12 and AVTZ, the new sets yielded better agreement with the reference CBS values by nearly a factor of 2, i.e., a MAD of 0.08 kcal/mol compared to 0.17 kcal/mol with AVTZ (correlation contribution only). The maximum error in the correlation contribution was just −0.2 kcal/mol with cc-pVTZ-F12 while the AVTZ set exhibited errors as large as −0.5 kcal/mol. This work is currently being extended to a larger set of 50 reactions in conjunction with the investigation of more approximate MP2-F12 methods. These results will be reported in a separate publication.

The basis sets developed in this work will be available for download from one of the authors' website (http://tyr0.chem.wsu.edu/~kipeters/basissets/basis.html), as well as within the MOLPRO program (http://www.molpro.net) or the EMSL basis set exchange site (http://gnode2.pnl.gov/bse/portal).

ACKNOWLEDGMENTS

K.A.P. would like to thank the members of the Institute for Theoretical Chemistry in Stuttgart for their hospitality during his sabbatical visit when this work was initiated. This work was funded in the priority program 1145 by the Deutsche Forschungsgemeinschaft. The authors would also like to thank Wim Klopper, David Tew, and Frank Jensen for valuable discussions.

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