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On the accuracy limits of orbital expansion methods: Explicit effects of *k*-functions on atomic and molecular energies

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For selected first- and second-row atoms, correlation-optimized Gaussian k functions have been determined and used in the construction of septuple-ζ basis sets for the correlation-consistent cc-pVXZ and aug-cc-pVXZ series. Restricted Hartree–Fock (RHF) and second-order Møller–Plesset (MP2) total and pair energies were computed for H, N, O, F, S, H_2, N_2, HF, H_2O, and $(H_2O)_2$ to demonstrate the consistency of the new septuple-ζ basis sets as extensions of the established (aug)-cc-pVXZ series. The pV7Z and aug-pV7Z sets were then employed in numerous extrapolation schemes on the test species to probe the accuracy limits of the conventional MP2 method *vis-à-vis* explicitly correlated (MP2-R12/A) benchmarks. For (singlet, triplet) pairs, $(X+\frac{1}{2})^{-n}$ functional forms with $n=(3,5)$ proved best for extrapolations. The (mean abs. relative error, std. dev.) among the 73 singlet pair energies in the dataset is (1.96%, 0.54%) and (1.72%, 0.51%) for explicit computations with the pV7Z and aug-pV7Z basis sets, respectively, but only (0.07%, 0.09%) after two-point, 6Z/7Z extrapolations with the $(X+\frac{1}{2})^{-3}$ form. The effects of k functions on molecular relative energies were examined by application of the septuple-ζ basis sets to the barrier to linearity and the dimerization energy of water. In the former case, an inherent uncertainty in basis set extrapolations persists which is comparable in size to the error ($\approx 20\ \mathrm{cm}^{-1}$) in explicit aug-pV7Z computations, revealing fundamental limits of orbital expansion methods in the domain of subchemical accuracy ($0.1\ \mathrm{kcal\,mol}^{-1}$). [DOI: 10.1063/1.1566744]

I. INTRODUCTION

Ab initio computation of highly accurate molecular properties has witnessed a dramatic improvement in the quality of predictions in the past decade thanks to the development of advanced wave function approaches coupled with numerous algorithm and hardware improvements. Nevertheless such computations remain highly expensive. Less rigorous, pragmatic approaches to the problem which combine wave function and efficient Kohn–Sham (KS) density functional theory (DFT) exist too, such as the GN//B3LYP model chemistries,[1,2] which utilize KS DFT methods for geometric structures and vibrational frequencies with wave function methods for final energetics. The GN methods[3,4] are further "trained" to perform well for certain types of systems and properties by including empirical corrections. Such approaches aim at chemical accuracy, commonly defined as $\sim 1\ \mathrm{kcal\,mol}^{-1}$ for relative energies, and offer close to the target performance. More rigorous thresholds, such as subchemical and spectroscopic accuracy ($\sim 0.1\ \mathrm{kcal\,mol}^{-1}$ and $1\ \mathrm{cm}^{-1}$ for relative energies, respectively) are out of reach of any but the most sophisticated methods of theoretical chemistry which compute electronic wave functions directly.[5]

To achieve the subchemical and spectroscopic accuracy thresholds one has to take into account many factors that are usually left out of consideration, such as convergence with respect to the n- and one-particle basis sets, core correlation, relativity, and non-Born–Oppenheimer effects.[6] For molecules composed of light elements, the obstacle to be overcome most frequently is the unacceptably slow convergence of correlation energies with respect to the one-particle basis set used for constructing the n-particle expansion.[7] This difficulty is due to the inability of orbital product expansions to properly describe the electron–electron cusps of the exact wave function.[8]

A highly robust method of dealing with the cusp is to include the dependence on the interelectronic distances into the wave function explicitly. The Hylleraas ansatz[9,10] for the helium atom is effective to better than femtohartree accuracy.[11] Hylleraas-CI,[12] the transcorrelated method of

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Boys and Handy,[13] Gaussian geminals methods,[14,15] and the linear R12 methods of Kutzelnigg, Klopper and others[16,17] are examples of general ways to include r_{ij}-dependence into wave functions. Unfortunately, the associated, difficult multielectron integrals have hindered widespread application of explicitly correlated approaches. Linear R12 methods deal with the problem in an attractive manner, by means of standard approximations,[16] so that only nonstandard two-electron integrals[16,18,19] are required.

A somewhat less rigorous approach to the one-particle basis set problem is to extrapolate the electron correlation energy (or any other property) to the complete basis limit. A fundamental problem with such an approach is, of course, that only the selected property is improved, not the wave function. One also needs to carefully design a sequence of *practical* basis sets which leads to a *known* convergence pattern in order to apply the extrapolation method successfully, a rather formidable task. For example, the partial wave expansion of the energy[7]—a useful approach in the case of a two-electron atom[20]—is impractical for nontrivial molecular cases because of the cost of constructing a series of basis sets (nearly) saturated to a given angular momentum $L_{\max}$.

Numerous efforts to design extrapolation schemes in the spirit of the partial wave expansion have nevertheless been made. The correlation-consistent basis set families (aug)-cc-p(C)VXZ developed by Dunning and co-workers[21–23] are employed for such studies most often.[87] Various assumptions have been made about the rate of convergence of correlation energies computed with correlation-consistent basis sets. Feller[24] first used an exponential fit,

$$\Delta E(X)=a\exp(-bX), \tag{1}$$

where $\Delta E(X)=E(X)-E(\infty)$, which if applied for small values of X may underestimate the basis set limit severely. Martin[25] suggested several alternative fits to the energy,

$$\Delta E(X)=c(X+1/2)^{\alpha}, \tag{2}$$

$$\Delta E(X)=d(X+1/2)^{-4}+e(X+1/2)^{-6}, \tag{3}$$

$$\Delta E(X)=f(X+1/2)^{-4}, \tag{4}$$

which are reminiscent of the partial wave contribution formulas.[7,26–28] Similarly, Wilson and Dunning[29] explored a general asymptotic expression,

$$\Delta E(X)=B(X+d)^{-m}+C(X+d)^{-(m+1)}+D(X+d)^{-(m+2)}, \tag{5}$$

where m assumed values of 3 and 4, and d ranged from 0 to 1. They found[29] that the following two specializations of Eq. (5) were optimal:

$$\Delta E(X)=BX^{-3}+CX^{-5}, \tag{6}$$

$$\Delta E(X)=B(X+1)^{-4}+C(X+1)^{-5}. \tag{7}$$

In 1997, Helgaker *et al.*[30] advocated a very simple formula,

$$\Delta E(X)=gX^{-3}. \tag{8}$$

There are several reasons for the attractiveness of relation (8). First, given two energies computed with cc-pVxZ and cc-pVyZ basis sets, the energy in a complete basis set limit can be approximated using a linear combination,

$$E(\infty)=\frac{x^3E(x)-y^3E(y)}{x^3-y^3}. \tag{9}$$

The algebraic nature of the fit opens the possibility of applying Eq. (9) to entire potential energy surfaces[6] in a straightforward and consistent manner, which is technically and conceptually more difficult with the nonlinear least-squares fits to Eqs. (1) and (2). Second, Halkier and co-workers[31] have found evidence that Eq. (8) is the optimal two-parameter fit of the type

$$\Delta E(X)=a(X+\delta)^{\alpha}. \tag{10}$$

Furthermore, Klopper *et al.*[32] utilized the concept of *principal expansion* to arrive at a more rigorous theoretical motivation for exploring extrapolation formulas of the type

$$\Delta E(X)=aX^{-3}+bX^{-4}+\cdots. \tag{11}$$

Thus, in terms of simplicity and physical motivation, Eq. (8) is hard to surpass. A recent, interesting generalization[33,34] of Eq. (8) takes into account the different convergence rates for pair energies derived by Kutzelnigg and Morgan[7] to extrapolate singlet

$$\Delta\epsilon_{ij}^{1}=a_{ij}X^{-3} \tag{12}$$

and triplet

$$\Delta\epsilon_{ij}^{3}=a_{ij}X^{-5} \tag{13}$$

pair energies separately. Note that previous studies that examined pair energies analyzed total, not spin-adapted, correlation energies only[29] which may explain why the asymptotic fits to Eq. (6), including *both* X^{-3} and X^{-5} terms, were found to provide accurate estimates of CBS limits. Certainly, more empirical evidence is needed to demonstrate the effectiveness of the spin-adapted approach, which is well-motivated in theory.

The aforementioned expressions seem to work well when sufficiently large basis sets (cc-pVTZ or larger) are utilized to compute correlation energies.[31] However, extrapolations using the lowest members of the correlation-consistent families should be discouraged, because only *asymptotic* expressions arise from the partial wave analysis of atomic correlation energies. Nevertheless, a number of researchers have recently attempted to construct extrapolation schemes that work well with smaller basis sets. Truhlar and co-workers[35,36] have proposed the following expression to approximate the CBS limit for correlation energies:

$$E_{\mathrm{corr}}(\infty)=\frac{3^{\beta}E_{\mathrm{corr}}(3)-2^{\beta}E_{\mathrm{corr}}(2)}{3^{\beta}-2^{\beta}}, \tag{14}$$

where constant β is empirically determined for each level of electron correlation treatment. The simplicity and low cost of the scheme have substantial tradeoffs,[37] as the resulting RMS errors in atomization energies are rather large, viz., over 2 kcal mol^{-1}. Varandas[38] has suggested use of a more elaborate expression,

$$E_{\mathrm{corr}}(X)=E_{\mathrm{corr}}(\infty)+A_3X^{-3}(1+A_4X^{-1}), \tag{15}$$

TABLE I. Optimized orbital exponents for k-function Gaussian manifolds in the pV7Z and aug-pV7Z basis sets.

	pV7Z				aug-pV7Z[a]		
Atom	ZAPT2	OPT2[b]	CCSD	CISD	ZAPT2	OPT2[b]	CCSD
N	2.276	2.276	2.378	2.379	0.876	0.876	0.977
O	2.986	2.986	3.129	3.123	1.130	1.130	1.232
F	4.069	4.069	4.256	4.256	1.442	1.442	1.597
S	1.200	1.200	1.210	1.209	0.518	0.518	0.575

[a]The exponent of the diffuse k-manifold appended to the pV7Z set.
[b]All corresponding optimum ZAPT2 and OPT2 exponents differ by less than 0.001.

where A_4 depends on A_3 via an empirical function. Performance of this scheme is difficult to assess. An obvious problem with such smaller-basis approaches,[35,36,38] besides the fact that the extracted basis set limits do not achieve chemical accuracy, is that the use of empirical constants no longer allows one to approach the basis set limit in a consistent manner. In our opinion, the use of such schemes is questionable.[37]

The value of ''simple'' extrapolations that do not include empirically-adjusted constants is that they offer a uniform method of approaching the basis set limit. Such fits have been employed repeatedly in the focal-point approach of Allen and co-workers.[39–46] The accuracy of the computed CBS values seems to increase as higher and higher members of correlation-consistent basis set families are included in fits. A fundamental problem with the extrapolation approaches to dealing with the basis set incompleteness problem remains: the inexactness of asymptotic expressions for rates of convergence of molecular correlation energies computed with correlation-consistent series of basis sets. Naturally, a fundamental question arises. How far can the accuracy of energy predictions based on approximate extrapolation of conventional *ab initio* computations be pushed? To rephrase, can extrapolation schemes remain competitive with explicitly correlated methods in domains of subchemical and better accuracy? In this paper we address such fundamental questions by extending the correlation-consistent series of basis sets to the septuple-ζ members, which include Gaussian functions of angular momentum 7 on first- and higher-row elements, and then by examining the effect of such functions on explicitly evaluated and extrapolated (spin-adapted) absolute and relative energies in atoms and molecules. Particular objectives include the completion of the construction of the (aug)-pV7Z basis sets started by Feller and co-workers,[47] followed by an examination of the effects on atomic Hartree–Fock (HF) and correlation energies (H, N, O, F, S), absolute HF energies in molecules (H_2, N_2), absolute (pair) correlation energies in molecules (HF, N_2, H_2O), and relative energetics in molecules (barrier to linearity in H_2O, water dimerization energy).

II. TECHNICAL DETAILS

Atomic CISD and CCSD energies were computed with the quantum chemistry package PSI 3 (Ref. 48) and were converged to at least 10^{-10} E_h. Atomic spin-adapted perturbation theory energies [OPT2 (Ref. 49) and ZAPT2 (Ref. 50)] were computed with the massively parallel quantum chemistry code MPQC (Ref. 51) and were precise to at least 10^{-10} E_h. In all atomic correlated computations, the lowest-lying ($1s$;$1s2s2p$)-like orbitals of (N,O,F;S) were kept doubly occupied (frozen core approximation). Spherical harmonic Gaussian functions were used throughout this study. Due to program restrictions, it was only possible to enforce the highest Abelian point group, D_{2h}, in atomic computations.

The pV7Z and aug-pV7Z basis sets, lacking k-exponents on first- and second-row atoms,[47] were obtained from the Environmental Molecular Sciences Laboratory online Gaussian basis set database.[52] The exponent of the missing k-manifold for the pV7Z basis was optimized numerically using a fourth-order polynomial fit to the atomic correlation energies computed with the frozen-core CISD, OPT2, ZAPT2, and CCSD methods. Optimized exponents are listed in Table I.

In accord with the optimization procedure for the correlation-consistent basis sets, the optimal CISD k-manifold was appended to the incomplete pV7Z basis to finish its construction. Technically, the final pV7Z contractions are H($14s6p5d4f3g2h1i/7s6p5d4f3g2h1i$), N–F($18s12p6d5f4g3h2i1k/8s7p6d5f4g3h2i1k$), and S($27s18p6d5f4g3h2i1k/9s8p6d5f4g3h2i1k$). The CCSD exponents are nearly identical to the reference CISD exponents, whereas the exponents obtained with the perturbation methods are significantly lower. Surprisingly, the optimal exponents for the two perturbation methods (OPT2, ZAPT2) are identical to four significant figures. The aug-pV7Z sets are obtained by adding a single, uncontracted primitive shell to every angular momentum manifold of the pV7Z sets. Further optimization of the orbital exponent for the diffuse k-manifold of the aug-pV7Z basis sets proceeded in the usual manner by maximizing the magnitude of the atomic correlation energy difference between the anion and neutral.[21] Due to the intrinsic limitations of our CI code, we were unable to optimize diffuse exponents at the CISD level, and thus chose the CCSD method for this purpose. If the agreement between CISD and CCSD k-exponents in the pV7Z case is an indication, the optimized diffuse CCSD exponent should be very close to the CISD optimized exponent. The PT2 optimized diffuse k-exponents are slightly lower than the CCSD values.

We should note that the pV7Z basis for sulfur must be used with with caution. Correlation consistent series for second-row elements have been recently corrected by Dunning and co-workers[53] to include an extra high exponent d-shell. The (aug)-cc-pV(X+d)Z basis sets thus obtained describe core polarization in molecular environments properly and show improved convergence behavior, especially with the low-X members of the series. The higher members (QZ through 6Z) of the standard correlation consistent series are consistent among themselves and include enough high-exponent polarization functions already, as demonstrated most clearly by Fig. 2 of Ref. 53. Thus, the d-manifold of the pV7Z basis set would have to be adjusted accordingly to be utilized within the context of the improved series. We believe that the S pV7Z basis could still be used with the higher members (QZ, 5Z, and 6Z) of the standard correlation consistent series without modification.

All molecular energies were computed with the quantum chemistry package PSI 3 (Ref. 48) and were precise to at least 10^{-12} E_h. In all molecular correlated computations the lowest-lying 1s-like orbitals were kept doubly occupied. Correlation consistent basis sets (aug)-cc-pVXZ through sextuple-ζ (Refs. 21–23) were obtained once again from the Environmental Molecular Sciences Laboratory online Gaussian basis set database.[52] Occasional linear dependencies in basis sets were handled via the canonical orthogonalization procedure,[54] in which overlap eigenvectors with eigenvalues smaller than 10^{-6} were omitted.

Molecular MP2 pair energies for occupied spatial orbitals i and j were evaluated according to the conventional formula,

$$e_{ij}^{s}=\left(\frac{2s+1}{1+\delta_{ij}}\right)\sum_{a\leqslant b}\frac{[(ia|jb)+(-1)^{s}(ib|ja)]^{2}}{(1+\delta_{ab})(\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_j)},\quad \forall i\leqslant j, \tag{16}$$

where the ϵ_p are canonical RHF orbital energies, $s=0, 1$ for singlet and triplet pairs, respectively, and a and b run over virtual orbitals. Molecular second-order Møller–Plesset pair energies close to the basis set limit (e_{ij}^{ref}) were obtained using the MP2-R12/A method as implemented in the quantum chemistry package PSI 3.[48] A large uncontracted Gaussian basis designated as V1+ was used in such R12 calculations. Technically, V1+ is $[21s13p11d10f7g5h2i/13s11p9d7f5g1h]$ for [N,O,F/H].[88]

Basis set extrapolations for atomic and molecular Hartree–Fock energies were performed by least-squares fitting a set of (aug)-cc-pVXZ RHF energies to the formula

$$E_{\mathrm{SCF}}(X)=E_{\mathrm{SCF}}(\infty)+a\exp(-bX). \tag{17}$$

For brevity, we designate the $E_{\mathrm{SCF}}(\infty)$ limit obtained from a set of cc-pVXZ, cc-pV(X+1)Z, ..., cc-pVYZ HF energies as (X,X+1,...,Y). Similarly, (aX,a(X+1)...) stands for the limit obtained by fitting a set of aug-cc-pVXZ, aug-cc-pV(X+1)Z, ..., aug-cc-pVYZ HF energies to the above expression.

Basis set extrapolations for molecular second-order Møller–Plesset singlet and triplet pair energies were usually performed according to Eqs. (12) and (13), respectively, by fitting to a pair of (aug)-cc-pVXZ and (aug)-cc-pVYZ MP2 pair energies. We designate the basis set limits thus obtained as (X,Y) and (aX,aY). We also use this notation for total molecular MP2 energies obtained by summing the individually extrapolated singlet and triplet pair energies. In contrast, total MP2 correlation energies extrapolated according to Eq. (8) are designated with braces as $\{X,Y\}$ and $\{\mathrm{a}X,\mathrm{a}Y\}$.

The statistical analysis of errors in MP2 pair energies here is similar that of Halkier *et al.*[31] and Klopper;[33] however, we utilized *relative* errors in our study. Relative error in a computed or extrapolated MP2 pair energy e_{ij} is defined as

$$\delta e_{ij}=\frac{e_{ij}-e_{ij}^{\mathrm{ref}}}{|e_{ij}^{\mathrm{ref}}|}, \tag{18}$$

where e_{ij}^{ref} is the corresponding V1+MP2-R12/A energy. Mean relative error Δ, mean absolute relative error Δ_{abs}, RMS relative error Δ_{RMS}, and standard deviation Δ_{std} are evaluated according to standard formulas. In addition, we explored distribution of errors in pair energies further by computing skewness and kurtosis of the sets of relative errors. Skewness and kurtosis are related to third and fourth moments of distribution, respectively, and are evaluated as follows:[55]

$$\mathrm{Skew}(\{\delta e_{ij}\})=\frac{1}{N}\sum_{ij}^{N}\left[\frac{(\delta e_{ij}-\Delta)}{\Delta_{\mathrm{std}}}\right]^{3}, \tag{19}$$

$$\mathrm{Kurt}(\{\delta e_{ij}\})=\frac{1}{N}\sum_{ij}^{N}\left[\frac{(\delta e_{ij}-\Delta)}{\Delta_{\mathrm{std}}}\right]^{4}-3, \tag{20}$$

where N is the number of MP2 pairs of a given type under consideration. For the normal (Gaussian) distribution skewness and kurtosis are zero. Positive (negative) skewness indicates a nonsymmetrical distribution with a long tail extending toward more positive (negative) values. Positive kurtosis indicates a distribution with a sharp peak at the mean, while negative kurtosis corresponds to a distribution with a plateau. Thus skewness and kurtosis provide a simple way to test the null hypothesis, i.e., that the distribution of an observed set of errors is not Gaussian. Assuming a normal distribution the standard deviation of skewness and kurtosis are $\sqrt{6/N}$ and $\sqrt{24/N}$, respectively. Values of skewness and kurtosis of significantly greater magnitude signal sufficiently non-normal distributions.

We also analyzed linear correlation between sets of relative errors. The linear correlation coefficient r (also known as Pearson's r) for two sets of errors $\{\delta e_{ij}^{A}\}$ and $\{\delta e_{ij}^{B}\}$ is evaluated as[55]

$$r=\frac{\sum_{ij}^{N}(\delta e_{ij}^{A}-\Delta^{A})(\delta e_{ij}^{B}-\Delta^{B})}{(N-1)\Delta_{\mathrm{std}}^{A}\Delta_{\mathrm{std}}^{B}}. \tag{21}$$

Coefficients r range from -1 to 1. Values of r close to zero indicate no correlation between sets of errors, while values close to 1 in absolute magnitude indicate strong correlation. A positive (negative) sign of r describes the tendency of δe_{ij}^{B} to increase (decrease) with increasing δe_{ij}^{A}.

III. HARTREE–FOCK ENERGIES

Although not designed with consistent convergence of Hartree–Fock energies in mind, correlation-consistent basis sets have been used extensively to obtain basis set limits for

TABLE II. Explicitly computed and extrapolated spin-restricted Hartree–Fock atomic energies.[a]

	H		N		O		F		S	
Basis set	E	$\alpha(X)$	E	$\alpha(X)$	E	$\alpha(X)$	E	$\alpha(X)$	E	$\alpha(X)$
cc-pVQZ	−0.499 945 569	2.9	−54.400 175 899	2.3	−74.810 843 555	2.6	−99.408 951 852	2.7	−397.506 630 729	2.6
cc-pV5Z	−0.499 994 535	3.0	−54.400 852 504	4.5	−74.812 230 679	4.1	−99.411 170 832	4.0	−397.507 107 972	6.0
cc-pV6Z	−0.499 999 245	10.2	−54.400 923 448	9.8	−74.812 371 770	10.0	−99.411 379 469	10.3	−397.507 237 748	5.3
pV7Z	−0.499 999 733	12.2	−54.400 932 263	11.1	−74.812 390 277	10.8	−99.411 403 742	11.5	−397.507 260 179	9.2
aug-cc-pVQZ	−0.499 948 321	2.8	−54.400 224 914	2.1	−74.811 064 142	2.5	−99.409 209 021	2.6	−397.506 701 109	2.6
aug-cc-pV5Z	−0.499 994 785	2.9	−54.400 855 631	4.5	−74.812 257 558	4.2	−99.411 197 056	3.9	−397.507 133 537	6.0
aug-cc-pV6Z	−0.499 999 276	10.2	−54.400 923 663	9.7	−74.812 378 290	10.0	−99.411 385 708	10.3	−397.507 245 574	5.6
aug-pV7Z	−0.499 999 743	12.1	−54.400 932 322	11.0	−74.812 392 792	11.3	−99.411 407 611	11.5	−397.507 262 584	10.0
Extrapolated energies										
(Q,5,6)	−0.499 999 746		−54.400 932 62		−74.812 390 33		−99.411 403 96		−397.507 274 42	
(5,6,7)	−0.499 999 789		−54.400 933 51		−74.812 393 07		−99.411 406 94		−397.507 264 87	
(aQ,a5,a6)	−0.499 999 757		−54.400 931 89		−74.812 391 88		−99.411 405 49		−397.507 284 75	
(aQ,a5,a6,a7)	−0.499 999 778		−54.400 932 72		−74.812 393 30		−99.411 407 93		−397.507 274 11	
(a5,a6,a7)	−0.499 999 797		−54.400 933 59		−74.812 394 77		−99.411 410 49		−397.507 265 63	
HF limit	−0.500 000 000		−54.400 934[b]							

[a]Energies in E_h, subject to D_{2h} symmetry restrictions. $\alpha(X)$ values are effective decay exponents, as defined in Sec. III.
[b]Reference 82.

the Hartree–Fock method. Thus it is of interest to briefly examine how the septuple-ζ basis sets affect atomic and molecular Hartree–Fock energies. This assessment should also indicate how well our pV7Z and aug-pV7Z basis sets derived from Feller's original work fit into the established correlation-consistent series.

Series of atomic Hartree–Fock energies through the septuple-ζ level are given in Table II, and corresponding molecular energies for the H_2 and N_2 examples appear in Table III. An insightful analysis of these data may be performed by means of the ratio

$$r(X)=\frac{E(X)-E(X-1)}{E(X-1)-E(X-2)}. \tag{22}$$

If some power law

$$E(X)=E(\infty)+\frac{a}{X^{\alpha}} \tag{23}$$

is operative $(\alpha>0)$, then

$$r(X)=\frac{\left(1-\frac{1}{X}\right)^{\alpha}-1}{1-\left(1+\frac{1}{X-2}\right)^{\alpha}}. \tag{24}$$

For each $r(X)$ value, nonlinear Eq. (24) can be solved numerically to yield $\alpha(X)$, which would be constant if Eq. (23) holds. Alternatively, if the energy series obeys the exponential form,

$$E(X)=E(\infty)+a\exp(-bX), \tag{25}$$

then $r(X)=\exp(-b)$ is constant, and $\alpha(X)$ can be shown to be almost perfectly linear with a slope of b in the domain $X\geqslant 3$. In Tables II and III, $\alpha(X)$ clearly and strongly increases with X, the only local anomaly involving $\alpha(5)$ of H_2. Moreover, for $X=7$, large effective exponents of 9–12 are seen, well beyond any value expected from a simple, physically-based power law. In brief, the (aug)-cc-pVXZ Hartree–Fock energies exhibit approximate exponential behavior, and the septuple-ζ basis sets fall nicely into the existing series.

TABLE III. Explicitly computed and extrapolated spin-restricted Hartree–Fock energies for H_2 and N_2.[a]

	H_2		N_2	
Basis set	$E(X)$	$\alpha(X)$[b]	$E(X)$	$\alpha(X)$[b]
cc-pVTZ	−1.132 960 53	⋯	−108.984 093 43	⋯
cc-pVQZ	−1.133 459 04	5.0	−108.991 735 29	2.8
cc-pV5Z	−1.133 608 19	3.7	−108.993 419 84	4.8
cc-pV6Z	−1.133 625 51	9.3	−108.993 741 77	7.0
pV7Z	−1.133 627 54	11.4	−108.993 796 73	9.3
aug-cc-pVTZ	−1.133 026 85	⋯	−108.985 317 38	⋯
aug-cc-pVQZ	−1.133 473 02	5.2	−108.992 205 15	3.2
aug-cc-pV5Z	−1.133 610 65	3.5	−108.993 610 49	5.1
aug-cc-pV6Z	−1.133 626 53	9.4	−108.993 786 80	9.0
aug-pV7Z	−1.133 628 31	11.7	−108.993 814 74	9.7
Extrapolated energies[c]				
(T,Q,5)	−1.133 671 87	⋯	−108.993 896 2	⋯
(T,Q,5,6)	−1.133 645 58	⋯	−108.993 855 8	⋯
(Q,5,6)	−1.133 627 78	⋯	−108.993 817 8	⋯
(T,Q,5,6,7)	−1.133 637 72	⋯	−108.993 837 3	⋯
(Q,5,6,7)	−1.133 627 80	⋯	−108.993 812 8	⋯
(5,6,7)	−1.133 627 81	⋯	−108.993 808 0	⋯
(aT,aQ,a5)	−1.133 672 05	⋯	−108.993 970 7	⋯
(aT,aQ,a5,a6)	−1.133 645 91	⋯	−108.993 884 9	⋯
(aQ,a5,a6)	−1.133 628 59	⋯	−108.993 812 1	⋯
(aT,aQ,a5,a6,a7)	−1.133 638 17	⋯	−108.993 858 0	⋯
(aQ,a5,a6,a7)	−1.133 628 57	⋯	−108.993 815 9	⋯
(a5,a6,a7)	−1.133 628 54	⋯	−108.993 820 0	⋯
HF limit	−1.133 629 57[d]	⋯	−108.993 826[e]	⋯

[a]Energies in E_h, at bond distances for H_2 and N_2 of exactly 1.4 and 2.068 atomic units, respectively.
[b]Effective decay exponent, as defined in text.
[c]See text for notation.
[d]LCAO SCF HF limit from Ref. 83.
[e]Numerical HF limit from Refs. 84–86.

TABLE IV. Valence MP2 singlet pair energies (in mE_h) for the HF molecule.[a]

Pair	cc-pVQZ	cc-pV5Z	cc-pV6Z	pV7Z	(Q,5)	(5,6)	(6,7)	V1+ MP2-R12/A
$2\sigma^+\ 2\sigma^+$	−11.8962	−12.4186	−12.6593	−12.7962	−12.967	−12.990	−13.029	−13.070
$3\sigma^+\ 2\sigma^+$	−18.0622	−19.0458	−19.4829	−19.7255	−20.078	−20.083	−20.138	−20.161
$3\sigma^+\ 3\sigma^+$	−27.6993	−28.4191	−28.7509	−28.9395	−29.174	−29.207	−29.260	−29.274
$1\pi_x\ 2\sigma^+$	−17.4235	−18.5942	−19.1350	−19.4332	−19.822	−19.878	−19.940	−19.985
$1\pi_x\ 3\sigma^+$	−15.0239	−15.7489	−16.0804	−16.2591	−16.510	−16.536	−16.563	−16.576
$1\pi_y\ 1\pi_x$	−15.9501	−16.7874	−17.1823	−17.3962	−17.666	−17.725	−17.760	−17.780
$1\pi_y\ 1\pi_y$	−24.5198	−25.5271	−26.0063	−26.2699	−26.584	−26.665	−26.718	−26.763
Total	−187.542	−196.411	−200.519	−202.782	−205.716	−206.162	−206.631	−206.932
	aug-cc-pVQZ	aug-cc-pV5Z	aug-cc-pV6Z	aug-pV7Z	(aQ,a5)	(a5,a6)	(a6,a7)	V1+ MP2-R12/A
$2\sigma^+\ 2\sigma^+$	−11.9783	−12.4619	−12.6872	−12.8125	−12.969	−12.997	−13.026	−13.070
$3\sigma^+\ 2\sigma^+$	−18.2708	−19.1486	−19.5447	−19.7648	−20.070	−20.089	−20.139	−20.161
$3\sigma^+\ 3\sigma^+$	−27.8531	−28.5091	−28.8079	−28.9778	−29.197	−29.218	−29.267	−29.274
$1\pi_x\ 2\sigma^+$	−17.7384	−18.7526	−19.2308	−19.4887	−19.817	−19.888	−19.927	−19.985
$1\pi_x\ 3\sigma^+$	−15.2956	−15.8798	−16.1560	−16.3061	−16.493	−16.535	−16.561	−16.576
$1\pi_y\ 1\pi_x$	−16.2916	−16.9671	−17.2893	−17.4618	−17.676	−17.732	−17.755	−17.780
$1\pi_y\ 1\pi_y$	−24.9039	−25.7298	−26.1295	−26.3459	−26.596	−26.679	−26.714	−26.763
Total	−190.270	−197.811	−201.367	−203.299	−205.723	−206.252	−206.585	−206.932

[a]Geometry as in Ref. 33: $r_{HF}=0.915\,769$ Å.

Among the extrapolations in Tables II and III, the spread of basis set limits determined with $X=$Q and higher data is (0.05,1.8,7.0,9.4) μE_h for (H, N, O, F) and (0.8,12) μE_h for (H_2, N_2), indicating good internal agreement. Addition of the septuple-ζ basis sets in the fits generally lowers the extrapolated Hartree–Fock limits and improves agreement with exactly known numerical values. In contrast, inclusion of (aug)-cc-pVTZ RHF energies in the fits noticeably worsens the accuracy of the extrapolations. In the limited cases analyzed here, the septuple-ζ basis sets are sufficiently complete that the errors in the explicitly computed RHF energies are of the same order of magnitude as the errors in associated extrapolations, the latter displaying a tendency to underestimate exact Hartree–Fock limits. The difficulty of extrapolating out the last microhartrees of error is likely a consequence of Gaussian basis sets not having the proper exponential form at large and small nuclear–electron distances.

IV. MOLECULAR ABSOLUTE MP2 PAIR ENERGIES

A chief merit of the correlation-consistent families of basis sets is that they provide a solid foundation for studies of convergence of correlation energies. To elucidate the effect of higher cardinal number basis sets on absolute correlation energies, we performed a series of computations on HF, N_2, F_2, and two conformers of H_2O with the (aug)-cc-pVXZ series of basis sets. The convergence data for the MP2 pair energies of these species are collected in Tables IV–XIII. Conventional estimates for the complete basis set limit for singlet and triplet MP2 pair energies were obtained via two-point fits to Eqs. (12) and (13), respectively. Additionally, more general linear two-point fits

$$\Delta\epsilon_{ij}^{1}=a_{ij}(X+c)^{-3}, \tag{26}$$

$$\Delta\epsilon_{ij}^{3}=a_{ij}(X+c)^{-5}, \tag{27}$$

with $c=0.5$ and 1.0 were studied. Note that Eqs. (12) and (13) are instances of Eqs. (26) and (27), respectively, with $c=0.0$. For the complete basis set limit reference points, we utilized explicitly computed V1+MP2-R12/A pair energies. Tables XIV and XV summarize the statistical analysis of the data. Our approach to data analysis is reminiscent of previous methods by Wilson and Dunning[29] and Klopper.[33]

TABLE V. Valence MP2 triplet pair energies (in mE_h) for the HF molecule.[a]

Pair	cc-pVQZ	cc-pV5Z	cc-pV6Z	pV7Z	(Q,5)	(5,6)	(6,7)	V1+ MP2-R12/A
$3\sigma^+\ 2\sigma^+$	−8.4971	−8.7044	−8.7629	−8.7866	−8.805	−8.802	−8.807	−8.810
$1\pi_x\ 2\sigma^+$	−8.9701	−9.2551	−9.3352	−9.3672	−9.394	−9.389	−9.395	−9.400
$1\pi_x\ 3\sigma^+$	−27.7110	−28.0592	−28.1636	−28.2020	−28.229	−28.234	−28.235	−28.240
$1\pi_y\ 1\pi_x$	−28.0542	−28.4987	−28.6360	−28.6862	−28.715	−28.728	−28.729	−28.740
Total	−109.913	−111.832	−112.396	−112.611	−112.767	−112.775	−112.796	−112.831
	aug-cc-pVQZ	aug-cc-pV5Z	aug-cc-pV6Z	aug-pV7Z	(aQ,a5)	(a5,a6)	(a6,a7)	V1+ MP2-R12/A
$3\sigma^+\ 2\sigma^+$	−8.5582	−8.7214	−8.7695	−8.7896	−8.801	−8.802	−8.807	−8.810
$1\pi_x\ 2\sigma^+$	−9.0712	−9.2817	−9.3458	−9.3724	−9.384	−9.389	−9.395	−9.400
$1\pi_x\ 3\sigma^+$	−27.9112	−28.1186	−28.1862	−28.2133	−28.220	−28.232	−28.237	−28.240
$1\pi_y\ 1\pi_x$	−28.3430	−28.5882	−28.6721	−28.7059	−28.708	−28.728	−28.735	−28.740
Total	−110.869	−112.110	−112.506	−112.667	−112.715	−112.772	−112.806	−112.831

[a]Geometry as in Ref. 33: $r_{HF}=0.915\,769$ Å.

TABLE VI. Valence MP2 singlet pair energies (in mE_h) for the N_2 molecule.[a]

Pair	cc-pVQZ	cc-pV5Z	cc-pV6Z	pV7Z	(Q,5)	(5,6)	(6,7)	V1+ MP2-R12/A
$2\sigma_g^+\ 2\sigma_g^+$	−14.7065	−15.5174	−15.9046	−16.1117	−16.368	−16.436	−16.464	−16.521
$2\sigma_u^+\ 2\sigma_g^+$	−4.8714	−5.0927	−5.1929	−5.2486	−5.325	−5.331	−5.343	−5.369
$2\sigma_u^+\ 2\sigma_u^+$	−16.6113	−17.0615	−17.2735	−17.3921	−17.534	−17.565	−17.594	−17.638
$3\sigma_g^+\ 2\sigma_g^+$	−10.9145	−11.5191	−11.7976	−11.9467	−12.153	−12.180	−12.200	−12.224
$2\sigma_u^+\ 3\sigma_g^+$	−24.5047	−25.3783	−25.7844	−26.0166	−26.295	−26.342	−26.412	−26.491
$3\sigma_g^+\ 3\sigma_g^+$	−16.7894	−17.3007	−17.5369	−17.6778	−17.837	−17.861	−17.917	−17.956
$1\pi_{u,x}\ 2\sigma_g^+$	−16.6774	−17.5389	−17.9548	−18.1692	−18.443	−18.526	−18.534	−18.588
$1\pi_{u,x}\ 2\sigma_u^+$	−12.6042	−13.0967	−13.3355	−13.4539	−13.613	−13.664	−13.655	−13.687
$1\pi_{u,x}\ 3\sigma_g^+$	−10.6045	−11.0076	−11.1958	−11.2975	−11.431	−11.454	−11.470	−11.489
$1\pi_{u,y}\ 1\pi_{u,x}$	−21.7369	−22.2564	−22.5127	−22.6454	−22.801	−22.865	−22.871	−22.901
$1\pi_{u,y}\ 1\pi_{u,y}$	−29.9907	−30.6248	−30.9378	−31.1009	−31.290	−31.368	−31.378	−31.428
Total	−249.888	−258.662	−262.851	−265.082	−267.868	−268.605	−268.876	−269.485
	aug-cc-pVQZ	aug-cc-pV5Z	aug-cc-pV6Z	aug-pV7Z	(aQ,a5)	(a5,a6)	(a6,a7)	V1+ MP2-R12/A
$2\sigma_g^+\ 2\sigma_g^+$	−14.8252	−15.5882	−15.9487	−16.1333	−16.389	−16.444	−16.447	−16.521
$2\sigma_u^+\ 2\sigma_g^+$	−4.9074	−5.1118	−5.2047	−5.2562	−5.326	−5.332	−5.344	−5.369
$2\sigma_u^+\ 2\sigma_u^+$	−16.7354	−17.1350	−17.3175	−17.4212	−17.554	−17.568	−17.598	−17.638
$3\sigma_g^+\ 2\sigma_g^+$	−10.9868	−11.5613	−11.8259	−11.9597	−12.164	−12.189	−12.187	−12.224
$2\sigma_u^+\ 3\sigma_g^+$	−24.7362	−25.5201	−25.8764	−26.0786	−26.343	−26.366	−26.422	−26.491
$3\sigma_g^+\ 3\sigma_g^+$	−16.8868	−17.3663	−17.5856	−17.7109	−17.869	−17.887	−17.924	−17.956
$1\pi_{u,x}\ 2\sigma_g^+$	−16.8835	−17.6615	−18.0278	−18.2142	−18.478	−18.531	−18.531	−18.588
$1\pi_{u,x}\ 2\sigma_u^+$	−12.7810	−13.1925	−13.3849	−13.4865	−13.624	−13.649	−13.659	−13.687
$1\pi_{u,x}\ 3\sigma_g^+$	−10.7202	−11.0728	−11.2362	−11.3243	−11.443	−11.461	−11.474	−11.489
$1\pi_{u,y}\ 1\pi_{u,x}$	−21.9490	−22.3902	−22.5925	−22.6992	−22.853	−22.870	−22.881	−22.901
$1\pi_{u,y}\ 1\pi_{u,y}$	−30.2532	−30.7850	−31.0330	−31.1658	−31.343	−31.374	−31.392	−31.428
Total	−252.303	−260.096	−263.715	−265.641	−268.272	−268.686	−268.917	−269.485

[a]Geometry as in Ref. 33: $r_{NN}=1.098\,119$ Å.

Perusal of the compiled data reveals consistent lowering of explicitly computed (aug)-pVXZ MP2 pair energies as the cardinal quantum number X of the basis is increased. As a result, the mean relative error Δ, mean absolute relative error Δ_{abs}, RMS relative error Δ_{RMS}, maximum absolute relative error Δ_{max}, and relative error standard deviation Δ_{std} all decrease monotonically with X (Table XIV). The average absolute relative error for singlet and triplet pair energies computed with the aug-pV7Z/pV7Z set is 1.719%/1.963% and 0.178%/0.265%, respectively. These septuple-ζ errors are smaller than the corresponding (aug)-cc-pV6Z values by 35% for singlet and 50% for triplet pairs. The trends in error statistics in Table XIV demonstrate that the pV7Z and aug-pV7Z sets are excellent extensions of the existing (aug)-cc-pVXZ sets in the computation of correlation energies, in addition to Hartree–Fock energies (Sec. III). In general, relative errors observed in singlet MP2 pair energies are 3–8 times greater than respective errors in triplet energies.

TABLE VII. Valence MP2 triplet pair energies (in mE_h) for the N_2 molecule.[a]

Pair	cc-pVQZ	cc-pV5Z	cc-pV6Z	pV7Z	(Q,5)	(5,6)	(6,7)	V1+ MP2-R12/A
$2\sigma_u^+\ 2\sigma_g^+$	−5.0143	−5.1311	−5.1673	−5.1806	−5.188	−5.192	−5.192	−5.194
$3\sigma_g^+\ 2\sigma_g^+$	−4.4994	−4.6351	−4.6727	−4.6885	−4.701	−4.698	−4.702	−4.705
$2\sigma_u^+\ 3\sigma_g^+$	−4.0589	−4.1344	−4.1601	−4.1686	−4.171	−4.177	−4.176	−4.177
$1\pi_{u,x}\ 2\sigma_g^+$	−11.5767	−11.7690	−11.8292	−11.8531	−11.863	−11.870	−11.874	−11.876
$1\pi_{u,x}\ 2\sigma_u^+$	−14.2222	−14.4043	−14.4717	−14.4937	−14.493	−14.517	−14.513	−14.515
$1\pi_{u,x}\ 3\sigma_g^+$	−22.1726	−22.3199	−22.3651	−22.3846	−22.392	−22.395	−22.401	−22.403
$1\pi_{u,y}\ 1\pi_{u,x}$	−39.4770	−39.6973	−39.7710	−39.8002	−39.805	−39.821	−39.825	−39.830
Total	−148.993	−150.584	−151.103	−151.301	−151.359	−151.452	−151.471	−151.495
	aug-cc-pVQZ	aug-cc-pV5Z	aug-cc-pV6Z	aug-pV7Z	(aQ,a5)	(a5,a6)	(a6,a7)	V1+ MP2-R12/A
$2\sigma_u^+\ 2\sigma_g^+$	−5.0534	−5.1458	−5.1725	−5.1831	−5.191	−5.190	−5.192	−5.194
$3\sigma_g^+\ 2\sigma_g^+$	−4.5141	−4.6397	−4.6751	−4.6896	−4.701	−4.699	−4.702	−4.705
$2\sigma_u^+\ 3\sigma_g^+$	−4.0961	−4.1496	−4.1647	−4.1707	−4.176	−4.175	−4.176	−4.177
$1\pi_{u,x}\ 2\sigma_g^+$	−11.6204	−11.7865	−11.8367	−11.8566	−11.867	−11.870	−11.874	−11.876
$1\pi_{u,x}\ 2\sigma_u^+$	−14.3454	−14.4560	−14.4890	−14.5024	−14.510	−14.511	−14.514	−14.515
$1\pi_{u,x}\ 3\sigma_g^+$	−22.1971	−22.3297	−22.3708	−22.3877	−22.394	−22.398	−22.402	−22.403
$1\pi_{u,y}\ 1\pi_{u,x}$	−39.5761	−39.7402	−39.7902	−39.8107	−39.820	−39.824	−39.828	−39.830
Total	−149.565	−150.820	−151.196	−151.348	−151.432	−151.449	−151.479	−151.495

[a]Geometry as in Ref. 33: $r_{NN}=1.098\,119$ Å.

TABLE VIII. Valence MP2 singlet pair energies (in mE_h) for the F_2 molecule.[a]

Pair	cc-pVQZ	cc-pV5Z	cc-pV6Z	pV7Z	(Q,5)	(5,6)	(6,7)	V1+ MP2-R12/A
$2\sigma_g^+\ 2\sigma_g^+$	−8.4106	−8.7629	−8.9333	−9.0306	−9.133	−9.167	−9.196	−9.228
$3\sigma_g^+\ 2\sigma_g^+$	−13.7592	−14.5486	−14.9243	−15.1338	−15.377	−15.440	−15.490	−15.518
$3\sigma_g^+\ 3\sigma_g^+$	−50.3983	−50.9825	−51.2460	−51.3995	−51.595	−51.608	−51.661	−51.685
$1\pi_{g,x}\ 2\sigma_g^+$	−9.2283	−9.8459	−10.1346	−10.2927	−10.494	−10.531	−10.562	−10.591
$1\pi_{g,x}\ 3\sigma_g^+$	−13.0495	−13.5098	−13.7227	−13.8380	−13.993	−14.015	−14.034	−14.048
$1\pi_{g,y}\ 1\pi_{g,x}$	−9.2129	−9.6803	−9.9032	−10.0241	−10.171	−10.209	−10.230	−10.243
$1\pi_{g,y}\ 1\pi_{g,y}$	−14.4265	−15.0024	−15.2797	−15.4317	−15.607	−15.661	−15.690	−15.718
$2\sigma_u^+\ 2\sigma_g^+$	−9.9155	−10.4074	−10.6406	−10.7709	−10.923	−10.961	−10.993	−11.046
$2\sigma_u^+\ 3\sigma_g^+$	−14.2760	−14.9587	−15.2842	−15.4615	−15.675	−15.731	−15.763	−15.795
$2\sigma_u^+\ 1\pi_{g,x}$	−11.5299	−12.2649	−12.6079	−12.7950	−13.036	−13.079	−13.113	−13.145
$2\sigma_u^+\ 2\sigma_u^+$	−9.0327	−9.3592	−9.5135	−9.5998	−9.702	−9.725	−9.747	−9.778
$1\pi_{u,y}\ 2\sigma_g^+$	−9.0217	−9.6760	−9.9919	−10.1667	−10.362	−10.426	−10.464	−10.495
$1\pi_{u,y}\ 3\sigma_g^+$	−9.5319	−10.0244	−10.2605	−10.3893	−10.541	−10.585	−10.608	−10.619
$1\pi_{u,y}\ 1\pi_{g,x}$	−7.6476	−8.0739	−8.2770	−8.3873	−8.521	−8.556	−8.575	−8.588
$1\pi_{u,y}\ 1\pi_{g,y}$	−23.4809	−24.5056	−25.0016	−25.2753	−25.581	−25.683	−25.741	−25.796
$1\pi_{u,y}\ 2\sigma_u^+$	−9.9037	−10.5516	−10.8548	−11.0207	−11.231	−11.271	−11.303	−11.334
$1\pi_{u,x}\ 1\pi_{u,y}$	−7.0940	−7.5264	−7.7381	−7.8555	−7.980	−8.029	−8.055	−8.069
$1\pi_{u,x}\ 1\pi_{u,x}$	−11.6485	−12.1802	−12.4380	−12.5814	−12.738	−12.792	−12.825	−12.854
Total	−361.036	−377.495	−385.321	−389.632	−394.763	−396.071	−396.964	−397.739
	aug-cc-pVQZ	aug-cc-pV5Z	aug-cc-pV6Z	aug-pV7Z	(aQ,a5)	(a5,a6)	(a6,a7)	V1+ MP2-R12/A
$2\sigma_g^+\ 2\sigma_g^+$	−8.5058	−8.8200	−8.9705	−9.0506	−9.150	−9.177	−9.187	−9.228
$3\sigma_g^+\ 2\sigma_g^+$	−14.0407	−14.7111	−15.0232	−15.1869	−15.414	−15.452	−15.465	−15.518
$3\sigma_g^+\ 3\sigma_g^+$	−50.5317	−51.0554	−51.2999	−51.4304	−51.605	−51.636	−51.652	−51.685
$1\pi_{g,x}\ 2\sigma_g^+$	−9.3488	−9.9128	−10.1771	−10.3165	−10.505	−10.540	−10.554	−10.591
$1\pi_{g,x}\ 3\sigma_g^+$	−13.2044	−13.5857	−13.7683	−13.8660	−13.986	−14.019	−14.032	−14.048
$1\pi_{g,y}\ 1\pi_{g,x}$	−9.3362	−9.7501	−9.9470	−10.0511	−10.184	−10.217	−10.228	−10.243
$1\pi_{g,y}\ 1\pi_{g,y}$	−14.5711	−15.0848	−15.3321	−15.4639	−15.624	−15.672	−15.688	−15.718
$2\sigma_u^+\ 2\sigma_g^+$	−9.9800	−10.4471	−10.6667	−10.7861	−10.937	−10.968	−10.989	−11.046
$2\sigma_u^+\ 3\sigma_g^+$	−14.4617	−15.0622	−15.3436	−15.4968	−15.692	−15.730	−15.757	−15.795
$2\sigma_u^+\ 1\pi_{g,x}$	−11.6945	−12.3553	−12.6635	−12.8266	−13.049	−13.087	−13.104	−13.145
$2\sigma_u^+\ 2\sigma_u^+$	−9.0857	−9.3900	−9.5328	−9.6112	−9.709	−9.729	−9.745	−9.778
$1\pi_{u,y}\ 2\sigma_g^+$	−9.2261	−9.7935	−10.0648	−10.2092	−10.389	−10.437	−10.455	−10.495
$1\pi_{u,y}\ 3\sigma_g^+$	−9.7483	−10.1423	−10.3305	−10.4310	−10.556	−10.589	−10.602	−10.619
$1\pi_{u,y}\ 1\pi_{g,x}$	−7.7723	−8.1436	−8.3201	−8.4136	−8.533	−8.563	−8.573	−8.588
$1\pi_{u,y}\ 1\pi_{g,y}$	−23.7420	−24.6585	−25.1002	−25.3361	−25.620	−25.707	−25.737	−25.796
$1\pi_{u,y}\ 2\sigma_u^+$	−10.0516	−10.6322	−10.9047	−11.0493	−11.241	−11.279	−11.295	−11.334
$1\pi_{u,x}\ 1\pi_{u,y}$	−7.2798	−7.6351	−7.8056	−7.8978	−8.008	−8.040	−8.055	−8.069
$1\pi_{u,x}\ 1\pi_{u,x}$	−11.8707	−12.3040	−12.5149	−12.6300	−12.759	−12.805	−12.826	−12.854
Total	−365.681	−380.096	−386.942	−390.595	−395.220	−396.346	−396.808	−397.739

[a]Geometry as in Ref. 33: $r_{FF}=1.411\,336$ Å.

This phenomenon is a very clear indication that the asymptotic rates of convergence for singlet and triplet pair energies are very different, in accord with previous evidence.[7,33]

Basis set extrapolation of pair energies according to Klopper's formulas (12) and (13) brings much better agreement with the reference MP2-R12/A values. On average, extrapolation decreases statistical measures of errors by roughly an order of magnitude, compared to the corresponding explicitly computed values. Moreover, two-point extrapolations with successively higher $(X,X+1)$ pairs consistently and substantially reduce all error statistics. For example, for singlet pairs the (mean abs. relative error, std. dev.) in the cc-pV$(X,X+1)$Z extrapolations with the X^{-3} form are reduced by factors of (0.29, 0.36) in going from (Q,5) to (6,7). Addition of diffuse functions to the one-particle basis does generally improve extrapolation accuracy and reduce all statistical measures of error, but the (6,7) versus (a6,a7) case for singlet pairs constitutes an exception.

Somewhat unexpectedly, pair energies extrapolated using Klopper's approach are almost always smaller in absolute value than their reference values. Only 2 out of 73 (6,7) singlet pair energies are larger in magnitude than their R12/A reference energies, and there are no such occurrences in the (Q, 5) and (5, 6) cases. This behavior is characteristic of the triplet pair energies also, but to a lesser degree. One might argue that the apparent underestimation of magnitudes is simply due to the reference values being more negative than the basis set limit since MP2-R12/A pair energies typically converge from below. However, thorough examination of Klopper's data[33] reveals that even when MP2-R12/B pair energies (which typically converge from above) are used as a reference, extrapolated singlet MP2 pair energies are still consistently higher than their reference values. This phenomenon is not found for CCD and CCSD pair energies.

The observed persistent underestimation of the absolute values of singlet MP2 pair energies extrapolated using Eqs. (12) and (13) is conveyed most clearly by linear correlation

TABLE IX. Valence MP2 triplet pair energies (in mE_h) for the F_2 molecule.[a]

Pair	cc-pVQZ	cc-pV5Z	cc-pV6Z	pV7Z	(Q,5)	(5,6)	(6,7)	V1+ MP2-R12/A
$3\sigma_g^+\ 2\sigma_g^+$	−5.7313	−5.8583	−5.8951	−5.9101	−5.920	−5.920	−5.923	−5.926
$1\pi_{g,x}\ 2\sigma_g^+$	−5.0864	−5.2542	−5.3074	−5.3294	−5.336	−5.343	−5.348	−5.353
$1\pi_{g,x}\ 3\sigma_g^+$	−27.8669	−28.0900	−28.1525	−28.1778	−28.199	−28.194	−28.200	−28.203
$1\pi_{g,y}\ 1\pi_{g,x}$	−16.2669	−16.4767	−16.5456	−16.5726	−16.579	−16.592	−16.596	−16.601
$2\sigma_u^+\ 2\sigma_g^+$	−1.3052	−1.3450	−1.3603	−1.3662	−1.364	−1.371	−1.371	−1.372
$2\sigma_u^+\ 3\sigma_g^+$	−11.2817	−11.4691	−11.5386	−11.5642	−11.560	−11.585	−11.586	−11.591
$2\sigma_u^+\ 1\pi_{g,x}$	−5.9047	−6.0757	−6.1276	−6.1485	−6.159	−6.162	−6.166	−6.171
$1\pi_{u,y}\ 2\sigma_g^+$	−4.4489	−4.6141	−4.6644	−4.6852	−4.695	−4.698	−4.703	−4.706
$1\pi_{u,y}\ 3\sigma_g^+$	−17.3902	−17.6029	−17.6684	−17.6938	−17.707	−17.712	−17.716	−17.719
$1\pi_{u,y}\ 1\pi_{g,x}$	−13.5478	−13.7494	−13.8166	−13.8435	−13.848	−13.862	−13.867	−13.872
$1\pi_{u,y}\ 1\pi_{g,y}$	−0.8164	−0.8877	−0.9126	−0.9226	−0.922	−0.929	−0.931	−0.933
$1\pi_{u,y}\ 2\sigma_u^+$	−5.5606	−5.7303	−5.7816	−5.8023	−5.813	−5.816	−5.820	−5.824
$1\pi_{u,x}\ 1\pi_{u,y}$	−12.6207	−12.8465	−12.9211	−12.9502	−12.957	−12.971	−12.975	−12.981
Total	−208.449	−212.004	−213.123	−213.569	−213.737	−213.875	−213.953	−214.033
	aug-cc-pVQZ	aug-cc-pV5Z	aug-cc-pV6Z	aug-pV7Z	(aQ,a5)	(a5,a6)	(a6,a7)	V1+ MP2-R12/A
$3\sigma_g^+\ 2\sigma_g^+$	−5.7562	−5.8666	−5.8987	−5.9117	−5.920	−5.920	−5.923	−5.926
$1\pi_{g,x}\ 2\sigma_g^+$	−5.1368	−5.2741	−5.3166	−5.3340	−5.341	−5.345	−5.349	−5.353
$1\pi_{g,x}\ 3\sigma_g^+$	−27.9677	−28.1114	−28.1620	−28.1883	−28.181	−28.196	−28.211	−28.203
$1\pi_{g,y}\ 1\pi_{g,x}$	−16.3471	−16.5042	−16.5581	−16.5795	−16.581	−16.594	−16.598	−16.601
$2\sigma_u^+\ 2\sigma_g^+$	−1.3328	−1.3573	−1.3654	−1.3686	−1.369	−1.371	−1.371	−1.372
$2\sigma_u^+\ 3\sigma_g^+$	−11.3913	−11.5205	−11.5596	−11.5752	−11.583	−11.586	−11.589	−11.591
$2\sigma_u^+\ 1\pi_{g,x}$	−5.9483	−6.0924	−6.1349	−6.1523	−6.163	−6.163	−6.167	−6.171
$1\pi_{u,y}\ 2\sigma_g^+$	−4.5079	−4.6353	−4.6740	−4.6896	−4.697	−4.700	−4.703	−4.706
$1\pi_{u,y}\ 3\sigma_g^+$	−17.5017	−17.6370	−17.6826	−17.7006	−17.703	−17.713	−17.716	−17.719
$1\pi_{u,y}\ 1\pi_{g,x}$	−13.6376	−13.7826	−13.8320	−13.8519	−13.853	−13.865	−13.869	−13.872
$1\pi_{u,y}\ 1\pi_{g,y}$	−0.9045	−0.9212	−0.9275	−0.9305	−0.929	−0.932	−0.933	−0.933
$1\pi_{u,y}\ 2\sigma_u^+$	−5.6165	−5.7506	−5.7904	−5.8067	−5.816	−5.817	−5.821	−5.824
$1\pi_{u,x}\ 1\pi_{u,y}$	−12.7616	−12.8976	−12.9437	−12.9623	−12.964	−12.975	−12.978	−12.981
Total	−210.031	−212.555	−213.366	−213.693	−213.785	−213.911	−213.975	−214.033

[a]Geometry as in Ref. 33: $r_{FF}=1.411\,336$ Å.

TABLE X. Valence MP2 singlet pair energies (in mE_h) for the C_{2v} structure of the H_2O molecule.[a]

Pair	cc-pVQZ	cc-pV5Z	cc-pV6Z	pV7Z	(Q,5)	(5,6)	(6,7)	V1+ MP2-R12/A
$2a_1\ 2a_1$	−12.2973	−12.7524	−12.9613	−13.0803	−13.230	−13.248	−13.283	−13.307
$3a_1\ 2a_1$	−15.9773	−16.7603	−17.1177	−17.3163	−17.582	−17.609	−17.654	−17.674
$3a_1\ 3a_1$	−24.1001	−24.8794	−25.2370	−25.4373	−25.697	−25.728	−25.778	−25.809
$1b_2\ 2a_1$	−16.8092	−17.7909	−18.2472	−18.4955	−18.821	−18.874	−18.918	−18.941
$1b_2\ 3a_1$	−15.3622	−16.1052	−16.4420	−16.6210	−16.885	−16.905	−16.925	−16.940
$1b_2\ 1b_2$	−24.2798	−25.2023	−25.6376	−25.8783	−26.170	−26.236	−26.288	−26.314
$1b_1\ 2a_1$	−19.4759	−20.3314	−20.7034	−20.9082	−21.229	−21.214	−21.257	−21.261
$1b_1\ 3a_1$	−16.8108	−17.2921	−17.5021	−17.6201	−17.797	−17.791	−17.821	−17.820
$1b_1\ 1b_2$	−13.3652	−13.9608	−14.2236	−14.3616	−14.586	−14.585	−14.596	−14.597
$1b_1\ 1b_1$	−24.4893	−25.0479	−25.2955	−25.4319	−25.634	−25.636	−25.664	−25.665
Total	−182.967	−190.123	−193.376	−195.150	−197.631	−197.844	−198.167	−198.328
	aug-cc-pVQZ	aug-cc-pV5Z	aug-cc-pV6Z	aug-pV7Z	(aQ,a5)	(a5,a6)	(a6,a7)	V1+ MP2-R12/A
$2a_1\ 2a_1$	−12.3682	−12.7928	−12.9851	−13.0968	−13.238	−13.249	−13.287	−13.307
$3a_1\ 2a_1$	−16.1573	−16.8593	−17.1755	−17.3568	−17.596	−17.610	−17.665	−17.674
$3a_1\ 3a_1$	−24.3770	−25.0241	−25.3244	−25.4989	−25.703	−25.737	−25.796	−25.809
$1b_2\ 2a_1$	−17.1030	−17.9393	−18.3309	−18.5509	−18.817	−18.869	−18.925	−18.941
$1b_2\ 3a_1$	−15.7009	−16.2676	−16.5343	−16.6826	−16.862	−16.901	−16.935	−16.940
$1b_2\ 1b_2$	−24.6810	−25.4101	−25.7612	−25.9584	−26.175	−26.243	−26.294	−26.314
$1b_1\ 2a_1$	−19.6497	−20.4194	−20.7528	−20.9409	−21.227	−21.211	−21.261	−21.261
$1b_1\ 3a_1$	−16.9329	−17.3571	−17.5409	−17.6460	−17.802	−17.793	−17.825	−17.820
$1b_1\ 1b_2$	−13.6239	−14.0790	−14.2876	−14.4028	−14.556	−14.574	−14.599	−14.597
$1b_1\ 1b_1$	−24.5898	−25.1060	−25.3307	−25.4563	−25.648	−25.639	−25.670	−25.665
Total	−185.184	−191.255	−194.023	−195.590	−197.625	−197.825	−198.255	−198.328

[a]Geometry as in Ref. 43: $r_{OH}=0.958\,85$ Å, $\theta_{HOH}=104.343°$.

TABLE XI. Valence MP2 triplet pair energies (in mE_h) for the C_{2v} structure of the H_2O molecule.[a]

Pair	cc-pVQZ	cc-pV5Z	cc-pV6Z	pV7Z	(Q,5)	(5,6)	(6,7)	V1+ MP2-R12/A
$3a_1\ 2a_1$	−8.1998	−8.3975	−8.4524	−8.4736	−8.494	−8.489	−8.492	−8.494
$1b_2\ 2a_1$	−9.0259	−9.2786	−9.3484	−9.3753	−9.402	−9.395	−9.398	−9.401
$1b_2\ 3a_1$	−26.0911	−26.4945	−26.6162	−26.6586	−26.691	−26.698	−26.695	−26.700
$1b_1\ 2a_1$	−7.9344	−8.0705	−8.1091	−8.1248	−8.137	−8.135	−8.138	−8.140
$1b_1\ 3a_1$	−23.4857	−23.7283	−23.8009	−23.8265	−23.847	−23.850	−23.849	−23.850
$1b_1\ 1b_2$	−25.2268	−25.5485	−25.6442	−25.6773	−25.705	−25.709	−25.706	−25.709
Total	−99.964	−101.518	−101.971	−102.136	−102.275	−102.275	−102.278	−102.294
	aug-cc-pVQZ	aug-cc-pV5Z	aug-cc-pV6Z	aug-pV7Z	(aQ,a5)	(a5,a6)	(a6,a7)	V1+ MP2-R12/A
$3a_1\ 2a_1$	−8.2820	−8.4201	−8.4601	−8.4770	−8.487	−8.487	−8.492	−8.494
$1b_2\ 2a_1$	−9.1417	−9.3099	−9.3595	−9.3806	−9.392	−9.393	−9.399	−9.401
$1b_2\ 3a_1$	−26.3925	−26.5872	−26.6500	−26.6754	−26.682	−26.692	−26.697	−26.700
$1b_1\ 2a_1$	−7.9688	−8.0807	−8.1129	−8.1266	−8.135	−8.135	−8.138	−8.140
$1b_1\ 3a_1$	−23.6295	−23.7717	−23.8161	−23.8338	−23.841	−23.846	−23.849	−23.850
$1b_1\ 1b_2$	−25.4512	−25.6159	−25.6687	−25.6896	−25.696	−25.704	−25.708	−25.709
Total	−100.866	−101.785	−102.067	−102.183	−102.233	−102.256	−102.283	−102.294

[a]Geometry as in Ref. 43: $r_{OH}=0.958\,85$ Å, $\theta_{HOH}=104.343°$.

TABLE XII. Valence MP2 singlet pair energies (in mE_h) for the $D_{\infty h}$ structure of the H_2O molecule.[a]

Pair	cc-pVQZ	cc-pV5Z	cc-pV6Z	pV7Z	(Q,5)	(5,6)	(6,7)	V1+ MP2-R12/A
$2\sigma_g^+\ 2\sigma_g^+$	−11.4851	−11.9005	−12.0912	−12.1987	−12.336	−12.353	−12.382	−12.409
$1\sigma_u^+\ 2\sigma_g^+$	−20.0378	−20.8744	−21.2354	−21.4318	−21.752	−21.731	−21.766	−21.773
$1\sigma_u^+\ 1\sigma_u^+$	−24.8661	−25.3946	−25.6251	−25.7515	−25.949	−25.942	−25.966	−25.965
$1\pi_{u,x}\ 2\sigma_g^+$	−16.8421	−17.8373	−18.2919	−18.5359	−18.881	−18.916	−18.951	−18.980
$1\pi_{u,x}\ 1\sigma_u^+$	−12.6662	−13.2232	−13.4693	−13.5966	−13.808	−13.807	−13.813	−13.816
$1\pi_{u,y}\ 1\pi_{u,x}$	−16.6330	−17.4339	−17.8048	−17.9991	−18.274	−18.314	−18.330	−18.352
$1\pi_{u,y}\ 1\pi_{u,y}$	−24.7198	−25.6429	−26.0782	−26.3131	−26.611	−26.676	−26.713	−26.754
Total	−181.478	−189.010	−192.435	−194.272	−196.912	−197.140	−197.396	−197.599
	aug-cc-pVQZ	aug-cc-pV5Z	aug-cc-pV6Z	aug-pV7Z	(aQ,a5)	(a5,a6)	(a6,a7)	V1+ MP2-R12/A
$2\sigma_g^+\ 2\sigma_g^+$	−11.5578	−11.9365	−12.1128	−12.2132	−12.334	−12.355	−12.384	−12.409
$1\sigma_u^+\ 2\sigma_g^+$	−20.1917	−20.9434	−21.2733	−21.4585	−21.732	−21.726	−21.773	−21.773
$1\sigma_u^+\ 1\sigma_u^+$	−24.9178	−25.4238	−25.6432	−25.7655	−25.955	−25.945	−25.974	−25.965
$1\pi_{u,x}\ 2\sigma_g^+$	−17.1580	−17.9851	−18.3764	−18.5907	−18.853	−18.914	−18.955	−18.980
$1\pi_{u,x}\ 1\sigma_u^+$	−12.8759	−13.3169	−13.5195	−13.6296	−13.780	−13.798	−13.817	−13.816
$1\pi_{u,y}\ 1\pi_{u,x}$	−17.0484	−17.6460	−17.9290	−18.0806	−18.273	−18.318	−18.338	−18.352
$1\pi_{u,y}\ 1\pi_{u,y}$	−25.1537	−25.8692	−26.2145	−26.4038	−26.620	−26.689	−26.726	−26.754
Total	−184.091	−190.292	−193.179	−194.766	−196.798	−197.145	−197.465	−197.599

[a]Geometry as in Ref. 43: $r_{OH}=0.934\,11$ Å.

TABLE XIII. Valence MP2 triplet pair energies (in mE_h) for the $D_{\infty h}$ structure of the H_2O molecule.[a]

Pair	cc-pVQZ	cc-pV5Z	cc-pV6Z	pV7Z	(Q,5)	(5,6)	(6,7)	V1+ MP2-R12/A
$1\sigma_u^+\ 2\sigma_g^+$	−7.1128	−7.2321	−7.2659	−7.2793	−7.290	−7.289	−7.291	−7.292
$1\pi_{u,x}\ 2\sigma_g^+$	−8.8226	−9.0809	−9.1512	−9.1774	−9.207	−9.198	−9.200	−9.203
$1\pi_{u,x}\ 1\sigma_u^+$	−25.1543	−25.4460	−25.5278	−25.5565	−25.588	−25.583	−25.581	−25.582
$1\pi_{u,y}\ 1\pi_{u,x}$	−26.9692	−27.5131	−27.6741	−27.7306	−27.778	−27.782	−27.779	−27.787
Total	−102.036	−103.799	−104.298	−104.478	−104.658	−104.633	−104.633	−104.649
	aug-cc-pVQZ	aug-cc-pV5Z	aug-cc-pV6Z	aug-pV7Z	(aQ,a5)	(a5,a6)	(a6,a7)	V1+ MP2-R12/A
$1\sigma_u^+\ 2\sigma_g^+$	−7.1439	−7.2398	−7.2687	−7.2806	−7.287	−7.288	−7.291	−7.292
$1\pi_{u,x}\ 2\sigma_g^+$	−8.9540	−9.1141	−9.1629	−9.1828	−9.192	−9.196	−9.200	−9.203
$1\pi_{u,x}\ 1\sigma_u^+$	−25.3412	−25.4962	−25.5452	−25.5645	−25.572	−25.578	−25.581	−25.582
$1\pi_{u,y}\ 1\pi_{u,x}$	−27.4397	−27.6572	−27.7293	−27.7581	−27.763	−27.778	−27.783	−27.787
Total	−103.174	−104.118	−104.414	−104.636	−104.578	−104.613	−104.827	−104.649

[a]Geometry as in Ref. 43: $r_{OH}=0.934\,11$ Å.

TABLE XIV. Mean value (Δ), mean absolute value (Δ_{abs}), RMS value (Δ_{RMS}), maximum absolute value (Δ_{max}), standard deviation (Δ_{std}), skewness (Skew), and kurtosis (Kurt) of relative errors in explictly computed and extrapolated valence MP2 pair energies in molecules under study.[a]

Basis set	Δ	Δ_{abs}	Δ_{RMS}	Δ_{max}	Δ_{std}	Skew[b]	Kurt[c]
			Singlet pairs				
cc-pVQZ	9.058	9.058	9.380	14.041	2.454	−0.184	−0.249
cc-pV5Z	4.940	4.940	5.120	7.807	1.354	−0.147	−0.228
cc-pV6Z	3.014	3.014	3.124	4.797	0.830	−0.125	−0.218
pV7Z	1.963	1.963	2.036	3.132	0.544	−0.129	−0.224
aug-cc-pVQZ	7.847	7.847	8.149	12.094	2.211	−0.038	−0.433
aug-cc-pV5Z	4.289	4.289	4.457	6.688	1.221	−0.049	−0.416
aug-cc-pV6Z	2.621	2.621	2.725	4.103	0.749	−0.051	−0.409
aug-pV7Z	1.719	1.719	1.792	2.727	0.507	−0.011	−0.483
				X^{-3} fit			
(Q,5)	0.620	0.620	0.681	1.266	0.283	−0.164	−0.331
(5,6)	0.367	0.367	0.402	0.767	0.165	0.213	−0.638
(6,7)	0.177	0.177	0.204	0.482	0.103	0.458	0.324
(aQ,a5)	0.555	0.555	0.598	1.016	0.223	−0.273	−0.366
(a5,a6)	0.330	0.330	0.357	0.700	0.136	0.418	−0.258
(a6,a7)	0.186	0.188	0.227	0.512	0.131	0.376	−0.588
				$(X+1/2)^{-3}$ fit			
(Q,5)	−0.046	0.171	0.229	0.591	0.225	−0.554	−0.024
(5,6)	0.053	0.109	0.144	0.423	0.135	0.567	0.430
(6,7)	0.004	0.072	0.093	0.304	0.093	0.830	0.866
				$(X+1)^{-3}$ fit			
(Q,5)	−0.716	0.716	0.773	1.247	0.293	−0.088	−0.990
(5,6)	−0.263	0.275	0.305	0.520	0.156	0.677	−0.288
(6,7)	−0.168	0.177	0.198	0.310	0.106	0.684	−0.282
			Triplet pairs				
cc-pVQZ	3.348	3.348	4.047	12.479	2.296	2.458	7.403
cc-pV5Z	1.196	1.196	1.485	4.835	0.888	2.721	8.663
cc-pV6Z	0.527	0.527	0.660	2.166	0.403	2.677	8.366
pV7Z	0.265	0.265	0.333	1.093	0.204	2.650	8.221
aug-cc-pVQZ	2.193	2.193	2.453	4.216	1.110	0.348	−1.291
aug-cc-pV5Z	0.792	0.792	0.884	1.509	0.397	0.347	−1.311
aug-cc-pV6Z	0.358	0.358	0.401	0.686	0.183	0.361	−1.312
aug-pV7Z	0.178	0.178	0.201	0.355	0.095	0.391	−1.181
				X^{-5} fit			
(Q,5)	0.147	0.153	0.270	1.109	0.228	3.079	10.091
(5,6)	0.076	0.078	0.111	0.372	0.081	1.945	4.526
(6,7)	0.039	0.039	0.052	0.170	0.035	2.194	5.699
(aQ,a5)	0.109	0.109	0.132	0.371	0.074	1.808	3.874
(a5,a6)	0.066	0.066	0.077	0.139	0.041	0.455	−1.316
(a6,a7)	0.024	0.029	0.034	0.069	0.025	−0.097	−0.167
				$(X+1/2)^{-5}$ fit			
(Q,5)	−0.049	0.110	0.148	0.410	0.141	1.296	2.966
(5,6)	0.013	0.034	0.045	0.121	0.043	0.506	−0.125
(6,7)	0.014	0.015	0.022	0.068	0.017	1.315	1.461
				$(X+1)^{-5}$ fit			
(Q,5)	−0.250	0.250	0.288	0.563	0.145	−0.381	−0.696
(5,6)	−0.050	0.050	0.062	0.133	0.036	−0.803	−0.383
(6,7)	−0.011	0.012	0.016	0.045	0.011	−0.665	0.483

[a] Δ, Δ_{abs}, Δ_{RMS}, Δ_{max}, and Δ_{std} in percents.
[b] The standard deviation of Skew assuming normal distribution is 0.287 and 0.350 for singlet and triplet pair sets, respectively.
[c] The standard deviation of Kurt assuming normal distribution is 0.573 and 0.700 for singlet and triplet pair sets, respectively.

coefficients r between relative errors in cc-pVXZ and extrapolated (X, Y) energies (Table XV). The r values for the singlet X^{-3} fits lie in the 0.44–0.79 range, indicating strong correlation between the sets of errors. Also, strong correlation between extrapolated pair energies (X, Y) suggests that higher-order terms in the principal expansion of pair correlation energies can be used to improve extrapolated values. The correlation coefficients between relative errors in explicitly computed and extrapolated MP2 pair energies are even larger for triplet pairs.

The observed underestimation of MP2 pair energies is a systematic trend that can be exploited for designing better extrapolation schemes for at least singlet pairs. We investigated improving Klopper's approach by fits to Eqs. (26) and

TABLE XV. Linear correlation coefficients (Pearson's r values)[a] between sets of relative errors in explictly computed and extrapolated valence MP2 pair energies in molecules under study.

X	5	6	7	(Q,5)	(5,6)	(6,7)
			Singlet pairs			
			X^{-3} fit			
Q	0.997	0.991	0.983	0.677	0.603	0.436
5		0.998	0.993	0.731	0.650	0.488
6			0.998	0.763	0.697	0.532
7				0.791	0.730	0.581
(Q,5)					0.885	0.814
(5,6)						0.855
			$(X+1/2)^{-3}$ fit			
Q	0.997	0.991	0.983	0.060	0.097	-0.025
5		0.998	0.993	0.134	0.156	0.033
6			0.998	0.184	0.218	0.083
7				0.228	0.264	0.142
(Q,5)					0.794	0.758
(5,6)						0.793
			$(X+1)^{-3}$ fit			
Q	0.997	0.991	0.983	-0.567	-0.468	-0.470
5		0.998	0.993	-0.503	-0.415	-0.420
6			0.998	-0.459	-0.357	-0.373
7				-0.417	-0.312	-0.318
(Q,5)					0.830	0.804
(5,6)						0.824
			Triplet pairs			
			X^{-5} fit			
Q	0.996	0.995	0.994	0.861	0.931	0.949
5		0.999	0.998	0.903	0.934	0.956
6			1.000	0.901	0.949	0.964
7				0.902	0.953	0.970
(Q,5)					0.841	0.879
(5,6)						0.967
			$(X+1/2)^{-5}$ fit			
Q	0.996	0.995	0.994	0.480	0.701	0.805
5		0.999	0.998	0.556	0.703	0.815
6			1.000	0.555	0.733	0.831
7				0.557	0.742	0.844
(Q,5)					0.382	0.518
(5,6)						0.842
			$(X+1)^{-5}$ fit			
Q	0.996	0.995	0.994	-0.439	-0.441	-0.453
5		0.999	0.998	-0.358	-0.444	-0.444
6			1.000	-0.358	-0.405	-0.420
7				-0.355	-0.391	-0.398
(Q,5)					0.147	0.279
(5,6)						0.682

[a]See Eq. (21) for the definition of r.

TABLE XVI. Average effective decay exponents[a] of valence MP2 pair energies for molecules under study.

X	$\overline{\alpha(X)}$ Singlet pairs	Triplet pairs
	$X^{-\alpha}$ fit	
6	2.7	4.7
7	2.6	4.6
a6	2.7	4.6
a7	2.6	4.2
	$(X+1/2)^{-\alpha}$ fit	
6	3.1	5.3
7	2.9	5.1
a6	3.1	5.2
a7	2.9	4.7
	$(X+1)^{-\alpha}$ fit	
6	3.5	5.9
7	3.2	5.6
a6	3.5	5.8
a7	3.2	5.1

[a]See Eq. (28) for the definition of $\alpha(X)$.

(27), which include Klopper's formulas as a special case with $c=0.0$. The use of $c=0.5$ for extrapolation of MP2 singlet pair energies decreases the mean relative error and mean absolute relative error most dramatically. For example, in the cc-pV$(X,X+1)$Z extrapolations, Δ_{abs} for [(Q,5),(5,6),(6,7)] is (0.620%, 0.367%, 0.177%) for $c=0.0$ and (0.171%, 0.109%, 0.072%) for $c=0.5$. The RMS relative error and maximum absolute relative error are also reduced with $c=0.5$, whereas the standard deviation of relative error does not vary with c very much. Perhaps most strikingly, the improvement in the extrapolated MP2 singlet pair energies from the use of Eqs. (26) and (27) with $c=0.5$ reduces dramatically the correlation between relative errors in explicitly computed and extrapolated singlet pair energies. Specifically, in Table XV the mean absolute value of the linear correlation coefficients for explicit versus extrapolated errors goes from 0.62 to 0.11 when c is changed from 0.0 to 0.5. Note that the use of $c=1.0$ overshoots the target, yielding negative r values comparable in size to the $c=0.0$ case. In the case of triplet pairs, once again the statistical measures improve and the correlation coefficients r are reduced when $c=0.5$ is employed. Thus, our data indicate that use of $c=0.5$ in Eqs. (26) and (27) offers statistically significant improvements *vis-à-vis* Klopper's approach, and thus should be used for MP2 pair energy extrapolations.

Effective decay exponents $\alpha(X)$ that correspond to asymptotic expressions (26) and (27) were computed for $c=0.0$, 0.5, 1.0 by solving the following nonlinear equation:

$$\frac{\epsilon(X)-\epsilon(X-1)}{\epsilon(X-1)-\epsilon(X-2)}=\frac{\left(1-\dfrac{1}{X+c}\right)^{\alpha}-1}{1-\left(1+\dfrac{1}{X-2+c}\right)^{\alpha}} \tag{28}$$

for α. The effective exponents were averaged for singlet and triplet pairs separately (Table XVI). Singlet and triplet pairs have clearly different convergence rates which approach their ''ideal'' values of 3 and 5 most closely when $c=0.5$, in accord with the observed minimum of statistical measures of errors in valence MP2 pair energies at $c=0.5$ (Table XIV). We believe that this is another indication that asymptotic fits (26) and (27) are optimal for MP2 pair energies when $c=0.5$.

One of the natural assumptions behind analyses of errors in total and pair correlation energies is the normal distribution of a (finite) set of errors. We test the assumption quantitatively by computing skewness and kurtosis (see Sec. II) of the sets of relative errors (Table XIV). Assuming an asymptotic limit of normal distribution of errors, we can compute standard deviations for Skew and Kurt of sets of relative errors (see footnotes of Table XIV). In all cases,

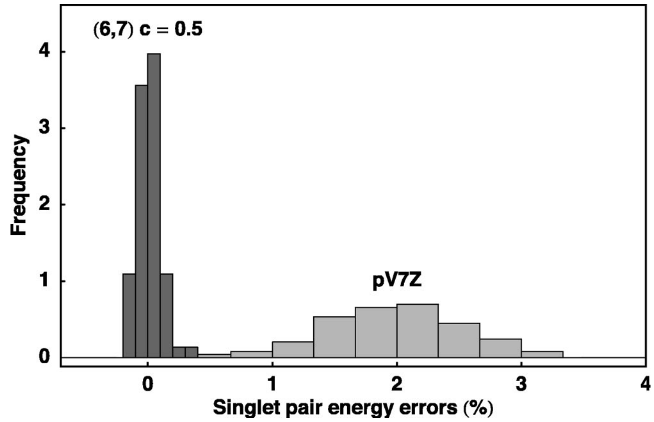

FIG. 1. Histogram of relative errors in valence singlet MP2 pair energies for the pV7Z basis and the (6,7) CBS extrapolations according to Eq. (26) with $c=0.5$.

skewness and kurtosis for sets of relative errors in non-extrapolated singlet pair energies are significantly less than the standard deviation different from zero, their value for a normal distribution. Figure 1 presents a histogram of relative errors for singlet MP2 pair energies in our dataset, both for explicit pV7Z computations and $(X+\frac{1}{2})^{-3}$ (6, 7) extrapolations. Both the dramatic error reduction upon extrapolation and the approximate normal distributions are evident. The analysis of Skew and Kurt is less useful for errors in triplet pair energies since the distribution of such errors is too narrow to make high-order moments of distributions meaningful. With the much faster convergence of triplet pair energies in mind, we conclude that the observed distributions of *relative* errors in MP2 pair energies are not significantly different from normal. Our tests of sets of *absolute* errors in MP2 pair energies indicate poorer resemblance to the normal distribution, with significantly higher values of Skew and Kurt.

By the time the large septuple-ζ basis sets are used to extrapolate basis sets limits for MP2 pair energies, the standard deviation of error becomes comparable (within a factor of 2) to the mean absolute and RMS errors. Significant further improvement upon extrapolation schemes would thus require reduction in the standard deviation of errors, which will be difficult to impossible without developing higher members of the correlation-consistent series or designing a new series of basis sets for extrapolations. Explicitly correlated methods such as the linear R12 methods of Kutzelnigg, Klopper, and co-workers[16,56] become a much more promising approach to the basis set problem in this regime. The cost of conventional second-order energy computations with (aug)-pV7Z basis sets can already be as large as that of significantly more accurate computations with the MP2-R12 method, even when the latter is not implemented with the more robust dual-basis formalism.[57]

V. MOLECULAR RELATIVE ENERGIES

A. Barrier to linearity of water

A challenging problem for orbital expansion methods is the barrier to linearity of water, which has been shown in several recent studies[42–44] to exhibit a torpid approach to the complete basis set limit. This barrier is a key feature of the ground-state potential energy (hyper)surface of water, which has received renewed interest due to greatly improved spectroscopic capabilities for detecting higher-lying bending states, intrigue over the extremely dense manifold of rovibrational states recorded and recently analyzed in the sunspot spectrum of water, and the pervasiveness of water in combustion systems, the interstellar medium, and the atmospheres of planets and cool stars.[58–71] Recently,[44,72] an *ab initio* barrier height of $11\,122\pm13$ cm^{-1} was deduced from careful focal-point analyses incorporating extremely large basis sets,[42–44] explicitly correlated R12 computations,[43,44] full CI calibrations of higher-order coupled-cluster methods,[43] and corrections for core correlation,[42,43] special relativity (the mass–velocity and one-electron Darwin terms),[42,43] and first-order non-Born–Oppenheimer effects.[43,72] An independent *ab initio* treatment of the ground state surface of water by Polyansky *et al.*,[5] which incorporated additional effects of relativity (the Breit interaction and the two-electron Darwin term)[73] and nonadiabaticity,[74] produced a value of $11\,123.3\pm5$ cm^{-1}; remarkably, this surface yields rovibrational energy levels with a mean error less than 1 cm^{-1}. These arduous theoretical results[5,44,72] are in almost ideal agreement with each other but slightly higher than the most recent empirical barrier of $11\,105\pm5$ cm^{-1} derived from spectroscopic fits.[75]

A key to solving the water barrier problem is the determination of the complete basis set limit of the MP2 contribution (δ[MP2]) to the barrier. A collection of δ[MP2] increments from this work and previous studies[42–44] appears in Table XVII. Using the R12/A method and specially designed [O/H] basis sets as large as K4^{3i} $=[19s13p11d9f7g5h3i/13s11p9d7f5g3h]$, a limit of δ[MP2]$=-357$ cm^{-1} is surmised. In explicit, conventional MP2 computations, this increment starts at $+352$ cm^{-1} with the cc-pVDZ basis[42] and slowly migrates to (-305, -330) cm^{-1} with the (cc-pV6Z, aug-cc-pV6Z) set. The new pV7Z and aug-pV7Z basis sets yield the improved values of -321 and -335 cm^{-1}, respectively, the latter being the lowest explicit, conventional result to date. However, the aug-pV7Z increment is remarkably still more than 20 cm^{-1} from the apparent MP2 limit. Pinpointing the water barrier by extrapolations of conventional MP2 energies has been plagued in past studies[42,43] by an unacceptably large sensitivity to details of the procedure. As shown in Table XVII, this sensitivity persists when the septuple-ζ basis sets are employed. Regardless of whether the extrapolation involves augmented basis sets or not, or whether total energies or individual pair energies are extrapolated, the (6,7) results generally underestimate the size of δ[MP2] almost as much as their (5,6) counterparts overestimate it. Moreover, despite the improved physical underpinnings of Klopper's approach [Eqs. (12) and (13)], extrapolation of individual pair energies does not yield improved estimates of the MP2-limit contribution to the water barrier.

In Table XVIII appears a pair-energy breakdown of the second-order correlation increment to the water barrier, wherein the convergence difficulties are clearly seen to be isolated in the singlet pairs. The singlet-pair contribution to

TABLE XVII. Valence MP2 correlation increments (cm^{-1}) to the barrier to linearity of the water molecule.[a,b]

Explicit		Extrapolated[c]		R12	
cc-pV5Z	−256	{4,5,6}	−382	K1 R12/A	−429
cc-pV6Z	−305	{5,6}	−371	K1 R12/B	−354
pV7Z	−321	{6,7}	−350	K2 R12/A	−410
aug-cc-pV5Z	−301	{a5,a6}	−370	K2 R12/B	−336
aug-cc-pV6Z	−330	{a6,a7}	−344	K2+ICP R12/A	−353
aug-pV7Z	−335	(5,6)	−367	K2+ICP R12/B	−344
$\mathrm{K3}^{1i}$	−310	(6,7)	−344	$\mathrm{K3}^{1i}$ R12/A	−353
$\mathrm{V1}^{2i}$	−320	(a5,a6)	−368	$\mathrm{V1}^{2i}$ R12/A	−356
$\mathrm{K4}^{3i}$	−325	(a6,a7)	−343	$\mathrm{K4}^{3i}$ R12/A	−357

[a]The [O/H] basis sets designed for explicitly correlated computations are K1 $[13s8p6d5f/7s5p4d]$, K2 $[15s9p7d5f/9s7p5d]$, $\mathrm{K3}^{1i}$ $[17s11p9d7f5g3h1i/11s9p7d5f3g1h]$, $\mathrm{V1}^{2i}$ $[21s13p11d10f7g5h2i/13s11p9d7f5g1h]$, and $\mathrm{K4}^{3i}$ $[19s13p11d9f7g5h3i/13s11p9d7f5g3h]$, as specified in Refs. 43 and 44. ICP denotes intramolecular counterpoise correction.
[b]Reference geometries as in Tables X–XIII.
[c]For notation, see Sec. II.

δ[MP2] systematically decreases in explicit calculations from $+327$ to $+181\ \mathrm{cm}^{-1}$ in going from cc-pVQZ to aug-pV7Z, but the latter is still $21\ \mathrm{cm}^{-1}$ above the $\mathrm{K4}^{3i}$ MP2-R12/A benchmark ($-160\ \mathrm{cm}^{-1}$). In extrapolations, the singlet-pair term of δ[MP2] is not very sensitive to the extrapolation function once larger basis sets are employed. Therefore, despite the marked improvements afforded in individual pair-energy extrapolations by using $c=0.5$ in Eq. (26), there is disappointingly no resulting improvement in the overall δ[MP2], due to the insidious nature of the collective residual errors. In particular, the (a6,a7) extrapolations with the X^{-3} and $(X+\frac{1}{2})^{-3}$ forms differ by less than $1\ \mathrm{cm}^{-1}$, and are both 13–14 cm^{-1} higher than the presumed $-160\ \mathrm{cm}^{-1}$ limit. In stark contrast, for the triplet-pair portion of δ[MP2], accuracy to the $2\ \mathrm{cm}^{-1}$ level is achieved by aug-cc-pV6Z, pV7Z, and aug-pV7Z explicit computations, as well as virtually all extrapolations past (Q,5), regardless of the functional form.

In summary, while the best explicit (aug-pV7Z) MP2 increment to the water barrier is about $20\ \mathrm{cm}^{-1}$ in error, a scatter of almost $30\ \mathrm{cm}^{-1}$ is observed among the various results from high-level extrapolations of both the total energy and individual pair energies. As in the case of individual pair energies (Sec. IV), once the septuple-ζ mark is reached in conventional correlation treatments, the standard deviation of extrapolation errors presents a fundamental obstacle for significant improvements in the determination of the basis set limit. Therefore, explicitly correlated methods are necessary to push the accuracy limit further.

B. Dimerization energy of water

The interaction energies D_e of hydrogen-bonded species provide another stringent challenge to correlated electronic structure methods. Halkier *et al.* noted[37] slow unsystematic basis set convergence of correlation contributions to D_e of several hydrogen-bonded dimers as a function of the cardinal number X of correlation-consistent basis sets. The unsystematic pattern is due to the interplay of both basis set superposition error (BSSE) and the asymptotic $O(X^{-3})$ convergence of correlation energy. Once BSSE was removed via the counterpoise correction, the contributions converged slowly, but systematically, allowing extrapolation using the usual techniques.[37] One of the systems studied by Halkier *et al.* was the global minimum on the ground state PES of water dimer, one of the simplest prototypical hydrogen-bonded systems and a cornerstone for structure and thermodynamics of bulk water. Water dimer has been studied in great detail by theoretical chemists.[89] High accuracy studies have become possible[76–78] with the introduction of Dunning's correlation consistent basis sets. Most recently, the dissociation energy at the equilibrium geometry has been established with the lowest-to-date uncertainty of $0.2\ \mathrm{kJ\,mol}^{-1}$ with the aid of explicitly correlated methods by Klopper *et al.*[76] The rest of the PES of water dimer has been investigated less thoroughly. Unsystematic basis set convergence, similar to that found by Halkier *et al.*,[37] has been noted in a recent study by Tschumper *et al.*[77] on relative energies of several key stationary points on the ground state surface of water dimer. It is

TABLE XVIII. Pair-energy breakdown of the valence MP2 correlation contribution (cm^{-1}) to the barrier to linearity of the water molecule.[a]

Basis	Singlet pairs	Triplet pairs	Total
cc-pVQZ	326.8	−454.8	−128.0
cc-pV5Z	244.2	−500.6	−256.4
cc-pV6Z	204.6	−510.7	−306.1
pV7Z	192.7	−514.0	−321.3
aug-cc-pVQZ	239.8	−506.6	−266.8
aug-cc-pV5Z	211.3	−511.9	−300.6
aug-cc-pV6Z	185.3	−515.1	−329.7
aug-pV7Z	180.9	−515.8	−334.9
		$X^{-3,5}$ fit	
(Q,5)	157.6	−522.9	−365.4
(5,6)	150.1	−517.5	−367.3
(6,7)	172.5	−516.8	−344.3
(aQ,a5)	181.4	−514.4	−333.0
(a5,a6)	149.6	−517.2	−367.6
(a6,a7)	173.4	−516.4	−343.1
		$(X+\frac{1}{2})^{-3,5}$ fit	
(Q,5)	144.2	−527.1	−382.9
(5,6)	143.7	−518.4	−374.8
(6,7)	170.6	−517.1	−346.5
(aQ,a5)	176.8	−514.9	−338.1
(a5,a6)	145.4	−517.5	−372.1
(a6,a7)	172.6	−516.5	−343.8
		$(X+1)^{-3,5}$ fit	
(Q,5)	130.8	−531.4	−400.6
(5,6)	137.2	−519.4	−382.2
(6,7)	168.6	−517.4	−348.8
(aQ,a5)	172.1	−515.4	−343.3
(a5,a6)	141.1	−517.9	−376.7
(a6,a7)	171.9	−516.5	−344.6
		Explicitly correlated (MP2-R12/A)	
$\mathrm{K3}^{1i}$	163.5	−516.4	−352.8
$\mathrm{V1}^{2i}$	160.2	−516.7	−356.5
$\mathrm{K4}^{3i}$	159.6	−516.7	−357.1

[a]See footnotes to Table XVII.

TABLE XIX. Valence MP2 contribution to the dissociation energy of the water dimer (cm^{-1}).[a]

Basis	δD_e (MP2)
aug-cc-pVTZ	+582
aug-cc-pVQZ	+559
aug-cc-pV5Z	+548
aug-cc-pV6Z	+540
aug-pV7Z	+527
Extrapolated according to Eq. (8)	
(Q,5)	+536
(5,6)	+529
(6,7)	+504
K2 MP2-R12/A	+525
$K2^{1h}$ MP2-R12/A	+532

[a]At the TZ2P(f,d)+dif CCSD(T) optimized geometry of Ref. 77. The [O/H] basis sets designed for explicitly correlated computations are K2 $[15s9p7d5f/9s7p5d]$ and $K2^{1h}$ $[15s9p7d5f3g1h/9s7p5d3f1g]$ as specified in Ref. 80.

clear that to construct a global PES for water dimer one has to address carefully issues of the basis set convergence of correlation energy and basis set superposition error. While the former can be dealt with using extrapolation techniques, the latter is difficult to eradicate consistently across a surface. It is not evident that even the largest basis sets utilized in conventional computations will be sufficient to render the BSSE negligible and attain high accuracy in this situation. Thus we decided to apply the newly developed aug-pV7Z basis set to the global minimum of water dimer to examine whether the brute force approach is sufficient to obtain the correlation contribution to the dissociation energy accurate to a few cm^{-1}.

Valence MP2 contributions to the dissociation energy of water dimer computed with the series of correlation-consistent basis sets augmented with diffuse functions are listed in Table XIX. The explicitly computed MP2 contributions diminish monotonically with X; however, all successive values differ by at least 8 cm^{-1}. Not surprisingly, convergence is not very systematic. Most notably, the δD_e(a7) $-\delta D_e$(a6) difference of -13 cm^{-1} is larger than the a6 $-$a5 difference of -8 cm^{-1}, contrary to the notion of asymptotic convergence. As a result, the extrapolated CBS $(X,X+1)$ contributions in Table XIX are far from consistent. The valence MP2 contributions obtained with the explicitly correlated MP2-R12/A method converge much faster to the basis set limit and are less susceptible to BSSE.[79] In addition to the previously published K2 MP2-R12/A result of Ref. 77, we computed the MP2-R12/A contribution with a much larger $K2^{1h}$ basis set,[80] which is technically $[15s9p7d5f3g1h/9s7p5d3f1g]$ for [O/H]. The resulting benchmark $K2^{1h}$ δD_e[MP2] increment is $+532$ cm^{-1}. The difference between the K2 and $K2^{1h}$ R12/A values is only 7 cm^{-1}, but still somewhat higher than expected. The conventional aug-pV7Z MP2 prediction thus appears to be an improvement over that of the established aug-cc-pV6Z basis. However, an uncertainty of 10 cm^{-1} or more in the CBS limit somewhat muddles the comparison, and the brute force approach appears unreliable in converging the interaction energy to a few cm^{-1}.

VI. CONCLUSIONS

(1) The following correlation-optimized Gaussian k-function exponents have been determined for use with correlation-consistent valence septuple-ζ (pV7Z) basis sets: $\alpha_k(\mathrm{N})=2.379$, $\alpha_k(\mathrm{O})=3.123$, $\alpha_k(\mathrm{F})=4.256$, and $\alpha_k(\mathrm{S})=1.209$. Corresponding diffuse function exponents for aug-pV7Z basis sets are $\alpha_k(\mathrm{N})=0.977$, $\alpha_k(\mathrm{O})=1.232$, $\alpha_k(\mathrm{F})=1.597$, and $\alpha_k(\mathrm{S})=0.575$. These results provide optimal k-manifolds that complete the construction of the pV7Z and aug-pV7Z basis sets for the selected atoms.

(2) The CISD and CCSD methods were found to give virtually identical valence-optimized k-function exponents, whereas less highly correlated, open-shell second-order perturbation theories (ZAPT2, OPT2) provide exponents 1%–4% smaller. For diffuse k orbitals, the (ZAPT2, OPT2) methods give exponents about 10% smaller than CCSD.

(3) For Hartree–Fock computations, qualitative inspections show that results from the new septuple-ζ basis sets fit well into an exponential approach of (aug)-cc-pVXZ energies toward the CBS limit. A detailed mathematical analysis confirms this behavior, revealing a linear increase of effective decay-exponents with X extending beyond values reasonable for any simple, physically-based power law.

(4) A complete collection of valence MP2 pair energies has been generated for the cc-pVXZ and aug-cc-pVXZ series through the septuple-ζ level for the HF, N_2, F_2, and H_2O molecules, for the purpose of examining the torpid convergence behavior of correlation energies. In addition, explicitly-correlated MP2-R12/A computations with prodigious $[(\mathrm{N,O,F})/\mathrm{H}]=[21s13p11d10f7g5h2i/13s11p9d7f5g1h]$ basis sets have been performed to provide benchmark pair energies. The mean absolute relative error for conventional MP2 with the (pV7Z, aug-pV7Z) basis set is (1.96%, 1.72%) and (0.26%, 0.18%) for singlet and triplet pair energies, respectively. These errors are smaller than the corresponding sextuple-ζ values by 35% for singlet and 50% for triplet pairs.

(5) Extrapolation of conventional valence MP2 pair energies with $(X+c)^{-n}$ functional forms, where $n=(3,5)$ for (singlet, triplet) pairs and $c=\frac{1}{2}$, provides dramatic improvements in accuracy, measured with respect to the MP2-R12/A benchmarks, and corrects systematic underestimations of absolute CBS MP2 limits found in $c=0$ extrapolations. Comparison to the results of a previous study of coupled cluster pair energies by Klopper[33] reveals that the improvements are specific to the case of MP2 pair energies. Two-point 6Z/7Z $(X+\frac{1}{2})^{-n}$ extrapolations reduce the mean absolute MP2 pair energy errors to 0.07% and 0.02% for singlet and triplet pairs, respectively. Moreover, the use of $c=\frac{1}{2}$ brings the effective decay exponents of the MP2 pair correlation energies

into the best accord with the ideal values predicted by Kutzelnigg and Morgan[7] via partial-wave analyses.

(6) Analysis of the skewness and kurtosis of the relative pair energy errors reveals distributions not significantly different from normal, at least for singlet pairs. The effect of extrapolation is to greatly sharpen the distribution and move it toward zero error, while maintaining an approximate Gaussian shape. Absolute errors show less resemblance to the normal distribution.

(7) The new septuple-ζ basis sets have been applied to the well-studied and problematic barrier to linearity of water, whose correlation energy component is known to exhibit protracted basis set convergence. For the δ[MP2] increment to the barrier, the aug-pV7Z basis set yields $-335\ \mathrm{cm}^{-1}$, the best explicit conventional result to date. Nonetheless, this prediction is still more than $20\ \mathrm{cm}^{-1}$ from the MP2 limit ($-357\ \mathrm{cm}^{-1}$) determined from extensive R12/A computations.[44] Remarkably, this error cannot be significantly reduced in even the best conventional extrapolations, because the standard deviation of extrapolation errors results in a $\pm 15\ \mathrm{cm}^{-1}$ scatter about the apparent CBS limit.

(8) A final, preliminary application of septuple-ζ basis sets has been made to the dimerization energy of water. Once again, aug-pV7Z MP2 computations provided the lowest conventional second-order correlation increment ($+527\ \mathrm{cm}^{-1}$) to date for the hydrogen-bond energy, a value lying within a roughly $10\ \mathrm{cm}^{-1}$ range of uncertainty about the CBS limit. While the series of aug-cc-pVXZ, noncounterpoise-corrected binding energies displays a monotonic decrease toward the apparent CBS limit, the decrements are erratic and extrapolations are suspect, presumably because of basis set superposition error.

(9) In the H_2O and $(H_2O)_2$ examples investigated here, conventional correlation-consistent computations through the septuple-ζ level with k-manifolds in the basis set, conjoined with the best physically-based extrapolations therefrom, do allow one to enter the domain of subchemical accuracy ($0.1\ \mathrm{kcal\,mol}^{-1}$), but not to reliably penetrate it beyond the $10\ \mathrm{cm}^{-1}$ level. The latter target is likely a fundamental accuracy obstacle of orbital expansion methods that may only be breached by explicitly correlated methods.[87–89]

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[88] The V1+ basis set for O and H has been described in detail in Ref. 44, and the sets for N and F can be obtained from authors upon request.
[89] It would be futile to even attempt to cite all landmark theoretical studies of water dimer. A good review of the subject is available in Ref. 81.