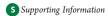


Accurate Interaction Energies for Problematic Dispersion-Bound Complexes: Homogeneous Dimers of NCCN, P₂, and PCCP

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ABSTRACT: All intermolecular interactions involve London dispersion forces. The accurate treatment of dispersion is essential for the computation of realistic interaction potentials. In general, the most reliable method for computing intermolecular interactions is coupled-cluster singles and doubles with perturbative triples [CCSD(T)] in conjunction with a sufficiently flexible Gaussian atomic orbital basis set, a combination which is not routinely applicable due to its excessive computational demands (CPU time, memory, storage). Recently, many theoretical methods have been developed that attempt to account for dispersion in a more efficient manner. It is well-known that dispersion interactions are more difficult to compute in some systems than others; for example, $\pi-\pi$ dispersion is notoriously difficult, while alkane—alkane dispersion is relatively simple to compute. In this work, numerous theoretical methods are tested for their ability to compute reliable interaction energies in particularly challenging systems, namely, the P_2 , PCCP, and NCCN dimers. Symmetry-adapted perturbation theory (SAPT) is applied to these dimers to demonstrate their sensitivity to the treatment of dispersion. Due to the small size of these systems, highly accurate CCSD(T) potential energy curves could be estimated at the complete basis set limit. Numerous theoretical methods are tested against the reliable CCSD(T) benchmarks. Methods using a treatment of dispersion that relies on time-dependent density functional theory (TDDFT) response functions are found to be the most reliable.

1. INTRODUCTION

Molecules with large, delocalized π orbitals are ubiquitous throughout chemistry. Not surprisingly, noncovalent interactions involving these types of molecules are important in the stacking of bases in DNA, 1-8 interactions between graphene sheets, the structure and energetics of certain organic crystals, 10-13 and some side chain interactions within proteins. 14-18 Unfortunately, the interactions between these highly polarizable molecules are notoriously difficult to study. Even seemingly simple systems, such as the benzene dimer or indole-benzene complex, can prove extremely challenging for all but the most robust quantum mechanical methods. 19-21 The most reliable standard method for treating these types of systems is coupled-cluster singles and doubles with perturbative triples [CCSD(T)]. 22,23 However, due to the computational expense associated with this method, it can only be applied to systems roughly the size of a nucleic acid base pair (with a medium-sized basis set).

The difficulty, in many cases, is to accurately capture London dispersion forces, which are critical for the study of noncovalent interactions. For even a qualitatively correct description of the interaction of neutral, nonpolar molecules, a reasonable treatment of dispersion is required. Of the four interaction components (electrostatics, induction, dispersion, and exchange-repulsion), the dispersion interaction is the most difficult for quantum mechanical methods to include in a reliable, yet computationally efficient manner. The quantum mechanical treatment of electrostatics, exchange-repulsion, and induction proves effective, at least

semiquantitatively, via Hartree—Fock (HF) or density functional theory (DFT). $^{24-26}$ Focusing on wave-function-based methods, second-order Møller—Plesset perturbation theory (MP2) is the simplest method that contains some account of dispersion. However, in many cases (especially those involving delocalized π orbitals), MP2 grossly overestimates the magnitude of dispersion interactions. 27,28 The usually robust coupled-cluster singles and doubles (CCSD) method 22 also struggles to describe dispersion in difficult cases, usually underestimating its magnitude in the cases where MP2 overestimates. 29 The inclusion of a perturbative triples correction is required for quantitatively correct results. 29

There are many approximate methods that attempt to correct the description of dispersion by MP2 or CCSD. The spin-component scaled (SCS) methods, originally introduced by Grimme, attempt to correct the correlation energy by empirically scaling the same- and opposite-spin components. There are several different parametrizations of MP2, including some specifically for noncovalent interactions; 32,33 unfortunately, it is not clear that any one set of parameters is reliable for all types of interactions. The SCS-CCSD method 31 has been shown to be much more reliable than SCS-MP2 for treating all types of noncovalent interactions. However, this method requires an iterative $\mathcal{O}\left(N^6\right)$ procedure to compute an interaction energy, which limits its applicability. The MP2.5 method of Hobza and

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co-workers³⁵ is comparable to SCS-CCSD with regard to accuracy and only requires a noniterative $\mathcal{O}(N^6)$ energy evaluation. Of the reliable, approximate wave-function-based methods, the least computationally expensive [noniterative $\mathcal{O}(N^5)$] and the most physically justified is the MP2C method of Hesselmann. This method attempts to correct the behavior of MP2 by evaluating dispersion with frequency-dependent polarizabilities from time-dependent density functional theory (TDDFT).

For the study of molecular interactions in even larger systems, much lower-scaling methods need to be applied. One very popular and effective approach is to augment traditional density functionals with a damped R^{-6} term. $^{38-41}$ This DFT-D approach uses the density functional to account for short-range electron correlation and the empirical correction to capture the long-range correlation that the functional neglects. The recently developed -D3 correction⁴² includes R^{-6} and R^{-8} terms computed with atomic dispersion coefficients that depend on the chemical environment (through the steric numbers of the atoms). A possible improvement to DFT-D methods is to apply the dispersion correction to long-range corrected functionals that are parametrized in the presence of the dispersion correction; ω B97X-D is such a functional⁴³ and appears to be particularly robust for noncovalent interactions when used with augmented triple- ζ basis sets.⁴⁴ The so-called "double hybrid" functionals contain an MP2-like term that accounts for dispersion. These functionals also appear well suited to describe noncovalent interactions. The B2PLYP and XYG3 functionals are two examples of double hybrid functionals that have been shown to perform well.44-48

The methods described above are *supermolecular* approaches to computing an interaction energy. It is also possible to compute interaction energies directly through a perturbative approach; the most rigorous of these methods is the symmetry-adapted perturbation theory (SAPT).⁴⁹ At this point, it should be noted that MP2C is a hybrid of supermolecular and perturbative approaches. SAPT exists in both wave-function-based and DFT-based forms [with the latter termed SAPT(DFT)]. The wave-function-based SAPT, which relies on a many-body perturbation theory (MBPT) expansion, has traditionally been too expensive to apply to large systems, since it scales as $\mathcal{O}(N')$ when all second-order intramonomer correlation terms are included. However, through densityfitting (DF) and natural orbital (NO) based approximations, it can be applied to systems with roughly 50 atoms. 50,51 The simplest SAPT method, SAPT0, consists of a Hartree-Fock interaction energy and an MP2-like dispersion term; this method can be applied to systems with over 100 atoms. The SAPT(DFT) method systems with over 100 atoms. The SAPT(DFT) method systems as $\mathcal{O}(N^5)$ after DF approximations are applied. SAPT(DFT) is quickly becoming the preferred method for describing dispersion in difficult systems with as many as 72 atoms.

One of the most accurate methods for obtaining a dispersion energy via a perturbative approach was developed in the mid-1990s by Williams et al. Their CCD-based approach is similar to the supermolecular CCD+ST(CCD) method developed by Raghavachari. The evaluation of CCD+ST(CCD) dispersion requires the iterative solution of five sets of doubles amplitudes, all of which scale as $\mathcal{O}(N^6)$. Finally, these amplitudes are used to evaluate a perturbative triples correction scaling $\mathcal{O}(N^7)$. Due to the expense of this method, it has remained virtually unused since its development. Recently, we have implemented the CCD+ST(CCD) dispersion while taking advantage of modern DF and NO approximations. These approximations allow

CCD+ST(CCD) dispersion energies to be computed for systems that are orders of magnitude larger than those which were previously accessible. A similarly accurate method for computing dispersion energies, due to Korona and Jeziorski, exists; however, it also scales as $\mathcal{O}(N^7)$ (if density fitting approximations are applied).

With the number of recently developed methods aimed at describing noncovalent interactions, it is important to have reliable and challenging benchmarks available. One of the most popular is the S22 test set of Hobza and co-workers. This set of benchmark interaction energies has been used extensively to test and train new methods. For most wave-function-based methods, two of the most difficult systems in this test set are the stacked benzene dimer and indole—benzene complexes. Even the original benchmark energy for the stacked indole—benzene differs by approximately 15% from the best estimates currently available. It is useful to study systems that contain dispersion interactions similar to the stacked aromatic $\pi-\pi$ complexes in the S22 test set, but for which more accurate benchmarks can be established.

In this work, we examine NCCN, P_2 , and PCCP dimers as such model systems. All three of these systems are much smaller than the benzene dimer or indole—benzene, allowing for the computation of the nonrelativistic, electronic interaction energy in the complete basis set limit. We apply our new CCD+ST(CCD) SAPT program to examine the nature of the dispersion interactions present in NCCN, P_2 , and PCCP dimers compared to those in stacked aromatic $\pi-\pi$ complexes. Through this analysis, the problems encountered by finite-order perturbation theory are explored. Furthermore, we compare the molecular interaction between an extensive set of the aforementioned methods and our new benchmark data over multiple slices of the interaction potential for these three dimers.

2. METHODS

Rigid, linear monomer geometries were adopted for all computations. Experimental bond lengths were taken from Herzberg 68,69 for P_2 and NCCN $[R(PP)=1.8943~\text{Å},\,R(CC)=1.3839~\text{Å},\,\text{and}\,R(CN)=1.1578~\text{Å}]$. Although PCCP has been observed experimentally, structural characterization was not feasible, and no experimentally inferred geometrical parameters were reported. As such, the bond lengths for PCCP used in this study [R(CC)=1.35560~Å and R(CP)=1.58597~Å] were obtained from a low-level geometry optimization (details in the Supporting Information). These values, however, are entirely consistent with CCSD(T) optimizations with correlation consistent triple- ζ basis sets. 71

Potential energy curves (PECs) of the dimer structures were computed in three different configurations: cross (X), parallel-displaced (PD), and T-shaped (T) that belong to the D_{2d} , C_{2h} , and $C_{2\nu}$ point groups, respectively. These configurations are depicted in Figure 1 for (PCCP)₂, but the general definitions of the intermolecular geometrical parameters also apply to $(P_2)_2$ and $(NCCN)_2$. The D_{2d} cross configuration is depicted in Figure 1a, where the arrow indicates the intermolecular distance (R) between the midpoints of the central bond of each monomer. For the $C_{2\nu}$ T-shaped structures, the arrow shown in Figure 1b denotes the intermolecular distance (R) from the midpoint of the central bond that is perpendicular to the C_2 rotational axis of symmetry to the nearest atom in the other monomer that lies on the C_2 axis of symmetry. The C_{2h} parallel displaced structures are defined by two intermolecular parameters. R is again used to indicate the

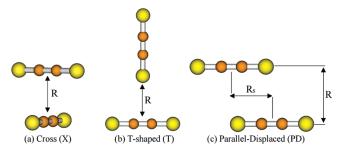


Figure 1. Three prototypical dimer configurations of NCCN, PCCP, and P₂ dimers included in this study.

separation between the monomers, specifically the distance between the two parallel lines defined by the linear monomers (denoted by the vertical arrow in Figure 1c). The other intermolecular geometrical parameter for the PD configurations is the displacement of the monomers along the aforementioned parallel lines relative to a rectangular (or sandwich) D_{2h} structure. In Figure 1c, this "horizontal slip" distance is labeled R_S and denoted by the horizontal arrow. The R_S coordinate was fixed at a value of 2.80 Å for (NCCN)₂, 2.31 Å for (P₂)₂, and 2.66 Å for (PCCP)₂. These values roughly correspond to the average of MP2 and CCSD(T) optimized R_S parameters (details in the Supporting Information).

The PECs in this work were generated by scanning over R for each configuration of the three homogeneous dimers. HF, MP2, CCSD, and CCSD(T) electronic energies were computed at each point along the curve with the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets. Larger, aug-cc-pV(X+d)Z-type basis sets were determined to provide nearly identical results (details in the Supporting Information). The 1s-like core orbitals of C and N were constrained to be doubly occupied during the electron correlation computations, whereas this constraint was applied to the 1s-, 2s-, and 2p-like core orbitals of P (i.e., the frozen core approximation). The electronic energies were converged to at least $1 \times 10^{-10} \, \text{E}_h$ for the SCF and $1 \times 10^{-8} \, \text{E}_h$ for the coupled-cluster procedures. The single point energy computations were performed using both the 2006.1 and 2010.1 versions of the Molpro software package. The single point energy computations of the molpro software package.

Electronic interaction energies were computed at the complete basis set (CBS) limit along the PECs for the X, PD, and T configurations of $(NCCN)_2$, $(P_2)_2$, and $(PCCP)_2$ by extrapolating the energy with respect to the cardinal number of the basis set. Within the supermolecular approach, CBS-limit interaction energies are computed by subtracting the extrapolated monomer electronic energies from the extrapolated electronic energies of the complex. Extrapolations were performed for the monomer energies in the monomer basis and for the dimer energies in the dimer basis. The electronic energy was separated into Hartree-Fock and correlation energies. HF energies were extrapolated with aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ according to a three-parameter formula. 73,74 The correlation energies were extrapolated to the CBS limit using the two-point formula of Halkier et al. with aug-cc-pVTZ and aug-cc-pVQZ basis sets.

The simplest wave-function-based methods tested in this work are the spin-component scaled MP2 methods. These methods have been shown to be capable of accurately computing non-covalent interactions with a triple- ζ quality basis. ^{30,33,34} In this work, the original parametrization, SCS-MP2, and a molecular

interaction specific parametrization, SCS(MI)-MP2, are tested. 30,33 The SCS- and SCS(MI)-MP2 computations in this work use the cc-pVTZ basis; 76,77 the HF and MP2 computations are performed under the DF approximation using the cc-pVTZ-JK and cc-pVTZ-RI auxiliary basis sets, respectively.^{78,79} The spin-component scaled CCSD method of Takatani et al., SCS-CCSD,31 and its recent reparameterization for molecular interactions, SCS-(MI)-CCSD, 80 are also tested. The SCS-CCSD method has been found to yield excellent results with large basis sets; 26 in the present work, SCS-CCSD/aug-cc-pVQZ and SCS(MI)-CCSD/aug-cc-pVQZ interaction energies are computed. The SCS parameters for these methods can be found in the Supporting Information. The midground in terms of computation expense between SCS-MP2 and SCS-CCSD is the scaled MP3 method (MP2.5) of Pitoňak et al.³⁵ This method includes half of the third-order correction to MP2 (or, equivalently, averages MP2 and MP3 energies). Similarly to SCS-CCSD, this method performs well with large basis sets, and MP2.5/aug-cc-pVQZ interaction energies are reported. The counterpoise correction is applied to these wave-function-based methods.81 These computations are performed with Molpro. 72

We also test the promising MP2C method. ^{36,37} This method is a composite of a counterpoise corrected MP2 interaction energy and dispersion energies from intermolecular perturbation theory. The uncoupled Hartree–Fock (UCHF) dispersion energy contained in MP2 is replaced with a dispersion energy computed with time-dependent density functional theory (TDDFT) response functions.

$$E_{\text{MP2C}} = E_{\text{MP2}} - E_{\text{disp}}(\text{UCHF}) + E_{\text{disp}}(\text{TDDFT})$$
 (1)

The $E_{\rm disp}({
m TDDFT})$ term would be exact if the exact exchangecorrelation potential could be used to evaluate the response functions. 55 In lieu of the exact exchange-correlation potential, the PBE0 functional in conjuction with the adiabatic local density approximation (ALDA) kernel has been shown to yield highly accurate dispersion energies.³⁷ The MP2C interaction energies are computed with an aug-cc-pVQZ basis and use aug-cc-pVQZ-JK and aug-cc-pVQZ-RI auxiliary basis sets (details in the Supporting Information). For the PCCP dimer, aug-cc-pVTZ, aug-cc-pVTZ-JK, and aug-cc-pVTZ-RI basis sets were used. A related method (in terms of its description of dispersion) is density-functional-based symmetry-adapted perturbation theory, SAPT (DFT). 53-57 Here, we use PBE0 with local HF exchange to describe the monomers. One caveat of SAPT(DFT) is that the monomer DFT computations need to be asymptotically corrected in order to produce accurate interaction energies; this requires the ionization potential of the monomers, which we compute at the PBEO/TZVPP level. The SAPT(DFT) computations use the DF approximation and the same basis sets as the MP2C computations. The MP2C and SAPT(DFT) computations are performed with Molpro.72

Many DFT methods have been developed in recent years that attempt to accurately describe noncovalent interactions. ⁸² Here, we test two hybrid meta-GGA functionals, M05-2X and M06-2X. ^{83–85} These functionals have been found to perform well when paired with the aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively. ⁴⁴ Meta-GGA's are known to be susceptible to numerical errors related to the integration grid. ⁸⁶ For this reason, we use a large, 100 302 (radial points, angular points) grid for the M05-2X and M06-2X computations. The ω B97X-D method of

Chai and Head-Gordon 43 and Grimme's B97-D3 method 40 are both evaluated with aug-cc-pVTZ basis sets. 44 A dense numerical integration grid was employed for the ω B97X-D computations, a pruned grid composed of 99 radial shells and 590 angular points per shell. We also test two double-hybrid DFT methods that include a perturbative MP2-like correlation correction, specifically, B2PLYP-D3/aug-cc-pVTZ and XYG3/6-311+G(3df,2p). 44,45,47 The XYG3 functional is evaluated with B3LYP orbitals and densities. 87 Only the ω B97X-D interaction energies are counterpoise-corrected. The M05-2X and M06-2X computations were performed with QChem 3.2. 88 The ω B97X-D computations were performed with the Gaussian 09 software package. 89 The B97-D3, B2PLYP-D3, and XYG3 computations were performed with NWChem 6.0. 90

Wave-function-based SAPT computations were performed with a development version of the PSI4 program. S2,91 All SAPT computations use the density fitting approximation. SAPT computations were performed with the aug-cc-pVQZ basis and use the aug-cc-pVQZ-RI auxiliary basis (with the exception of the PCCP dimer, where aug-cc-pVTZ and aug-cc-pVTZ-RI sets were used). To reduce the expense of including triple excitations, a truncated virtual space constructed from MP2 natural orbitals is used. This approximation has been shown to greatly improve efficiency without introducing significant errors. A similar approximation can be applied to the evaluation of the CCD dispersion energy and will be discussed in a forthcoming publication. The highest level of SAPT applied in this work is denoted SAPT2+3(CCD), which is defined as follows:

$$\begin{split} E_{\text{SAPT2+3(CCD)}} &= E_{\text{elst, resp}}^{(10)} + E_{\text{elst, resp}}^{(12)} + E_{\text{elst, resp}}^{(13)} \\ &+ E_{\text{exch}}^{(10)} + E_{\text{exch}}^{(11)}(S^2) + E_{\text{exch}}^{(12)}(S^2) \\ &+ E_{\text{exch}}^{(20)} + E_{\text{exch-ind, resp}}^{(20)}(S^2) \\ &+ E_{\text{ind}}^{(30)} + E_{\text{exch-ind}}^{(30)}(S^2) + {}^tE_{\text{ind}}^{(22)} \\ &+ {}^tE_{\text{exch-ind}}^{(22)} \\ &+ \varepsilon_{\text{disp}}^{(2)}[\text{CCD} + \text{ST(CCD)}] \\ &+ E_{\text{disp}}^{(30)} + E_{\text{exch-disp}}^{(30)} + E_{\text{exch-disp}}^{(30)} \\ &+ E_{\text{ind-disp}}^{(30)} + E_{\text{exch-ind-disp}}^{(30)} \end{split}$$

The supermolecular HF interaction energy is not included in the SAPT energy, since the third-order treatment of induction is expected to be sufficient when nonpolar monomers are considered. A thorough discussion of the supermolecular HF interaction energy in the context of SAPT can be found in ref 92. Approximate exchange terms are scaled according to $E_{\rm exch}^{(10)}/E_{\rm exch}^{(10)}(S^2)$ in order to account for higher-order exchange effects that are neglected in the S^2 approximation. At equilibrium, this scaling adds, at most, 0.03 kcal mol $^{-1}$ of exchange to the interaction energy. At shorter intermolecular separations, for the first repulsive configuration considered (the potential energy curves are computed in 0.1 Å increments), this scaling can add as much as 1 kcal mol $^{-1}$ to the exchange energy; the largest contributions come from scaling the $E_{\rm exch-ind}^{(30)}(S^2)$ term.

Table 1. Magnitude of the Dispersion Energy Relative to the Total SAPT2+3(CCD) Interaction Energy at Estimated CCSD(T)/CBS Limit Equilibrium Geometries

	NCCN	PCCP	P_2
cross	333%	205%	240%
PD	116%	216%	250%
T-shaped	96%	194%	234%

3. RESULTS

3.1. SAPT Analysis of the Dispersion Energy. The SAPT computations on the NCCN, PCCP, and P2 dimers allow the dispersion energy to be analyzed separately from the total interaction energy. The dependence of interaction energies on the theoretical treatment of dispersion can be estimated from the relative importance of the dispersion component. To identify which systems would most likely be sensitive to the treatment of dispersion, Table 1 shows the magnitude of the dispersion energy relative to the total SAPT2+3(CCD) interaction energy computed at the estimated CCSD(T)/CBS limit equilibrium geometry. In the cross configurations of the NCCN, PCCP, and P₂ dimers, for example, the magnitude of the dispersion energy is 2-3 times larger than the total interaction energy. The relative contribution from dispersion is appreciably smaller for the PD and T-shaped configurations of the NCCN dimer but remains large for P₂ and PCCP dimers. From this simple analysis, one would expect the PCCP and P₂ dimers to be more sensitive to the treatment of dispersion than the NCCN dimer.

A more detailed analysis of the dispersion energy in these complexes can be found in Table 2. Here, the dispersion energy is reported as computed at various truncations of the MBPT expansion. For the moment, we will consider only the $E_{\text{disp}}(2)$, $E_{\text{disp}}(4)$, and $E_{\text{disp}}(\text{CCD})$ treatments of the dispersion energy. The $E_{\text{disp}}(2)$ term is an MP2-like (UCHF) dispersion energy. The $E_{\text{disp}}(4)$ term contains perturbative intramonomer correlation corrections to dispersion through second order. The $E_{\text{disp}}(CCD)$ dispersion is the most reliable and uses CCD wave functions to correct the dispersion energy for intramonomer correlation. The dispersion energies are also presented as a percentage of the $E_{\text{disp}}(2)$ dispersion energy. These percentages can be used as a means of gauging how difficult the dispersion energies in a given complex are to compute. For simple systems, there will be little change between $E_{\rm disp}(2)$ and $E_{\rm disp}({\rm CCD})$. For more difficult systems, there will be a significant difference between $E_{\rm disp}(2)$ and $E_{\rm disp}(4)$, but not $E_{\rm disp}(4)$ and $E_{\rm disp}({\rm CCD})$. For the most difficult systems, there will be large differences between all three of these treatments of dispersion.

For the sake of comparison with more commonly studied systems, the methane dimer, methane—benzene, and benzene dimer dispersion energies are also presented in Table 2. For typical interactions, such as these, the $E_{\rm disp}(4)$ treatment of dispersion has been found previously to be quite reliable. ⁵⁰ The dispersion interactions between alkanes can be treated accurately with $E_{\rm disp}(2)$. The interactions involving π orbitals are more difficult and require, at least, the $E_{\rm disp}(4)$ treatment of dispersion. Dispersion within the NCCN dimer is comparable to the dispersion in the benzene dimer. There is a large difference between $E_{\rm disp}(2)$ and $E_{\rm disp}(4)$ and a small difference between $E_{\rm disp}(4)$ and $E_{\rm disp}(CCD)$. The P_2 dimer differs in that there is an even larger difference between $E_{\rm disp}(2)$ and $E_{\rm disp}(4)$, but the $E_{\rm disp}(CCD)$ correction is unimportant.

Table 2. Dispersion Energies Computed with Various Levels of SAPT^a

	$E_{ m disp}(2)^b$	$E_{\rm disp}(3)^c$	$E_{\rm disp}(2.5)^d$	$E_{\rm disp}(4)^e$	$E_{\rm disp}({\it CCD})^f$		
(NCCN) ₂ cross	-2.3	-1.5 (65%)	-1.9 (83%)	-2.0 (85%)	-1.9 (81%)		
(NCCN) ₂ PD	-2.9	-1.8 (65%)	-2.4 (82%)	-2.5 (87%)	-2.3 (82%)		
(NCCN) ₂ T-shaped	-2.5	-1.6 (66%)	-2.1 (83%)	-2.3 (92%)	-2.2 (87%)		
(PCCP) ₂ cross	-8.0	-3.9 (49%)	-6.0 (74%)	-6.3 (79%)	-5.8 (72%)		
(PCCP) ₂ PD	-7.9	-3.7 (47%)	-5.8 (73%)	-6.5 (82%)	-5.8 (73%)		
(PCCP) ₂ T-shaped	-4.7	-2.6 (55%)	-3.7 (77%)	-4.0 (85%)	-3.7 (78%)		
$(P_2)_2$ cross	-3.2	-1.9 (58%)	-2.5 (79%)	-2.4 (74%)	-2.4 (75%)		
$(P_2)_2$ PD	-3.6	-2.1 (58%)	-2.8 (79%)	-2.8 (78%)	-2.8 (78%)		
$(P_2)_2$ T-shaped	-2.0	-1.2 (58%)	-1.6 (79%)	-1.7 (82%)	-1.6 (79%)		
$(CH_4)_2$	-1.3	-1.2 (97%)	-1.2 (99%)	-1.3 (103%)	-1.3 (106%)		
CH ₄ -Bz	-2.9	-2.4 (82%)	-2.7 (91%)	-2.7 (93%)	-2.7 (93%)		
$(Bz)_2$ PD	-7.9	-5.2 (65%)	-6.6 (83%)	-6.7 (84%)	-6.5 (82%)		
^a Dispersion energies are given in kcal mol ⁻¹ and as percentages of $E_{\text{disp}}(2)$. ${}^{b}E_{\text{disp}}(2) = E_{\text{disp}}(20)$. ${}^{c}E_{\text{disp}}(3) = E_{\text{disp}}(30) + E_{\text{disp}}(30) + E_{\text{disp}}(30) + E_{\text{disp}}(20)$.							
$E_{\text{disp}}^{(20)} + (1)/(2)(E_{\text{disp}}^{(30)} + E_{\text{disp}}^{(21)}). \ ^{e}E_{\text{disp}}(4) = E_{\text{disp}}^{(20)} + E_{\text{disp}}^{(30)} + E_{\text{disp}}^{(31)} + E_{\text{disp}}^{(21)} + E_{\text{disp}}^{(21)} + E_{\text{disp}}^{(22)}(CCD) = E_{\text{disp}}^{(22)}(CCD) + E_{\text{disp}}^{(22)}(ST)(CCD).$							

The PCCP dimer has the most difficult dispersion interactions to compute. In this case, not only is the difference between $E_{\rm disp}(2)$ and $E_{\rm disp}(4)$ large, but the difference between $E_{\rm disp}(4)$ and $E_{\rm disp}(CCD)$ can be as large as 0.7 kcal mol⁻¹. This analysis shows that only the most robust methods will be capable of accurately computing dispersion interactions within the PCCP dimer.

3.2. Performance of Supermolecular Methods. The methods tested in this work can be grouped in terms of their treatments of the dispersion interaction. We test four methods that contain highly parametrized dispersion corrections (M05-2X, M06-2X, B97-D3, and ω B97X-D). We test four methods that contain empirically corrected MP2-like dispersion terms (SCS-MP2, SCS(MI)-MP2, XYG3, and B2PLYP-D3). The other methods compute dispersion with more robust techniques than MP2: MP2.5 contains contributions from MP3; SCS- and SCS(MI)-CCSD contain a CCSD treatment of dispersion; and MP2C and SAPT(DFT) use TDDFT-based dispersion corrections.

First, we will consider the M05-2X and M06-2X density functionals. Although these functionals do not contain the correct physics to describe long-range dispersion interactions, through extensive parametrization, they appear to capture "medium-range" dispersion (up to perhaps 4-5 Å). $^{44,84,93-96}$ This deficiency is evident in Figures 3-5; M05-2X tends to predict reasonable interaction energies near equilibrium and underbinds at long range. M06-2X often predicts reasonable interaction energies but equilibrium distances that are too short; at long range, the performance of M06-2X degrades quickly. The PD PCCP dimer (Figure 4) is an example of typical behavior for M05-2X and M06-2X. Although lacking long-range dispersion interactions, these functionals can provide reasonable interaction energies for small, closely interacting complexes with relatively low computational expense. In Figure 2, the average errors of each method are presented for the equilibrium configurations of the nine dimers considered in this work. For these equilibrium geometries, the performance of M05-2X and M06-2X is slightly better than the DFT-D methods. Their performance for the difficult dispersion interactions included in this work is similar to their performance for less difficult dispersion bound systems included in other test sets (e.g., the S22 and NBC10 test sets).⁴⁴ The fact that the accuracy of these functionals does not degrade for more difficult systems is a desirable characteristic. These functionals can be a

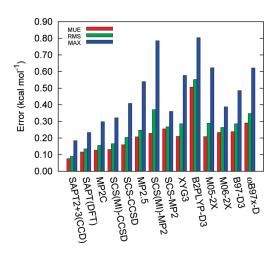


Figure 2. Errors in interaction energies for NCCN, PCCP, and P_2 dimers computed at equilibrium with various methods.

practical solution for studying near-equilibrium configurations of dispersion bound complexes.

The B97-D3 and ω B97X-D methods rely entirely on pairwise C_6R^{-6} terms to account for dispersion. Therefore, the accuracy of these functionals for dispersion-bound complexes is tied to the empirical parametrization of these -D terms. B97-D3 uses C_6 coefficients that provide some information about the chemical environment of each atom. 42 This is done through a rather ingenious atom-typing procedure that is completely black-box and varies continuously with the molecular geometry. The performance of these DFT-D methods at equilibrium is not as good as that for the M0N-2X methods; however, at long range, the behavior of these functionals improves rather than degrades (see Figure 3–5). ω B97X-D tends to be underbound relative to the CCSD(T) benchmark, which could be indicative of C_6 coefficients that are not optimal for these highly polarizable molecules. Overall, the B97-D3 functional outperforms ω B97X-D for the dimers considered in this work. This is a useful result, since the B97-D3 functional exhibits $\mathcal{O}(N^3)$ scaling as opposed to the $\mathcal{O}(N^4)$ scaling of the hybrid ω B97X-D method.

Two promising double hybrid density functionals, XYG3 and B2PLYP-D3, were applied to the NCCN, P₂, and PCCP dimers.

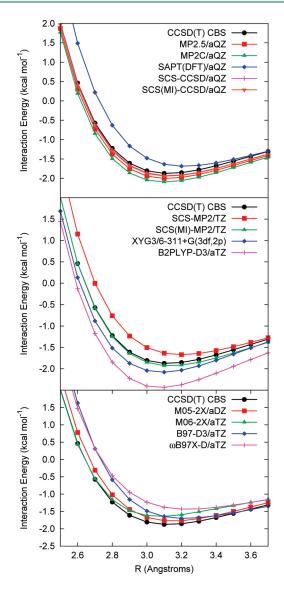


Figure 3. T-shaped NCCN dimer potential energy curves computed with various methods.

XYG3 accounts for dispersion with an MP2-like term that is evaluated using B3LYP orbitals and scaled by 0.3211. This small scaling parameter is required because short-range correlation is included elsewhere in the functional; additionally, the DFT orbitals have, relative to Hartree-Fock orbitals, a smaller HOMO-LUMO gap, resulting in a larger perturbative correction. The B2PLYP functional contains a similar scaled perturbative correction but still requires a small empirical dispersion correction in order to provide accurate results for dispersion bound complexes. The results for B2PLYP-D3 for these dimers is very poor. Perhaps the limited data set used to parametrize this functional, which contains no third row elements, contributes to this failing. This poor performance is unusual, as the B2PLYP-D3 method is typically reliable for treating dispersion dominated interactions. 44 XYG3 performs as well as any DFT-based method that was tested; this is consistent with previous findings for other test sets. 44,48 Unfortunately, it merely equals the performance of M05-2X and M06-2X, which both scale as $\mathcal{O}(N^4)$, whereas XYG3 scales as $\mathcal{O}(N^5)$ due to the perturbative correction. An important observation is that XYG3 does not inherit the poor

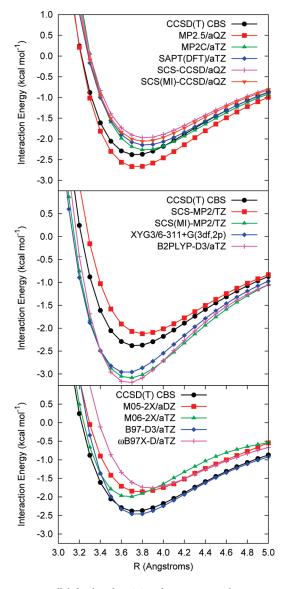


Figure 4. Parallel-displaced PCCP dimer potential energy curves computed with various methods.

performance of MP2 in its own perturbative correction, even for these particularly difficult cases. This can be attributed to the small fraction of the perturbative correction that needs to be included.

The SCS-MP2 methods we tested offer tremendous improvement over unscaled MP2 interaction energies. However, their performance is erratic; SCS(MI)-MP2, which was parametrized against the S22 test set, performs brilliantly for NCCN and P_2 dimers but severely overbinds the PCCP dimer. The SCS-MP2 method is more consistent but underbinds every dimer considered. It is probable that SCS-MP2/aug-cc-pVTZ would provide better results than SCS-MP2/cc-pVTZ, which is tested here. However, SCS-MP2 methods have an underlying problem that prevents any single parametrization from providing accurate results for a wide variety of dispersion bound complexes. The leading dispersion term, $E_{\rm disp}^{(2O)}$, which is included in MP2, is composed of 1/2 same-spin and 1/2 opposite-spin correlation (assuming a closed shell reference). For an SCS-MP2 method, this means that the scaling of the dispersion term is effectively an

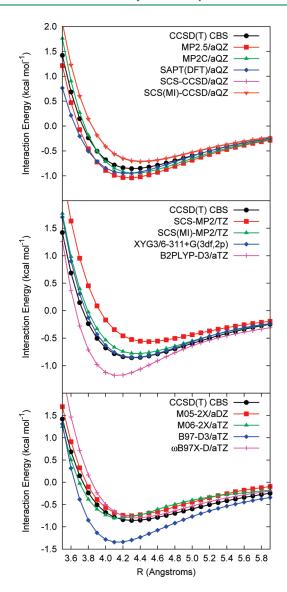


Figure 5. Cross P_2 dimer potential energy curves computed with various methods.

average of the same-spin and opposite-spin parameters, i.e.,

$$E_{\rm disp}^{(20)}({\rm SCS-MP2}) = \frac{S_{\rm os} + S_{\rm ss}}{2} E_{\rm disp}^{(20)}({\rm MP2}) \eqno(3)$$

With this in mind, the percentages of $E_{\rm disp}^{(20)}$ in Table 2 given for $E_{\rm disp}({\rm CCD})$ represent nearly ideal values of $(S_{\rm os}+S_{\rm ss})/2$ for each dimer considered. For the dimers in Table 2, the ideal value for $(S_{\rm os}+S_{\rm ss})/2$ ranges from 1.06 to 0.72. In SCS-MP2 and SCS-(MI)-MP2, these averaged values are 0.77 and 0.96, respectively. The use of a nonaugmented basis set, cc-pVTZ, essentially has the same effect as scaling the dispersion energy. The realization that the dispersion energy is scaled by a single parameter shows that it is not possible to find one set of SCS parameters that will provide consistent results for a diverse set of nonbonded interactions.

The problems encountered by SCS-MP2 methods are a result of the inconsistent behavior of MP2 for treating dispersion interactions. The SCS-CCSD methods circumvent this problem by attempting to correct a method that behaves in a much more consistent manner. Previous benchmarking of SCS-CCSD has shown that the only drawback is the $\mathcal{O}(N^6)$ scaling of CCSD;

admittedly, this is a considerable limitation. The tests of SCS- and SCS(MI)-CCSD for the NCCN dimer were consistent with previous results; indeed, the SCS-CCSD methods provide interaction energies within the uncertainties of the CCSD(T) benchmarks. For the P2 and PCCP dimers, however, their performance was not as good. Both parametrizations of SCS-CCSD consistently underbind both of these dimers. Despite this slight problem, the overall performance of both SCS-CCSD methods was still excellent. The new SCS(MI) parametrization outperforms the original SCS-CCSD parameters for nearly all of the test cases, but, on average, only by a few hundredths of 1 kcal mol⁻¹. The parameters themselves are very similar: the original oppositeand same-spin scaling parameters of 1.27 and 1.13, respectively, and the SCS(MI) parameters of 1.11 and 1.28. The apparent insensitivity of SCS-CCSD methods to the choice of parameters is an obvious advantage of SCS-CCSD over SCS-MP2 and a desirable trait in general for an SCS method to possess.

In a similar spirit to SCS-MP2 and SCS-CCSD, MP2.5 attempts to correct the behavior of MP2 and MP3 by combining their energies in an empirical manner. MP2.5 is an average of MP2 and MP3 interaction energies; equivalently, it is also MP2 plus half of the third-order correction. The motivation for this method is obvious from the results in Table 2. The third-order dispersion energy $[E_{\text{disp}}(3)]$ is always higher than the second-order dispersion energy $[E_{\text{disp}}(2)]$. In the cases where the second-order dispersion energy is a good estimate of the CCD dispersion energy $[E_{\text{disp}}(CCD)]$, the third-order correction to the dispersion energy is small. Where there is a large difference between the second-order dispersion energy and the CCD dispersion energy, there is an even larger difference between the second-order and third-order dispersion energies. We also report the second-order dispersion energy with half of the third-order correction included [$E_{\text{disp}}(2.5)$]. There is excellent agreement between $E_{\text{disp}}(2.5)$ and our best estimate of the dispersion energy, $E_{\text{disp}}(CCD)$; this is the origin of the excellent performance of MP2.5 for dispersion-bound complexes. For the complexes considered in this work, the performance of MP2.5 is slightly better than SCS-MP2 methods and slightly worse than SCS-CCSD methods. MP2.5 tends to overbind somewhat relative to the CCSD(T) benchmark. For more typical interactions, the simple averaging of MP2 and MP3 in the MP2.5 method provides rather accurate results.²⁶ For these more difficult dispersion bound complexes, a larger fraction of MP3 would need to be included for similar accuracy.

The least empirical method tested for these complexes is the MP2C method of Hesselmann. 36,37 This method uses TDDFT response functions to correct the account of dispersion in MP2. The initial tests of this method have been very promising. 26,37 Here, we apply MP2C to more difficult systems than were included in the previous tests. The performance of this method, however, does not degrade for these systems. The performance of MP2C is slightly better than the SCS-CCSD methods at greatly reduced cost. A related method, in terms of the treatment of dispersion, SAPT(DFT) also performs extremely well for these complexes. These methods perform better than any of the other approximate methods tested in this work. Additionally, both MP2C and SAPT(DFT) scale as $\mathcal{O}(N^3)$, which is better than or equivalent to all but the DFT methods (excluding the double hybrids). SAPT(DFT) is slightly better than MP2C, and this is likely due to a more accurate treatment of dispersion and a more rigorous treatment of exchange-dispersion. Both of these methods contain a treatment of the dispersion energy that does not degrade for more difficult systems. They can both be recommended as generally applicable for the study of nonbonded interactions.

4. CONCLUSIONS

We have introduced the NCCN, P_2 , and PCCP dimers as model systems for dispersion dominated $\pi-\pi$ interactions. These dimers involve dispersion interactions that are problematic to study computationally. Dispersion interactions of this type are typically found in much larger complexes (e.g., benzene dimer or indole—benzene). SAPT computations show that the dispersion in the NCCN dimer is similar in nature to the dispersion in the benzene dimer, while dispersion in P_2 and PCCP dimers is potentially more difficult to accurately characterize. The advantage of these model systems lies in their relatively small size; near complete basis set limit CCSD(T) interaction energies were obtained for NCCN, P_2 , and PCCP dimers.

The performance of many recently developed quantum mechanical methods was tested for the NCCN, P2, and PCCP dimers. DFT-based methods provide reasonable results at relatively low computational expense. An advantage of these methods is that their performance does not degrade for these more difficult systems. Spin-component scaled methods perform much better than their unscaled, parent methods; although generally good, the performance of SCS methods can be somewhat erratic. The best results for the NCCN, P2, and PCCP dimers come from the methods that use TDDFT response functions to describe dispersion interactions, MP2C and SAPT(DFT). These methods provide accuracy that could otherwise only be achieved through the inclusion of the effect of triple excitations on the dispersion energy. However, there are some limitations for general applicability of MP2C and SAPT(DFT) due to their roots in intermolecular perturbation theory (i.e., the need to fragment the system and the current lack of analytic gradients). Despite this, both methods are very promising for accurately characterizing π - π dispersion interactions in extended systems.

ASSOCIATED CONTENT

Supporting Information. Additional information regarding the monomer and dimer geometries, testing of aug-cc-pV(X +d)Z basis sets, and all nine of the PCCP, P₂ and NCCN dimer potential energy curves computed with various methods is available. This information is available free of charge via the Internet at http://pubs.acs.org/.

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