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CENTENNIAL FEATURE ARTICLE

An Assessment of Theoretical Methods for Nonbonded Interactions: Comparison to Complete Basis Set Limit Coupled-Cluster Potential Energy Curves for the Benzene Dimer, the Methane Dimer, Benzene−Methane, and Benzene−H_2S[†]

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Large, correlation-consistent basis sets have been used to very closely approximate the coupled-cluster singles, doubles, and perturbative triples [CCSD(T)] complete basis set potential energy curves of several prototype nonbonded complexes, the sandwich, T-shaped, and parallel-displaced benzene dimers, the methane−benzene complex, the H_2S−benzene complex, and the methane dimer. These benchmark potential energy curves are used to assess the performance of several methods for nonbonded interactions, including various spin-component-scaled second-order perturbation theory (SCS-MP2) methods, the spin-componet-scaled coupled-cluster singles and doubles method (SCS-CCSD), density functional theory empirically corrected for dispersion (DFT-D), and the meta-generalized-gradient approximation functionals M05-2X and M06-2X. These approaches generally provide good results for the test set, with the SCS methods being somewhat more robust. M05-2X underbinds for the test cases considered, while the performances of DFT-D and M06-2X are similar. Density fitting, dual basis, and local correlation approximations all introduce only small errors in the interaction energies but can speed up the computations significantly, particulary when used in combination.

I. Introduction

Drug binding, protein folding, self-assembly, and crystal packing are all phenomena governed by nonbonded interactions.[1,2] Despite the central importance of such processes to chemistry, biology, and materials science, our current understanding of the underlying nonbonded interactions is far from complete. Although certain prototypical nonbonded interactions such as $\pi-\pi$, cation$-\pi$, CH$-\pi$, and S$-\pi$ interactions have been noted,[3] other significant classes of nonbonded interactions may not have been recognized yet. Moreover, even for the types of interactions which are known, questions remain about their strength, directionality, and how they are influenced by substituents or heteroatoms. Answering such questions is challenging because these nonbonded interactions are typically studied in complex environments, where many such interactions occur simultaneously and it is difficult to determine information about any particular single interaction. In several key studies of $\pi-\pi$ interactions, model systems have been synthesized and studied by techniques such as NMR to provide partial information about energetics and substituent effects.[4−11] However, the interpretation of these experiments is not always straightforward as solvation effects and secondary interactions can complicate matters.[11−13] Theoretical studies can thus be immensely valuable in elucidating the fundamental nature of the various types of nonbonded interactions.

High-level ab initio quantum mechanical studies have been instrumental in understanding important prototype systems such as the benzene dimer. Studies by our group[14] and Tsuzuki and co-workers[15] were the first to use sufficiently high levels of electronic structure theory (namely, coupled-cluster theory through perturbative triples, CCSD(T), in conjunction with corrections for basis set effects) to approach convergence toward the ab initio limit. These studies overturned the conventional wisdom in some circles that the T-shaped dimer is significantly more stable than the parallel-displaced configuration (see Figure 1). Instead, these two configurations are nearly isoenergetic. Moreover, the most commonly quoted experimental binding energy of the gas-phase benzene dimer,[16] 1.6 ± 0.2 kcal mol^{-1}, was shown to be clearly underestimated compared to the best theoretical estimates of around 2.5 kcal mol^{-1} (the theoretical results are, however, in agreement with an often-overlooked experimental study by Grover et al.[17] yielding $D_0 = 2.4 \pm 0.4$ kcal mol^{-1}).

Often using our binding energies[14] and subsequent potential energy curves[18] as a guide, several recent studies have used more approximate methods to examine a wider array of geometrical configurations for the benzene dimer.[19−22] One of the most interesting conclusions of these studies is that of the three configurations receiving the most interest historically (the sandwich, T-shaped, and parallel-displaced configurations), only the parallel-displaced appears to correspond to a local potential energy minimum.[19,22] The global minimum appears to be a

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[†] 2008 marked the Centennial of the American Chemical Society's Division of Physical Chemistry. To celebrate and to highlight the field of physical chemistry from both historical and future perspectives, *The Journal of Physical Chemistry* is publishing a special series of Centennial Feature Articles. These articles are invited contributions from current and former officers and members of the Physical Chemistry Division Executive Committee and from *J. Phys. Chem.* Senior Editors.

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slightly tilted T-shaped configuration;[19,20,22,23] however, the tilt provides only a very small additional energetic stabilization. The theoretical data indicate that the potential energy surface is very flat, and interconversion among various configurations should be facile, leading to a fluxional structure. Indeed, in one of the most complete recent examinations of stationary points on the benzene dimer potential surface,[22] Gräfenstein and Cremer show that all of the stationary points in the T-shaped and parallel-displaced region of the potential surface lie within ~0.12 kcal mol^{-1} of each other. Although there are lower-energy stationary points, the conventionally studied higher-symmetry configurations of the benzene dimer are important for theoretical benchmarking studies and as limiting cases in understanding how $\pi-\pi$ interactions vary across the potential energy surface.

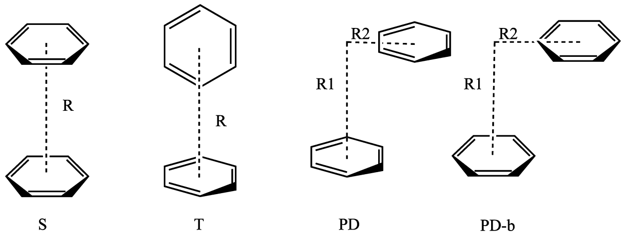

Figure 1. Orientation for the sandwich, T-shaped, and two parallel displaced benzene dimer configurations.

The benzene dimer and other prototypes of nonbonded interactions have captured the interest of many theorists and computational chemists over the past few years, resulting in a large number of studies. Some of this recent work is summarized in review articles by Lee et al.[24] and by Tschumper.[25] Recent studies of nonbonded interactions in our group have used high levels of theory to examine substituent effects in benzene dimers;[26,27] the additivity of $\pi-\pi$ interactions;[28] CH$-\pi$ interactions between methane and benzene, phenol, and indole;[29] the correspondence between S$-\pi$ interactions in H_2S−benzene and those observed in the Protein Data Bank (PDB);[30] the lattice energy of crystalline benzene;[31] and the effect of heteroatoms on $\pi-\pi$ interactions in pyridine−benzene and the pyridine dimer.[32]

High-level theoretical results for prototypes such as the benzene dimer are useful not only for understanding the physics of particular types of nonbonded interactions and how they affect energetics and geometries in larger systems, but they are also useful as benchmarks for calibrating and testing more approximate theoretical approaches. This is particularly important given that the computational cost of the CCSD(T) method formally scales as $\mathcal{O}(N^7)$, where N is proportional to the system size; this makes conventional CCSD(T) inapplicable to systems much larger than the benzene dimer. Moreover, even for those systems where CCSD(T) energies are feasible, optimized geometries or vibrational frequencies are often infeasible due to their even greater computational demands. Given the importance of nonbonded interactions to so many areas of molecular science and the need for reliable theoretical results, there is therefore a great interest in developing new theoretical tools which might provide results of near-CCSD(T) quality but at a greatly reduced computational expense.

In this work, we review the efficiency and reliability of several theoretical models and approximations as applied to nonbonded interactions. The performance of standard force field methods has been assessed recently in separate work.[33] Here, we consider a number of quantum mechanical models, including density functional theory (DFT) approaches, empirically corrected DFT, and spin-component-scaled (SCS) MP2[34−36] and CCSD.[37] We also consider approximations such as local correlation, dual basis techniques, and resolution-of-the-identity (RI) or density fitting (DF). These approximations are evaluated by comparison to

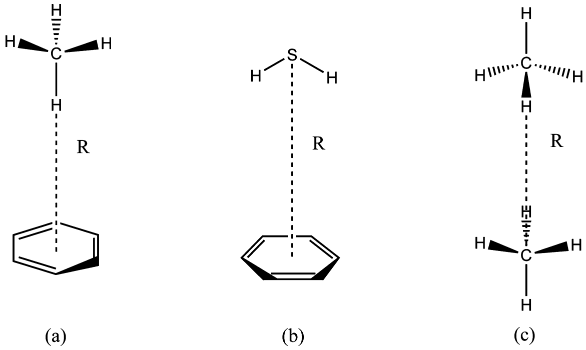

Figure 2. Orientations for (a) methane−benzene, (b) H_2S−benzene, and (c) methane dimer.

benchmarks near the ab initio limit for several prototypes of noncovalent interactions. Given the demonstrated level of interest in such benchmark data, we have performed significantly larger computations in order to improve our previously published benchmark potential curves for the benzene dimer,[18] H_2S−benzene,[30,38] and CH_4−benzene.[29] Here, we present high-quality estimates of the CCSD(T) potential curves extrapolated to the complete basis set limit. In addition, we consider some additional questions which have arisen about benzene dimer benchmarks, including (a) whether horizontal displacement over a vertex is more favorable energetically than horizontal displacement over a bond in parallel-displaced configurations,[39] (b) whether the aug-cc-pVDZ basis is large enough to converge the coupled-cluster correction, ΔCCSD(T), defined as the difference between CCSD(T) and second-order perturbation theory, MP2, and (c) how the binding energies of the prototype sandwich, T-shaped, and parallel-displaced configurations compare to the binding energies of dimers found in crystalline benzene.

II. Theoretical Methods

The MOLPRO[40] and PSI3[41] ab initio program packages were used to generate all ab initio potential energy curves (PECs). For the benzene dimer configurations (Figure 1), the benzene monomer geometries were set to those suggested by Gauss and Stanton, $R(C-C) = 1.3915$ Å and $R(C-H) = 1.0800$ Å.[42] For the methane dimer (Figure 2c) and the methane−benzene complex (Figure 2a), the methane geometries were set to those obtained at the MP2/cc-pVDZ level of theory of Ringer et al.[29] For the H_2S−benzene complex (Figure 2b), experimental equilibrium values were utilized for the H_2S monomer,[43] $R(S-H) = 1.3356$ Å and $\theta(H-S-H) = 92.12°$, and the Gauss−Stanton geometry[42] for benzene. Monomer geometries were kept frozen as the intermolecular distances were varied.

The spin-component-scaled methods result from Grimme's idea to scale same-spin and opposite-spin contributions to the correlation energy by separate scaling factors.[34] In addition to Grimme's original scaling factors for MP2 ($c_{SS} = 1/3$, $c_{OS} = 6/5$, SCS-MP2), we also consider the alternative scaling parameters which have been proposed for noncovalent interactions. Fitting to a test set of 10 nucleic acid base pairs, Hill and Platts recommend[35] $c_{SS} = 1.76$, $c_{OS} = 0$, which they denote SCSN-MP2; fitting to the S22 set of nonbonded interactions, Distasio and Head-Gordon recommend[36] $c_{SS} = 1.29$, $c_{OS} = 0.40$, which they denote SCS(MI)-MP2. We also consider the recently introduced spin-component-scaled coupled-cluster singles and doubles (SCS-CCSD) method,[37] with the recommended scale factors of $c_{SS} = 1.13$, $c_{OS} = 1.27$ obtained by fitting to essentially the same set of reaction energies employed by Grimme in the original SCS-MP2 parametrization.[34]

Computations applied the augmented correlation-consistent basis sets aug-cc-pVXZ (X = D,T,Q) of Dunning et al.[44,45] and the cc-pVXZ basis sets for the SCS(MI)-MP2[36] method. In some cases, we have explored truncations of the augmented correlation-consistent basis sets for greater computational efficiency (trunctations of correlation-consitent basis sets have also been tested by Wilson and co-workers for their effect on energies of small molecules).[46] In generating our earlier set of potential curves for the benzene dimer,[18] we evaluated CCSD(T) energies in a basis that we called aug-cc-pVDZ*, which is aug-cc-pVDZ for carbon and cc-pVDZ for hydrogen. Following Tschumper and co-workers,[47] in this work, we will call this a "heavy-aug-cc-pVDZ" basis, abbreviated haDZ, meaning that only the heavy (non-hydrogen) atoms are augmented by diffuse functions. (Such a basis is also sometimes denoted as aug′-cc-pVDZ.) Our previous work also sped up MP2 computations by truncating the aug-cc-pVQZ basis, removing g functions for carbon and f functions for hydrogen, yielding a basis that we called aug-cc-pVQZ*. Here, we compare to potentials generated with CCSD(T) in the full aug-cc-pVDZ basis or larger and with MP2 computed with the full aug-cc-pVQZ basis (allowing extrapolation to the complete basis set limit).

For all SCS-MP2 methods and variants, density fitting was applied to the Hartree−Fock and MP2 methods and extrapolated to the complete basis set (CBS) limit, adding a two-point extrapolation[48] of the aug-cc-pVTZ and aug-cc-pVQZ correlation energies to the aug-cc-pVQZ reference energy. For Hartree−Fock, density fitting employed the cc-pVXZ JK auxiliary[49] basis set, and for the MP2 correlation energy, density fitting employed the auxiliary MP2-fitting[50] basis set. The dual basis SCF approximation,[51] as implemented in Q-Chem 3.1,[52] employed corresponding basis subsets for the self-consistent field iterations. Core orbitals were constrained to remain doubly occupied in all correlated computations. All the above methods were counterpoise-corrected using the method of Boys and Bernardi.[53]

All density functional theory (DFT) computations were performed with Q-Chem 3.1[52] and MOLPRO.[40] Energy computations were performed with B3LYP,[54] PBE,[55] M05-2X,[56] and M06-2X[57,58] functionals along with Dunning's aug-cc-pVTZ basis set.[45] Computations using the M05-2X and M06-2X functionals utilized a Lebedev grid with 302 angular points for each of the 100 radial points included (100,302). This grid was chosen to avoid artifacts due to numerical integration for noncovalent interactions, particularly when using meta-GGA functionals.[59,60] In the case of the methane dimer, an even larger, (200,1202), grid was necessary to completely remove these artifacts. Empirical dispersion corrections were added to B3LYP and PBE to improve their performance for treating noncovalent complexes; we employed the dispersion corrections of Grimme,[61,62] as implemented in Q-Chem 3.2 by two of the authors (C.D.S. and E.G.H.). The empirical dispersion terms were scaled by 0.75 and 1.05 for PBE and B3LYP, respectively, as recommended by Grimme.[62] The dispersion-corrected functionals will be referred to as PBE-D and B3LYP-D for the remainder of this work. Counterpoise correction was not applied to the DFT computations.

The performance of these various methods and approximations is assessed by comparison to very accurate benchmark values which estimate the CCSD(T) binding energies at the complete basis set limit. For the smallest test system, the methane dimer, the CCSD(T)/CBS limit value is most easily estimated by the two-point extrapolation scheme of Halkier et al.[48] using the CCSD(T) energies in the aug-cc-pVTZ and aug-cc-pVQZ basis sets. This was the procedure used for the entire PEC for the methane dimer.

For larger benchmark systems, explicit CCSD(T)/aug-cc-pVQZ computations are much more difficult, and additional approximations are required. Because higher-order electron correlation effects converge rapidly with respect to basis set, it has become common practice to use an additive approximation

$$E_{\mathrm{CCSD(T)}}^{\text{large-basis}} \approx E_{\mathrm{MP2}}^{\text{large-basis}} + E_{\mathrm{CCSD(T)}}^{\text{small-basis}} - E_{\mathrm{MP2}}^{\text{small-basis}} \qquad (1)$$

In the present instance, we use Halkier's two-point extrapolation scheme to estimate MP2/CBS values from aug-cc-pVTZ and aug-cc-pVQZ basis sets. Next, we estimate the CCSD(T)/CBS result by adding a "coupled-cluster correction", ΔCCSD(T), evaluated as the difference between CCSD(T) and MP2 in a smaller basis set. In the past, we have argued that augmented double-ζ basis sets seem large enough to converge ΔCCSD(T).[18] However, recent work by Janowski and Pulay suggests that additional improvements in the basis can change the value of ΔCCSD(T) somewhat.[63] We further examine this question in the present study. The basis used to obtain ΔCCSD(T) is noted in parentheses after the CCSD(T)/CBS designation. Thus, CCSD(T)/CBS(ΔaDZ) indicates that ΔCCSD(T) is evaluated in an aug-cc-pVDZ basis. Similarly, CCSD(T)/CBS(Δha(DT)Z) indicates that the ΔCCSD(T) correction was evaluated using a haDZ/haTZ extrapolation. In practice, the ΔCCSD(T) term did not change much whether a (h)aTZ basis or a (h)aDZ/(h)aTZ extrapolation was used. For the benzene dimer, complete PECs were computed at the CCSD(T)/CBS(Δha(DT)Z) level. For the methane−benzene and H_2S−benzene complexes, complete PECs were computed at the CCSD(T)/CBS(Δa(DT)Z) level.

In tests of local correlation methods, localization procedures followed that of Hill et al.[64] The Pipek−Mezey[65] localization method was applied with the Newton−Raphson algorithm to ensure convergence. The contributions from the most diffuse basis functions were eliminated by setting the corresponding overlap matrix elements used in the Pipek−Mezey procedure to 0. A completeness criterion of 0.985 for the orbital domain selection was applied as described by Boughton and Pulay.[66] The π orbital domains of benzene were merged, and only atoms with Löwdin charges greater than 0.2 for hydrogen and 0.01 for all other atoms were included in the domain. Local methods have been shown to incur little basis set superposition error (BSSE) and therefore were not counterpoise (CP)-corrected.[67]

III. Results and Discussion

A. The Benzene Dimer. The present study employs considerably more complete computations than our previous benchmark study of 2004.[18] For the potential energy curves, we have used the full aug-cc-pVQZ basis for the MP2 computations, allowing an aTZ/aQZ extrapolation to the complete basis set limit. Moreover, we have used much larger basis sets to compute the ΔCCSD(T) correction; now, this correction is evaluated using haDZ/haTZ extrapolations. Figure 3 demonstrates convergence to the complete basis set limit of the MP2 component of the binding energy for the sandwich configuration of the benzene dimer as a function of the intermonomer separation. Basis set effects are largest for intermonomer distances around 4.5 Å or less. The counterpoise-corrected curves converge to the CBS limit from above, and the uncorrected curves converge from below. However, the counterpoise-corrected binding energies converge much more rapidly than the uncorrected ones. Thus, for the benchmark studies of noncovalent π interactions discussed here, subsequent results are counterpoise-corrected. The aug-cc-pVDZ results feature both a large basis set superposition error and a large basis set incompleteness error. The larger aug-cc-pVTZ basis still features a quite large basis set superposition error, and this error remains significant even for the aug-cc-pVQZ basis set. However, when the counterpoise correction is applied, the aug-cc-pVTZ and aug-cc-pVQZ basis sets provide results close to the CBS limit. Indeed, the counterpoise-corrected aQZ and CBS extrapolations lie nearly on top of each other on the curve, as does the uncorrected CBS extrapolation. This demonstrates a pleasing convergence of the results and indicates that the Halkier two-point extrapolation scheme is indeed effective at reaching the CBS limit.[48] Such convergence was not quite achieved in our previous work using only truncated aug-cc-pVQZ basis sets without extrapolation.[18]

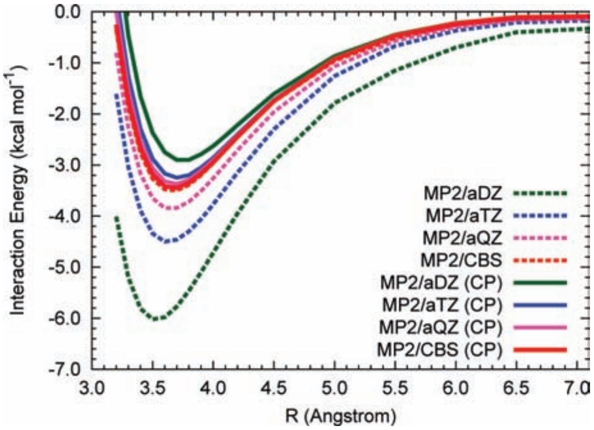

Figure 3. Effect of counterpoise (CP) correction on MP2 potential energy curves for the sandwich benzene dimer.

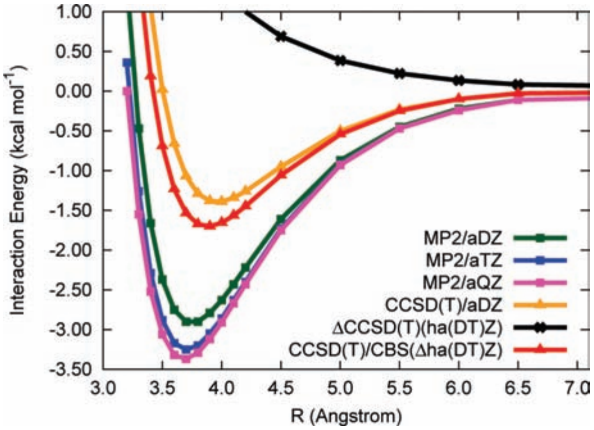

Figure 4. MP2 and CCSD(T) potential energy curves for the sandwich benzene dimer. ΔCCSD(T)(ha(DT)Z) denotes the difference between CCSD(T) and MP2, evaluated using extrapolated correlation energies determined in the haDZ and haTZ basis sets (see text). All results are counterpoise-corrected.

Figure 4 shows potential curves for the sandwich benzene dimer using both MP2 and CCSD(T) methods. The basis set and correlation effects for the T-shaped and parallel-displaced configurations are similar. Also plotted in Figure 4 is the difference between the haDZ/haTZ extrapolated CCSD(T) and MP2 correlation energies, labeled ΔCCSD(T)(ha(DT)Z). Here, we note that electron correlation effects are much larger than the basis set effects (when the counterpoise correction is applied), making the use of CCSD(T) critical for benchmark-quality binding energies. Adding the higher-order correlation corrections ΔCCSD(T)(ha(DT)Z) to the extrapolated MP2/CBS

TABLE 1: Benzene Dimer Intermolecular Distances (in Å)[a]

method	basis	S	T	PD R_1	PD R_2
MP2	aug-cc-pVDZ′	3.9	5.0	3.5	1.6
	heavy-aug-cc-pVDZ[b]	3.8	5.0	3.4	1.6
	aug-cc-pVDZ	3.7	4.9	3.4	1.6
	aug-cc-pVTZ	3.7	4.9	3.4	1.6
	aug-cc-pVQZ*[c]	3.7	4.9	3.4	1.6
	aug-cc-pVQZ[d]	3.7	4.9	3.4	1.5
	CBS(a(TQ)Z)[d,e]	3.7	4.8	3.4	1.5
CCSD(T)	heavy-aug-cc-pVDZ[b]	4.0	5.1	3.6	1.8
	aug-cc-pVDZ	4.0	5.1	3.6	1.8
	aug-cc-pVTZ[d]	3.9	5.0		
estd. CCSD(T)	aug-cc-pVQZ*[c]	3.9	5.0	3.6	1.6
QCISD(T)	aug-cc-pVTZ[f]	3.92	4.99	3.53	1.72
estd. CCSD(T)	CBS(ΔaDZ)[d]	3.9	5.0	3.5	1.7
estd. CCSD(T)	CBS(Δha(DT)Z)[d,g]	3.9	5.0	3.5	1.7
expt[h]			4.96		

[a] All intermonomer parameters obtained using rigid monomers (C−C = 1.3915, C−H = 1.0800 Å, ref 42). Data from ref 18, except as noted. [b] Diffuse functions are added to carbon but not to hydrogen. [c] This is the aug-cc-pVQZ less g functions for carbon and less f functions for hydrogen. [d] This work. [e] From aTZ/aQZ extrapolation. [f] From Janowski and Pulay.[63] [g] Using an extrapolated haDZ/haTZ ΔCCSD(T). [h] Reference 99.

TABLE 2: Estimates of the "Coupled-Cluster Correction", ΔCCSD(T) (in kcal mol^{-1}), for Various Configurations of the Benzene Dimer, with and without Counterpoise (CP) Correction[a]

basis	no CP S	no CP T	no CP PD	CP S	CP T	CP PD
cc-pVDZ	1.20	0.70	1.58	1.12	0.70	1.48
heavy-aug-cc-pVDZ[b]	1.36	0.71	1.74	1.42	0.78	1.85
aug-cc-pVDZ	1.34	0.62	1.69	1.41	0.76	1.84
heavy-aug-cc-pVTZ[b]	1.49	0.82	1.95	1.45	0.79	1.90
aug-cc-pVTZ	1.51	0.85	1.98	1.46	0.79	1.90
CBS(ha(DT)Z)[c]	1.54	0.87	2.04	1.47	0.80	1.93
CBS(a(DT)Z)[d]	1.58	0.94	2.10	1.47	0.80	1.93
heavy-aug-cc-pVQZ[b]	1.55	0.86	2.03	1.48	0.80	1.94
aug-cc-pVQZ	1.57	0.91		1.49		
CBS(ha(TQ)Z)[e]	1.60	0.89	2.08	1.51	0.81	1.96
CBS(a(TQ)Z)[f]	1.62	0.96		1.51		

[a] Evaluated at the estimated CCSD(T)/CBS(Δha(DT)Z) optimized intermonomer distances (see Table 1) and using the best estimates of the monomer geometry (C−C = 1.3915, C−H = 1.0800 Å, ref 42). [b] Diffuse functions added to carbon but not to hydrogen. [c] From haDZ/haTZ extrapolation. [d] From aDZ/aTZ extrapolation. [e] From haTZ/haQZ extrapolation. [f] From aTZ/aQZ extrapolation.

energies yields an estimated potential curve labeled ΔCCSD(T)/CBS(Δha(DT)Z), which we expect to be within about 0.05 kcal mol^{-1} of the true CCSD(T)/CBS curve (see below), except perhaps at short intermolecular distances. Additional small errors will exist with respect to the ab initio limit due to the approximate treatment of three-body electron correlation and the neglect of four-body or higher electron correlations. From studies of smaller systems by Hopkins and Tschumper,[68] it appears that the effect of quadruple electron correlations can be as large as 27% of the effect of triples. For the sandwich benzene dimer, this could be as large as 0.2 kcal mol^{-1} around equilibrium. However, recent work by Pitoňák et al.[23] using factorized quadruple approximations suggests that the corrections are much smaller than this, around 0.04 kcal mol^{-1} (although this contribution may be underestimated by the small 6-31G*(0.25) basis set used).

Due to a favorable cancellation of errors between the MP2 component and the ΔCCSD(T) component of the binding energies, our estimated CCSD(T)/CBS(Δha(DT)Z) potential curves for the sandwich, T-shaped, and parallel-displaced configurations are quite similar to our previous estimated CCSD(T)/aug-cc-pVQZ* results.[18] Around equilibrium, the differences in interaction energies are typically less than 0.1 kcal mol^{-1}. They grow to only a few tenths of 1 kcal mol^{-1} at shorter intermolecular distances. These differences are comparable to or less than the errors usually associated with new methods for nonbonded interactions which have been calibrated against our previously published curves; thus, there is probably not a large improvement to be gained by reparameterizing these methods against the current curves. Howevever, we suggest using the present potentials for parametrization and calibration of new methods in future studies.

Although the binding energies in Figure 4 vary considerably depending on the method used, the equilibrium intermonomer separation is rather similar for each of the curves, falling between 3.7 and 4.0 Å. Table 1 presents the optimum intermolecular distances at each level of theory for the sandwich, T-shaped, and parallel-displaced configurations. In conjunction with its overestimation of binding energies, MP2 tends to underestimate the intermolecular distances (by around 0.2 Å) compared to CCSD(T). Our best estimates of the geometries of the sandwich and T-shaped configurations are identical (within 0.1 Å) to those obtained in our previous benzene dimer potential curves study.[18] For the parallel-displaced configuration, our new estimates of the vertical and horizontal displacements are shorter and longer, respectively, by 0.1 Å. Our best estimates also agree very closely with the recent QCISD(T)/aug-cc-pVTZ results of Janowski and Pulay.[63]

One serious question about additivity schemes such as the one employed here [i.e., adding a "coupled-cluster correction" ΔCCSD(T) to an MP2/CBS energy] is whether the small basis used to evaluate the correction is large enough to obtain a converged value. Fortunately, higher-order correlation effects tend to converge more rapidly with respect to the basis set than lower-order ones such as those captured by MP2, and this justifies the use of such approaches. These additive schemes have been called "focal-point" methods by Allen and coworkers,[69,70] and they form the basis of the successful Gaussian-*n*[71,72] and Weizmann-*n*[73] thermochemical methods. Previously, we had shown the importance of including diffuse functions in the evaluation of ΔCCSD(T),[18] and our results with a truncated aug-cc-pVTZ basis set suggested that basis sets of aug-cc-pVDZ quality are sufficient to converge ΔCCSD(T) within a few hundredths of 1 kcal mol^{-1}. However, computations of unprecedented size by Janowski and Pulay [namely, explicit QCISD(T)/aug-cc-pVQZ computations] indicate that ΔCCSD(T) can continue to grow by almost 0.1 kcal mol^{-1} when extrapolated to the CBS limit. While this is not a large difference, it is important when benchmark-quality results are desired. Because of these results, we have examined the basis set convergence of the ΔCCSD(T) correction in more detail.

Table 2 presents the ΔCCSD(T) correction for a variety of basis sets at the estimated CCSD(T)/CBS(Δha(DT)Z) intermolecular geometries of the sandwich, T-shaped, and parallel-displaced configurations. Note first that the counterpoise-corrected values are much more consistent than those without counterpoise correction; for this reason, we have always used counterpoise-corrected ΔCCSD(T) values in our benchmark studies. Note also that the cc-pVDZ values (without diffuse functions) are far off from all of the other values in the table. In general, all of the other counterpoise-corrected values of

ΔCCSD(T) are within a few hundredths of 1 kcal mol^{-1} for a given dimer configuration. However, in the case of the sandwich, where we were able to perform explicit CCSD(T)/aug-cc-pVQZ computations to allow an aTZ/aQZ extrapolation, ΔCCSD(T) is about 0.1 kcal mol^{-1} larger than it is with an aug-cc-pVDZ or heavy-aug-cc-pVDZ basis set, in agreement with the QCISD(T) results of Janowski and Pulay.[63] Thus, for benchmark-quality studies, it is desirable to go beyond the aug-cc-pVDZ basis set in evaluating ΔCCSD(T); unfortunately, it seems unlikely that this will be routine in the near future for systems as large as the benzene dimer because the computational difficulty would be great. Upon increasing the basis from aug-cc-pVDZ to aug-cc-pVTZ, the ΔCCSD(T) term increases by 0.05, 0.03, and 0.06 kcal mol^{-1} for the sandwich, T-shaped, and parallel-displaced configurations, respectively.

To explore an alternative to the usual sequence aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ for the evaluation of ΔCCSD(T), we have also performed computations with "heavy-augmented" basis sets, which do not add diffuse functions to hydrogens. Table 2 indicates that these heavy-aug-cc-pVXZ basis sets are in fact very effective at approximating the full aug-cc-pVXZ results for ΔCCSD(T), particularly when the counterpoise correction is applied. The largest difference between aug-cc-pVDZ and heavy-aug-cc-pVDZ is 0.02 kcal mol^{-1} for counterpoise-corrected ΔCCSD(T), and this drops to 0.01 kcal mol^{-1} for the triple-ζ basis sets. In addition to having a reduced computational cost, these heavy-augmented basis sets might also be useful in avoiding linear dependency problems which could arise for the larger basis sets (we experienced difficulty in converging the CCSD equations with some of the larger basis sets).

Using the aug-cc-pVDZ and aug-cc-pVTZ MP2 and CCSD(T) energies, one can perform two-point D−T extrapolations to the CBS limit and evaluate ΔCCSD(T) from these values. These results, labeled CBS(a(DT)Z) in the table, further increase the size of ΔCCSD(T) by another 0.01−0.03 kcal mol^{-1} compared to the aug-cc-pVTZ values (or more, if one considers the values without counterpoise correction). Fortunately, the analogous procedure using heavy-augmented basis sets gives the same values for counterpoise-corrected ΔCCSD(T). It is debatable whether the D−T extrapolation represents enough of an improvement to be preferred over the plain (heavy)-aug-cc-pVTZ values.

Having explored the basis set dependence of the ΔCCSD(T) correction, let us turn to benchmark values for the interaction energies of the prototype benzene dimer configurations, presented in Table 3. Note that all interaction energies are evaluated at geometries from the same level of theory (see Table 1), unless noted otherwise. From the table, we see that all MP2 energies (even with counterpoise correction) are significantly overbound, with the exception of the MP2/aug-cc-pVDZ′ results. This basis is the same as heavy-aug-cc-pVDZ minus diffuse d functions on carbon, and it leads to a favorable cancellation of errors such that the interaction energies are fairly close to the estimated CCSD(T)/CBS results. If one wishes to use a strictly conventional, relatively inexpensive ab initio method for systems like the benzene dimer, this would appear to be a good compromise, although this level of theory overestimates the energy difference between the T-shaped and parallel-displaced configurations. Even with the smallest basis sets considered, CCSD(T) will generally be more reliable and robust than MP2. However, below, we discuss several relatively inexpensive electronic structure approximations which can be more reliable than either MP2/aug-cc-pVDZ′ or small-basis CCSD(T).

TABLE 3: Interaction Energies (kcal mol^{-1}) for the Benzene Dimer[a]

method	basis	S	T	PD
MP2	aug-cc-pVDZ′	−1.88	−2.35	−2.89
	heavy-aug-cc-pVDZ[b]	−2.83	−3.00	−4.12
	aug-cc-pVDZ	−2.90	−3.07	−4.22
	aug-cc-pVTZ	−3.25	−3.44	−4.65
	aug-cc-pVQZ*[c]	−3.35	−3.48	−4.73
	aug-cc-pVQZ	−3.37	−3.53	−4.65
	CBS(a(TQ)Z)[d,e]	−3.45	−3.62	−4.91
CCSD(T)	heavy-aug-cc-pVDZ[b]	−1.33	−2.24	−2.22
	aug-cc-pVDZ[d]	−1.39	−2.31	−2.30
	aug-cc-pVTZ[d,f]	−1.60	−2.53	−2.54
estd. CCSD(T)	aug-cc-pVQZ*[c]	−1.70	−2.61	−2.63
estd. CCSD(T)	CBS(ΔaDZ)[d,g]	−1.76	−2.73	−2.79
estd. CCSD(T)	CBS(Δha(DT)Z)[d,e,h]	−1.70	−2.70	−2.71
estd. CCSD(T)	CBS(Δa(DT)Z)[d,e,f,i]	−1.70	−2.70	−2.71
QCISD(T)	CBS(a(TQ)Z)[j]	−1.65	−2.68	−2.66
estd. CCSD(T)	CBS(Δa(TQ)Z-OVOS)[k]	−1.68	−2.71	−2.73
CCSD(T)	CBS(ha(TQ)Z)[d,f,l]	−1.65	−2.69	−2.67
CCSD(T)	CBS(a(TQ)Z)[d,f,m]	−1.66		

[a] Unless otherwise noted, all computations used intermonomer distances optimized at each level of theory with rigid monomers (C−C = 1.3915, C−H = 1.0800 Å, ref 42). Data from ref 18, except as noted. [b] Diffuse functions are added to carbon but not to hydrogen. [c] This is the aug-cc-pVQZ less g functions for carbon and less f functions for hydrogen. [d] This work. [e] From aTZ/aQZ extrapolation for MP2 contribution. [f] At the estd. CCSD(T)/CBS-(Δha(DT)Z) optimal interfragment distances. [g] Using ΔCCSD(T) evaluated in the aug-cc-pVDZ basis. [h] Using an extrapolated haDZ/haTZ ΔCCSD(T). [i] Using an extrapolated aDZ/aTZ ΔCCSD(T). [j] From Janowski and Pulay,[63] using an aTZ/aQZ QCISD(T) extrapolation at the QCISD(T)/aug-cc-pVTZ optimized geometries. [k] From Pitoňák et al.,[23] using an aQZ/a5Z extrapolation of MP2 energies with a ΔCCSD(T) correction evaluated via aTZ/aQZ extrapolation and the OVOS approximation. [l] CCSD(T) haTZ/haQZ extrapolation. [m] CCSD(T) aTZ/aQZ extrapolation.

The various estimates of CCSD(T)/CBS in Table 3 are in good agreement with each other. Using a D−T extrapolation (with either the aug-cc-pVXZ or heavy-aug-cc-pVXZ basis sets) for ΔCCSD(T) reduces the magnitude of the interaction energies by 0.03−0.08 kcal mol^{-1} compared to their CCSD(T)/CBS(ΔaDZ) values. However, differences between our estimated CCSD(T)/CBS(a(DT)Z) interaction energies and the QCISD(T)/CBS(a(TQ)Z) values of Janowski and Pulay are only 0.02−0.05 kcal mol^{-1}. Compared to the estimated CCSD(T)/CBS values of Pitoňák et al.[23] obtained using the OVOS method, our results agree to 0.01−0.02 kcal mol^{-1}. This indicates that all of these results are essentially converged to the CCSD(T)/CBS limit. Compared to the improved benchmarks, our earlier estimated CCSD(T)/aug-cc-pVQZ* values appear to be about right for the sandwich and slightly underbound (by 0.1 kcal mol^{-1} or less) for the T-shaped and parallel-displaced configurations.

Before moving on to discuss how various recent approximations perform compared to these and other benchmark values, we would like to discuss two remaining questions about the benzene dimer. First, two different parallel-displaced configurations have been considered in the literature. In the one used by us, one benzene is displaced horizontally over a C−C bond in the other benzene. Others, including Tsuzuki and co-workers,[15] have considered configurations which displace one benzene horizontally over a carbon (vertex) of the other ring. Park and Lee[39] suggest that binding energies for the oververtex geometry may be significantly larger than those for the overbond geometry.[39] However, according to CCSD(T)/CBS(ΔaDZ) interaction energies for a grid of points around the equilibrium geometry for the overbond (PD) and oververtex (PD-b) con-

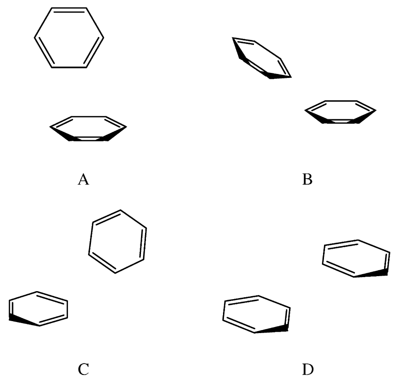

Figure 5. Geometries of nearest-neighbor pairs in crystalline benzene.

figurations (see Figure 1 and Table S28 of the Supporting Information), there is no significant difference. The PD-b configuration is lower by only 0.01−0.02 kcal mol^{-1} for the smaller horizontal displacements and 0.02−0.05 kcal mol^{-1} for the larger horizontal displacements. At the equilibrium geometry (3.5, 1.7 Å), the energy difference is 0.02 kcal mol^{-1}. These findings are in accord with the high-level results of Pitoňák et al.[23] for the minimum geometries, published while this work was in preparation.

Finally, we compare the benchmark energies for our three high-symmetry, prototype configurations to the C_1 geometries of benzene pairs found in crystalline benzene. We recently reported what appears to be the first high-accuracy, fully ab initio computation of the lattice energy of a neutral organic (benzene) using coupled-cluster methods.[31] The four nearest-neighbor pairs are illustrated in Figure 5, and they have center-to-center distances of 5.02, 5.81, 5.99, and 6.81 Å in the neutron diffraction structure of Bacon et al.[74] These compare to center-to-center distances of 3.9, 5.0, and 3.9 Å for the prototype sandwich, T-shaped, and parallel-displaced configurations, respectively. The estimated CCSD(T)/CBS(ΔaDZ) binding energies of the four nearest-neighbors are 2.75, 1.81, 1.43, and 0.46 kcal mol^{-1}, compared to 1.76, 2.73, and 2.79 kcal mol^{-1} for the symmetric sandwich, T-shaped, and parallel-displaced configurations at the same level of theory. Crystal pair A resembles a tilted T-shaped configuration; it has a similar intermonomer distance to the symmetric T-shaped configuration, and its binding energy is very similar (2.75 versus 2.73 kcal mol^{-1}); the difference is somewhat smaller than the 0.09 kcal mol^{-1} difference between the T and tilted-T configurations studied by Pitoňák et al.[23] Crystal configuration B is intermediate between the T and PD configurations, but its larger intermolecular separation leads to a smaller binding energy. The remaining crystal pairs have even larger intermolecular separations and smaller binding energies.

B. Density Fitting, Local Correlation, and Dual Basis Approximations. In this section, we consider several approximations which are meant to speed up conventional ab initio electronic structure methods while introducing negligible errors. These approximations are analyzed specifically for their effectiveness in the context of noncovalent interactions.

The resolution-of-the-identity (RI) approximation speeds up the computation of the two-electron integrals by introducing an auxiliary basis set and expressing four-index integrals as products of three-index integrals and two-index electron repulsion integrals[49]

$$(\mu\nu|\rho\sigma) \approx \sum_{PQ} (\mu\nu|P)(P|Q)^{-1}(Q|\rho\sigma) \qquad (2)$$

The two-index quantity $(P|Q)$ is also an electron repulsion integral, not an overlap

$$(P|Q) = \int P(\mathbf{r}_1)\frac{1}{r_{12}}Q(\mathbf{r}_2)\mathrm{d}^3\mathbf{r}_1\mathrm{d}^3\mathbf{r}_2 \qquad (3)$$

This RI approach is closely related to the pseudospectral aproximation,[75,76] which uses a grid instead of atom-centered functions for the auxiliary basis. This way of expressing the two-electron integrals can be helpful for more effective factorizations of Hartree−Fock,[49,77] MP2,[78,79] and other kinds of quantum chemistry computations. The effectiveness of this approach for MP2 is magnified when combined with local correlation approximations.[79] In recent years, the RI approximation has also been called density fitting (DF).[79] We will use both terms here.

Another very fruitful avenue of research has examined local correlation approximations.[79−88] Introduced by Pulay and Saebø in the 1980s,[80−82] these approaches are based on the use of localized molecular orbitals. Electron motions should only be correlated if the electrons reside in orbitals that are spatially close to each other. Moreover, virtual (unoccupied) orbitals can be neglected if they are not spatially close to the occupied orbitals in a given excitation. Local correlation methods have the extra advantage that they neglect some of the terms leading to basis set superposition error,[67] and hence, counterpoise correction is generally not necessary.

Tables 4 and 5 show the effectiveness for RI/DF and local correlation approximations as observed in the MOLPRO[40] and Q-Chem[52] packages. Here, we compare errors and computational times against a canonical MP2/aug-cc-pVTZ computation for the sandwich benzene dimer (828 basis functions) using a standard 3.2 GHz Intel Woodcrest EM64T Linux workstation. For MOLPRO, the canonical computation requires 23.0 h, including the counterpoise correction computation. Spatial symmetry was not used for these tests (which would reduce the time to 12.7 h) because the density fitting and local correlation approximations implemented in MOLPRO do not use spatial symmetry; this is unlikely to be a drawback in studies of large molecules, which are unlikely to have much, if any, symmetry to exploit. Density fitting the MP2 correlation energy (DF-MP2/HF) incurs essentially no error and reduces the computational time to 19 h. Localizing the MP2 correlation energy (LMP2/HF) leads to a slight increase in computational time (to 28.7 h), probably because this test case is too small for the benefits of local correlation to make up for the additional overhead costs. However, it is encouraging to note that the LMP2/HF result incurs an error of only 0.015 kcal mol^{-1}. Such an error is quite small and should not be of any practical concern for most studies. Using local correlation in conjunction with density fitting for MP2 reduces the computational cost compared to DF-MP2/HF by 1.5 h.

Density fitting the Hartree−Fock procedure only (MP2/DF-HF) requires about one-quarter of the time of the standard MP2 method and incurs an error of 0.006 kcal mol^{-1}. This signifies that the time-consuming part for this test case is the SCF iterations. The DF-MP2/DF-HF method dramatically reduces the computational time to under 2 h, with an error of only 0.005 kcal mol^{-1}. Given this result, density fitting both the MP2 and HF parts of the computation is recommended for routine or even

TABLE 4: Effectiveness of Density Fitting and Local Correlation Approximations for the Sandwich Benzene Dimer[a]

MP2		SCF		
DF	LOC[b]	DF	error	time
			0.000	23.0
X			−0.001	19.2
	X		0.015	28.7
		X	0.006	6.2
X	X		0.011	17.7
X		X	0.005	1.7
X	X	X	0.013	3.2

[a] Errors are versus MP2/aug-cc-pVTZ in kcal mol^{-1} and time in h. Evaluated at an intermolecular separation of 3.8 Å, using the cc-pVTZ JK and MP2-fitting basis sets as the auxiliary basis sets for the Hartree−Fock and MP2 procedures, respectively. Timings using the MOLPRO 2006.1 program[40] obtained on a 3.2 GHz Intel Woodcrest EM64T workstation. An X denotes the use of the given approximation. All computations evaluated without use of spatial symmetry. [b] Not counterpoise-corrected.

TABLE 5: Effectiveness of Resolution-of-the-Identity (RI) MP2 and Dual Basis Self-Consistent Field (SCF) Approximations for the Sandwich Benzene Dimer[a]

MP2	SCF		
RI	DB	error	time
		0.000	24.3
X		−0.001	12.2
	X	0.012	16.6
X	X	0.010	2.8

[a] Errors are versus MP2/aug-cc-pVTZ in kcal mol^{-1} and time in h. Evaluated at an intermolecular separation of 3.8 Å, using the cc-pVTZ MP2-fitting basis set as the auxiliary basis set for the MP2 procedure and the default Q-Chem basis subset for the dual basis SCF procedure. Timings using the Q-Chem 3.1 program[52] obtained on a 3.2 GHz Intel Woodcrest EM64T workstation. An X denotes the use of the given approximation. All computations evaluated without use of spatial symmetry.

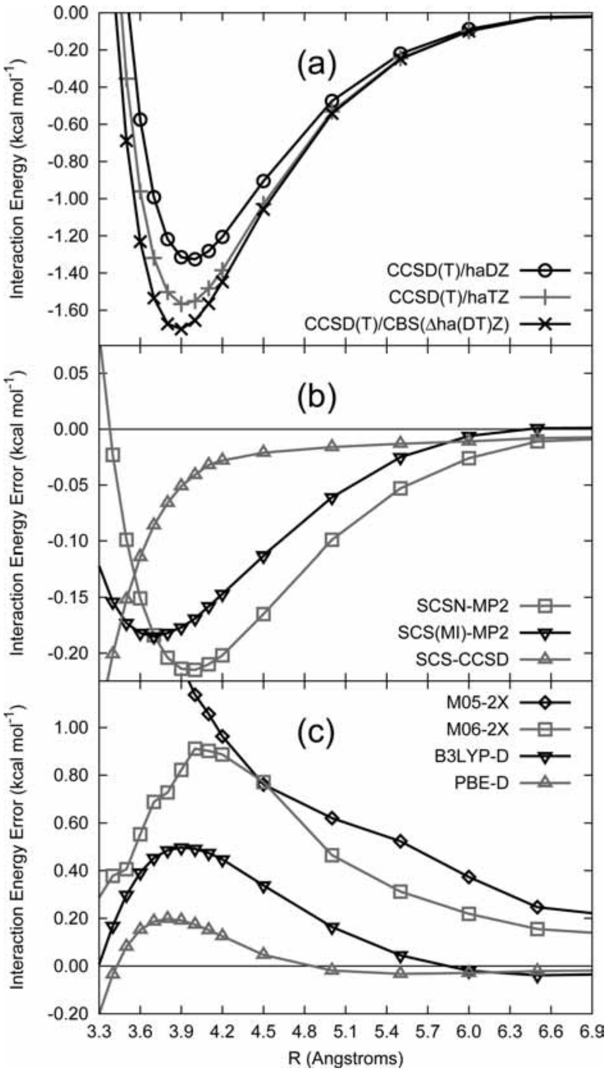

Figure 6. (a) CCSD(T) PECs for the sandwich benzene dimer. Interaction energy errors for (b) SCS-type approximations and (c) DFT methods compared to the CCSD(T)/CBS(Δha(DT)Z) interaction energies.

benchmark-quality computations. Although we focus here on the errors near the equilibrium geometry, we have also examined the error of the DF-MP2/DF-HF method as a function of intermolecular distance (see Table S27 of the Supporting Information). The error is larger at shorter intermolecular distances and decays rapidly for larger separations. At the minimum separation considered, 3.2 Å, the error is still only 0.012 kcal mol^{-1}. Adding local correlation (DF-LMP2/DF-HF) increases the computational time somewhat, probably because of overhead, which is not recovered for such a small molecular system.

As noted above, the SCF procedure can be one of the major time-consuming steps in an MP2 computation. Another technique for reducing this cost is the dual basis SCF procedure of Head-Gordon and co-workers,[51] which is implemented in the Q-Chem program.[52] Table 5 examines the RI and dual basis (DB) SCF approximations. In Q-Chem, the reference MP2/aug-cc-pVTZ computation on the sandwich benzene dimer requires 24.3 h to complete using the same hardware as that used above (again, we are not utilizing spatial symmetry in these comparisons). Applying the RI approximation to the MP2 method (RI-MP2) (equivalent to density fitting) requires about half of the time of the standard MP2 method and incurs an extremely small error of −0.001 kcal mol^{-1}. The MP2 method combined with the dual basis SCF (MP2/DB-SCF) approximation decreases the time to 16.6 h and incurs a somewhat greater (but still negligible) error of 0.012 kcal mol^{-1}. The most efficient approximation tested in Q-Chem is the combined RI-MP2 and DB-SCF procedures (RI-MP2/DB-SCF). The RI-MP2/DB-SCF method has an error of 0.01 kcal mol^{-1} with a computational time of 2.8 h. It would be interesting to also apply the RI procedure to the SCF iterations in combination with the dual basis and RI-MP2 approximations to further decrease computational costs.

C. Evaluation of Spin-Component-Scaled Methods. With the reliability of the CCSD(T)/CBS(ΔaDZ) and CCSD(T)/CBS(Δa(DT)Z) approximations established for the benzene dimer, we computed potential energy curves for the CH_4−benzene and H_2S−benzene complexes with the CCSD(T)/CBS(Δa(DT)Z) approach. For the smaller methane dimer, T−Q extrapolations of CCSD(T) energies were possible. Using these benchmark potential curves, we now evaluate the reliability of various approximate methods which have arisen in the past few years and which promise to make accurate quantum chemistry applicable to larger systems.

Figures 6−8 depict for the benzene dimer test cases (a) the convergence of the (explicit or estimated) CCSD(T) binding energies with respect to basis set, (b) the errors in interaction energies for spin-component-scaled methods, and (c) the errors

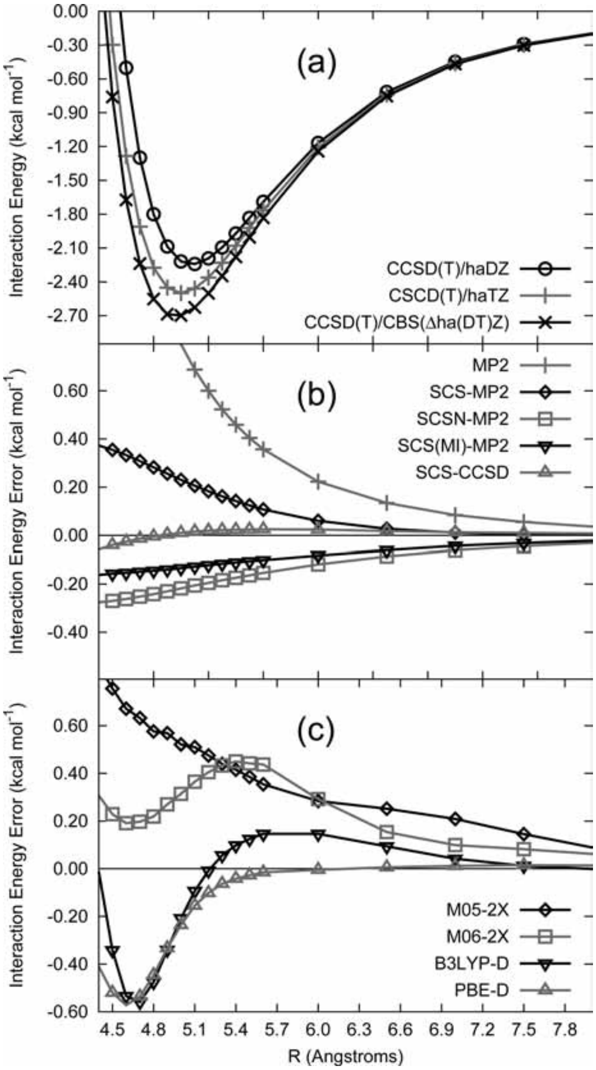

Figure 7. (a) CCSD(T) PECs for the T-shaped benzene dimer. Interaction energy errors for (b) SCS-type approximations and (c) DFT methods compared to the CCSD(T)/CBS(Δha(DT)Z) interaction energies.

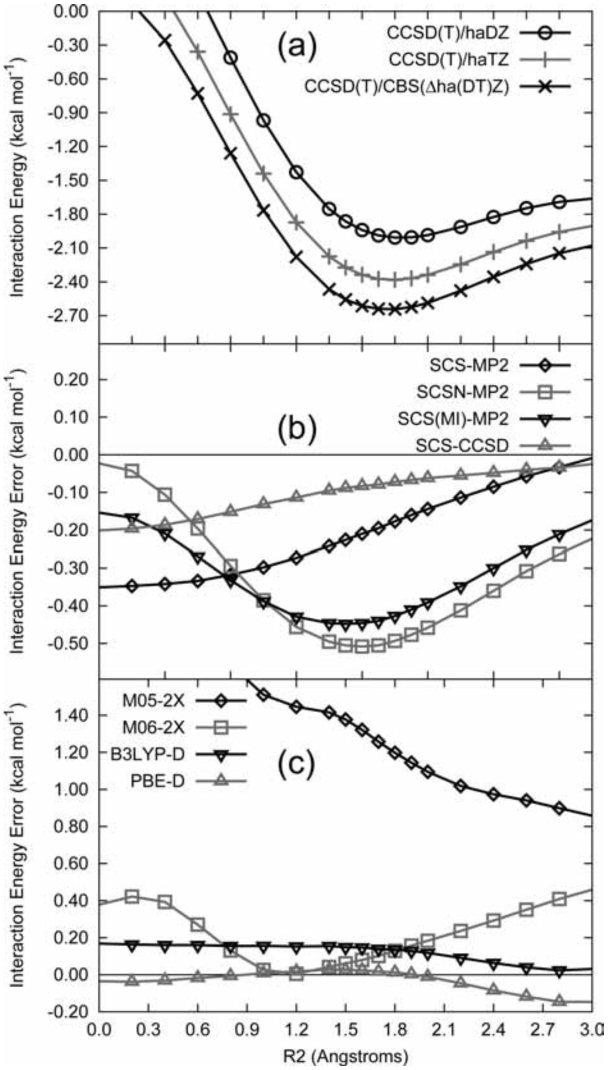

Figure 8. (a) CCSD(T) PECs for the PD benzene dimer at an R_1 displacement of 3.4 Å. Interaction energy errors for (b) SCS-type approximations and (c) DFT methods compared to the CCSD(T)/CBS(Δha(DT)Z) interaction energies.

in various DFT approximations. In this section, we will focus our attention on the performance of the SCS methods.

Of all of the SCS or DFT methods considered in this work, the only one which uniformly exhibits a high degree of accuracy is the SCS-CCSD method (it is, not surprisingly, also the most computationally expensive, having the same cost as conventional CCSD). The magnitude of the interaction energy error is below 0.2 kcal mol^{-1} for any of the points considered along the benzene dimer PECs; it only approaches this value at short intermolecular distances, where electron correlation effects are largest (and where most other approximate methods also have increasing errors). The SCS- and SCSN-MP2 methods do not perform nearly as well, having errors of 1 to several tenths of 1 kcal mol^{-1}. While the SCS-MP2 error is generally a monotonic function of intermolecular separation in Figures 6−8, the SCSN-MP2 error is more erratic and can increase or decrease with distance. The SCS(MI)-MP2 error curves have a similar shape to those from SCSN-MP2, but the magnitude of the error is generally smaller.

Figures 9 and 10 show results of the SCS and DFT approximations for the methane−benzene and H_2S−benzene complexes. Again, the SCS-CCSD method does extremely well, with errors of about 0.1 kcal mol^{-1} or less across the PECs. The SCS(MI)-MP2 errors again mimic the SCSN-MP2 errors, but they are generally somewhat better. The SCS-MP2 method exhibits errors of a couple tenths of 1 kcal mol^{-1} at equilibrium distances for both complexes.

Interaction energy errors for the methane dimer exhibit a different behavior than the other noncovalent complexes, as shown Figure 11. In this case, the unaltered MP2 method reproduces the benchmark PEC to less than four hundredths of 1 kcal mol^{-1}. Because MP2 typically overbinds van der Waals complexes, the SCS methods typically scale the interaction energy to make it smaller in magnitude; unfortunately, because MP2 is actually correct in this case, the scaling overcorrects. Thus, all scaled MP2 values are underbound up to about 3.9 Å (particularly SCS-MP2). Around the equilibrium distance, the scaled MP2 methods all underestimate the binding energy by 0.2 kcal mol^{-1}. The SCS-CCSD method reliably incurs errors of less than 0.1 kcal mol^{-1} across the PEC.

Table 6 shows the interaction energies and optimum equilibrium distances for the various methods utilized for the PECs. For all systems, the SCS-CCSD method reproduces CCSD(T) interaction energies reliably with errors of less than a tenth of 1 kcal mol^{-1}, and it obtains the proper intermolecular separations. The scaled MP2 methods generally yield intermolecular

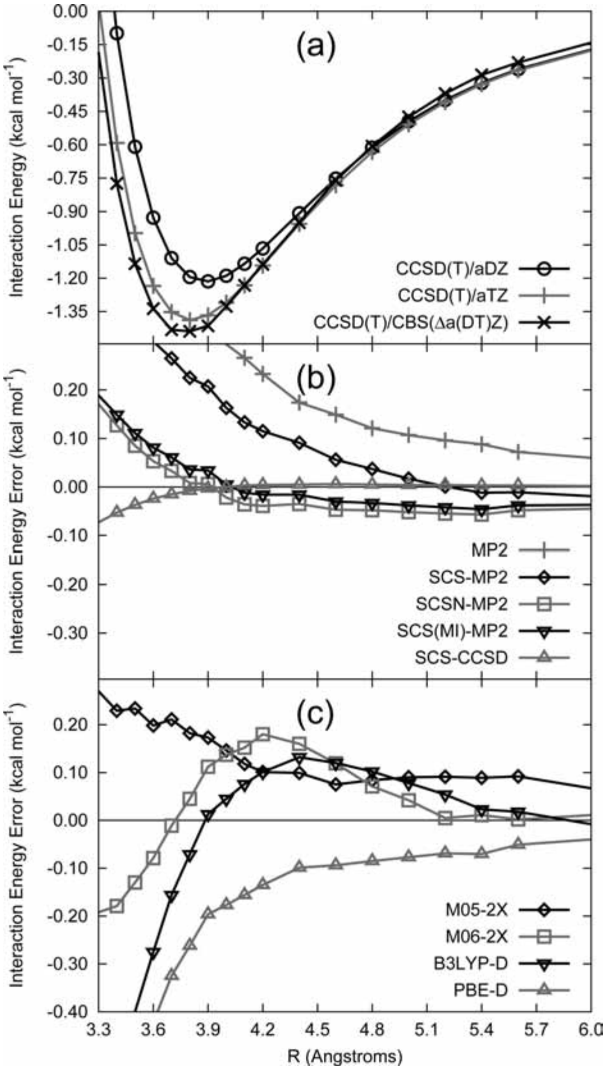

Figure 9. (a) CCSD(T) PECs for the methane−benzene complex. Interaction energy errors for (b) SCS-type approximations and (c) DFT methods compared to the CCSD(T)/CBS(Δa(DT)Z) interaction energies.

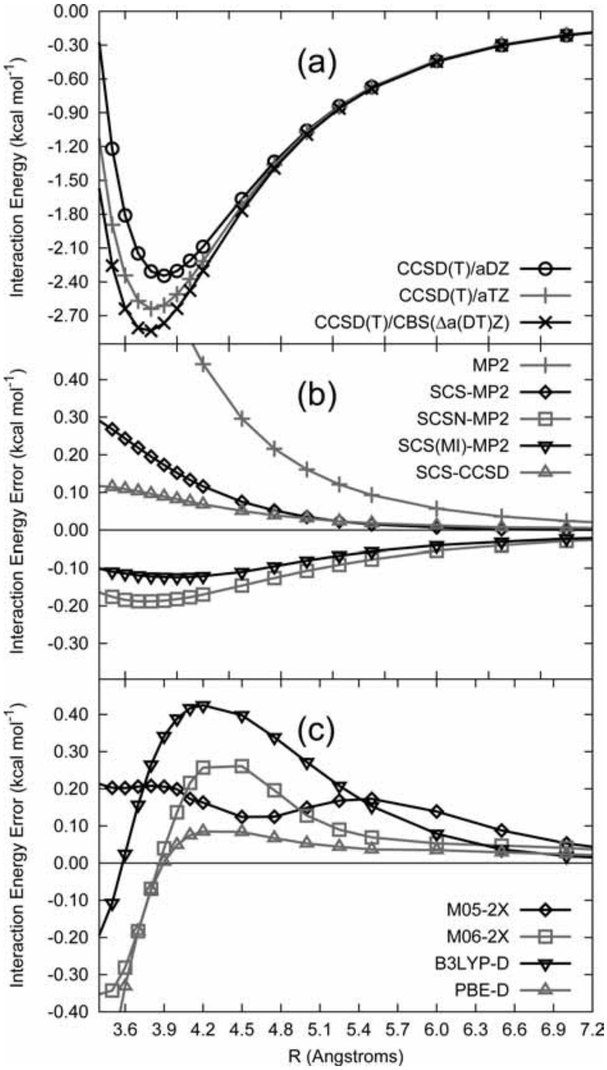

Figure 10. (a) CCSD(T) PECs for the H_2S−benzene complex. Interaction energy errors for (b) SCS-type approximations and (c) DFT methods compared to the CCSD(T)/CBS(Δa(DT)Z) interaction energies.

distances correct within 0.1 Å, except for the methane dimer, which exhibits an error of 0.2 Å. Interestingly, the SCS(MI)-MP2 method seems to be the most reliable among the MP2-type methods for the interaction energies, even though nonaugmented basis sets were used for this method. This is likely because the SCS(MI)-MP2 method was fit to the S22 test set[89] (which contains four of the six complexes tested here) with nonaugmented basis sets. It is therefore recommended that the SCS-CCSD method be used when computationally feasible. Otherwise, the scaled MP2 approaches appear similar for these test cases, but the performance of the SCS(MI)-MP2 method is perhaps somewhat better, and it is also more compuationally efficient because it has been parametrized with the smaller nonaugmented basis sets.

D. Evaluation of Density Functional Approximations. The lower panel of Figure 11 shows the performance of four DFT methods for the methane dimer. The methane dimer is the smallest of the six test cases considered and the most dominated by dispersion interactions. PBE and B3LYP cannot accurately describe binding in this dimer without correction for dispersion interactions; however, the addition of empirical dispersion terms should provide reasonable results. Unfortunately, PBE-D does not perform well for the methane dimer, overbinding at all geometries considered, particularly around equilibrium. B3LYP-D improves over PBE-D near the equilibrium geometry; at larger separations, however, PBE-D performs somewhat better. On an absolute scale, the errors for both PBE-D and B3LYP-D are modest (0.3 kcal mol^{-1} or less, except at very short intermolecular separations), but they are significant compared to a total CCSD(T)/CBS binding energy of only 0.54 kcal mol^{-1}.

M05-2X and M06-2X appear to implicitly model the interaction energy of the methane dimer without the addition of empirical terms. These functionals tend to overestimate the binding of the methane dimer at short intermonomer separations, but they perform well at the equilibrium geometry. M05-2X significantly underbinds at larger intermonomer separations; at distances larger the 5 Å, the error between M05-2X and CCSD(T) begins to behave like R^{-6}. M06-2X incurs almost no error from 4.6 to 5.8 Å, although it exhibits some underbinding at larger distances.

The methane−benzene complex is the next largest of the six included in this study; this complex includes important electrostatic interactions as well as dispersion interactions. The behavior of the four DFT methods for methane−benzene (see Figure 9c) is similar to that for the methane dimer; this

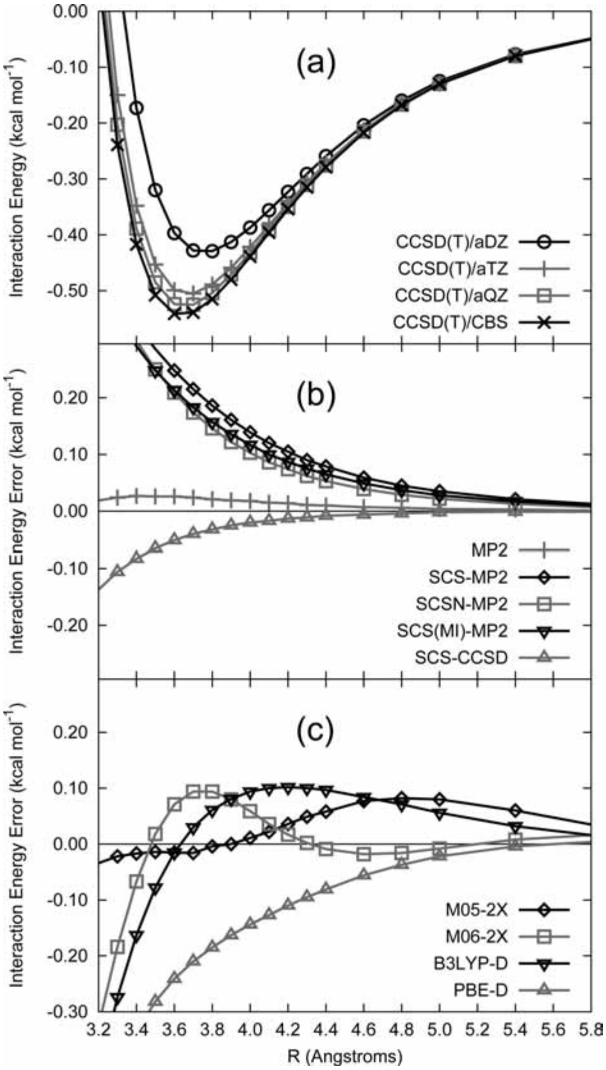

Figure 11. (a) CCSD(T) PECs for the methane dimer. Interaction energy errors for (b) SCS- and MP2-type approximations and (c) DFT methods compared to the CCSD(T)/CBS interaction energies.

is perhaps not surprising because both complexes contain only carbon and hydrogen atoms, and the same three types of pair potentials are included in the dispersion correction. PBE-D again overestimates the attractive interactions in the complex, incurring significant errors at small intermonomer separations. B3LYP-D performs well around the equilibrium geometry but underestimates the strength of the attractive interactions within the complex at larger separations. As in the methane dimer, M06-2X performs well for configurations near equilibrium but overestimates binding at short intermolecular separations. Compared to M06-2X, the error curve for M05-2X is flatter for methane−benzene and methane dimer, but it is shifted up to somewhat larger errors for methane−benzene and underestimates binding at all separations.

Compared to the methane dimer and methane−benzene, the H_2S−benzene complex contains stronger electrostatic contributions.[29,38] Thus, one might expect this case to be easier for DFT methods than the previous two considered. Figure 10c displays the errors in the interaction energies. Here, PBE-D performs well; for the equilibrium geometry and separations beyond equilibrium, PBE-D incurs errors of less than 0.10 kcal mol^{-1}. B3LYP-D underestimates the strength of the interaction and does not perform as well as PBE-D except at intermonomer distances shorter than the equilibrium distance. M05-2X performs similarly for this complex as it does for methane−benzene, consistently underestimating the attractive interactions. In this case, M05-2X incurs errors of 0.2 kcal mol^{-1} or less across the PEC. M06-2X appears to capture a larger portion of the dispersion interactions than does M05-2X as it overestimates the attractive interactions around equilibrium and at shorter separations. M06-2X also outperforms M05-2X at distances larger than 5 Å. Again, the error curve for M06-2X is somewhat more erratic than that for M05-2X with respect to intermolecular separation.

The benzene dimer has already been used as a challenging test case to assess the performance of new density functional approximations[57,90−98] because its potential energy surface is not reproduced by standard functionals.[59] The performance of the DFT approaches considered here for three configurations of the benzene dimer can be seen in Figures 6−8. As was seen for the three smaller complexes, PBE-D tends to predict more attractive interaction energies than does B3LYP-D. Of the three configurations, the DFT-D methods perform best for the parallel-displaced case. Here, PBE-D and B3LYP-D incur absolute errors of less than 0.20 kcal mol^{-1} across the PEC. M05-2X and M06-2X do not perform nearly as well for the benzene dimer as they did for the three smaller complexes. M05-2X performs particularly poorly for the sandwich and parallel-displaced configurations, where it underestimates the strength of the interaction by over 1.00 kcal mol^{-1} at the equilibrium geometries. In the sandwich and T-shaped configurations, the error grows at larger intermolecular separations and then decreases as the magnitude of the interaction energy decreases. In the sandwich configuration, after a separation of 4.5 Å, the error between M06-2X and CCSD(T) appears to be dominated by neglected dispersion interactions. For the T-shaped configuration, this occurs at about 5.5 Å. Thus, the benzene dimer is a more challenging system for M05-2X and M06-2X than the three smaller complexes examined in this work. Somewhat better performance was reported for M05-2X for the parallel-displaced and T-shaped configurations in the work of Zhao and Truhlar,[98] who used the 6-311+G(2df,2p) basis set. That basis is somewhat smaller than aug-cc-pVTZ, leading to larger basis set superposition errors, which partially cancel the underbinding exhibited by M05-2X (this is consistent with the significantly decreased binding observed by Zhao and Truhlar when they applied the counterpoise correction).

Thus, the M05-2X and M06-2X functionals appear to implicitly capture some of the effects of “medium-range” dispersion interactions. For the smaller systems (methane dimer, methane−benzene, and H_2S−benzene), M05-2X and M06-2X work well, performing as well or better than PBE-D and B3LYP-D. However, for the slightly larger benzene dimer test case, the performance of these methods is not as good; M05-2X significantly underbinds at shorter intermolecular distances (although this could be partially compensated for by using a smaller basis set), and both M05-2X and M06-2X fail to capture the attraction due to dispersion at large intermolecular distances.

IV. Conclusions

By improving the basis sets used for the MP2 and CCSD(T) components of our additive scheme for nonbonded interactions, benchmark potential energy curves have been obtained which should very closely approximate the CCSD(T) complete basis set (CBS) limit for several important prototypes of noncovalent

TABLE 6: Interaction Energies (kcal mol^{-1}) at Optimum Intermolecular Separations (Å, in Parentheses) for Prototype Nonbonded Complexes

method	S	T	PD[a]	CH_4−benzene	H_2S−benzene	CH_4−CH_4
CCSD(T)[b]	−1.65 (3.9)	−2.69 (5.0)	−2.67 (3.5,1.7)	−1.47 (3.8)	−2.83 (3.8)	−0.54 (3.6)
SCS-CCSD[c]	−1.75 (3.9)	−2.69 (5.0)	−2.77 (3.5,1.7)	−1.48 (3.8)	−2.74 (3.8)	−0.58 (3.6)
SCS-MP2[d]	−1.87 (3.9)	−2.47 (5.0)	−2.87 (3.5,1.6)	−1.21 (3.8)	−2.64 (3.8)	−0.32 (3.8)
SCSN-MP2[d]	−1.92 (3.9)	−2.92 (4.9)	−3.17 (3.5,1.7)	−1.43 (3.8)	−3.02 (3.8)	−0.36 (3.8)
SCS(MI)-MP2[e]	−1.88 (3.9)	−2.83 (5.0)	−3.10 (3.5,1.7)	−1.40 (3.8)	−2.96 (3.8)	−0.35 (3.8)
M05−2X[f]	−0.52 (4.0)	−2.18 (5.0)	−1.57 (3.5,2.0)	−1.26 (3.8)	−2.63 (3.8)	−0.54 (3.7)
M06−2X[f]	−0.95 (3.8)	−2.42 (4.9)	−2.54 (3.4,1.7)	−1.44 (3.7)	−2.99 (3.7)	−0.47 (3.5)
B3LYP-D[f]	−1.20 (3.9)	−3.03 (4.9)	−2.51 (3.4,1.8)	−1.61 (3.6)	−2.65 (3.7)	−0.56 (3.5)
PBE-D[f]	−1.51 (3.9)	−3.02 (4.9)	−2.63 (3.4,1.8)	−1.76 (3.6)	−2.99 (3.7)	−0.77 (3.5)

[a] Optimized distances given as (R_1,R_2) in Å. [b] Estimated CCSD(T)/CBS(Δha(TQ)Z) results for the benzene dimer. CCSD(T)/CBS results using aTZ/aQZ extrapolation for other cases. [c] Estimated SCS-CCSD/CBS(Δ aDZ) results for the benzene dimer. SCS-CCSD/CBS results using aTZ/aQZ extrapolation for other cases. [d] From an aTZ/aQZ extrapolation to the CBS limit. [e] TZ/QZ extrapolation to the CBS limit. [f] Evaluated with the aug-cc-pVTZ basis.

interactions; the sandwich, T-shaped, and parallel-displaced benzene dimers, the methane−benzene complex, the H_2S−benzene complex, and the methane dimer.

The new benchmarks answer several questions about the benzene dimer. First, our results validate the findings of Janowski and Pulay[63] that the aug-cc-pVDZ basis is not quite large enough to make the error in the ΔCCSD(T) contribution less than 0.1 kcal mol^{-1} for the benzene dimer. However, evaluating this term from extrapolated aug-cc-pVDZ and aug-cc-pVTZ basis sets (with or without augmented functions on hydrogen) is sufficient to bring the error down to just a few hundredths of 1 kcal mol^{-1}. Second, there is only a very small energetic difference between parallel-displaced configurations in which a benzene is displaced (a) over a bond or (b) over a vertex; this difference is 0.01−0.05 kcal mol^{-1} for the geometries considered, or 0.02 kcal mol^{-1} at equilibrium. Third, the interaction energies of these idealized geometries have been compared to those from dimers in crystalline benzene. Of the crystal pairs, only one of them has a binding energy as strong as those of the symmetric dimers; the rest are farther apart in the crystal and do not interact as strongly.

The very high-quality benchmarks presented here will be useful in testing new, computationally efficient approaches for nonbonded interactions. In this work, we evaluated several methods including spin-component-scaled MP2 and CCSD, density functional theory empirically corrected for dispersion interactions (DFT-D), and the meta-generalized gradient approximation functionals M05-2X and M06-2X. Generally speaking, these approaches provided reasonable results for the prototype test cases (errors of a few tenths of 1 kcal mol^{-1} across the potential energy curves), although typically, the spin-component-scaled wave function techniques performed better than the density functional approximations. M05-2X significantly underbound the benzene dimer when used with the fairly large aug-cc-pVTZ basis without counterpoise correction (this error could be partially canceled by using smaller basis sets, which exhibit larger basis set superposition errors). The performance of M06-2X and the DFT-D methods is roughly comparable, although DFT-D tends to be more reliable at large intermolecular distances. Intermolecular distances are well-predicted by the methods considered, although DFT-D tended to slightly underestimate these distances by about 0.1 Å. M05-2X and M06-2X are more sensitive to the integration grid than standard density functionals.[59,60]

Several general approximations for electronic structure theory were also tested in the context of nonbonded interactions, including density fitting/resolution-of-the-identity, local correlation approximations for MP2, and the dual basis approach of Head-Gordon and co-workers.[51,52] The errors introduced by these approximations are negligible for the cases that we have considered, and they can lead to significant reductions in the computational cost, up to a factor of seven when density fitting is used for both the Hartree−Fock and MP2 steps in an MP2/aug-cc-pVTZ computation for the sandwich benzene dimer, even when the canonical computation is allowed to use spatial symmetry (which the density fitting computations do not).

Future work should consider a wider array of noncovalent interaction prototypes. However, the combination of general approximations, which significantly reduce computational time, and new approximate electronic structure methods, which provide fairly reliable results for the nonbonded interactions examined here, suggest that trustworthy computations are now possible for much larger chemical systems. This should substantially accelerate progress in studies of molecular recognition, crystal engineering, and supramolecular chemistry.

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Supporting Information Available: Cartesian coordinates for equilibrium geometries and potential energy curves of the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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