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Push it to the limit: characterizing the convergence of common sequences of basis sets for intermolecular interactions as described by density functional theory

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(Dated: 29 April 2016)

With the aim of systematically characterizing the convergence of common families of basis sets such that general recommendations for basis sets can be made, we have tested a wide variety of basis sets against complete-basis binding energies across the S22 set of intermolecular interactions – noncovalent interactions of small and medium-sized molecules consisting of first- and second-row atoms – with three distinct density functional approximations: SPW92, a form of local-density approximation; B3LYP, a global hybrid generalized gradient approximation; and B97M-V, a meta-generalized gradient approximation with nonlocal correlation. We have found that it is remarkably difficult to reach the basis set limit; for the methods and systems examined, the most complete basis is Jensen's pc-4. The Dunning correlation-consistent sequence of basis sets converges slowly relative to the Jensen sequence. The Karlsruhe basis sets are quite cost effective, particularly when a correction for basis set superposition error (BSSE) is applied: counterpoise-corrected def2-SVPD binding energies are better than corresponding energies computed in comparably sized Dunning and Jensen bases, and on par with uncorrected results in basis sets 3-4 times larger. These trends are exhibited regardless of the level of density functional approximation employed. A sense of the magnitude of the intrinsic incompleteness error of each basis set not only provides a foundation for guiding basis set choice in future studies, but also facilitates quantitative comparison of existing studies on similar types of systems.

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I. INTRODUCTION

The past two decades have seen an explosion of interest in Kohn-Sham density functional theory (DFT),[1] largely due to the potential of approximations within the formalism to strike a nice balance between computational expense and accuracy. Twenty years ago, state-of-the-art methods were generalized gradient approximations (GGA) with few, if any, nonempirical parameters.[2–6] Nowadays, density functionals abound: the most successful relics of the past (e.g. PBE, B3LYP) still live on, but the quest for the ultimate density functional continues;[7–12] recent work by Mardirossian and Head-Gordon involved exploration of a space of over a billion meta-GGAs, a space orders of magnitude larger than the space of previously-existing density functionals (yet still a tiny fraction of the unexplored space of B97-esque functionals).[13] Needless to say, there has been – and continues to be – a tremendous amount of effort dedicated to the development and testing of novel density functional approximations.

Although settling on a method is arguably the most important step one makes prior to running an electronic structure calculation, there remain other decisions that can significantly impact results, most notably grid – in the case of numerical calculations, as in DFT – and basis set. The issue of grid is relatively trivial to resolve: a standard semilocal DFT calculation is linear in the number of grid points, and so it is feasible to employ incredibly dense grids. The issue of basis set is a bit stickier, however, since it is the size of the basis that dominates the scaling. In extended and periodic systems, plane waves constitute the natural choice of basis function, though the delocalized nature of plane waves renders them ineffective at describing localized densities, e.g. core electrons. As a result, periodic calculations tend to employ some form of additonal approximation to describe the effects of core electrons.[14] In calculations on molecular systems, local atomic orbital (AO) basis sets are arguably more physically relevant; common representations of AOs include Slater orbitals[15] and Gaussian-type orbitals (GTOs)[16]. The latter are typically preferred; the Gaussian Product Theorem renders the necessary integrals more computationally tractable. The focus of this work will thus be GTO basis sets.

Even limiting oneself to existing GTO basis sets, the space of possibilities is enormous. There are a vast number of hierarchical basis sets that are in common use; for details pertaining to their construction, see Jensen's recent review.[17] The fact that so many basis sets are

regularly employed is a testament to the fact that there really is no unambiguously *best* basis set of a given size. Here, we focus primarily on three families of GTO basis sets: the Dunning correlation-consistent sequence,[18–20] the Jensen polarization-consistent sequence,[21–23] and the Karlsruhe property-optimized basis sets.[24,25] The correlation-consistent basis sets have been designed to exploit the fact that the correlation energy converges as an inverse power series in the highest angular momentum of the basis;[26,27] the result is systematic convergence with the cardinal number of the basis set. In the case of DFT, however, the convergence patterns of these basis sets lack the same theoretical underpinnings. Similarly, the convergence behaviors of the Jensen and Karlsruhe sequences, particularly in the context of intermolecular interactions – the domain of many interesting problems in modern chemistry – are not well-documented.

When local basis sets are utilized, two interrelated types of basis set incompleteness errors (BSIE) emerge: basis set superposition error (BSSE), which arises from the inconsistent treatment of a supersystem and its constituent fragments,[28,29] and what we will call the remaining basis set incompleteness error (rBSIE), the leftover incompleteness error once BSSE is removed that is due to the fact that the Schrödinger equation is being solved in just a fraction of the full Hilbert space. We will here briefly address the issue of BSSE, since unlike rBSIE it can be relatively cheaply eliminated. For a more detailed discussion of basis set errors, particularly in the context of small basis sets, the reader is referred to a recent review article by Sure et al.[30] BSSE is often removed by performing fragment calculations in the full supersystem basis; this constitutes the counterpoise correction (CP) approach of Boys and Bernardi,[29] though the downside of this approach is that there must exist some natural partitioning of the full supersystem into fragments. The validity of this and other BSSE correction schemes has long been a contentious issue,[31–35] though a comprehensive review article by van Duijneveldt, van Duijneveldt-van de Rijdt, and van Lenthe[36] temporarily resolved the debate in favor of CP. Recent years have seen a resurgence of arguments against CP,[37,38] though it has been demonstrated that some of the data used to formulate the conclusions of Kalescky, Kraka, and Cremer[38] were impacted significantly by unrelated issues, namely mismatches between the choices of basis sets and the extent of correlation included.[39] Linear dependency issues in calculations involving ghost atoms may have affected the results, as well. Some authors have proposed a compromise – a half-CP approach, wherein uncorrected and counterpoise-corrected binding energies are averaged –

on the basis of its stellar performance for certain methods.[40] Needless to say, the field has yet to reach a consensus on how BSSE should be addressed.

In this work, we have endeavored to fill in various gaps in the literature, to characterize the convergence patterns of several common hierarchical families of basis sets in the context of noncovalent interactions as described by DFT. We have further distinguished between the two manifestations of basis set error, BSSE and rBSIE. Characterizing these errors in conventional basis sets enables us to make recommendations regarding which basis sets to use when studying noncovalent interactions with DFT.

II.   COMPUTATIONAL METHODS

We have examined basis set errors of a wide variety of standard GTO basis sets in the context of density functional theory calculations on noncovalent interactions. Specifically, we have considered several Pople split-valence basis sets: 6-31G*, 6-31++G**, 6-311++G**, and 6-311++G(3df,3pd);[41–48] the correlation-consistent basis sets of Dunning, cc-pVXZ, as well as their augmented variants aug-cc-pVXZ, with X=D,T,Q,5,[18–20] the doubly-augmented versions d-aug-cc-pVDZ and d-aug-cc-pVTZ,[18,19,49] the core-valence sets aug-cc-pCVDZ and aug-cc-pCVTZ,[18,19,50] and Truhlar's pruned jun-cc-pVXZ analogues;[51] the Karlsruhe sequence def2-SVP, def2-TZVP, and def2-QZVP,[24] as well as the augmented variants def2-SVPD, def2-TZVPD, and def2-QZVPD;[25] and the Jensen polarization-consistent sequences pc-n and aug-pc-n.[21–23] We have utilized three density functional approximations: SPW92,[1,52–54] a local-density approximation; B3LYP,[2–5] a global hybrid generalized gradient approximation; and B97M-V,[13] a meta-generalized gradient approximation incorporating VV10 long-range correlation.[55] This set of approximations was chosen because it spans the space of complexity in common density functionals: SPW92 is one of the simplest Kohn-Sham density functionals; B3LYP is a bit more complex due to its incorporation of the gradient of the electron density, as well as a portion of exact exchange; and B97M-V is a state-of-the-art method with all the accompanying bells and whistles, most notably an explicit nonlocal correlation kernel. Calculations have been performed on the S22 set of molecules,[56] depicted in Figure 1.

All calculations were performed with a development version of Q-Chem 4.3.[57] The DIIS error was converged to 10^{-8}, integral threshholds of 10^{-14} were used, and no symmetry
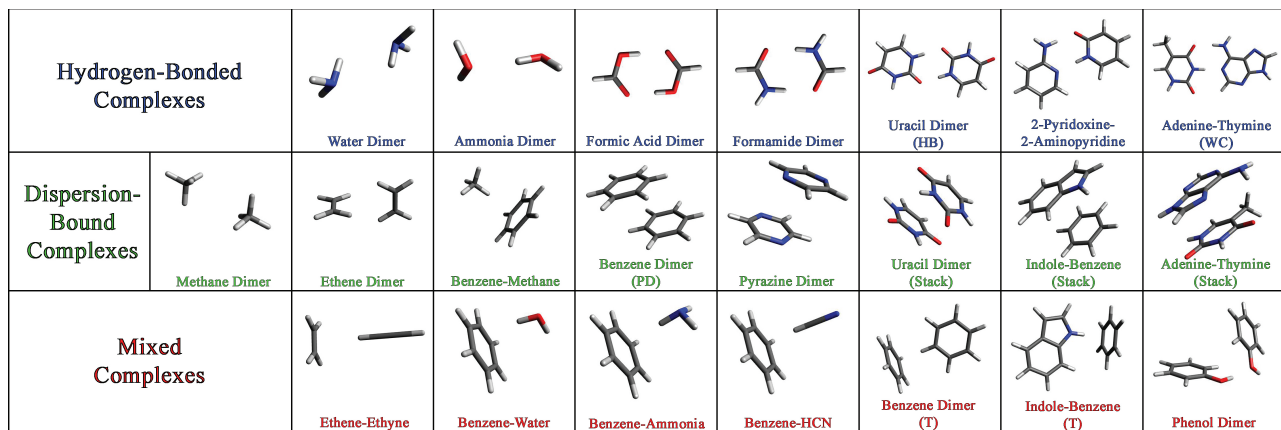
FIG. 1. Structures of the systems in the S22 dataset. The systems are classified by interaction type as per the original work.[56]

was exploited. Molecular structures were generated with Avogadro.[58] For all systems, binding energies were determined both with and without the Boys and Bernardi correction for BSSE.[29] The occupied orbital resolution-of-the-identity approximation (occ-RI-K) was utilized to accelerate construction of the exact exchange matrix in B3LYP.[59] For the cc-pVXZ and def2- basis sets, optimized auxiliary basis sets from Weigend were used, though i functions were omitted.[60,61] Auxiliary basis sets for the aug-cc-pVXZ basis sets were generated by adding an even-tempered diffuse function to each primitive set; the (aug-)cc-pVDZ auxiliary bases were generated by removing the highest angular momentum functions from the (aug-)cc-pVTZ auxiliary bases; and for the (aug-)pc-n and Pople basis sets, the corresponding Dunning auxiliary basis sets were used, e.g. cc-pVTZ-jkfit for pc-2.

Due to the constraints of double precision floating point numbers and linear-dependency issues in calculations on some systems with the larger basis sets, the precision to which we report all binding energies is 0.01 kcal/mol. For the smaller basis sets we could meaningfully reproduce binding energies to a much greater level of precision, but the same is not true for larger basis sets; this is particularly an issue in basis sets rife with diffuse functions, e.g. aug-pc-3. The desired level of precision dictates the grids necessary: a Lebedev integration grid consisting of 99 radial points and 590 angular points per atom was utilized to compute the semilocal exchange-correlation components of the energy, and the coarser SG-1 grid was used for nonlocal correlation in B97M-V.[62] This combination of grids yields binding energies that are converged to within 0.01 kcal/mol across the entire S22 set, as can be seen within

the supplemental material[63].

III. RESULTS AND DISCUSSION

Although the principal objective of this study has been to elucidate the convergence patterns of various standard GTO basis sets in the context of density functional theory applied to intermolecular interactions, in the course of this work we have, at three different levels of density functional theory, established what we deem to be complete-basis (CBS) binding energies for every system in S22. These CBS binding energies correspond to counterpoise-corrected values in the pc-4 basis. We justify this choice of CBS limit – counterpoise-corrected pc-4 – in three ways: firstly, the pc-4 basis is the only basis examined for which the mean BSSE across the S22 set of molecules is not larger than the chosen level of precision, 0.01 kcal/mol; secondly, pc-4 absolute energies for any given system are lower than those computed with any other basis set in this study, and as such pc-4 is variationally the most complete basis examined; thirdly, counterpoise-corrected pc-4 SPW92 binding energies are converged to within 0.01 kcal/mol relative to those calculated in the much larger aug-pc-4 basis set, as is illustrated in the supplemental material[63] – in fact, even pc-4 absolute energies are converged to roughly this level of precision. Any reference to basis set limit SPW92, B3LYP, or B97M-V results henceforth corresponds to counterpoise-corrected pc-4, and all errors – unless otherwise noted – are expressed relative to the basis set limit result for the relevant method. Since complete-basis results are costly to obtain and are of interest for e.g. anyone testing a novel basis set in one of these methods, we present them in Table I. Reference CCSD(T)/CBS values generated by Marshall, Burns, and Sherrill[64] are also provided for comparison.

Now that benchmarks for each method have been established, it is possible to assess the qualities of various standard local quantum chemistry basis sets in the context of noncovalent interactions as described by density functional theory. Note that the most meaningful point of comparison for each method-basis combination is the CBS limit for that method; by comparing to reference CCSD(T)/CBS results, we would be confounding method error with basis set error, whereas by comparing to CBS results within each method we are able to isolate basis set errors. The uncorrected (noCP) and counterpoise-corrected (CP) root mean square errors (RMSEs) versus the CBS limit for SPW92 are illustrated in Figure 2 for a

TABLE I. Complete basis set (CBS) binding energies for each system in S22 at various levels of theory. For the density functional approximations, counterpoise-corrected pc-4 constitutes the CBS limit. Benchmark CCSD(T)/CBS results from Marshall, Burns, and Sherrill[64] are provided for comparison.

System	SPW92	B3LYP	B97M-V	CCSD(T)[a]
Ammonia dimer	-5.07	-2.19	-3.09	-3.13
Water dimer	-7.81	-4.51	-5.00	-4.99
Formic acid dimer	-26.98	-17.45	-18.69	-18.75
Formamide dimer	-21.92	-14.07	-15.62	-16.06
Uracil dimer h-bonded	-26.27	-17.99	-20.11	-20.64
2-pyridoxine 2-aminopyridine complex	-22.89	-13.83	-16.39	-16.93
Adenine thymine Watson-Crick complex	-22.08	-12.91	-15.82	-16.66
Methane dimer	-0.83	0.39	-0.43	-0.53
Ethene dimer	-2.47	0.48	-1.31	-1.47
Benzene - Methane complex	-2.02	0.76	-1.34	-1.45
Benzene dimer parallel displaced	-2.60	3.72	-2.53	-2.65
Pyrazine dimer	-4.43	2.45	-3.85	-4.26
Uracil dimer stack	-10.14	-0.95	-9.76	-9.81
Indole benzene complex stack	-4.36	4.64	-4.35	-4.52
Adenine thymine complex stack	-11.95	1.29	-11.75	-11.73
Ethene ethyne complex	-2.27	-0.66	-1.50	-1.50
Benzene water complex	-4.44	-1.20	-3.10	-3.28
Benzene ammonia complex	-3.04	-0.11	-2.13	-2.31
Benzene HCN complex	-5.82	-1.97	-4.21	-4.54
Benzene dimer T-shaped	-3.05	0.98	-2.33	-2.72
Indole benzene T-shape complex	-6.27	-0.55	-5.02	-5.63
Phenol dimer	-9.01	-2.99	-6.57	-7.10

[a] CCSD(T) values taken from Marshall, Burns, and Sherrill[64]

variety of basis sets. Basis sets are listed in order of increasing size: the basis with the fewest functions (6-31G*) is at the top and that with the most (aug-cc-pV5Z) is at the bottom. Also noteworthy is the fact that there are two axes, one which corresponds to the uncorrected RMSE (top, blue), and one which corresponds to the counterpoise-corrected RMSE (bottom, gold); the scales of these axes differ by roughly a factor of four in order to compensate for the fact that the CP RMSEs are significantly smaller, on average, than the noCP RMSEs.
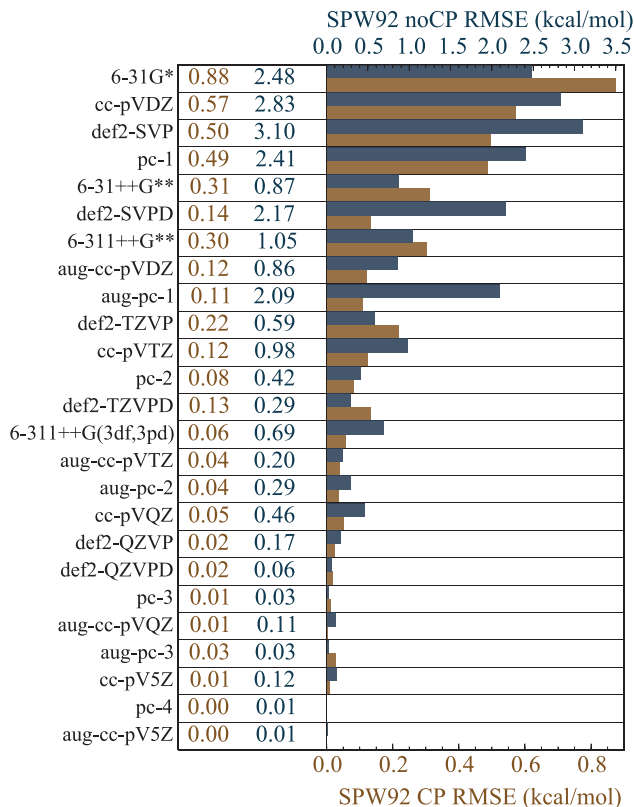
SPW92 noCP RMSE (kcal/mol)

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5

Basis set	CP	noCP
6-31G*	0.88	2.48
cc-pVDZ	0.57	2.83
def2-SVP	0.50	3.10
pc-1	0.49	2.41
6-31++G**	0.31	0.87
def2-SVPD	0.14	2.17
6-311++G**	0.30	1.05
aug-cc-pVDZ	0.12	0.86
aug-pc-1	0.11	2.09
def2-TZVP	0.22	0.59
cc-pVTZ	0.12	0.98
pc-2	0.08	0.42
def2-TZVPD	0.13	0.29
6-311++G(3df,3pd)	0.06	0.69
aug-cc-pVTZ	0.04	0.20
aug-pc-2	0.04	0.29
cc-pVQZ	0.05	0.46
def2-QZVP	0.02	0.17
def2-QZVPD	0.02	0.06
pc-3	0.01	0.03
aug-cc-pVQZ	0.01	0.11
aug-pc-3	0.03	0.03
cc-pV5Z	0.01	0.12
pc-4	0.00	0.01
aug-cc-pV5Z	0.00	0.01

0.0 0.2 0.4 0.6 0.8

SPW92 CP RMSE (kcal/mol)

FIG. 2. Uncorrected (noCP) and counterpoise-corrected (CP) root mean square errors (RMSE) in SPW92 binding energies across the S22 set of molecules. Errors are expressed relative to SPW92/CBS. Blue corresponds to noCP, gold to CP. The bars are a visual representation of the actual RMSEs, which are tabulated for each basis set on the left side of the figure. Basis sets are listed in order of increasing number of basis functions. Note the difference between noCP (top) and CP (bottom) axes.

From Figure 2, it is immediately evident that for any given basis set, the CP RMSE is significantly smaller than the noCP RMSE; that is, counterpoise-corrected binding energies across S22 are closer to the basis set limit than uncorrected ones. Since the counterpoise correction is designed to alleviate BSSE, the CP RMSE is a quantitative measure of the remaining basis set incompleteness error (rBSIE). The noCP RMSE, on the other hand, encompasses the entirety of the BSIE, i.e. both rBSIE and BSSE. Basis sets exhibiting a small CP RMSE can then be said to have a low intrinsic rBSIE: their spans form a good approximation to the full Hilbert spaces of the systems in the S22 set. It is worth noting that when discussing basis set quality, rBSIE is arguably a more important metric than BSSE,

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since BSSE can be relatively cheaply removed – at least in the context of intermolecular interactions.

As the size of the basis increases, computed energies generally approach the basis set limit. This is trivially true within a given variational space, as exemplified by the difference between e.g. cc-pVDZ and aug-cc-pVDZ. The trend also weakly holds even when the spaces are different: a quadruple-zeta basis is usually closer to the basis set limit than a triple-zeta basis. Nevertheless, the different families of basis sets exhibit different rates of convergence to the basis set limits, such that it is possible for a basis set in one family to be smaller yet more complete than one in another family (compare def2-QZVPD to aug-cc-pVQZ). Certain basis sets are particularly cost-effective. This is represented within Figure 2 by smaller bars higher up, e.g. CP def2-SVPD. Other basis sets – most notably those in the Pople sequence, e.g. 6-31++G** – outperform their similarly-sized competitors when not corrected for BSSE, but dramatically underperform once a counterpoise correction is employed. Thus, different conclusions regarding relative qualities of basis sets may be drawn based on whether or not counterpoise correction is desired, which is evidenced by different trends between the gold and blue bars in Figure 2. Nevertheless, correcting for basis set superposition error is useful, particularly in the case of smaller basis sets. For instance, calculating a counterpoise-corrected binding energy for a dimer in the def2-SVPD basis entails less than 20% of the effort required to calculate the corresponding uncorrected energy in the aug-cc-pVTZ basis, despite the fact that the CP def2-SVPD calculation is – as evidenced by these data – more accurate.

Similar trends regarding the qualities of the various basis sets are observed for the other density functional approximations, B3LYP and B97M-V, as is illustrated by comparison with Figures 3 and 4, respectively. There are, of course, some exceptions: for instance, in the case of B97M-V, the noCP aug-pc-n results are disproportionately worse, which may simply be an artifact of its training. Nevertheless, a significant degree of transferability is expected for any density functional with a well-behaved inhomogeneity correction factor (ICF), regardless of whether exact exchange is incorporated or not. All bets are off, however, when considering functionals with strongly oscillatory ICFs; for more details, see Mardirossian and Head-Gordon.[65]

One particularly interesting aspect of the similarities among functionals observed in this study is that the nonlocal VV10 correlation of B97M-V is no more sensitive to basis set
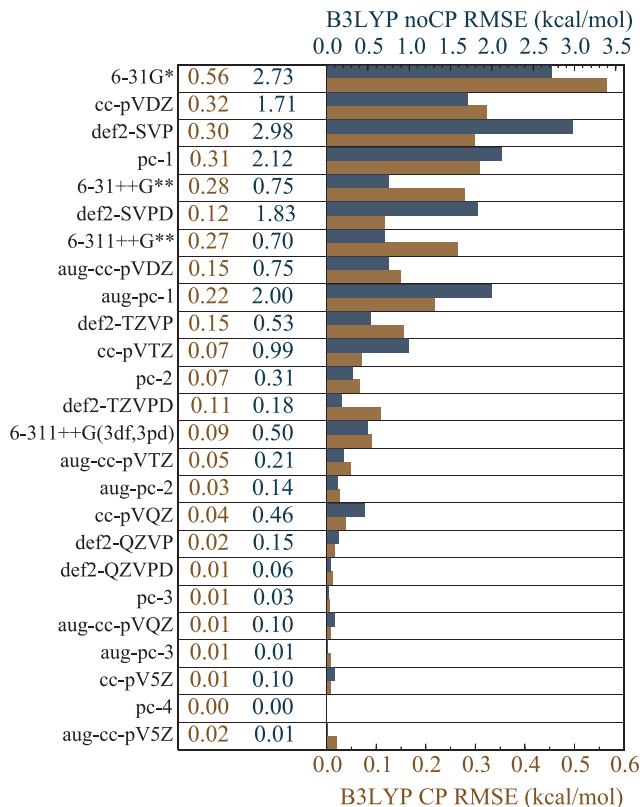
FIG. 3. Uncorrected (noCP) and counterpoise-corrected (CP) root mean square errors (RMSE) in B3LYP binding energies across the S22 set of molecules. For further details, see Figure 2.

than the semilocal exchange and correlation components. In fact, VV10 nonlocal correlation is vastly *less* sensitive to basis set size than even the local exchange and correlation of SPW92: there is effectively no difference between VV10 nonlocal contributions to binding energies in the def2-SVPD and pc-4 basis sets. Relevant data are provided in the supplemental material[63]. It has previously been established that nonlocal correlation energies are insensitive to grid[12,66], but to our knowledge this is the first time basis set insensitivity has been reported. This is a conceptually interesting phenomenon which could be exploited to greatly reduce the cost of electronic structure calculations with VV10; such will be the focus of work to come.

The convergence patterns of the Dunning, Jensen, and Karlsruhe basis sequences for uncorrected and counterpoise-corrected mean binding energies in S22 are summarized in Figures 5 and 6, respectively, at the local-density approximation level of DFT. For the Dunning and Jensen sequences, basis sets of double- through quintuple-zeta quality were employed
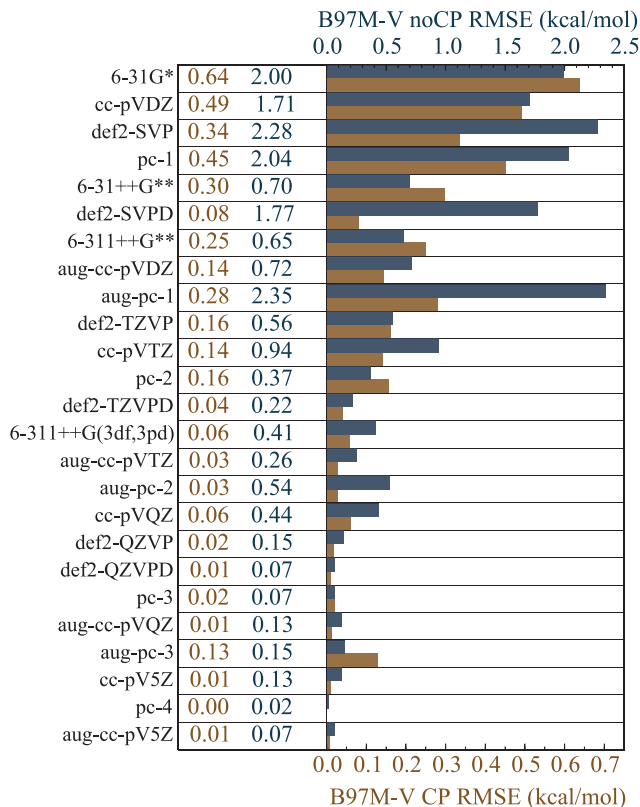
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	B97M-V noCP RMSE (kcal/mol)	
	0.0 0.5 1.0 1.5 2.0 2.5	
6-31G*	0.64	2.00
cc-pVDZ	0.49	1.71
def2-SVP	0.34	2.28
pc-1	0.45	2.04
6-31++G**	0.30	0.70
def2-SVPD	0.08	1.77
6-311++G**	0.25	0.65
aug-cc-pVDZ	0.14	0.72
aug-pc-1	0.28	2.35
def2-TZVP	0.16	0.56
cc-pVTZ	0.14	0.94
pc-2	0.16	0.37
def2-TZVPD	0.04	0.22
6-311++G(3df,3pd)	0.06	0.41
aug-cc-pVTZ	0.03	0.26
aug-pc-2	0.03	0.54
cc-pVQZ	0.06	0.44
def2-QZVP	0.02	0.15
def2-QZVPD	0.01	0.07
pc-3	0.02	0.07
aug-cc-pVQZ	0.01	0.13
aug-pc-3	0.13	0.15
cc-pV5Z	0.01	0.13
pc-4	0.00	0.02
aug-cc-pV5Z	0.01	0.07
	0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7	
	B97M-V CP RMSE (kcal/mol)	

FIG. 4. Uncorrected (noCP) and counterpoise-corrected (CP) root mean square errors (RMSE) in B97M-V binding energies across the S22 set of molecules. For further details, see Figure 2.

(with the exception of aug-pc-4, since those calculations could not all be converged). For the Karlsruhe sequences, basis sets of double-zeta through quadruple-zeta quality were used. Similar convergence patterns are observed for B3LYP and B97M-V; relevant figures may be found in the supplemental material[63]. It is evident that the counterpoise-corrected results converge significantly more quickly than the uncorrected results with respect to the number of basis functions, regardless of the choice of basis sequence; note the difference in scales between Figure 5 and Figure 6. However, this accelerated convergence comes at the cost of a loss of systematicity in the error: whereas complexes are always overbound when uncorrected for BSSE (as is guaranteed by the variational borrowing of fragment functions in supersystem calculations), they are not always underbound following application of the counterpoise correction.

It is clear from Figure 5 that the Dunning sequences of basis sets cc-pVXZ and aug-cc-pVXZ converge remarkably slowly to the basis set limit for DFT. In fact, even binding
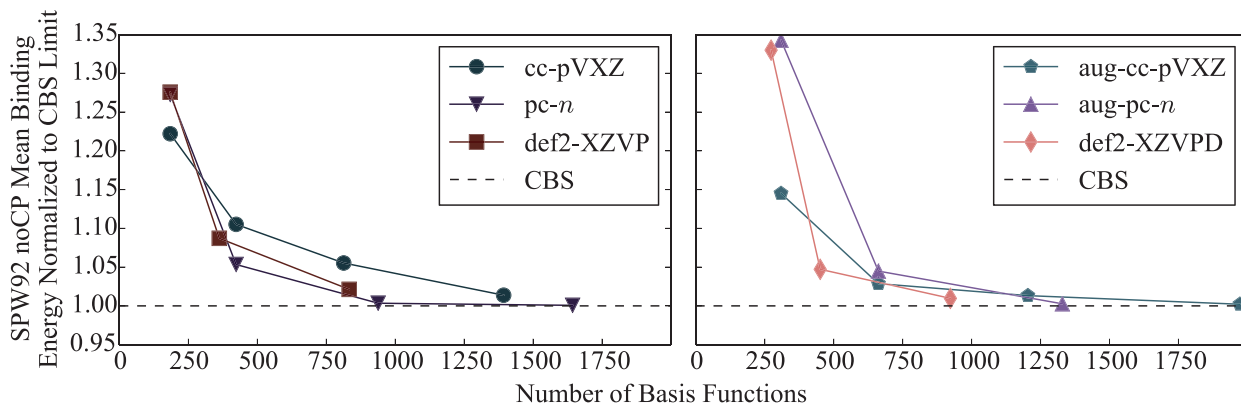
FIG. 5. Convergence of uncorrected (noCP) SPW92 normalized mean binding energies across the S22 set of molecules for the Dunning, Jensen, and Karlsruhe sequences of basis sets. Each binding energy was normalized to the corresponding SPW92/CBS value before averaging. The number of basis functions for each basis set was determined by averaging the number of basis functions for each system within each basis set across all systems in S22.
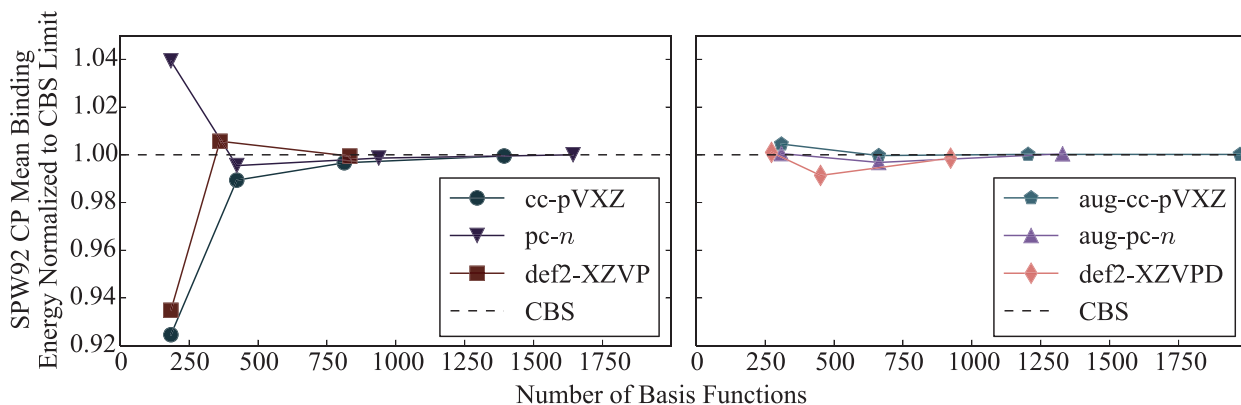

FIG. 6. Convergence of counterpoise-corrected (CP) SPW92 normalized mean binding energies across the S22 set of molecules for the Dunning, Jensen, and Karlsruhe sequences of basis sets. For further details, see Figure 5.

energies at the uncorrected aug-cc-pV5Z level are not fully converged: in this basis set, the mean BSSE across S22 ranges from 0.01 to 0.06 kcal/mol, depending on the method. The pc-4 basis set, on the other hand, is essentially BSSE-free to this level of precision, despite being roughly 17% smaller. Even binding energies in the def2-QZVPD basis are converged to approximately the same level as those in aug-cc-pV5Z, despite the fact that

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def2-QZVPD is less than half the size of aug-cc-pV5Z. The Dunning sequences of basis sets are undeniably inefficient for DFT; that being said, they were designed with correlated wavefunction-based methods in mind, so this is not altogether unexpected. When considering counterpoise-corrected results, the picture is not nearly as bleak, though the Jensen sequences of polarization-consistent basis sets still converge more quickly than the Dunning sequences, as is illustrated in Figure 6. On the basis of these results, it is difficult to justify the use of Dunning basis sets for density functional theory; for a given Dunning basis set, there exists a Jensen or Karlsruhe alternative that is simultaneously smaller and more accurate.

In their calendar basis set article, Papajak *et al.*[51] argue that the augmented Dunning basis sets contain more diffuse functions than are strictly necessary, and offer pruned versions at the double- through quadruple-zeta levels. We have thus examined one such sequence, the so-called jun-cc-pVXZ sequence of basis sets. The convergence pattern of this basis sequence with B97M-V across S22 is provided in Figure 7. At first glance, the jun-cc-pVXZ sequence seems superior to the aug-cc-pVXZ sequence, particularly in the absence of a correction for BSSE. Indeed, at the triple- and quadruple-zeta levels this is the case, but at the double-zeta level BSSE is simply being traded for rBSIE, as evidenced by the significantly increased CP RMSE in Table II. Additionally, even though the jun-cc-pVTZ and jun-cc-pVQZ basis sets outperform their fully-augmented counterparts, they can still not really be recommended. They are not bad basis sets – by all measures examined here, they are better than the corresponding fully-augmented Dunning basis sets – but they are still less cost-effective than the Karlsruhe and Jensen alternatives. As a final note, as is evident in Table II, other methods of altering the Dunning sequence, namely the addition of a new set of core functions (aug-cc-pCVXZ) or a set of diffuse functions (d-aug-cc-pVXZ), are also not useful for converging these binding energies. Again, these enhancements were optimized with other properties in mind, and cannot be expected to be effective in the present application.

Figures 8 and 9 illustrate the convergence behavior of the Dunning, Karlsruhe, and Jensen sequences of basis sets across various subsets of S22 at the SPW92 level of theory. The subsets are delineated by interaction type: there is a category for hydrogen-bonded complexes, one for dispersion-bound complexes, and one for complexes bound by a combination of dispersion and permanent electrostatics; see Figure 1 a breakdown of which systems within S22
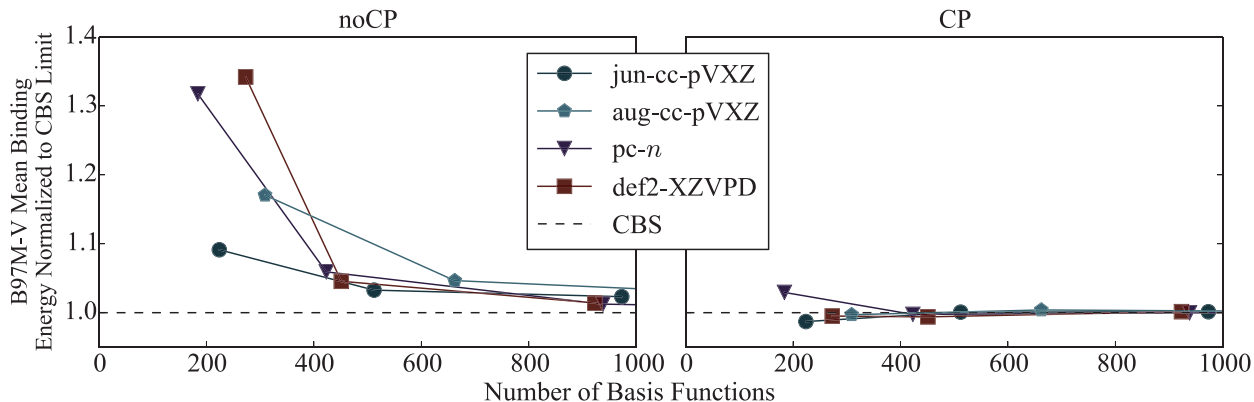
FIG. 7. Convergence of uncorrected (noCP) and counterpoise-corrected (CP) B97M-V normalized mean binding energies across the S22 set of molecules for the Truhlar, Dunning, Jensen, and Karlsruhe sequences of basis sets. Each binding energy was normalized to the corresponding B97M-V/CBS value before averaging.

TABLE II. Uncorrected (noCP) and counterpoise-corrected (CP) root mean square errors (RMSE) in B97M-V binding energies across S22 for variants of Dunning-style basis sets and comparably-sized Karlsruhe alternatives.

| Basis | RMSE (kcal/mol) | |
	noCP	CP
aug-cc-pVDZ	0.72	0.15
d-aug-cc-pVDZ	0.81	0.14
aug-cc-pCVDZ	0.75	0.13
jun-cc-pVDZ	0.57	0.39
def2-SVPD	1.77	0.08
aug-cc-pVTZ	0.26	0.03
d-aug-cc-pVTZ	0.32	0.03
aug-cc-pCVTZ	0.34	0.03
jun-cc-pVTZ	0.20	0.02
def2-TZVPD	0.22	0.04
aug-cc-pVQZ	0.13	0.01
jun-cc-pVQZ	0.14	0.01
def2-QZVPD	0.07	0.01

fall within each category. In these figures, the binding energies for each complex have been normalized to the SPW92 basis set limit – namely, counterpoise-corrected pc-4 – then these normalized binding energies have been averaged across each subset. Based on Figure 8, it is evident that in the absence of a correction for BSSE, the relatively slow convergence of

the Dunning basis sequences in comparison to the Jensen and Karlsruhe sequences cannot be attributed to a failure on any particular interaction type; it is observed regardless of the type of dominant interaction. Through comparison with Figure 9, it becomes clear that this issue is a consequence of disproportionately high BSSE rather than rBSIE; after application of the counterpoise correction, the Dunning sequences converge at a rate similar to that of the Jensen and Karlsruhe sequences.
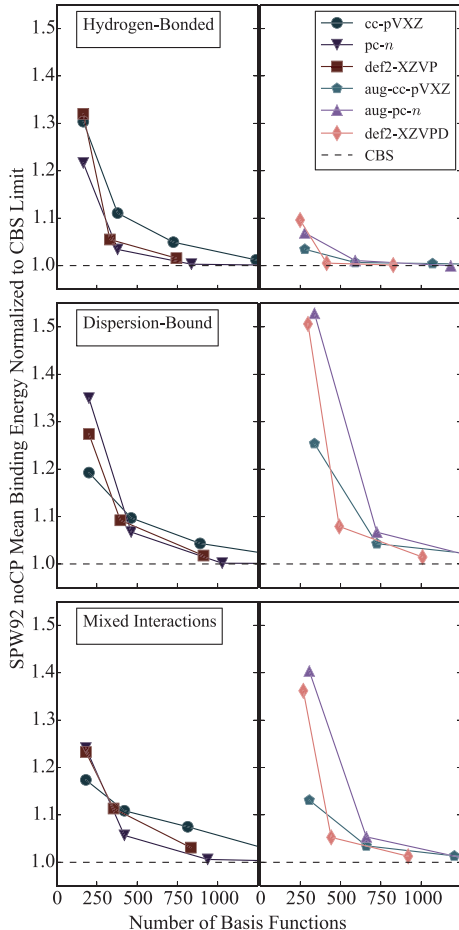

FIG. 8. Convergence of uncorrected (noCP) SPW92 normalized mean binding energies across subsets of the S22 set of molecules for the Dunning, Jensen, and Karlsruhe sequences of basis sets. Within each subset, each binding energy was normalized to the CBS limit (counterpoise-corrected pc-4) before averaging. The three subsets – hydrogen-bonded, dispersion-bound, and mixed interactions – are the same as those in Figure 1. The number of basis functions for each basis set was determined by averaging the number of basis functions for each system within each basis set across all systems in the relevant subset of S22.
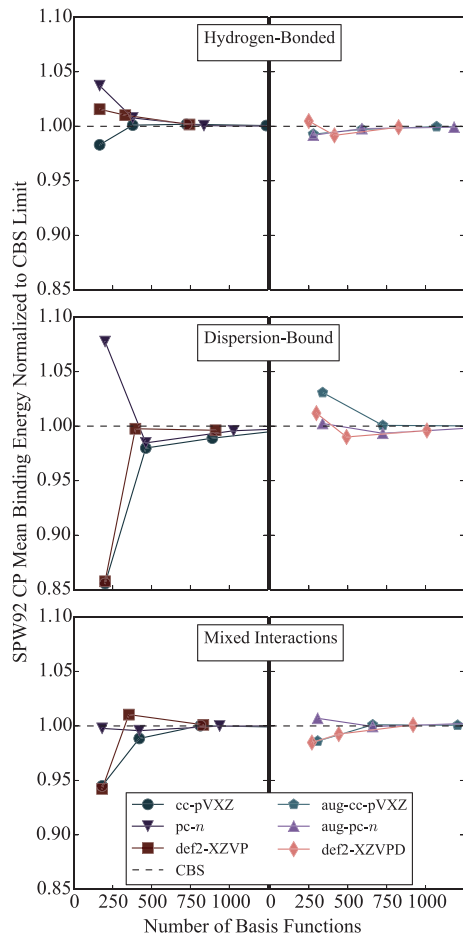
FIG. 9. Convergence of counterpoise-corrected (CP) SPW92 normalized mean binding energies across subsets of the S22 set of molecules for the Dunning, Jensen, and Karlsruhe sequences of basis sets. For further details, see Figure 8.

As is observed across the entirety of the S22 set (*cf.* Figures 5 and 6), comparison of Figures 8 and 9 demonstrates that the accelerated convergence counterpoise correction affords is observed regardless of interaction type, though again at a loss of systematicity. Thus, it stands to reason that BSSE is – for typical GTO basis sets in the context of typical noncovalent interactions – the predominant flavor of basis set error. One other particularly striking feature of Figure 9 is the relatively large deviation from the basis set limit exhibited by the unaugmented double-zeta basis sets. The performance across the hydrogen-bonded and mixed subsets of S22 is not strongly impacted by the decision to include diffuse functions, but for dispersion-bound complexes, particularly in the limit of smaller basis sets, the inclusion of diffuse functions is vital to eliminate rBSIE. This reinforces conventional

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wisdom: diffuse functions are necessary in order to accurately describe dispersion interactions, and, for certain classes of basis sets, other energetic properties.[67] In larger basis sets, additional diffuse functions may not be necessary depending on the system, since these basis sets tend to already contain basis functions with relatively small exponents, but in basis sets of double-zeta quality (def2-SVP, pc-1, cc-pVXZ), it is imperative to explicitly expand the basis sets to include such functions: def2-SVP is a terrible basis for describing dispersion.

One further interesting observation regarding basis set superposition error can be made on the basis of this work: BSSE is effectively extensive, growing with the number of significant interactions in the system. This is illustrated in Figure 10, where we have plotted BSSE versus the number of interacting atoms for three distinct method-basis pairings. We have defined the number of interacting atoms as simply the number of unique atoms within a given system for which the distance to another atom on a different molecule is less than 110% the sum of the van der Waals radii of the atoms. Even this incredibly simple and naive approach yields a striking correlation between BSSE and system size, as measured by the number of interacting atoms. This property of extensivity justifies the development and use of geometric approaches to predicting BSSE, such as the interaction-specific approach of Merz[68,69] and the more general approach of Grimme.[70,71]

Given this extensive nature of BSSE, it is possible to extract a meaningful measure of the BSSE associated with each method-basis pairing examined in this study, namely the mean BSSE per interacting atom across the S22 set. This is illustrated for a variety of basis sets with the SPW92, B3LYP, and B97M-V methods in Figure 11. Each column is color-coded from highest BSSE (dark red) to lowest BSSE (dark blue) for ease of reading; one thing that is immediately evident is that although the *absolute* BSSE within a given basis set is dependent on the density functional approximation employed, the *relative* BSSE is largely independent of method. Note that this extensivity does not extend to the remaining basis set incompleteness error: there is no such correlation between rBSIE and the number of interactions, as is illustrated in Figure 12.

A measure of mean BSSE per interaction effectively allows us to make back-of-the-envelope qualitative predictions of BSSE. For instance, for the equilibrium CO_2-benzene complex,[72] we predict using this naive approach a BSSE of 1.7 kcal/mol for B3LYP in the def2-SVPD basis, which is not too far removed from the actual value of 1.1 kcal/mol. If we consider a larger system, such as the parallel-displaced coronene dimer with an interplane
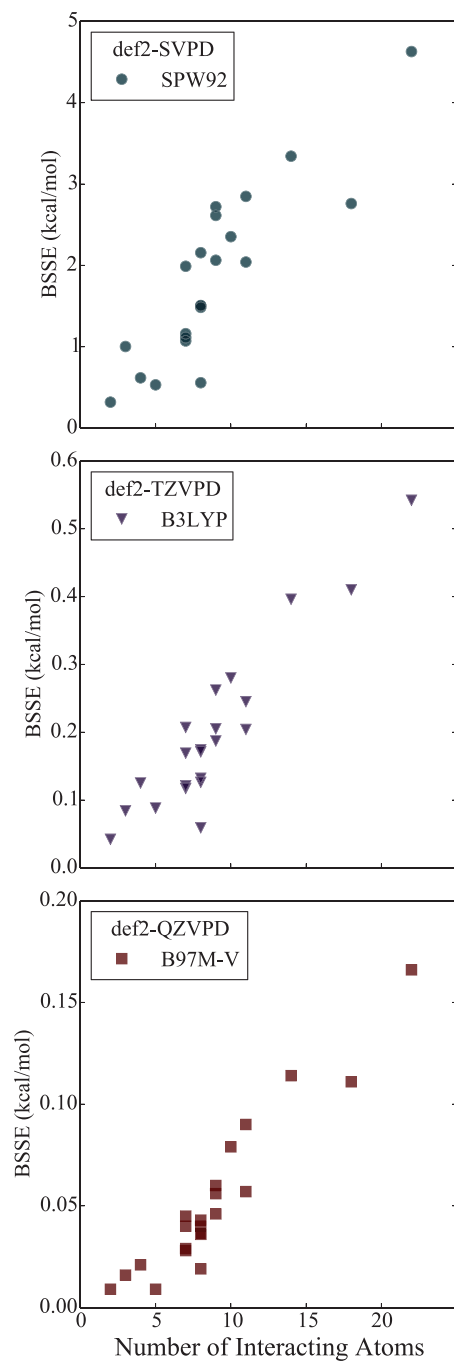
FIG. 10. Relationship between basis set superposition error (BSSE) and number of interacting atoms for several method/basis set combinations. The number of interacting atoms is defined as the number of unique atoms in each system for which the distance to another atom on a different fragment is less than 1.1 times the sum of the van der Waals radii of the atoms.

	Size[a]	Basis	Mean BSSE per Interaction (cal/mol)		
			SPW92	B3LYP	B97M-V
Pople	204	6-31G*	260.0	263.0	212.0
	300	6-31++G**	76.9	76.2	67.6
	348	6-311++G**	83.2	63.5	54.1
	684	6-311++G(3df,3pd)	64.8	52.8	40.7
Dunning	228	cc-pVDZ	310.0	296.0	249.0
	528	cc-pVTZ	109.0	104.0	102.0
	1020	cc-pVQZ	50.3	47.6	47.9
	1752	cc-pV5Z	12.2	10.8	12.8
	384	aug-cc-pVDZ	89.4	92.6	78.7
	828	aug-cc-pVTZ	19.8	20.9	21.1
	1512	aug-cc-pVQZ	9.1	8.0	11.9
	2484	aug-cc-pV5Z	1.4	1.7	6.1
Karlsruhe	228	def2-SVP	319.0	291.0	238.0
	444	def2-TZVP	62.2	54.5	53.4
	1044	def2-QZVP	17.4	15.0	14.4
	336	def2-SVPD	206.0	185.0	158.0
	552	def2-TZVPD	32.1	22.1	22.3
	1152	def2-QZVPD	5.9	4.5	5.4
Jensen	228	pc-1	206.0	194.0	182.0
	528	pc-2	41.2	28.4	35.6
	1176	pc-3	3.4	2.9	6.5
	2064	pc-4	0.6	0.4	1.7
	384	aug-pc-1	201.0	205.0	224.0
	828	aug-pc-2	29.9	12.4	44.4
	1668	aug-pc-3	1.1	1.5	8.7

[a]Size here indicates the number of basis functions used for the parallel-displaced benzene dimer.

FIG. 11. Mean basis set superposition error (BSSE) per interaction across the S22 set of molecules for SPW92, B3LYP, and B97M-V in a variety of basis sets. The number of interactions per system were determined as in Figure 10. Each column is color-coded with a gradient from dark red (highest BSSE) to white (median BSSE) to dark blue (lowest BSSE).

separation of 3.308 Å,[73,74] we predict a much larger BSSE: 9.9 kcal/mol for the SPW92 method in the def2-SVPD basis, which compares favorably with the actual value of 13.8 kcal/mol. This is not to suggest that the numbers in Figure 11 should be used for any quantitative purpose: they simply provide a rough indication of how much BSSE you can expect for a given system in a given basis set. In order to get a quantitative estimate of BSSE, it is necessary to be more clever in the counting of interactions, such as by incorporating an explicit distance dependence, as in the gCP approach of Kruse and Grimme.[70] Such a quantitative estimate has the potential to be incredibly useful, since for certain basis sets – e.g. the augmented Karlsruhe basis sets – BSSE constitutes the vast majority of basis set error. Thus, judicious choice of basis set could, in combination with some correction scheme for BSSE, yield effectively complete-basis results at a fraction of the effort.

Although this is intended to be primarily a study on basis sets, the availability of both DFT/CBS (Table I) and CCSD(T)/CBS[64] data allows us to make one more meaningful analysis: namely, we can distinguish between apparent error and method error, as has been
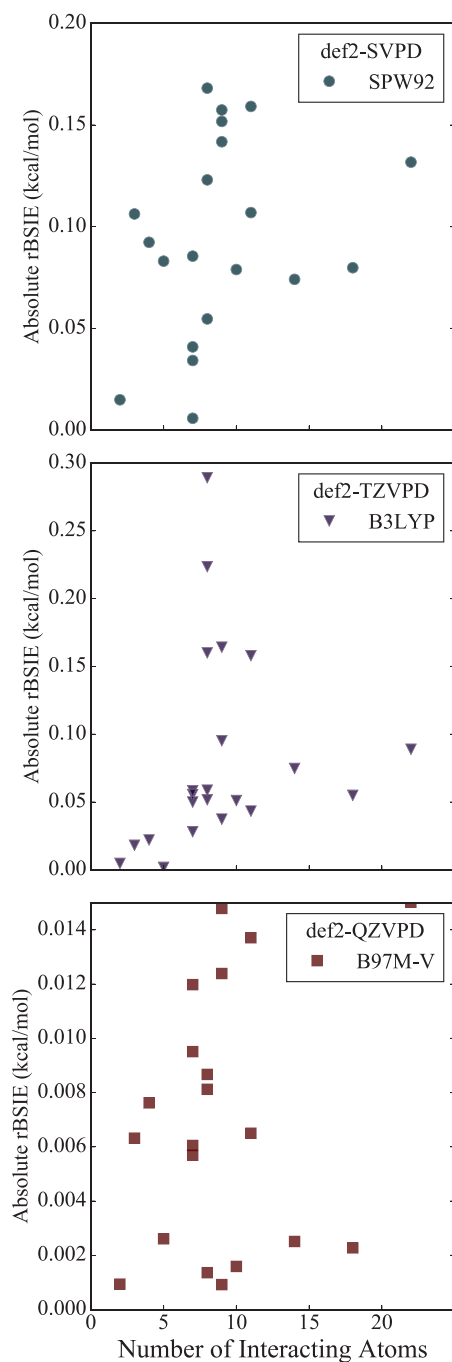
FIG. 12. Relationship between remaining basis set incompleteness error (rBSIE) and number of interacting atoms for several method/basis set combinations. The number of interactions per system were determined as in Figure 10.

done previously for wavefunction-based methods.[75–77] The convergences – within the pc-n sequence of basis sets – of uncorrected and counterpoise-corrected binding energies for each
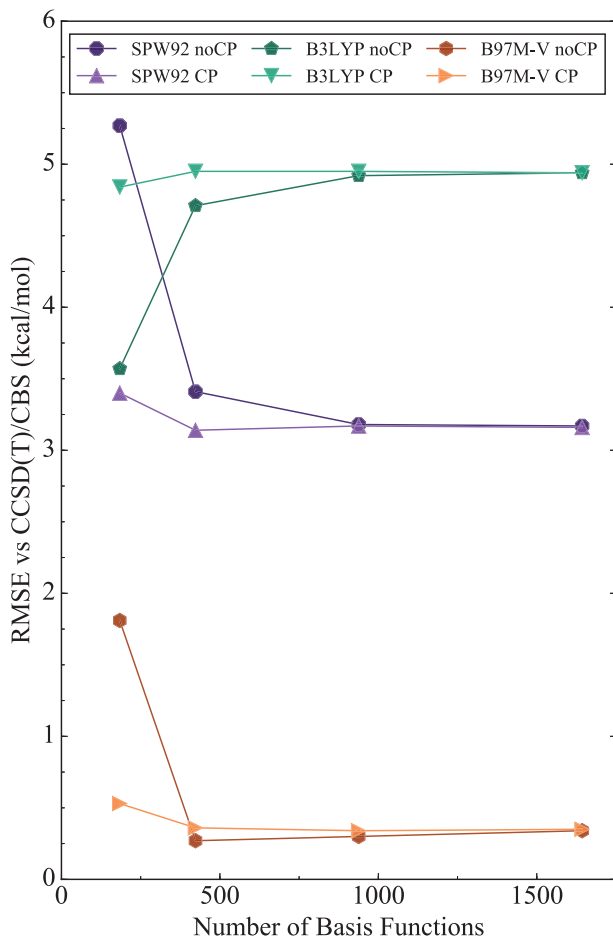
FIG. 13. Root mean square errors (RMSE) in uncorrected (noCP) and counterpoise-corrected (CP) binding energies for each method within the pc-*n* sequence of basis sets. Errors here correspond to errors relative to CCSD(T)/CBS results.[64] The number of basis functions is determined as in Figure 5.

method towards the CCSD(T)/CBS binding energies are visualized in Figure 13. Unlike RMSEs reported elsewhere in this study, the RMSEs in Figure 13 correspond to differences from "exact" binding energies. It is immediately evident that B97M-V is the most accurate of the methods examined, which is to be expected, given the nature of its construction and training. SPW92 and B3LYP are not intended to be used for the description of intermolecular interactions. SPW92 systematically overbinds across S22, and is subsequently worse in smaller basis sets without CP. B3LYP, on the other hand, overbinds hydrogen-bonded complexes in small basis sets and underbinds them in large basis sets and when a correction for BSSE is applied, which accounts for the seemingly bizarre fact that B3LYP appears to

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be "better" in smaller basis sets. This highlights one of the dangers of judging the merits of a functional on the basis of its apparent error: oftentimes a low apparent error is simply a product of a fortuitous cancellation of basis set error and method error. Such cancellation is also manifest in the behavior of B97M-V, which apparently performs "best" in the pc-2 basis without counterpoise correction. The B97M-V noCP RMSE increases from pc-2 to pc-3, then again from pc-3 to pc-4. This behavior is in stark contrast to that of B3LYP and SPW92, the noCP RMSE errors of which change monotonically with increasing basis size within the same family of basis set, and is directly a result of its training; B97M-V was trained in the aug-cc-pVTZ basis set without counterpoise correction, and hence compensation for aug-cc-pVTZ basis set error was implicitly built in to the functional.

IV. DISCUSSION AND CONCLUSION

In this work, we have examined the efficacies of various popular families of basis sets with regards to their abilities to approach complete-basis binding energies across the S22 set of noncovalent interactions. More specifically, we have tested a number of Pople split-valence basis sets, the Dunning sequence of correlation-consistent basis sets, the Karlsruhe def2-basis sets, and the Jensen polarization-consistent sequence of basis sets with three distinctly different density functional approximations: SPW92, a form of local-density approximation, B3LYP, a global hybrid GGA, and B97M-V, a meta-GGA with nonlocal correlation.

Although ours is the first systematic study of the convergence patterns of these basis sets in the context of intermolecular interactions as described by DFT, there have been several other relevant studies comparing the Dunning and Jensen sequences of basis sets in slightly different contexts in the past decade. Shahbazian and Zahedi[78] have demonstrated that polarization-consistent basis sets outperform correlation-consistent basis sets for binding energies of diatomic molecules at the Hartree-Fock level of theory; we show here that this behavior applies to other self-consistent methods, namely DFT, and larger molecular systems. Kupka and Lim[79] have concluded that the pc-n sequence is similarly well-suited to the calculation of molecular and spectroscopic properties, namely geometries and vibrational frequencies, so our particular basis set recommendations may be relevant in the context of such properties. Elsohly and Tschumper[80] have previously shown that binding energies computed with Møller-Plesset perturbation theory to second order (MP2)[81] in the

Dunning correlation-consistent sequence of basis sets converge more quickly than when the Jensen polarization-consistent sequence is employed. Correlation-consistent basis sets have their place; they reign supreme in the realm of correlated wavefunction-based calculations.

We have established that counterpoise correction accelerates convergence to the basis set limit for DFT in the context of noncovalent interactions – regardless of basis set sequence – though at the cost of a loss of systematicity of error. Previously, Eshuis and Furche[82] showed that counterpoise correction leads to faster convergence of random phase approximation (RPA) correlation energies across S22, though in the case of RPA, the corrected correlation errors have the added benefit of still being systematic. On the other hand, Elsohly and Tschumper[80] demonstrated that for five weakly bound clusters, counterpoise correction does not accelerate the convergence of MP2 correlation energies. We thus reiterate that our recommendation of counterpoise correction applies strictly to self-consistent methods, particularly well-behaved density functional approximations. We expect our conclusions to be transferable to Hartree-Fock (HF) theory[83,84]; after all, HF and DFT have been previously shown to have similar basis set requirements,[85] and here we have demonstrated that functionals with local and exact exchange within the Kohn-Sham formalism exhibit similar convergence patterns.

In this study, we have also established that it is remarkably difficult to truly reach the basis set limit; even the massive aug-cc-pV5Z basis is plagued by BSSE. In fact, in the context of S22 DFT binding energies, the only effectively BSSE-free basis set examined is pc-4. However, at 2064 basis functions for the benzene dimer, pc-4 is not a particularly pragmatic basis for day-to-day use. A more economical alternative is the Karlsruhe def2-SVPD basis set. With only 336 basis functions for the benzene dimer, def2-SVPD is relatively affordable; moreover, when corrected for BSSE, it yields results that are comparable to those obtained with the analogous Dunning and Jensen basis sets, aug-cc-pVDZ and aug-pc-1, despite being significantly smaller. In fact, for the S22 set of systems, counterpoise-corrected def2-SVPD binding energies are on par with those obtained with significantly larger basis sets: on the order of 0.1 kcal/mol error across the S22 set of molecules. This is consistent with the findings of Mardirossian and Head-Gordon,[13] who recommended counterpoise-corrected def2-SVPD as an alternative to aug-cc-pVTZ on the basis of its ability to reproduce reference coupled-cluster binding energies when combined with the B97M-V functional. We thus demonstrate here that this reproduction does not stem exclusively from fortuitous error cancellation,

but rather emerges as a result of the strength of B97M-V and the small intrinsic rBSIE of def2-SVPD in the context of noncovalent interactions.

The complete-basis data presented in Table I, Figure 13, and the supplemental material[63] shed light on an interesting aspect of functional development. The parameters of the functional B97M-V were optimized without counterpoise correction in the aug-cc-pVTZ basis set. As a result, B97M-V exhibits a smaller RMSE versus CCSD(T)/CBS across S22 without counterpoise correction in aug-cc-pVTZ than in any other basis, with or without a correction for BSSE: the noCP aug-cc-pVTZ RMSE of B97M-V is 0.23 kcal/mol, which is more than 30% smaller than the B97M-V/CBS RMSE of 0.35 kcal/mol. Similarly small RMSEs are exhibited for B97M-V in other basis sets of triple-zeta quality without counterpoise correction, such as noCP def2-TZVPD (0.25 kcal/mol). In larger basis sets, or when a correction for BSSE is applied, B97M-V systematically underbinds across the S22 set (with the exception of two systems: the uracil dimer stack and the ethene-ethyne complex, both of which are significantly overbound at the level of noCP aug-cc-pVTZ). Thus, in the case of methods trained in the presence of significant BSSE and rBSIE – such as B97M-V – it is not necessarily better to use a larger basis, since compensation for these basis set errors within the training basis has been implicitly built into the method. Consequently, we recommend future empirical methods be trained as close to the basis set limit as possible, such as in the def2-QZVPD basis set with counterpoise correction. When training in any finite basis, it is desirable to ensure that the method error is significantly larger than the basis set error; otherwise, the method will invariably rely on some cancellation of these errors and hence underperform when liberated from basis set error.

In addition to our previous small basis recommendation (CP def2-SVPD), we thus establish as our large basis of choice def2-QZVPD; when corrected for BSSE, this basis set is a practical alternative to pc-4. There is an argument to be made against training new density functionals in basis sets with significant rBSIE, since basis set error becomes confounded with method error, as is seen with B97M-V. Counterpoise-corrected def2-QZVPD thus constitutes an ideal level at which train new density functionals: it is sufficiently large to reproduce complete-basis results with errors an order of magnitude smaller than the intrinsic method errors, yet it is a small enough basis to be feasible. The principle downside of performing a counterpoise correction when training a new functional is the differential treatment of noncovalent interactions and thermochemistry; this could potentially be reme-

died by correcting for BSSE in a manner that allows for the consideration of intramolecular BSSE, such as by utilizing an atomic[86,87] or geometric[70] correction. Such will be the focus of work to come. An additional suitable course of future work would be to extend this study beyond second-row elements, to see whether the observed trends among and within the different sequences of basis sets hold for heavier atoms and transition metals.

ACKNOWLEDGMENTS

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