

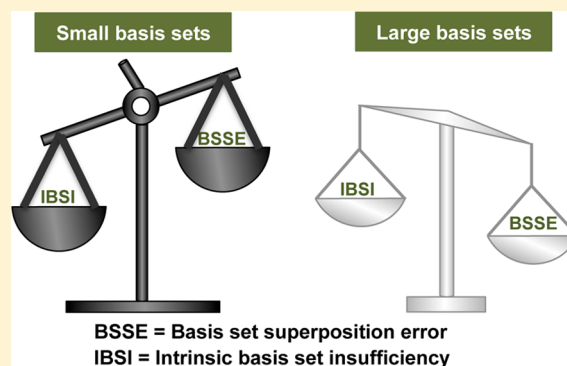
Some Observations on Counterpoise Corrections for Explicitly Correlated Calculations on Noncovalent Interactions

Brina Brauer, Manoj K. Kesharwani, and Jan M. L. Martin*

Department of Organic Chemistry, Weizmann Institute of Science, 76100 Rehovot, Israel

Supporting Information

ABSTRACT: The basis set convergence of explicitly correlated *ab initio* methods, when applied to noncovalent interactions, has been considered in the presence (and absence) of Boys–Bernardi counterpoise corrections, as well as using “half-counterpoise” (the average of raw and counterpoise-corrected values) as recently advocated in this journal [Burns, L. A.; Marshall, M. S.; Sherrill, C. D. *J. Chem. Theory Comput.* **2014**, *10*, 49–57]. Reference results were obtained using basis sets so large that BSSE (basis set superposition error) can be shown to be negligible. For the HF+CABS component, full counterpoise unequivocally exhibits the fastest basis set convergence. However, at the MP2-F12 and CCSD(T*)-F12b levels, surprisingly good *uncorrected* results can be obtained with small basis sets like cc-pVDZ-F12, owing to error compensation between basis set superposition error (which overbinds) and intrinsic basis set insufficiency (which underbinds). For intermediate sets like cc-pVTZ-F12, “half-half” averages work best, while for large basis sets like cc-pVQZ-F12, full counterpoise may be preferred but BSSE in uncorrected values is tolerably small for most purposes. A composite scheme in which CCSD(T)–MP2 “high level corrections” obtained at the CCSD(T*)-F12b/cc-pVDZ-F12 level are combined with “half-counterpoise” MP2-F12/cc-pVTZ-F12 interaction energies yields surprisingly good performance for standard benchmark sets like S22 and S66.



INTRODUCTION

BSSE (basis set superposition error¹) has been vexing quantum chemists for at least as long as they have been addressing noncovalent interactions (a.k.a. “weak chemical interactions”). The brute-force solution is of course to work in basis sets so large that BSSE becomes negligible, but this is only possible at present for the smallest systems. The Boys–Bernardi counterpoise method^{2–4} is therefore still one of the most widely used tools in the quantum chemical toolbox, with over 11 500 citations as of the time of writing. (We note in passing that a similar idea appears to have been introduced slightly earlier by Jansen and Ros.⁵) The counterpoise-corrected interaction energy of the dimer AB is defined as

$$-D_{\text{e,CP}} = E[\text{AB}] - E[\text{A(B)}] - E[\text{B(A)}] \quad (1)$$

while the nominal “raw” dissociation energy is found as

$$-D_{\text{e,raw}} = E[\text{AB}] - E[\text{A}] - E[\text{B}] \quad (2)$$

In these two equations, $E[\text{A(B)}]$ represents the total energy of monomer A in the presence of the basis functions on monomer B, and conversely for $E[\text{B(A)}]$. The BSSE (a term apparently first introduced by Liu and McLean¹) is then defined as

$$\begin{aligned} \Delta\text{CP} &= D_{\text{e,raw}} - D_{\text{e,CP}} \\ &= E[\text{A}] + E[\text{B}] - E[\text{A(B)}] - E[\text{B(A)}] \end{aligned} \quad (3)$$

There has been a long debate in the past about the formal correctness of the counterpoise correction, which was settled in the affirmative. For a review, see van Duijneveldt et al.⁶

However, in correlated *ab initio* calculations, it was noted numerous times (see, e.g., refs 7 and 8; for earlier observations with smaller basis sets, see, e.g., refs 9–13) that $D_{\text{e,raw}}$ tends to converge from above with increasing basis set size, while $D_{\text{e,CP}}$ tends to converge from below. This then automatically suggests averaging the two values as $D_{\text{e,half-half}} = (D_{\text{e,raw}} + D_{\text{e,CP}})/2$ (see, e.g., ref 14): most recently, this has been advocated by Sherrill and co-workers.¹⁵

Note that this suggestion does *not* imply that there is some formal problem with the Boys–Bernardi correction: rather, error compensation occurs between BSSE and what one might term “intrinsic basis set incompleteness” (what Dunning¹⁶ called “basis set convergence error”).

Following Davidson and Chakravorty,^{17,18} but simplifying the notation, let us define a complement basis set K as the orthogonal complement of the infinite basis set \mathcal{N} with the union of the monomer basis sets A and B, $K = \mathcal{N} \setminus (A \cup B)$. We assume in the following that no “bond functions”¹⁹ are employed in the dimer calculation (which would be intrinsically absent in the monomers).

Received: June 12, 2014

Published: July 23, 2014

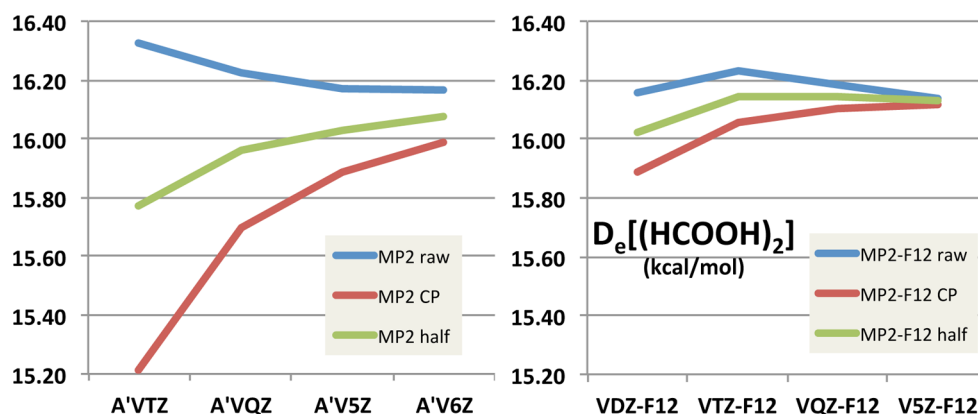


Figure 1. Dissociation energy (kcal/mol) of formic acid dimer using conventional MP2 and explicitly correlated MP2-F12, without and with counterpoise corrections.

The dissociation energy of the dimer AB at the complete basis set limit (where BSSE vanishes by definition) is then defined as

$$-D_{e,CBS} = E[AB(K)] - E[A(BK)] - E[B(AK)] \quad (4)$$

If we define the basis set incompleteness error (BSIE) as

$$\begin{aligned} \Delta BSIE &= -(D_{e,CBS} - D_{e,raw}) \\ &= E[AB(K)] - E[A(BK)] - E[B(AK)] - E[AB] \\ &\quad + E[A] + E[B] \end{aligned} \quad (5)$$

then we can partition it into two components:

$$\Delta BSIE = \Delta CP + \Delta IBSI \quad (6)$$

where the first is the Boys–Bernardi counterpoise correction for BSSE, eq 3, and we have defined a hypothetical correction for intrinsic basis set incompleteness (IBSI) as

$$\begin{aligned} \Delta IBSI &= E[AB(K)] - E[A(BK)] - E[B(AK)] - E[AB] \\ &\quad + E[A(B)] + E[B(A)] \end{aligned} \quad (7)$$

BSSE universally increases the dissociation energy and thus counterpoise correction ΔCP will reduce it, while generally the intrinsic basis set incompleteness will decrease the dissociation energy, and thus a putative correction for IBSI would increase it. Combining eqs 5 and 6 and rearranging, we obtain

$$-D_{e,CBS} = -D_{e,raw} + w\Delta CP \quad (8)$$

$$w = 1 + \frac{\Delta IBSI}{\Delta CP} = 1 - \left| \frac{\Delta IBSI}{\Delta CP} \right| \quad (9)$$

where w could be physically interpreted as a “Pauling point”²⁰ counterpoise weight. Following this argument, if the basis set ($A \cup B$) used is fairly close to the basis set limit for the property (and level of theory) at hand, then $\Delta IBSI$ will be very small, and $\Delta BSIE$ will be dominated by ΔCP , leading to $w \approx 1$, and “full counterpoise” will yield answers very close to the true basis set limit. If, however, ($A \cup B$) is still far away from the basis set limit for the property of interest (e.g., a covalent dissociation energy), then $\Delta IBSI$ will overwhelm ΔCP , and eq 9 might actually suggest a *negative* weight for the counterpoise correction! In fact, precisely *that* was proposed in the work of the NASA Ames group in the late 1980s, where they advocated^{21,22} using 3/2 of the calculated counterpoise correction as an estimate for residual basis set incompleteness.

(We wish to clarify that we do *not* advocate using w as some sort of “empirical counterpoise weight.” Rather, we will use it as a computational probe.)

In the present contribution, we shall consider the situation for explicitly correlated^{23–25} calculations on weakly interacting systems, for a number of representative test sets. Explicitly correlated calculations exhibit much faster basis set convergence than conventional orbital-based correlation methods and thus entail a much reduced BSSE—yet counterpoise corrections remain nontrivial for any basis set one can reasonably apply for medium-sized systems. (See Figure 1 for an illustration from the present work.)

Our goals in the present study are 4-fold. First, we wish to establish how BSSE behaves for different components of the interaction energy (SCF, MP2 correlation, post-MP2 correction) as well as (where possible) obtain interaction energies with basis sets so large that BSSE has been driven into insignificance. A second purpose is to rationalize the observed behavior. The third goal is to establish a reasonably inexpensive but accurate composite approach for medium-sized systems, while the fourth is to find the most economical option for more accurate benchmarks on smaller systems.

Concerning prior work, we note that BSSE in F12 calculations was considered in a recent study^{26,27} on some complexes of CO_2 . Ref 28 briefly discusses BSSE in F12 calculations in the context of covalent bond energies, while Boese et al.²⁹ discuss BSSE in their MP2-F12 study of the water, ammonia, and hydrogen fluoride dimers.

■ COMPUTATIONAL DETAILS

All calculations were carried out using MOLPRO 2012.1³⁰ running on the Faculty of Chemistry HPC cluster at the Weizmann Institute of Science.

In most calculations, we employed the cc-pVnZ-F12 correlation consistent basis sets ($n = D, T, Q$) optimized for F12 calculations³¹ and the auxiliary basis sets³² and CABS (complementary auxiliary basis sets)³³ developed for use with them, as well as the Weigend³⁴ JK-fitting basis sets, which are the MOLPRO default. Some additional calculations were performed using the very recently developed cc-pV5Z-F12 basis set.³⁵ The values recommended in refs 31 and 35 of the geminal exponent were used for them: 0.9 for cc-pVDZ-F12, 1.0 for cc-pVTZ-F12, 1.1 for cc-pVQZ-F12, and 1.2 for cc-pV5Z-F12. The SCF component was improved through the “CABS correction.”^{36,37}

Our discussion focuses on the CCSD-F12b approximation,^{36,38} but we also performed some exploratory calculations using the CCSD(F12*) (a.k.a., CCSD-F12c)³⁹ approximation. F12 approaches as presently practiced do not directly affect the connected quasiperturbative triples, so the basis set convergence behavior of the (T) contribution is effectively that of an orbital-based calculation. Marchetti and Werner⁴⁰ proposed convergence acceleration by scaling the (T) contribution by the MP2-F12/MP2 correlation energy ratio and found that this considerably improves calculated interaction energies for noncovalent complexes. (In a recent study, we found such scaling to be beneficial for F12 harmonic frequency calculations as well.⁴¹) The scaling proposed by Marchetti and Werner will be indicated by the notation (T*) instead of (T) in the present manuscript. The MP2-F12/MP2 ratios taper off fairly rapidly with the basis set: by way of illustration, for (HCOOH)₂ at the equilibrium geometry and cc-pVnZ-F12 basis sets, we obtain 1.220 (D), 1.089 (T), 1.043 (Q), and 1.026 (n = 5); for other molecules, similar values are found.

The MP2-F12 correlation energies discussed are those obtained with the 3C ansatz with fixed amplitudes,⁴² a.k.a. “3C(Fix)”.

The “frozen core” approximation was applied; i.e., all inner-shell orbitals were constrained to be doubly occupied.

The principal benchmark data sets employed are the S22,^{43,44} S22x5,^{43,44} and S66^{45,46} benchmark sets for weak interactions developed by the Hobza group. These sets were designed with a balance in mind between hydrogen-bonded, dispersion-bound (including π -stacking), and mixed-influence complexes. Specifically, S22 consists of seven hydrogen-bonded complexes, eight dispersive ones (seven π -stacks plus methane dimer), and seven “mixed-influence” complexes, while S66 contains 23 hydrogen-bonded, 23 dispersive (of which 10 π -stacks), and 20 mixed-influence dimers that are meant to be representative of weak interactions in biomolecules. Unless indicated otherwise, reference geometries were downloaded from the BEGBD Web site.⁴⁷

In addition, we considered the ADIM6 set of Grimme, which is one subset of large weak interaction⁴⁸ and general purpose⁴⁹ benchmarks by Grimme and co-workers. It consists of the dimers of the linear alkanes ethane through *n*-heptane. Reference geometries were taken from the Supporting Information of ref 49.

■ RESULTS AND DISCUSSION

a. S22/7x5 Data Set. As a first test case, we consider a reduced data set consisting of just 35 data points: from the S22x5 test set of Hobza and co-workers,^{43,44} we selected the complexes (NH₃)₂, (H₂O)₂, (HCOOH)₂, (HCONH₂)₂, (CH₄)₂, (C₂H₄)₂, and (C₂H₄)(C₂H₂), each taken at equilibrium and at geometries where the intermonomer distances were compressed to 90% and stretched by 120%, 150%, and 200%. (The stretched geometries in Grimme’s S130 set^{48,50} are similar but not identical.) cc-pVSZ-F12 calculations on the remaining systems were beyond the grasp of our hardware: in any case, the different stretched and compressed geometries cover not only a broader gamut of counterpoise corrections (an early observation of the increase in BSSE with decreasing intermonomer distance can be found in ref 10) but also of noncovalent bonding situations, as the different distance dependences of electrostatic, induction, exchange, and dispersion terms imply considerable shifts in the “balance of power” between them.

Due to hardware limitations, we were unable to compute all the counterpoise corrections with the cc-pVSZ-F12 basis set at the CCSD(T)-F12b level: however, we were able to obtain a complete set at the MP2-F12 level. Applying the MP2-F12 counterpoise corrections to the CCSD(T) energetics, we obtain a full set of CP-corrected data that agrees with the partial CP-CCSD(T*)-F12b/cc-pVSZ-F12 data set to within 0.001 kcal/mol RMS. Consequently, this is the manner in which we obtained the CCSD-F12b and CCSD(T*)-F12b reference data presented in Table 1. Full data at lower levels is given in the Supporting Information. Error statistics with and without counterpoise are given in Table 2.

First, let us consider the HF+CABS level. With the cc-pVSZ-F12 basis set, raw and counterpoise-corrected binding energies agree to within 0.001 kcal/mol RMSD, which means either could have been chosen as the reference. Inspection of Table 2 makes it clear that for cc-pVTZ-F12 and up, full counterpoise correction is the closer to the basis set limit of the three choices considered (raw, half–half, and full counterpoise). For cc-pVDZ-F12, half- and full-counterpoise yield similar RMSDs of about 0.014 kcal/mol, compared to 0.028 kcal/mol for the raw values. If one can afford cc-pVQZ-F12 calculations, then it basically becomes irrelevant for this component whether one does or does not apply counterpoise corrections.

We can now use the CP VSZ-F12 data as a reference and minimize the RMSD as a function of the “counterpoise weight factor” defined in eq 9. We reiterate that we are not advocating this as an “empirical counterpoise correction parameter,” but merely as a probe.

RMSD-minimized counterpoise weight factors thus obtained are 0.73 for VDZ-F12, 0.83 for VTZ-F12, and 0.82 for VQZ-F12, where for the two latter basis sets the counterpoise corrections are small enough that the difference between $w = 0.82$ and $w = 1$ is purely cosmetic.

Let us next consider the MP2-F12 correlation component. With the VSZ-F12 basis set, the RMSD between raw and counterpoise interaction energies is just 0.008 kcal/mol, the largest counterpoise corrections being 0.022 and 0.018 kcal/mol for (HCOOH)₂ at compressed and equilibrium geometries, respectively. In fact, the raw and counterpoise values for the set are close enough that selection of a reference level becomes somewhat arbitrary: if we choose the counterpoise VSZ-F12 data, then RMSD-minimized counterpoise weights become 0.14 for VDZ-F12, 0.55 for VTZ-F12, and 0.80 for VQZ-F12. For the total dissociation energy, the corresponding weights become 0.31 for VDZ-F12, 0.61 for VTZ-F12, and 0.81 for VQZ-F12: the difference for VDZ-F12 results from the behavior of the SCF component. Qualitatively speaking, the most cost-effective approach appears to be combining a raw MP2-F12/cc-pVDZ-F12 correlation component with counterpoise-corrected HF+CABS. For MP2-F12/cc-pVTZ-F12, half–half clearly agrees best with the basis set limit values, while for cc-pVQZ-F12, full counterpoise has a slight edge, even as the difference with half–half is negligible for all practical purposes, and even the difference with raw cc-pVQZ-F12 is largely of academic interest.

The performance penalty for counterpoise MP2-F12/cc-pVDZ-F12 is particularly large. This is even more the case for the CCSD-F12b total, which we are considering next. RMSD-minimized counterpoise fractions are −0.09(!) for VDZ-F12, 0.38 for VTZ-F12, and 0.74 for VQZ-F12. This then leaves “raw” as the best choice for VDZ-F12 and “half–half” for VTZ-

Table 1. Benchmark Dissociation Energies (kcal/mol) for the S22x5/7 Set Using the cc-pV5Z-F12 Basis Set with Full Counterpoise Correction^a

	HF +CABS	MP2- F12	CCSD- F12b	CCSD(T*)- F12b
at frozen S22x5 geometries				
(NH ₃) ₂ 0.9R	−0.348	2.469	1.966	2.392
(NH ₃) ₂ 1.0R	1.407	3.156	2.858	3.135
(NH ₃) ₂ 1.2R	1.656	2.363	2.242	2.359
(NH ₃) ₂ 1.5R	0.910	1.116	1.073	1.107
(NH ₃) ₂ 2.0R	0.321	0.357	0.346	0.351
(H ₂ O) ₂ 0.9R	2.282	4.330	3.958	4.319
(H ₂ O) ₂ 1.0R	3.585	4.960	4.730	4.990
(H ₂ O) ₂ 1.2R	3.436	4.037	3.947	4.071
(H ₂ O) ₂ 1.5R	2.147	2.302	2.275	2.310
(H ₂ O) ₂ 2.0R	0.958	0.951	0.945	0.945
(HCOOH) ₂ 0.9R	12.126	16.594	15.631	16.677
(HCOOH) ₂ 1.0R	15.295	18.547	17.892	18.758
(HCOOH) ₂ 1.2R	13.979	15.533	15.281	15.809
(HCOOH) ₂ 1.5R	8.776	9.168	9.139	9.358
(HCOOH) ₂ 2.0R	3.699	3.601	3.633	3.673
(HCONH ₂) ₂ 0.9R	8.970	14.230	13.326	14.377
(HCONH ₂) ₂ 1.0R	12.189	15.804	15.265 ^b	16.065 ^b
(HCONH ₂) ₂ 1.2R	11.640	13.264	13.102 ^b	13.542 ^b
(HCONH ₂) ₂ 1.5R	7.637	8.037	8.039	8.203
(HCONH ₂) ₂ 2.0R	3.578	3.487	3.524	3.544
(CH ₄) ₂ 0.9R	−1.319	0.276	0.109	0.331
(CH ₄) ₂ 1.0R	−0.366	0.491	0.401	0.527
(CH ₄) ₂ 1.2R	−0.031	0.241	0.211	0.252
(CH ₄) ₂ 1.5R	−0.003	0.061	0.054	0.063
(CH ₄) ₂ 2.0R	0.000	0.010	0.008	0.010
(C ₂ H ₄) ₂ 0.9R	−3.500	0.885	0.018	0.648
(C ₂ H ₄) ₂ 1.0R	−0.828	1.579	1.110	1.474
(C ₂ H ₄) ₂ 1.2R	0.067	0.835	0.684	0.806
(C ₂ H ₄) ₂ 1.5R	0.036	0.213	0.175	0.203
(C ₂ H ₄) ₂ 2.0R	0.004	0.031	0.025	0.029
(C ₂ H ₄) (C ₂ H ₂) 0.9R	−0.584	1.449	0.878 ^b	1.194 ^b
(C ₂ H ₄) (C ₂ H ₂) 1.0R	0.431	1.664	1.297	1.497
(C ₂ H ₄) (C ₂ H ₂) 1.2R	0.712	1.171	1.011 ^b	1.091 ^b
(C ₂ H ₄) (C ₂ H ₂) 1.5R	0.408	0.522	0.469	0.491
(C ₂ H ₄) (C ₂ H ₂) 2.0R	0.139	0.154	0.141	0.146
at equilibrium including geometry relaxation ^c				
(NH ₃) ₂	1.394	3.158	2.856	3.136
(H ₂ O) ₂	3.424	4.942	4.693	4.974
(HCOOH) ₂	11.565	16.119	15.064	16.154
(HCONH ₂) ₂	9.617	14.761	13.806	14.882
(CH ₄) ₂	−0.418	0.459	0.384	0.520
(C ₂ H ₄) ₂	−0.884	1.560	1.093	1.470
(C ₂ H ₄) (C ₂ H ₂)	0.317	1.646	1.264	1.488

^a0.9R, e.g., indicates a geometry where the intermonomer distance was scaled by a factor of 0.9. ^bCounterpoise correction obtained at the MP2-F12 level. ^cMonomer geometries optimized at same levels of theory as the respective dimers in ref 43.

F12, while for VQZ-F12 there is no real difference between half–half and full counterpoise.

Somewhat disappointingly, but not surprisingly (see, e.g., ref 51), the CCSD–MP2 difference converges rather slowly with the basis set, more slowly in fact than the CCSD(T)–MP2 difference. The same is true, in fact, of the (T) contribution (see Table ESI-1 in the Supporting Information). However, since CCSD–MP2 decreases D_e while (T) increases it, the basis

Table 2. RMS Deviations (kcal/mol) from the Basis Set Limit Values in Table 1 for Different Components, Basis Sets, and Counterpoise Corrections

	cc-pVDZ- F12	cc-pVTZ- F12	cc-pVQZ- F12	cc-pVSZ- F12
HF+CABS dissociation energy (D_e)				
raw	0.028	0.015	0.005	0.001
counterpoise	0.014	0.003	0.001	0.000
half–half	0.014	0.007	0.002	0.000
MP2-F12 correlation component of D_e				
raw	0.030	0.032	0.024	0.008
counterpoise	0.081	0.026	0.007	0.000
half–half	0.042	0.008	0.010	0.004
MP2-F12 total D_e				
raw	0.052	0.045	0.029	0.008
counterpoise	0.093	0.029	0.007	0.000
half–half	0.043	0.011	0.012	0.004
CCSD-F12b total D_e				
raw	0.046	0.030	0.019	0.008
counterpoise	0.155	0.048	0.007	0.002
half–half	0.092	0.013	0.007	0.005
CCSD(T*)-F12b total D_e				
raw	0.043	0.054	0.030	0.008
counterpoise	0.180	0.053	0.010	0.001
half–half	0.083	0.009	0.011	0.004
HLC on D_e				
raw	0.018	0.010	0.002	0.000
counterpoise	0.090	0.025	0.003	0.001
half–half	0.049	0.009	0.002	0.000
composite with raw CCSD(T*)-F12b/cc-pVDZ-F12 HLC ^a				
raw		0.043	0.031	
counterpoise		0.039	0.021	
half–half		0.019	0.020	
composite with raw CCSD(T*)-F12b/cc-pVTZ-F12 HLC ^a				
raw		0.054	0.038	
counterpoise		0.021	0.008	
half–half		0.020	0.022	
composite with half–half CCSD(T*)-F12b/cc-pVTZ-F12 HLC ^a				
raw			0.022	
counterpoise			0.015	
half–half			0.007	

^aAdditivity approximation $E[\text{MP2-F12/cc-pVnZ-F12}] + E[\text{CCSD(T*)-F12b/cc-pVmZ-F12}] - E[\text{MP2-F12/cc-pVmZ-F12}]$, $m < n$.

set errors largely cancel, and the “high level correction” (HLC), i.e., the CCSD(T)–MP2 difference, actually converges quite rapidly. With the VQZ-F12 basis set, all three choices yield negligible RMSDs of 0.002–3 kcal/mol, while with the even larger VSZ-F12 basis set the three choices are effectively indistinguishable. With the cc-pVTZ-F12 basis set, “half–half” HLCs just barely edge out their “raw” counterparts, and both (at about 0.01 kcal/mol RMSD) are clearly superior to full counterpoise. Of greatest practical interest is the behavior for the economical cc-pVDZ-F12 basis set: here, a felicitous error compensation between BSSE and IBSI is manifestly at work, with “raw” clearly yielding the lowest RMSD at 0.018 kcal/mol. This immediately suggests ccCA-type^{52–54} composite approximations where the HLC is computed “raw” in a small basis set, and the MP2-F12 D_e in a larger one.

RMSD values for such approximations, with and without counterpoise corrections, can be found in Table 2. The combination of half-counterpoise MP2-F12/cc-pVTZ-F12 with

raw CCSD(T*)-F12b/cc-pVDZ-F12 HLC is without a doubt the most cost-effective, at RMSD = 0.019 kcal/mol. The only approximation that performs better still is full counterpoise MP2-F12/cc-pVQZ-F12 combined with HLC at the raw CCSD(T*)-F12b/cc-pVTZ-F12 level, yielding an RMSD = 0.008 kcal/mol—functionally equivalent to a vastly more expensive CCSD(T*)-F12b/cc-pVQZ-F12 calculation. In situations where counterpoise corrections cannot be conveniently applied—such as conformer equilibria (e.g., refs 55 and 56)—the combination of raw MP2/VQZ-F12 with raw CCSD(T*)-F12b/VDZ-F12 HLC may be useful at RMSD = 0.031 kcal/mol. Finally, the combination of half-counterpoise MP2-F12/VQZ-F12 with half-counterpoise HLC/VTZ-F12 yields RMSD = 0.007 kcal/mol, which can effectively be regarded as benchmark quality.

Turning now to the single-level CCSD(T*)-F12b results, we see that the error tendencies in MP2-F12 and in HLC actually amplify each other, such that counterpoise-corrected VDZ-F12 now reaches RMSD = 0.18 kcal/mol. Raw CCSD(T*)-F12b/cc-pVDZ-F12 has an RMSD of just 0.043 kcal/mol despite its fairly low cost, while half-half with the VTZ-F12 basis set even falls below RMSD = 0.01 kcal/mol. For VQZ-F12, neither full counterpoise nor half counterpoise perform any better than half-half VTZ-F12, at 1 order of magnitude greater computational expense.

There are indications that basis set convergence for CCSD(F12*) is faster than for CCSD-F12b (see, e.g., ref 41). Would this also be true for the HLCs here? With the VTZ-F12 basis set we find (see Supporting Information) differences between CCSD(T*)-F12b and CCSD(T*)(F12*) HLCs to be insignificant, and basically nonexistent with the VQZ-F12 basis set. With the small VDZ-F12 basis set, however, individual differences of up to 0.1 kcal/mol can be seen for species like (HCOOH)₂, with the (F12*) results closer to the larger basis set HLCs. Nevertheless, substitution of (F12*) HLCs does not improve error statistics, either for the present sample or for the whole S22 set.

Finally, a reviewer commented on the fact that the cyclic C_{2h} geometry for (NH₃)₂ in the S22 set does not correspond to the global minimum, which is an eclipsed Cs structure. (Theoretical and experimental work on the ammonia dimer has been reviewed by Havenith.⁵⁷) In conventional CCSD(T)/aug'-cc-pV{Q,5}Z calculations,⁵⁸ as well as at the MP2-F12/aug-cc-pVQZ level,²⁹ the C_{2h} structure is found to lie just 0.01 kcal/mol above the global minimum. For the sake of completeness, we carried out CCSD(T*)-F12b/cc-pVTZ-F12 optimizations and harmonic frequency calculations on all five stationary points in ref 58. In addition, on just the global minimum and the cyclic structure, we performed CCSD(T*)-F12b/cc-pVQZ-F12 optimizations and CCSD(T*)-F12b/cc-pVSZ-F12 single-point energies. The calculated imaginary frequency of the saddle point is just 19i cm⁻¹: the energy difference is found to be 0.013, 0.007, and 0.009 kcal/mol for cc-pV{T,Q,5}Z-F12, respectively. Therefore, while the (NH₃)₂ geometry in the S22 set is indeed neither the global nor even a local minimum, the energy difference involved is insignificant compared to the uncertainty in the other reference values, and in practice this will not matter for the overall error statistics of a given method for the S22 set. Also, as concluded previously,⁵⁷ this is a nonrigid molecule that will exhibit large amplitude motions, for which the vibrationally averaged structure is qualitatively different from the *r_e* geometry.

b. ADIM6 Data Set. This data set^{48,49} consists of the *n*-alkane dimers C_{*n*}H_{2*n*+2} (*n* = 2–7). Unlike the previous one, it is entirely dominated by dispersive interactions.

Reference geometries were taken from the Supporting Information of ref 49. No optimization was attempted. Selected results can be found in Table 3, with full results given in the Supporting Information.

Table 3. RMS Deviations (kcal/mol) from the MP2-F12 Basis Set Limits for the ADIM6 Set and Best Estimate CCSD(T)-F12b Dissociation Energies (kcal/mol) from Composite Schemes

	cc-pVDZ-F12	cc-pVTZ-F12	cc-pVQZ-F12
HF+CABS dissociation energy (<i>D_e</i>)			
raw	0.084	0.019	0.003
counterpoise	0.003	0.001	0.000
half-half	0.041	0.009	0.002
MP2-F12 correlation component of <i>D_e</i>			
raw	0.040	0.014	0.004
counterpoise	0.106	0.037	0.011
half-half	0.073	0.025	0.004
MP2-F12 total <i>D_e</i>			
raw	0.047	0.009	0.007
counterpoise	0.109	0.038	0.011
half-half	0.033	0.016	0.003
composite HLC(smaller)+MP2-F12(larger)			Grimme ^{48,a}
HLC	VDZ-F12 raw	VTZ-F12 half	
MP2-F12	VTZ-F12 half	VQZ-F12 half	
(C ₂ H ₆) ₂	1.315	1.334	1.300
(C ₃ H ₈) ₂	1.979	1.984	1.970
(<i>n</i> -C ₄ H ₁₀) ₂	2.874	2.873	2.790
(<i>n</i> -C ₆ H ₁₂) ₂	3.767	3.758	3.680
(<i>n</i> -C ₆ H ₁₄) ₂	4.639	4.621	4.610
(<i>n</i> -C ₇ H ₁₆) ₂	5.589	5.559	5.600

^aOrbital MP2/cc-pVnZ extrapolation with HLC obtained at the CCSD(T)/cc-pVTZ level through (*n*-butane)₂ and linearly extrapolated for longer chains

For ADIM6, we were able to obtain MP2-F12/VnZ-F12 through *n* = Q, as well as CCSD(T*)-F12b/cc-pVDZ-F12 and cc-pVTZ-F12. For the MP2-F12 reference, we extrapolate the correlation component of MP2-F12/V{T,Q}Z-F12 results to the infinite basis set limit (where the counterpoise correction should vanish) using the familiar^{59,60} $E_{\infty} \approx E_L + (E_L - E_{L-1}) / [(L/L - 1)^{\alpha} - 1]$ formula with $\alpha = 4.071516$ given in Hill et al.⁶¹ The “raw” and “counterpoise” extrapolated results agree to within 0.003 kcal/mol RMSD: we have taken the counterpoise values (added to the CP HF+CABS/cc-pVQZ-F12) as the reference.

Once again, we see that “raw” works best for the MP2-F12/VDZ-F12 correlation component and that full counterpoise yields a fairly large RMSD with that basis set, but now (for this dispersion-driven problem) even for VTZ-F12 the “raw” values seem to be preferred; for VQZ-F12, once again, it does not really matter which are used.

For the HF+CABS component by itself, full counterpoise again is unequivocally preferred.

We were also able to obtain CCSD(T*)-F12b/cc-pVDZ-F12 and cc-pVTZ-F12 data with and without counterpoise corrections. (The counterpoise calculations for heptane were particularly demanding on account of the low symmetry. This calculation ran for over a week on 32 CPUs.) From these, we

can obtain CCSD(T)-MP2 corrections: these are (for the system at hand) very similar between cc-pVDZ-F12 and cc-pVTZ-F12, and monotonically vary with chain length from essentially nil for the ethane dimer to -0.31 kcal/mol for the *n*-heptane dimer. Our “best estimate” values combine half-half VTZ-F12 HLCs with half-half MP2-F12/VQZ-F12. The low-cost combination of raw VDZ-F12 HLC with half-counterpoise MP2-F12/VTZ-F12 agrees very well with that, as do both with Grimme’s wave function-based results. In fact, even the relatively inexpensive raw CCSD(T*)-F12b/cc-pVDZ-F12 calculations are within 0.06 kcal/mol of our best estimates.

c. S22 and S66 Data Sets. Error statistics for these two diverse data sets of 22 and 66 noncovalent complexes, respectively, can be found in Table 4. The S22 data set⁴³

Table 4. RMS Deviations (kcal/mol) for the S22 and S66 Data Sets Using Different Approximations

		S22	S22	S22	S66
BSSE on HLC		raw	CP	half-half	raw
MP2-F12 level	HLC level				
VDZ-F12 raw	same	0.117			0.091
VDZ-F12 CP	same		0.333		N/A
VDZ-F12 half	same			0.125	N/A
VTZ-F12 raw	same	0.085			N/A
VTZ-F12 CP	same		0.104		N/A
VTZ-F12 half	same			0.035	N/A
VTZ-F12 raw	VDZ-F12	0.110	0.061	0.053	0.086
VQZ-F12 raw	VDZ-F12	0.075	0.104	0.056	0.060
VTZ-F12 CP	VDZ-F12	0.081	0.199	0.134	0.077
VQZ-F12 CP	VDZ-F12	0.049	0.152	0.087	0.054
VTZ-F12 half	VDZ-F12	0.059	0.126	0.067	0.055
VQZ-F12 half	VDZ-F12	0.057	0.127	0.067	0.053
VQZ-F12 raw	VTZ-F12	0.070	0.027	0.045	N/A
VQZ-F12 CP	VTZ-F12	0.030	0.048	0.032	N/A
VQZ-F12 half	VTZ-F12	0.043	0.030	0.028	N/A
original S22 paper ⁴³		0.220			
Sherrill et al. ⁶²	reference				
original S66 paper ⁴⁵					0.106
S66 revision ⁴⁶					reference

includes several systems (such as the nucleic acid dimers in Watson–Crick and stacked configurations) where even the VDZ-F12 calculation turned out to be computationally quite demanding.

An energy breakdown between HF+CABS, MP2-F12 correlation, and HLC for the S22 and S66 sets reveals that hydrogen-bonded complexes (and some of the “mixed” complexes such as $C_2H_2 \cdots H_2O$) are associated with large percentages of D_e recovered at the HF+CABS level, while the dispersive (and most mixed) complexes are repulsive at the HF level and the π -stacks especially so. While HLCs for the hydrogen-bonded complexes are on the order of just 1–3% of D_e , especially large HLC percentages are seen for the π -stacks, reaching -3.6 kcal/mol for indole–benzene, -3.0 kcal/mol for stacked (adenine)(thymine), and -2.4 kcal/mol for the parallel-displaced benzene dimer. The “mixed” complexes represent an intermediate situation, while among the dispersive systems alkane–aromatic complexes have large HLC percentages and alkane–alkane complexes small ones. In short, these sets will be less “forgiving” of poor HLCs than the previous ones discussed above.

The best S22 reference values currently available appear to be the 2011 re-evaluation by Sherrill and co-workers.⁶² Compared to that, our “raw” CCSD(T*)-F12b/cc-pVDZ-F12 calculated values have a surprisingly low RMSD = 0.12 kcal/mol, compared to 0.33 kcal/mol counterpoise and 0.13 kcal/mol half-half, or for that matter 0.22 kcal/mol for the original S22 calculations.⁴³

We were able to perform CCSD(T*)/cc-pVTZ-F12 calculations with full and half-counterpoise correction for the 15 smallest systems (see Table ESI-2), while in the “raw” case we were able to additionally include the stacked uracil dimer. Here, “half-half” has the lowest RMSD = 0.035 kcal/mol, compared to 0.085 kcal/mol raw and 0.10 kcal/mol with full counterpoise.

Considering that for the largest systems, even CCSD(T)-F12b/VDZ-F12 calculations pushed the limits of our hardware, one would like to know the performance of a composite scheme combining HLCs calculated at that level with MP2-F12 in larger basis sets. This also brings us to the subsidiary question: whether or not to apply Marchetti–Werner scaling to the parenthetical triples (Table ESI-2). Both the HLCs and the connected triples components being substantially larger for the S22 set than for the subset considered in Tables 1, 2, and ESI-1, differences between different (T) approximations ought to be clearer. As a gauge for systematic bias, mean signed deviations (MSDs) have been given in Tables ESI-1 and ESI-2 alongside the RMSD values. In order to obtain reference values, we subtracted counterpoise-corrected MP2-F12/cc-p V{T,Q}Z-F12 extrapolated⁴¹ basis set limits from the Sherrill CCSD(T) limits⁶²—using the Marchetti and Werner MP2 limits⁴⁰ instead of the presently calculated ones yields similar results.

For the cc-pVDZ-F12 basis set, the smallest MSD (effectively nil) and RMSD (0.05 kcal/mol) are rendered by raw (T*). Unscaled (T) leads to systematic underestimates (MSD -0.12 kcal/mol) even for the raw values, which is exacerbated to -0.26 kcal/mol with full counterpoise. Indeed, with full counterpoise even (T*) has an MSD of -0.11 kcal/mol. (We considered an alternate (T) scaling formula

$$E[(Tb)] = E[(T)] \frac{E_{\text{corr}}[\text{CCSD} - \text{F12b}]}{E_{\text{corr}}[\text{CCSD}]} \quad (10)$$

While it may be useful in situations with significant static correlation where MP2 will work particularly poorly, no significant improvement in error statistics was found for the problem at hand.)

We were able to obtain CCSD(T*)/VTZ-F12 HLCs with full and half-counterpoise correction for a subset of 15 systems (see Table ESI-2), while for the raw VTZ-F12 HLCs, we were able to additionally include a stacked uracil dimer. We found (see Table ESI-2) that (T*) half-half has effectively zero MSDs with both variants of the Marchetti–Werner scaling. However, most other variations in Table ESI-2 yield acceptable error statistics with that basis set, with the exception of (T) with full counterpoise correction, which is clearly contraindicated. (We note that the Marchetti–Werner scaling factors obtained are considerably smaller, at 1.07 – 1.10 , than those for the cc-pVDZ-F12 basis set, 1.18 – 1.22 .)

With the “raw” HLC combined with raw MP2-F12/VTZ-F12, no improvement over the VDZ-F12 calculation by itself is seen—and combining full-counterpoise VTZ-F12 and HLC/VDZ-F12 actually *increases* the RMSD to 0.20 kcal/mol—but several other schemes reach low RMSDs of 0.05 – 0.06 kcal/mol

that are to be considered equivalent within the precision of the reference data and that are not much worse than a single-level CCSD(T*)-F12b/cc-pVTZ-F12 calculation, which is an order of magnitude more costly. Considering the high computational cost and resource demands of the CCSD(T)-F12b counterpoise calculations for the larger systems—and the relative ease of performing the corresponding MP2-F12 counterpoise calculations—it would appear that MP2-F12/VTZ-F12 half-counterpoise with a raw HLC/VDZ-F12 or MP2-F12/VQZ-F12 full counterpoise with a raw HLC/VDZ-F12 are the most attractive options, with raw MP2-F12/VQZ-F12 remaining for problems where counterpoise corrections would be difficult to implement.

While for much of the S22 data set, CCSD(T*)-F12b/cc-pVQZ-F12 is entirely out of reach, a CCSD(T*)-F12b/cc-VTZ-F12 HLC can be combined with an MP2-F12/cc-pVQZ-F12 calculation. As seen in Table 4, several such combinations reach RMSDs of about 0.03 kcal/mol, which are probably comparable to the uncertainty in the reference data themselves, and make them potential options for when still greater accuracy is required than achievable with a cc-pVDZ-F12 HLC.

As a further test for our composite approaches, we considered the S66 data set, which contains 23 hydrogen-bonded species, 10 π -stacked complexes, 13 dispersive complexes, and 20 “mixed” complexes (such as dipole–quadrupole interactions).

The difference between the original S66 reference values⁴⁵ and the later updated benchmark⁴⁶ is 0.106 kcal/mol RMS. For comparison, half–half MP2-F12/VTZ-F12 combined with a raw VDZ-F12 HLC agrees to RMSD = 0.055 kcal/mol with the revised reference values. An effectively equivalent RMSD = 0.060 kcal/mol would be obtained if raw VQZ-F12 were used instead. For comparison, RMSD = 0.091 kcal/mol is found for straightforward CCSD(T*)-F12b/cc-pVDZ-F12 without paying any further heed to basis set expansion.

CONCLUSIONS

We have considered the basis set convergence of “raw” (uncorrected), counterpoise-corrected, and “half–half” (averaged) noncovalent interaction energies for F12 methods.

For the HF+CABS component, it appears clear that full counterpoise correction results in the fastest basis convergence.

For MP2-F12 and CCSD(T)-F12b with small basis sets such as cc-pVDZ-F12, however, “raw” interaction energies are actually considerably closer to the basis set limit than their counterpoise-corrected counterparts. This is due to error compensation between BSSE (which artificially increases computed interaction energies) and intrinsic basis set incompleteness (which reduces them).

For MP2-F12 or CCSD(T)-F12b with intermediate basis sets like cc-pVTZ-F12, “half–half” appears to be closest to the basis set limit, while for cc-pVQZ-F12 and larger basis sets, the counterpoise corrections become sufficiently small that the choice between raw, “half–half,” and full counterpoise is somewhat academic.

For the problem at hand, while CCSD(F12*) appears to be closer to the basis set limit than CCSD-F12b if a cc-pVDZ-F12 basis set is used, the difference between the two approximations to CCSD-F12 becomes insignificant for cc-pVTZ-F12 and effectively vanishes for still larger basis sets.

The combination of “half–half” MP2-F12/cc-pVTZ-F12 or “raw” MP2-F12/cc-pVQZ-F12 with a “raw” higher-level correction at the CCSD(T*)-F12b/cc-pVDZ-F12 level appears

to perform very well for noncovalent interaction energies. From a pragmatic standpoint, the HLC(raw):MP2-F12/VTZ-F12-(half) combo may be preferable for weakly interacting dimers, while HLC(raw):MP2-F12/VQZ-F12(raw) would be preferable in situations where counterpoise calculations would be awkward or impossible—such as conformer equilibria.

Finally, the recommendation from ref 15 for orbital-based *ab initio* calculations on weak complexes—namely, to apply “half–half” counterpoise corrections—can be seen to apply for explicitly correlated calculations as well, except for small basis sets where raw energies are to be preferred.

ASSOCIATED CONTENT

Supporting Information

Complete ref 30; Tables ESI-1 and ESI-2 comparing performance for S22x5/7 and S22 HLC, respectively, with and without triples scaling; Table ESI-3 with energies, geometries, and harmonic frequencies for the five stationary points of (NH₃)₂; Excel spreadsheet containing calculated total and interaction energies for the various data sets discussed in the paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Fax: +972 8 9344142. E-mail: gershom@weizmann.ac.il.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank Drs. Daniel Boese (U. of Potsdam, Germany) and Sebastian Kozuch (U. of North Texas, Denton) and Profs. Martin Suhm (U. of Göttingen, Germany) and Amir Karton (U. of Western Australia, Perth) for helpful discussions, and the reviewers for valuable suggestions. This research was supported in part by the Lise Meitner-Minerva Center for Computational Quantum Chemistry and by the Helen and Martin Kimmel Center for Molecular Design.

REFERENCES

- (1) Liu, B.; McLean, A. D. Accurate Calculation of the Attractive Interaction of Two Ground State Helium Atoms. *J. Chem. Phys.* **1973**, *59*, 4557.
- (2) Boys, S. F.; Bernardi, F. The Calculation of Small Molecular Interactions by the Differences of Separate Total Energies. Some Procedures with Reduced Errors. *Mol. Phys.* **1970**, *19*, 553–566.
- (3) Boys, S. F.; Bernardi, F. (Reprinted) The Calculation of Small Molecular Interactions by the Differences of Separate Total Energies. Some Procedures with Reduced Errors. *Mol. Phys.* **2002**, *100*, 65–73.
- (4) Handy, N. C. Comment. *Mol. Phys.* **2002**, *100*, 63–63.
- (5) Jansen, H. B.; Ros, P. Non-Empirical Molecular Orbital Calculations on the Protonation of Carbon Monoxide. *Chem. Phys. Lett.* **1969**, *3*, 140–143.
- (6) Van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H. State of the Art in Counterpoise Theory. *Chem. Rev.* **1994**, *94*, 1873–1885.
- (7) Halkier, A.; Koch, H.; Jørgensen, P.; Christiansen, O.; Nielsen, I. M. B.; Helgaker, T. A Systematic Ab Initio Study of the Water Dimer in Hierarchies of Basis Sets and Correlation Models. *Theor. Chem. Acc.* **1997**, *97*, 150–157.

- (8) Halkier, A.; Klopper, W.; Helgaker, T.; Jørgensen, P.; Taylor, P. R. Basis Set Convergence of the Interaction Energy of Hydrogen-Bonded Complexes. *J. Chem. Phys.* **1999**, *111*, 9157.
- (9) Feller, D. Application of Systematic Sequences of Wave Functions to the Water Dimer. *J. Chem. Phys.* **1992**, *96*, 6104.
- (10) Klopper, W.; Noga, J. An Explicitly Correlated Coupled Cluster Calculation of the Helium–Helium Interatomic Potential. *J. Chem. Phys.* **1995**, *103*, 6127.
- (11) Van Mourik, T.; Wilson, A. K.; Peterson, K. A.; Woon, D. E.; Dunning, T. H. The Effect of Basis Set Superposition Error (BSSE) on the Convergence of Molecular Properties Calculated with the Correlation Consistent Basis Sets. *Adv. Quantum Chem.* **1998**, *31*, 105–135.
- (12) Feyereisen, M. W.; Feller, D.; Dixon, D. A. Hydrogen Bond Energy of the Water Dimer. *J. Phys. Chem.* **1996**, *100*, 2993–2997.
- (13) Peterson, K. A.; Dunning, T. H. Benchmark Calculations with Correlated Molecular Wave Functions. VII. Binding Energy and Structure of the HF Dimer. *J. Chem. Phys.* **1995**, *102*, 2032.
- (14) Schwabe, T.; Grimme, S. Double-Hybrid Density Functionals with Long-Range Dispersion Corrections: Higher Accuracy and Extended Applicability. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3397–3406.
- (15) Burns, L. A.; Marshall, M. S.; Sherrill, C. D. Comparing Counterpoise-Corrected, Uncorrected, and Averaged Binding Energies for Benchmarking Noncovalent Interactions. *J. Chem. Theory Comput.* **2014**, *10*, 49–57.
- (16) Dunning, T. H. A Road Map for the Calculation of Molecular Binding Energies. *J. Phys. Chem. A* **2000**, *104*, 9062–9080.
- (17) Davidson, E. R.; Chakravorty, S. J. A Possible Definition of Basis Set Superposition Error. *Chem. Phys. Lett.* **1994**, *217*, 48–54.
- (18) Davidson, E. R.; Chakravorty, S. J. Reply to Comment on “A Possible Definition of Basis Set Superposition Error. *Chem. Phys. Lett.* **1995**, *241*, 146–148.
- (19) Tao, F.-M. Bond Functions, Basis Set Superposition Errors and Other Practical Issues with Ab Initio Calculations of Intermolecular Potentials. *Int. Rev. Phys. Chem.* **2001**, *20*, 617–643.
- (20) Löwdin, P. O. Twenty-Five Years of Sanibel Symposia: A Brief Historic and Scientific Survey. *Int. J. Quantum Chem.* **1986**, *28*, 19–37.
- (21) Bauschlicher, C. W.; Langhoff, S. R.; Taylor, P. R. On the Dissociation Energy of BH. *J. Chem. Phys.* **1990**, *93*, 502.
- (22) Taylor, P. R. Accurate Calculations and Calibration. In *Lecture Notes in Chemistry* 58; Roos, B. O., Ed.; Springer: Berlin, 1992; pp 325–412.
- (23) Hättig, C.; Klopper, W.; Köhn, A.; Tew, D. P. Explicitly Correlated Electrons in Molecules. *Chem. Rev.* **2012**, *112*, 4–74.
- (24) Kong, L.; Bischoff, F. A.; Valeev, E. F. Explicitly Correlated R12/F12 Methods for Electronic Structure. *Chem. Rev.* **2012**, *112*, 75–107.
- (25) Ten-no, S.; Noga, J. Explicitly Correlated Electronic Structure Theory from R12/F12 Ansätze. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 114–125.
- (26) McMahon, J. D.; Lane, J. R. Explicit Correlation and Basis Set Superposition Error: The Structure and Energy of Carbon Dioxide Dimer. *J. Chem. Phys.* **2011**, *135*, 154309.
- (27) De Lange, K. M.; Lane, J. R. Explicit Correlation and Intermolecular Interactions: Investigating Carbon Dioxide Complexes with the CCSD(T)-F12 Method. *J. Chem. Phys.* **2011**, *134*, 034301.
- (28) Feller, D.; Peterson, K. A. An Expanded Calibration Study of the Explicitly Correlated CCSD(T)-F12b Method Using Large Basis Set Standard CCSD(T) Atomization Energies. *J. Chem. Phys.* **2013**, *139*, 084110.
- (29) Boese, A. D.; Jansen, G.; Torheyden, M.; Höfener, S.; Klopper, W. Effects of Counterpoise Correction and Basis Set Extrapolation on the MP2 Geometries of Hydrogen Bonded Dimers of Ammonia, Water, and Hydrogen Fluoride. *Phys. Chem. Chem. Phys.* **2011**, *13*, 1230–1238.
- (30) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; et al. *MOLPRO*, version 2012.1; University College Cardiff Consultants Ltd.: Cardiff, Wales, U.K., 2012.
- (31) Peterson, K. A.; Adler, T. B.; Werner, H.-J. Systematically Convergent Basis Sets for Explicitly Correlated Wavefunctions: The Atoms H, He, B-Ne, and Al-Ar. *J. Chem. Phys.* **2008**, *128*, 084102.
- (32) Yousaf, K. E.; Peterson, K. A. Optimized Auxiliary Basis Sets for Explicitly Correlated Methods. *J. Chem. Phys.* **2008**, *129*, 184108.
- (33) Yousaf, K. E.; Peterson, K. A. Optimized Complementary Auxiliary Basis Sets for Explicitly Correlated Methods: Aug-Cc-pVnZ Orbital Basis Sets. *Chem. Phys. Lett.* **2009**, *476*, 303–307.
- (34) Weigend, F. Hartree-Fock Exchange Fitting Basis Sets for H to Rn. *J. Comput. Chem.* **2008**, *29*, 167–175.
- (35) Peterson, K. A.; Martin, J. M. L. The cc-pV5Z-F12 Basis Set for Explicitly Correlated Calculations near the Basis Set Limit [working Title]. To be published.
- (36) Adler, T. B.; Knizia, G.; Werner, H.-J. A Simple and Efficient CCSD(T)-F12 Approximation. *J. Chem. Phys.* **2007**, *127*, 221106.
- (37) Noga, J.; Šimunek, J. On the One-Particle Basis Set Relaxation in R12 Based Theories. *Chem. Phys.* **2009**, *356*, 1–6.
- (38) Knizia, G.; Adler, T. B.; Werner, H.-J. Simplified CCSD(T)-F12 Methods: Theory and Benchmarks. *J. Chem. Phys.* **2009**, *130*, 054104.
- (39) Hättig, C.; Tew, D. P.; Köhn, A. Communications: Accurate and Efficient Approximations to Explicitly Correlated Coupled-Cluster Singles and Doubles, CCSD-F12. *J. Chem. Phys.* **2010**, *132*, 231102.
- (40) Marchetti, O.; Werner, H.-J. Accurate Calculations of Intermolecular Interaction Energies Using Explicitly Correlated Wave Functions. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3400–3409.
- (41) Martin, J. M. L.; Kesharwani, M. K. Assessment of CCSD(T)-F12 Approximations and Basis Sets for Harmonic Vibrational Frequencies. *J. Chem. Theory Comput.* **2014**, *10*, 2085–2090.
- (42) Ten-no, S. Initiation of Explicitly Correlated Slater-Type Geminal Theory. *Chem. Phys. Lett.* **2004**, *398*, 56–61.
- (43) Jurecka, P.; Sponer, J.; Cerný, J.; Hobza, P. Benchmark Database of Accurate (MP2 and CCSD(T) Complete Basis Set Limit) Interaction Energies of Small Model Complexes, DNA Base Pairs, and Amino Acid Pairs. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985–1993.
- (44) Gráfová, L.; Pitoňák, M.; Řezáč, J.; Hobza, P. Comparative Study of Selected Wave Function and Density Functional Methods for Noncovalent Interaction Energy Calculations Using the Extended S22 Data Set. *J. Chem. Theory Comput.* **2010**, *6*, 2365–2376.
- (45) Řezáč, J.; Riley, K. E.; Hobza, P. S66: A Well-Balanced Database of Benchmark Interaction Energies Relevant to Biomolecular Structures. *J. Chem. Theory Comput.* **2011**, *7*, 2427–2438.
- (46) Řezáč, J.; Riley, K. E.; Hobza, P. Extensions of the S66 Data Set: More Accurate Interaction Energies and Angular-Displaced Non-equilibrium Geometries. *J. Chem. Theory Comput.* **2011**, *7*, 3466–3470.
- (47) Řezáč, J.; Jurečka, P.; Riley, K. E.; Černý, J.; Valdes, H.; Pluháčková, K.; Berka, K.; Řezáč, T.; Pitoňák, M.; Vondrášek, J.; Hobza, P. Quantum Chemical Benchmark Energy and Geometry Database for Molecular Clusters and Complex Molecular Systems (www.begdb.com): A Users Manual and Examples. *Collect. Czechoslov. Chem. Commun.* **2008**, *73*, 1261–1270.
- (48) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
- (49) Goerigk, L.; Grimme, S. Efficient and Accurate Double-Hybrid-Meta-GGA Density Functionals—Evaluation with the Extended GMTKN30 Database for General Main Group Thermochemistry, Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2011**, *7*, 291–309.
- (50) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- (51) Barnes, E. C.; Petersson, G. A.; Feller, D.; Peterson, K. A. The CCSD(T) Complete Basis Set Limit for Ne Revisited. *J. Chem. Phys.* **2008**, *129*, 194115.
- (52) DeYonker, N. J.; Cundari, T. R.; Wilson, A. K. The Correlation Consistent Composite Approach (ccCA): An Alternative to the Gaussian-n Methods. *J. Chem. Phys.* **2006**, *124*, 114104.

- (53) DeYonker, N. J.; Wilson, B. R.; Pierpont, A. W.; Cundari, T. R.; Wilson, A. K. Towards the Intrinsic Error of the Correlation Consistent Composite Approach (ccCA). *Mol. Phys.* **2009**, *107*, 1107–1121.
- (54) Mahler, A.; Wilson, A. K. Explicitly Correlated Methods within the ccCA Methodology. *J. Chem. Theory Comput.* **2013**, *9*, 1402–1407.
- (55) Fogueri, U. R.; Kozuch, S.; Karton, A.; Martin, J. M. L. The Melatonin Conformer Space: Benchmark and Assessment of Wave Function and DFT Methods for a Paradigmatic Biological and Pharmacological Molecule. *J. Phys. Chem. A* **2013**, *117*, 2269–2277.
- (56) Kozuch, S.; Bachrach, S. M.; Martin, J. M. L. Conformational Equilibria in Butane-1,4-Diol: A Benchmark of a Prototypical System with Strong Intramolecular H-Bonds. *J. Phys. Chem. A* **2014**, *118*, 293–303.
- (57) Havenith, M. $(\text{NH}_3)_2$ — a Prototype of Hydrogen Bonding? In *Infrared Spectroscopy of Molecular Clusters*; Springer Tracts in Modern Physics; Springer: Berlin, 2002; Vol. 176, pp 97–110.
- (58) Boese, A. D.; Chandra, A.; Martin, J. M. L.; Marx, D. From Ab Initio Quantum Chemistry to Molecular Dynamics: The Delicate Case of Hydrogen Bonding in Ammonia. *J. Chem. Phys.* **2003**, *119*, 5965.
- (59) Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. Basis-Set Convergence in Correlated Calculations on Ne, N_2 , and H_2O . *Chem. Phys. Lett.* **1998**, *286*, 243–252.
- (60) Martin, J. M. L. Ab Initio Total Atomization Energies of Small Molecules — towards the Basis Set Limit. *Chem. Phys. Lett.* **1996**, *259*, 669–678.
- (61) Hill, J. G.; Peterson, K. A.; Knizia, G.; Werner, H.-J. Extrapolating MP2 and CCSD Explicitly Correlated Correlation Energies to the Complete Basis Set Limit with First and Second Row Correlation Consistent Basis Sets. *J. Chem. Phys.* **2009**, *131*, 194105.
- (62) Marshall, M. S.; Burns, L. A.; Sherrill, C. D. Basis Set Convergence of the Coupled-Cluster Correction, $\delta(\text{MP2})(\text{CCSD}-(\text{T}))$: Best Practices for Benchmarking Non-Covalent Interactions and the Attendant Revision of the S22, NBC10, HBC6, and HSG Databases. *J. Chem. Phys.* **2011**, *135*, 194102.