

Convergent Partially Augmented Basis Sets for Post-Hartree–Fock Calculations of Molecular Properties and Reaction Barrier Heights

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Abstract: We present sets of convergent, partially augmented basis set levels corresponding to subsets of the augmented “aug-cc-pV($n+d$)Z” basis sets of Dunning and co-workers. We show that for many molecular properties a basis set fully augmented with diffuse functions is computationally expensive and almost always unnecessary. On the other hand, unaugmented cc-pV($n+d$)Z basis sets are insufficient for many properties that require diffuse functions. Therefore, we propose using intermediate basis sets. We developed an efficient strategy for partial augmentation, and in this article, we test it and validate it. Sequentially deleting diffuse basis functions from the “aug” basis sets yields the “jul”, “jun”, “may”, “apr”, etc. basis sets. Tests of these basis sets for Møller–Plesset second-order perturbation theory (MP2) show the advantages of using these partially augmented basis sets and allow us to recommend which basis sets offer the best accuracy for a given number of basis functions for calculations on large systems. Similar truncations in the diffuse space can be performed for the aug-cc-pVxZ, aug-cc-pCVxZ, etc. basis sets.

1. Introduction

In quantum mechanical electronic structure calculations, the orbitals in configuration state functions may be represented as linear combinations of contracted functions, which in turn are linear combinations of spherical harmonics times radial functions with preoptimized exponential parameters. The radial functions can be Gaussian or Slater-type functions. Slater-type functions are more physical, but for ease of computation of the two-electron integrals, Slater-type functions are usually replaced by linear combinations of Gaussian-type functions.^{1,2} The so-called ζ level reflects the degree of decontraction of the primitive Gaussian functions used to represent valence orbitals. For example, for carbon, valence double- ζ denotes two contracted functions designed to represent 2s orbitals and two contracted subshells to represent 2p orbitals, whereas valence triple- ζ denotes three, etc. Since the core is single- ζ quality in most modern basis sets, one often says “double- ζ ” instead of “valence double- ζ ”, and so

forth for triple, quadruple, etc. Double-, triple-, and quadruple- ζ are usually abbreviated DZ, TZ, and QZ, respectively. The contraction coefficients and exponential parameters for standard basis sets are available as lists called basis sets. Standard basis sets usually include polarization functions (e.g., d functions for carbon, p functions for hydrogen) and sometimes include diffuse functions.

The choice of the basis set for a given problem is critical, because it greatly affects the quality of the results as well as the cost of acquiring them. A basis set that is too large can make higher-level methods unaffordable for a given system or a given level unaffordable for larger systems. On the other hand, too small of a basis set can prevent taking full advantage of the potential accuracy of an otherwise very accurate electronic structure level. We have been especially interested in the requirements for diffuse basis functions as they play an important role in calculations of such commonly computed molecular properties as electron affinities, non-covalent interaction energies, and barrier heights for chemical reactions. Diffuse functions are characterized by very small exponential parameters, which allow the electrons to be

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Table 1. Angular Momenta Included in the Diffuse Space in Tested Basis Sets

basis set ^a	Li through Ca	H and He
aug-cc-pV(Q+d)Z	s p d f g	s p d f
jul-cc-pV(Q+d)Z	s p d f g	
jun-cc-pV(Q+d)Z	s p d f	
may-cc-pV(Q+d)Z	s p d	
apr-cc-pV(Q+d)Z ^b	s p	
cc-pV(Q+d)Z		
aug-cc-pV(T+d)Z	s p d f	s p d
jul-cc-pV(T+d)Z	s p d f	
jun-cc-pV(T+d)Z	s p d	
may-cc-pV(T+d)Z ^c	s p	
cc-pV(T+d)Z		
aug-cc-pV(D+d)Z	s p d	s p
jul-cc-pV(D+d)Z	s p d	
jun-cc-pV(D+d)Z ^d	s p	
cc-pV(D+d)Z		

^a The same diffuse functions can be employed for month-cc-pV(*n*+*d*)Z or cc-pV(*n*+*d*)Z and for month-cc-pV*n*Z or cc-pV*n*Z. ^b Same as maug-cc-pV(Q+d)Z. ^c Same as maug-cc-pV(T+d)Z. ^d Same as maug-cc-pV(D+d)Z.

further away from the nuclei, so they are crucial for many systems and properties involving anions, transition states, excited states, and polarizability. However, if an unnecessarily large set of diffuse functions is used, the calculations may become unfeasible or unnecessarily expensive.

Three approaches to supplying basis sets with diffuse functions have emerged and have been widely used. In basis sets developed by Pople, Schleyer, and co-workers^{3,4} (sometimes called Pople-type basis sets), *s* and *p* diffuse functions are added on atoms heavier than He, which is indicated by “+” in the name of the basis set. A second “+” in the name indicates that in addition to the diffuse functions on the nonhydrogenic atoms, diffuse *s* functions are added on the hydrogen atoms. Correlation consistent basis sets by Dunning and co-workers (including cc-pV*n*Z^{5–9} and cc-pV(*n*+*d*)Z¹⁰) are augmented with gradually increasing sets of diffuse functions for increasing decontraction of the valence space (aug-cc-pV*n*Z^{5–9,11,12} and aug-cc-pV(*n*+*d*)Z¹⁰). The angular momentum quantum numbers included in the diffuse spaces of aug-cc-pV*n*Z and aug-cc-pV(*n*+*d*)Z basis sets for *n* = D, T, and Q are listed in Table 1. The other rows of this table (other than “aug-”) will be explained below. In a third approach, Jensen recommended including sets of diffuse functions (on all atoms) such that the number of diffuse functions increases with increasing *n*.¹³ The Pople strategy is not convergent in the diffuse space, in that the number of diffuse functions is not systematically increased when the ζ level is increased, whereas the Dunning and Jensen approaches are convergent.

We will use the term “augmentation” to denote adding diffuse functions to a basis (whereas “extension” means raising the ζ level or adding polarization functions), and we will use “full augmentation” to denote adding a diffuse function for every angular momentum present in the unaugmented basis set. The aug- basis sets are fully augmented. It has been known for a long time that augmentation on hydrogen atoms is less important than augmentation on nonhydrogenic atoms (e.g., Schleyer and co-workers defined the “+” basis sets that omit augmentation on hydrogen

atoms;³ del Bene and Shavitt¹⁴ showed that they could converge proton affinities and hydrogen bonding energies with respect to basis set without diffuse functions on H; and Lynch and one of the authors¹⁵ showed that diffuse functions are not needed on H even in molecules where H has a partial negative charge), and the present article is mainly concerned with the level of augmentation on nonhydrogenic atoms. We have previously shown that the full augmentation of nonhydrogenic atoms in the basis sets defined by Dunning and co-workers often leads to unnecessary expense in calculations by density functional theory (DFT).^{16,17} In particular, we showed that the nonconvergent “+” approach is often sufficient for DFT calculations, and a basis set obtained by deleting all diffuse functions in aug- basis sets except the diffuse *s* and *p* functions on non-hydrogenic atoms has been called minimally augmented, denoted by the prefix maug.¹⁶ However, we have also seen that wave function theory (WFT) calculations are more sensitive than DFT calculations to the saturation of the diffuse space in the nonhydrogenic basis space as well as to the size of the basis set in general.^{16,17} This is because correlation energy in WFT converges very slowly with respect to the number of one-electron basis functions, and this slow convergence occurs because products of one-electron functions in a Slater-determinant poorly describe the cusps in the two-electron densities as the interelectronic distance approaches zero. The most slowly convergent part of the electron correlation energy is the part covered by second-order Møller–Plesset perturbation theory¹⁸ (MP2). The reason for this is that although higher-order corrections are important, the contributions of the weakly coupled virtual orbitals at second order are quantitatively larger,^{19,20} and it is important to understand how to include them efficiently. In practical work, in order to obtain as accurate results as one can afford using WFT for a given system, it is a common practice^{21–26} to calculate the MP2 energy part at the complete basis set limit and to add higher-order corrections (e.g., the difference between an MP2 calculation and a calculation by the coupled cluster method with single and double excitations and a quasiperturbative treatment of connected triple excitations²⁷ CCSD(T)) calculated with a smaller basis set. Therefore, achieving the MP2 CBS limit is of a great practical interest.

One popular way to determine the MP2 CBS limit is extrapolation.^{28–30} Recently, Møller–Plesset perturbation calculations employing basis functions that depend explicitly on electron–electron distances (MP2-R12 or MP2-F12^{31–44}) have provided a powerful, alternative way to approach the MP2 basis set limit in a very efficient way, by explicitly improving the description of the cusp. MP2-F12 is very rapidly convergent with respect to the size of the one-electron basis set. In some key studies, the rapid convergence of the MP2-F12 method has often been established on the basis of heats of formation,⁴⁵ absolute correlation energy,⁴⁸ and energies of reaction,⁴⁸ but we note that, for neutral molecules and cations, heats of formation and energies of reaction are typically insensitive to the inclusion of the diffuse basis functions; thus a more recent study by Werner et al.⁴⁶ that examined not only reaction energies and atomization energies but also electron affinities, ionization potentials, equilibrium

structures, vibrational frequencies, and intermolecular interaction energies and a study by Kjaergaard et al.⁴⁷ on hydrogen bonded systems are more relevant to the question of how many diffuse functions one should use for a diverse set of molecular properties (Werner et al. also cite earlier diverse benchmarking studies). Recently, basis sets have been prepared specifically for use in F12 calculations.⁴⁸ Those basis sets are specifically limited to minimal augmentation, but the reader was informed that “the inclusion of just *s* and *p* diffuse functions may not be sufficient” in all cases, and “further extension of the higher angular momentum functions might then be considered.” Werner et al.⁴⁶ employed these minimally augmented basis sets and fully augmented ones in their F12 benchmarking but did not consider intermediate augmentation. In the present article, we will consider this; in particular, we systematically explore various levels of partial augmentation in both MP2 and MP2-F12 calculations with databases for atomization energies, barrier heights, hydrogen bond energies, ionization potentials, and electron affinities.

It is an oversimplification to assume that “the more diffuse functions, the better.” The size of the diffuse space of a basis set is just one of the parameters of a basis set, and it must be considered in conjunction with the space spanned by primitive valence functions, the level of contraction, and the number of polarization functions. Full augmentation with many diffuse functions that make only a small difference in the property to be calculated increases the size (and, one hopes, the accuracy) of the basis set a given ζ level, but the gain may be small relative to other ways to increase the accuracy such as increasing the ζ level. In practice, when attempting to improve a basis set, one should ask which aspect of the basis set is most limiting at any given level, and then one should improve that specific part of the basis set first. We have found that this is not always the way calculations are done. Very often, basis sets are fully augmented or fully augmented on nonhydrogenic atoms while staying at given ζ level when it would be more efficient to do only a partial augmentation on nonhydrogenic atoms and spend the saved resources by going to a higher ζ level or adding more polarization functions.

The questions we are attempting to answer are the following:

- Which molecular properties are most sensitive to the level of augmentation of the diffuse space? What level of augmentation is advisable for these properties?
- At what point is saturation of the diffuse space reached for key properties such as barrier heights, electron affinities, ionization potentials, noncovalent interaction energies, atomization energies, and bond energies?
- What is the right order of steps in improving the basis set for a given problem? At a given ζ level and for a given property, is it more beneficial to add more diffuse functions or to attempt to go to the higher ζ sooner with a minimal or intermediate number of diffuse functions?

A variety of *ad hoc* partially augmented basis sets have been used for specific calculations in various publications. Here, we put forward a systematic partial augmentation scheme and test it carefully for MP2 and MP2-F12 calculations.

The naming convention for the systematically partially augmented basis sets is based on the months and involves successively truncating the “aug” basis sets of Dunning and co-workers to well-defined levels called “jul,” “jun,” “may,” etc.

A second objective of the present article is to allow us to compare the accuracy of MP2-F12 to that of MP2.

2. Definition of the New Basis Sets

In our calculations, we use the correlation consistent cc-pV(*n*+*d*)Z basis sets of Dunning and co-workers with spherical harmonic *d*, *f*, and *g* subshells. Notice that a cc-pV(*n*+*d*)Z basis set for an atom lighter than Al is defined to be the same as cc-pV(*n*+*d*)Z.¹⁰ Table 1 defines the diffuse spaces of the fully and partially augmented basis sets. As seen in the table, deleting all diffuse basis functions on hydrogen and helium atoms from “aug” basis sets yields the “jul” basis set, which has already been defined.¹⁷ The “jun”, “may”, etc. basis sets are obtained by sequentially removing the diffuse subshells on the heavy atoms, where “heavy atoms” is used here as a synonym for atoms heavier than He. The new basis sets are systematically convergent in that, just as aug-cc-pV(*n*+*d*)Z converges to a fully augmented complete-valence basis set as *n* increases, jun-cc-pV(*n*+*d*)Z converges to a fully heavy-atom-augmented complete-valence basis set as *n* increases, and so does may- or apr-. As discussed in the Introduction, it has been known for a long time that augmentation on heavy atoms is less important than augmentation on hydrogen atoms.

3. Methods and Databases

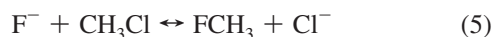
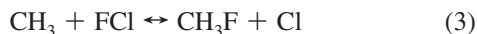
All of the MP2 calculations for this paper (except when timing MP2-F12 vs MP2) were carried out using the *Gaussian 03*⁴⁹ and *Gaussian 09*⁵⁰ program packages. All of the MP2-F12 calculations were performed using the *MolPro 2009*⁵¹ program.

In order to test the performance of the partially augmented basis sets, we have used previously optimized geometries of the species contained in the DBH24/08,^{52,53} HB6/04,⁵⁴ EA13/3,^{55,56} IP13/3,^{55,56} and AE6⁵⁷ databases.

These databases contain, respectively, 24 diverse barrier heights, six hydrogen bond energies (four of which were used for the present tests), 13 electron affinities, 13 ionization potentials, and six atomization energies.

We carried out restricted single-point-energy MP2 and MP2-F12 calculations for both open- and closed-shell species. Results of these MP2 and MP2-F12 single-point calculations using basis sets ranging from aug-cc-pV(*n*+*d*)Z through partially augmented basis sets to nondiffuse cc-pV(*n*+*d*)Z were then compared to MP2-F12/aug-cc-pV(*Q*+*d*)Z values that should be close to the complete basis set limit and that serve as a reference. MP2-F12/aug-cc-pV(*Q*+*d*)Z data were generated for the following properties:

- 24 (forward and backward) barrier heights using quadratic configuration interaction with single and double excitations QCISD/MG3S geometries (listed in the DBH24/08 database^{52,53}) for the species (reactants, transition states, and products) involved in the following 12 reactions:



• the hydrogen bonding energy calculations for the $\text{NH}_3\text{--NH}_3$, HF--HF , $\text{H}_2\text{O--H}_2\text{O}$, and $\text{NH}_3\text{--H}_2\text{O}$ dimers for the MC-QCISD/3 geometries; this subset of the HB6/04 database⁵⁴ will be called HB4

• the electron affinities for C, S, O, Si, P, Cl, OH, SH, PH, PH_2 , O_2 , S_2 , and Cl_2 using QCISD/MG3S geometries listed in EA13/3 database^{55,56}

• the ionization potentials of the same 13 atoms and molecules as for electron affinities for the QCISD/MG3S geometries listed in the IP13/3 database^{55,56}

• the atomization energies per bond for SiH_4 , SiO , S_2 , propyne (C_3H_4), glyoxal ($\text{C}_2\text{H}_2\text{O}_2$), and cyclobutane (C_4H_8) were calculated using the QCISD/MG3S geometries in the AE6 database.⁵⁷

In all of our calculations, the Born–Oppenheimer electronic energies including nuclear repulsion were considered; vibrational contributions were not included. Spin–orbit energies were added (when nonzero) as in previous work.^{16,17}

For this article, all of the MP2-F12/aug-cc-pV(n+d)Z calculations were carried out using the aug-cc-pVnZ/JKFIT⁵⁸ and aug-cc-pVnZ/MP2FIT^{59,60} density-fitting basis sets. For all of the calculations involving nondiffuse (cc-pV(n+d)Z) orbital basis sets, cc-pVnZ/JKFIT⁵⁸ and cc-pVnZ/MP2FIT^{59,60} density fitting basis sets were used. In order to reduce the cost of the calculations and at the same time pose a bigger challenge for the partially augmented (month-cc-pV(n+d)Z) sets, we used the density fitting basis sets recommended for the cc-pVnZ basis sets. The density fitting basis sets might not be completely converged for all basis sets, but they should be close enough to convergence that their small extent of incompleteness does not affect our conclusions.

All of the MP2-F12 calculations use the 3C ansatz with orbital invariant amplitudes and were carried out with a full nonlinear fit of the geminal expansion.

4. Results

In order to allow the assessment of computational costs (computer time and storage) of the various basis sets, Table

2 lists the total numbers of contracted basis functions for all of the calculations carried out for this article. This provides representative relative numbers for typical applications. Table 3 summarizes relative computer timings normalized to the least expensive basis set used (cc-pV(D+d)Z). For the ease of estimating computational savings by using partially instead of fully augmented basis sets at the same ζ level, we also list timings normalized to the unaugmented basis set for the same n .

Basis sets in the first column of all tables are listed in order of decreasing size. In each case, the basis set listed above the unaugmented basis set is the minimally augmented (maug) basis set containing s and p functions on heavy atoms (which means heavier than He) and no diffuse functions on H and He atoms. Subminimal augmentation (diffuse s functions on heavy atoms) gives results at best slightly better than no augmentation and is not recommended. Therefore, in this article, except for unaugmented results, no results are presented for subminimal augmentation.

Both MP2 and MP2-F12 results are compared with MP2-F12/aug-cc-pVQZ values. Tables 4–8 list mean signed deviation (MSD) and mean unsigned deviation (MUD) from this reference. Except for atomization energies, we define MSD and MUD as

$$\text{MSD} = \frac{1}{N} \sum_{i=1}^N d_i \quad (13)$$

$$\text{MUD} = \frac{1}{N} \sum_{i=1}^N |d_i| \quad (14)$$

where N is the number of energetic data computed (24 for barrier heights, 4 for hydrogen bonding energies, 13 for electron affinities and ionization potentials), and d_i is the deviation (in kcal/mol) of the i th value from the reference value.

In order to report MSD and MUE for atomization energies on per-bond basis, mean deviations, computed using eqs 13 and 14, were divided by the average number of bonds in the AE6 database as in eqs 15 and 16.

$$\text{MSD} = \frac{1}{4.83N} \sum_{i=1}^N d_i \quad (15)$$

$$\text{MUD} = \frac{1}{4.83N} \sum_{i=1}^N |d_i| \quad (16)$$

Root mean square deviation values (RMSD) for all of the properties are available in the Supporting Information. In Tables 4–8, we provide mean deviations of MP2 (Tables 4–6) and MP2-F12 (Tables 6–8) results from the reference values. We have also listed maximum unsigned deviations (MaxUD) for completeness.

Counterpoise corrections⁶¹ are sometimes used to estimate corrections for basis set superposition error, but such corrections are problematic in terms of accuracy⁶² and become increasingly complex as one considers systems with more components⁶³ and hence are often omitted. In Table 5, we present an analog of the triple- ζ results in Table 4 for

Table 2. Number of Basis Functions Used in MP2 Calculations

	N_{bf}^a					sum		
	DBH24/08	HB4	EA13/3	IP13/3	AE6	total ^b	norm. ^c	rel. ^d
aug-cc-pV(Q+d)Z	9129	4068	3218	3218	2528	22161	5.7	1.5
jul-cc-pV(Q+d)Z	7865	3460	3058	3058	2224	19665	5.1	1.3
jun-cc-pV(Q+d)Z	7262	3199	2770	2770	2044	18045	4.6	1.2
may-cc-pV(Q+d)Z	6793	2996	2546	2546	1904	16785	4.3	1.1
apr-cc-pV(Q+d)Z	6458	2851	2386	2386	1804	15885	4.1	1.0
cc-pV(Q+d)Z	6190	2735	2258	2258	1724	15165	3.9	1.0
aug-cc-pV(T+d)Z	5034	2208	1900	1900	1411	12453	3.2	1.5
jul-cc-pV(T+d)Z	4323	1866	1810	1810	1240	11049	2.8	1.4
jun-cc-pV(T+d)Z	3854	1663	1586	1586	1100	9789	2.5	1.2
may-cc-pV(T+d)Z	3519	1518	1426	1426	1000	8889	2.3	1.1
cc-pV(T+d)Z	3251	1402	1298	1298	920	8169	2.1	1.0
aug-cc-pV(D+d)Z	2387	1009	1024	1024	685	6129	1.6	1.6
jul-cc-pV(D+d)Z	2071	857	984	984	609	5505	1.4	1.4
jun-cc-pV(D+d)Z	1736	712	824	824	509	4605	1.2	1.2
cc-pV(D+d)Z	1468	596	696	696	429	3885	1.0	1.0

^a Number of contracted basis functions used for all of the calculations in the database. ^b Sum of N_{bf} over all five databases. ^c Sum normalized to cc-pV(D+d)Z. ^d Sum relative to cc-pV(n +d)Z for the same n .

Table 3. Timing Summary for MP2 and MP2-F12 for All Species in the Databases

basis set ^a	MP2		MP2-F12		
	norm. ^b	rel. ^c	norm. (MP2) ^b	norm. ^d	rel. ^e
aug-QZ	388.9	6.3	942.6	46.9	3.4
jul-QZ	154.4	2.5	492.4	24.5	1.8
jun-QZ	112.9	1.8	402.7	20.0	1.4
may-QZ	88.3	1.4	337.9	16.8	1.2
apr-QZ	72.3	1.2	303.0	15.1	1.1
QZ	62.1	1.0	278.4	13.9	1.0
aug-TZ	30.1	5.0	144.2	7.2	2.8
jul-TZ	15.6	2.6	80.3	4.0	1.5
jun-TZ	10.4	1.7	65.7	3.3	1.3
may-TZ	7.8	1.3	57.8	2.9	1.1
TZ	6.0	1.0	51.9	2.6	1.0
aug-DZ	2.4	2.4	38.1	1.9	1.9
jul-DZ	1.8	1.8	24.8	1.2	1.2
jun-DZ	1.3	1.3	22.1	1.1	1.1
DZ	1.0	1.0	20.1	1.0	1.0

^a Labels month- n Z or n Z denote month-cc-pV(n +d)Z or cc-pV(n +d)Z. ^b Sum normalized to MP2 with the same program on the same machine with the smallest basis set used (cc-pV(D+d)Z). ^c Sum relative to MP2 with the same program on the same machine with the smallest basis set with the same n . ^d Sum relative to MP2-F12 with the same program on the same machine with the smallest basis set used. ^e Sum relative to MP2-F12 with the same program on the same machine with the smallest basis set with the same n .

the HB4 database. In comparison with the results given in Table 4, the counterpoise-corrected results do not show different trends or lead to different conclusions on augmentation, and the errors are increased upon making the “correction”. Therefore, to make the rest of the convergence tests as straightforward as possible, no counterpoise corrections are applied in Tables 4 or 6–8.

5. Discussion

In the Discussions and Conclusions (as in Table 3), we abbreviate cc-pV(D+d)Z, cc-pV(T+d)Z, and cc-pV(Q+d)Z as DZ, TZ, and QZ, respectively. Similarly, month-cc-pV(n +d)Z is abbreviated in the text as month- n Z.

Tables 4–6 show the mean deviations of MP2 energies computed with augmented, partially augmented, and not

augmented basis sets from the near-CBS reference values. In all cases, for triple- and quadruple- ζ basis sets, the difference in MUD for jul- and jun- basis sets compared to aug- is usually small compared to the absolute value of the deviations, and in most cases they are negligibly small. The same holds true for jul-DZ.

The tables show many outstanding successes of partial augmentation, especially for barrier heights and hydrogen bond energies. For example, for barrier heights, aug-QZ, apr-QZ, and QZ differ from the near-CBS reference value by 0.2, 0.3, and 1.2 kcal/mol, respectively, but Table 2 shows that aug-QZ has about 50% more basis functions than apr-QZ. A similar observation can be made for may-TZ. For hydrogen bond energies, apr-QZ, may-TZ, and jul-DZ are all more accurate than aug-QZ. *The key point is not that they are more accurate, which (obviously) arises mainly from cancellation of errors, but that they are not significantly less accurate.*

A comparison of Tables 4 and 6 to Tables 7 and 8 shows that MP2 results converge more slowly with respect to the saturation of the diffuse space of the basis set than do MP2-F12 calculations, as expected from the discussion in section 1. Tables 7 and 8 show that in MP2-F12 calculations, only triple- and quadruple- ζ atomization energy calculations seem to be insensitive to the addition of diffuse basis functions. This is probably due to the fact that the underlying cc-pV(n +d)Z basis set is sufficiently diffuse for $n = \{T \text{ or } Q\}$ and not diffuse enough for $n = D$ for the calculation of bond energies. However, the inclusion of diffuse functions seems to be crucial for all other properties, including (perhaps surprisingly) ionization potentials.

It is interesting that for the tested properties the aug basis sets never offer any significant improvement at either the MP2 or MP2-F12 level over jul- basis sets. On the other hand, the unaugmented basis sets usually have much higher MUDs than partially augmented basis sets. Therefore, partially augmented basis sets provide intermediate options that are more balanced than either fully augmented or unaugmented basis sets with respect to the computational cost and the quality of the results.

Table 4. Mean and Maximum Deviations of MP2 Barrier Height (kcal/mol), Hydrogen Bonding Energy (kcal/mol), and Electron Affinity (kcal/mol) from Reference Value

	barrier height			hydrogen bonding			electron affinity		
	MSD	MUD	MaxUD	MSD	MUD	MaxUD	MSD	MUD	MaxUD
aug-cc-pV(Q+d)Z	-0.03	0.15	0.43	0.09	0.09	0.13	0.64	1.36	2.64
jul-cc-pV(Q+d)Z	0.06	0.19	0.57	0.01	0.01	0.02	0.68	1.41	2.64
jun-cc-pV(Q+d)Z	0.13	0.20	0.61	-0.01	0.02	0.03	1.14	1.70	3.18
may-cc-pV(Q+d)Z	0.20	0.25	0.78	-0.03	0.03	0.04	1.50	1.93	3.49
apr-cc-pV(Q+d)Z	0.20	0.29	0.89	0.01	0.02	0.04	1.97	2.28	3.93
cc-pV(Q+d)Z	-0.40	1.18	8.27	0.38	0.38	0.49	7.18	7.18	3.18
aug-cc-pV(T+d)Z	0.01	0.49	1.05	0.17	0.17	0.21	1.90	2.28	4.29
jul-cc-pV(T+d)Z	0.19	0.58	1.39	0.04	0.04	0.08	2.01	2.38	4.29
jun-cc-pV(T+d)Z	0.49	0.66	2.14	-0.03	0.04	0.07	3.04	3.10	5.60
may-cc-pV(T+d)Z	0.65	0.79	3.05	0.05	0.09	0.10	4.47	4.47	6.96
cc-pV(T+d)Z	-0.18	2.15	11.10	0.88	0.88	1.05	14.83	14.83	32.17
aug-cc-pV(D+d)Z	-0.28	1.21	3.25	0.34	0.34	0.48	4.09	4.64	8.95
jul-cc-pV(D+d)Z	0.20	1.44	4.41	0.10	0.10	0.19	4.36	4.91	8.95
jun-cc-pV(D+d)Z	1.27	2.16	5.50	0.31	0.31	0.45	8.94	8.94	13.36
cc-pV(D+d)Z	0.08	3.92	15.81	1.93	1.93	2.44	30.26	30.26	61.09

Table 5. Mean and Maximum Deviations of MP2 Counterpoise-Corrected Hydrogen Bonding Energy (kcal/mol) from the Reference Value

	hydrogen bonding		
	MSD	MUD	MaxUD
aug-cc-pV(T+d)Z	-0.24	0.24	0.28
jul-cc-pV(T+d)Z	-0.29	0.29	0.36
jun-cc-pV(T+d)Z	-0.38	0.38	0.45
may-cc-pV(T+d)Z	-0.45	0.45	0.56
cc-pV(T+d)Z	-0.51	0.51	0.81

Table 6. Mean and Maximum Deviations of MP2 Ionization Potentials (kcal/mol) and Atomization Energies per Bond (kcal/mol per Bond) from Reference Value

	ionization potential			atomization energy		
	MSD	MUD	MaxUD	MSD	MUD	MaxUD
aug-cc-pV(Q+d)Z	-2.00	2.26	7.52	-1.03	1.03	1.82
jul-cc-pV(Q+d)Z	-2.02	2.27	7.52	-1.09	1.09	1.97
jun-cc-pV(Q+d)Z	-2.27	2.47	7.86	-1.21	1.21	2.12
may-cc-pV(Q+d)Z	-2.38	2.55	8.09	-1.26	1.26	2.18
apr-cc-pV(Q+d)Z	-2.43	2.60	8.19	-1.28	1.28	2.19
cc-pV(Q+d)Z	-2.55	2.70	7.86	-1.28	1.28	2.17
aug-cc-pV(T+d)Z	-3.26	3.28	7.80	-2.44	2.44	4.28
jul-cc-pV(T+d)Z	-3.28	3.30	7.80	-2.60	2.60	4.68
jun-cc-pV(T+d)Z	-3.89	3.89	8.67	-2.86	2.86	5.08
may-cc-pV(T+d)Z	-4.20	4.20	9.17	-2.98	2.98	5.19
cc-pV(T+d)Z	-4.55	4.55	10.40	-3.01	3.01	5.09
aug-cc-pV(D+d)Z	-6.25	6.25	10.99	-7.38	7.38	13.87
jul-cc-pV(D+d)Z	-6.31	6.31	10.99	-7.69	7.69	14.68
jun-cc-pV(D+d)Z	-8.65	8.65	13.81	-8.51	8.51	15.87
cc-pV(D+d)Z	-10.23	10.23	19.13	-8.62	8.62	15.57

At any given ζ level (n) and augmentation level ($month$ -), if one can afford additional cost and wishes to improve the quality of the calculations by increasing the size of the basis set, one would only be interested in doing so if the larger basis set offered significantly lower mean deviations. Mean deviations in electron affinity listed in Table 7 show that only partially augmented basis sets offer such an advantage. To see this for MP2-F12 calculations, recall that in the tables each basis set is larger than all those below it (as shown quantitatively in Table 2). Then, consider starting with DZ and moving up. The error in Table 7 decreases significantly as we increase the basis set only through jun- and jul-, but

not for aug-. The higher, triple- ζ unaugmented basis set also does not offer a decrease in error relative to that of jul-DZ. Therefore, aug-DZ and -TZ should be skipped. The next basis set to offer an improvement in the quality of the results is jun-TZ. The jul-TZ basis set offers further improvement. Then, aug-TZ and QZ can be skipped until improvement is again found with apr-QZ. Similar conclusions are drawn from other tables, for both MP2 and MP2-F12, except for atomization energies at the triple- and quadruple- ζ levels (Tables 6 and 8), which do not seem to require diffuse functions.

The trend is even more striking for calculations without F12. Consider, for example, the barrier height calculations in Table 4. One achieves higher accuracy with apr-QZ than with aug-TZ, jul-TZ, jun-TZ, or may-TZ, but simply going to QZ without any diffuse functions is less accurate than any of these triple- ζ levels. Table 3 shows that the cost savings in using apr-QZ rather than aug-QZ to include the diffuse space is more than a factor of 5. This is one of the main lessons of the present study and is more important than the small deviations from one MUD to another in the 0.5–0.8 kcal/mol range or the small deviations from one MUD to another in the 0.15–0.3 kcal/mol range. Similarly, now considering barrier heights in Table 4, TZ is inaccurate, but may-TZ is more accurate than aug-DZ and is less expensive than aug-TZ by about a factor of 4. Thus, in calculations where one cannot afford to go all the way to aug-TZ, the errors may be decreased considerably compared to TZ by using intermediate augmentation. As a third example, consider hydrogen bonding in Table 4. The main point is not the small differences from one MUD to another in the range 0.01–0.17 kcal/mol but rather the fact that even apr-QZ accounts well for the effect of diffuse functions at the quadruple- ζ level. Even may-TZ accounts well for them at the TZ level, and even jun-DZ accounts well for them at the DZ level. Usually, when diffuse functions are important, we find that $(n+1)Z$ is not more accurate than jul- nZ or jun- nZ . In other words, the fully augmented and unaugmented basis sets hardly ever seem to be good choices as compared to the new intermediate basis set levels, and in almost all cases,

Table 7. Mean and Maximum Deviations of MP2-F12 Barrier Height (kcal/mol), Hydrogen Bonding Energy (kcal/mol), and Electron Affinity from Reference Value

	barrier height						hydrogen bonding				electron affinity		
	MSE			MUD			MaxUD						
	DBH24	(DBH06 ^a)	(DBH18 ^b)	DBH24	(DBH06 ^a)	(DBH18 ^b)		MSE	MUD	MaxUD	MSD	MUD	MaxUD
aug-cc-pV(Q+d)Z	0.00 ^c	(0.00 ^c)	(0.00 ^c)	0.00 ^c	(0.00 ^c)	(0.00 ^c)	0.00 ^c	0.00 ^c	0.00 ^c	0.00 ^c	0.00 ^c	0.00 ^c	0.00 ^c
jul-cc-pV(Q+d)Z	0.02	(0.00)	(0.02)	0.03	(0.02)	(0.03)	0.08	0.02	0.02	0.03	0.03	0.04	0.13
jun-cc-pV(Q+d)Z	0.02	(0.00)	(0.03)	0.03	(0.01)	(0.03)	0.08	0.02	0.02	0.02	0.10	0.10	0.14
may-cc-pV(Q+d)Z	0.03	(0.01)	(0.04)	0.04	(0.04)	(0.04)	0.10	0.02	0.02	0.03	0.27	0.27	0.42
apr-cc-pV(Q+d)Z	0.00	(−0.12)	(0.05)	0.08	(0.12)	(0.06)	0.40	0.08	0.08	0.10	0.71	0.71	0.91
cc-pV(Q+d)Z	−0.51	(−2.07)	(0.00)	0.87	(3.04)	(0.15)	7.09	0.46	0.46	0.57	4.88	4.88	13.63
aug-cc-pV(T+d)Z	0.06	(−0.06)	(0.10)	0.11	(0.07)	(0.12)	0.77	0.04	0.04	0.04	0.23	0.23	0.36
jul-cc-pV(T+d)Z	0.09	(−0.04)	(0.14)	0.16	(0.09)	(0.18)	0.69	0.14	0.14	0.15	0.33	0.33	0.56
jun-cc-pV(T+d)Z	0.13	(0.03)	(0.16)	0.18	(0.14)	(0.20)	0.75	0.14	0.14	0.15	0.62	0.62	1.07
may-cc-pV(T+d)Z	0.16	(0.00)	(0.21)	0.25	(0.22)	(0.26)	1.12	0.24	0.24	0.28	1.86	1.86	2.47
cc-pV(T+d)Z	−0.56	(−2.53)	(0.10)	1.44	(4.37)	(0.46)	9.24	1.09	1.09	1.27	9.79	9.79	22.66
aug-cc-pV(D+d)Z	0.03	(0.13)	(0.00)	0.26	(0.32)	(0.25)	0.69	0.08	0.08	0.10	1.02	1.02	1.83
jul-cc-pV(D+d)Z	0.15	(0.21)	(0.13)	0.39	(0.40)	(0.39)	1.32	0.38	0.38	0.46	1.18	1.18	1.78
jun-cc-pV(D+d)Z	0.54	(1.31)	(0.28)	0.84	(1.37)	(0.66)	2.19	0.56	0.56	0.70	4.27	4.27	5.71
cc-pV(D+d)Z	−0.54	(−2.14)	(0.00)	2.66	(6.76)	(1.29)	12.38	2.31	2.31	2.86	19.64	19.64	39.98

^a Reactions containing anions ($\text{Cl}^- \cdots \text{CH}_3\text{Cl}$, $\text{F}^- \cdots \text{CH}_3\text{Cl}$, $\text{OH}^- \cdots \text{CH}_3\text{F}$). ^b The rest of the reactions in DBH24/08 (not listed in a). ^c Zero by definition.

Table 8. Mean and Maximum Deviations of MP2-F12 Ionization Potentials (kcal/mol) and Atomization Energies per Bond (kcal/mol per Bond) from Reference Value

	ionization potential			atomization energy		
	MSD	MUD	MaxUD	MSD	MUD	MaxUD
aug-cc-pV(Q+d)Z	0.00 ^a	0.00 ^a	0.00 ^a	0.00 ^a	0.00 ^a	0.00 ^a
jul-cc-pV(Q+d)Z	−0.01	0.02	0.04	0.01	0.01	0.02
jun-cc-pV(Q+d)Z	−0.04	0.04	0.06	0.00	0.01	0.01
may-cc-pV(Q+d)Z	−0.09	0.09	0.13	−0.01	0.01	0.02
apr-cc-pV(Q+d)Z	−0.15	0.15	0.23	−0.01	0.01	0.03
cc-pV(Q+d)Z	−0.31	0.31	0.90	0.01	0.02	0.05
aug-cc-pV(T+d)Z	−0.13	0.14	0.26	−0.03	0.04	0.06
jul-cc-pV(T+d)Z	−0.17	0.17	0.25	−0.01	0.03	0.06
jun-cc-pV(T+d)Z	−0.35	0.35	0.58	−0.03	0.04	0.08
may-cc-pV(T+d)Z	−0.68	0.68	1.02	−0.04	0.04	0.11
cc-pV(T+d)Z	−1.28	1.28	2.77	0.06	0.07	0.18
aug-cc-pV(D+d)Z	−0.74	0.80	1.50	−0.19	0.22	0.46
jul-cc-pV(D+d)Z	−0.99	1.01	1.62	−0.10	0.19	0.33
jun-cc-pV(D+d)Z	−2.86	2.86	5.36	−0.06	0.23	0.35
cc-pV(D+d)Z	−4.91	4.91	9.08	0.24	0.34	0.87

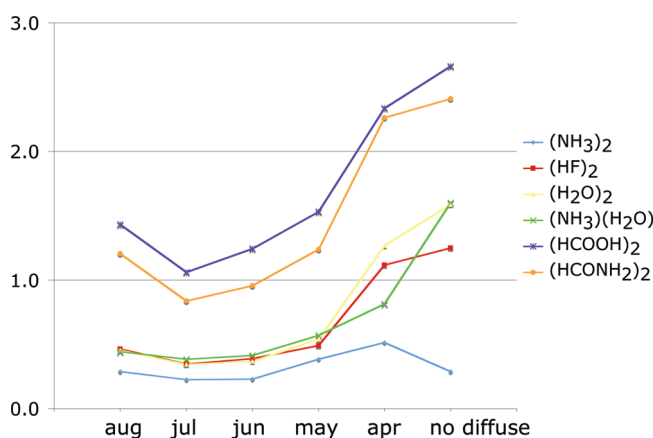
^a Zero by definition.

truncation to a basis set intermediate between unaugmented or fully augmented on only heavy atoms is the best choice.

An excessive number of diffuse functions not only increases the cost but also often leads to difficult SCF convergence, and as shown in Figure 1, it can increase the basis set superposition error.

The fact that the aug-*n*Z basis sets approach the CBS limit in a systematic way is often correctly considered to be one of their chief advantages. However, if one accepts that diffuse functions are not needed on hydrogenic atoms, a basis set sequence such as jun-XZ (*x* = D, T, Q, etc.) also approaches the CBS limit systematically (i. e., is “convergent”), and it does so in a more efficient manner. Thus, partially augmented basis sets would appear to be very useful for focal point^{23,64} analysis.

We have not examined reduction in the number of polarization functions, but previous work⁶⁵ shows that savings are possible in that area as well.

**Figure 1.** Counterpoise corrections [kcal/mol] for hydrogen-bonded dimers for triple- ζ basis sets.

Another possible use of the partially augmented basis sets is in dual-basis calculations where Hartree–Fock calculations are performed in a small basis set and the post-Hartree–Fock calculation is performed in a large set.^{66,67}

The second objective of this article is to compare MP2-F12 to MP2. Both kinds of calculations converge to the same MP2 CBS limit, but at different rates. Comparing Table 4 to Table 7 shows that, for barrier heights, MP2-F12/jul-DZ is more accurate than MP2/aug-TZ or MP2/aug-QZ. Furthermore, MP2-F12/may-TZ is as accurate as MP2/jul-QZ. For ionization potentials (Tables 6 and 8), MP2-F12/jul-DZ is more accurate than MP2/jun-QZ. For atomization energies (Tables 6 and 8), we find that MP2-F12/DZ is more accurate than MP2/aug-QZ. However, MP2-F12 is not more accurate than MP2 for hydrogen bonding.

6. Conclusions

Of all of the energetic molecular properties considered here, unaugmented basis sets are adequate only for atomization energies at the triple- and quadruple- ζ levels.

Both MP2 and MP2-F12 theories are sensitive to the saturation of the diffuse space; however, in most cases

presented here, the full augmentation is unnecessary. Instead of using fully augmented (aug) or unaugmented basis sets, we recommend using the new partially augmented basis sets.

For MP2 calculations of properties requiring diffuse basis functions, we recommend jun-QZ, jul-TZ, and jul-DZ for especially reliable results, but the tables show that, except for electron affinities (and therefore probably for most properties involving anions), one can usually cut back to may-QZ or jun-TZ.

In MP2-F12 calculations of properties sensitive to the number of diffuse functions, we recommend using may-QZ, jun-TZ, and jul-DZ, which offer considerable savings compared to aug- basis sets and significant improvement over unaugmented cc-pV(*n*+d)Z basis sets.

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Supporting Information Available: Root mean square errors for all the properties in this article. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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