

Extrapolation and Scaling of the DFT-SAPT Interaction Energies toward the Basis Set Limit

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 Supporting Information

ABSTRACT: The dispersion energy term in the symmetry-adapted perturbation theory based on the density functional theory (DFT-SAPT) converges rather slowly with basis set size. Accurate results for large complexes, where only calculations in small basis sets are practical, can be obtained by extrapolation to the complete basis set limit (CBS). In this paper, we propose an extrapolation scheme with the variable exponent optimized specifically for the DFT-SAPT calculations in correlation-consistent basis sets with diffuse functions. Another way to improve the accuracy term at no additional cost is to scale the dispersion term by a fixed amount. We present the scaling factors averaged over a balanced set of 10 model complexes. The results of these schemes are compared to the high-quality DFT-SAPT/CBS interaction energies in small complexes obtained by fitting to a series of basis sets up to aug-cc-pV5Z and to the CCSD(T)/CBS interaction energies. It is shown that even the cheapest extrapolation scheme yields results that are limited by the accuracy of the DFT-SAPT approach rather than by the basis set convergence. Scaling the dispersion term allows accurate interaction energies as well as their components to be obtained using just the aug-cc-pVDZ basis set; such a calculation can be applied to complexes consisting of up to 50 first-row atoms.

The symmetry-adapted perturbation theory based on density functional theory^{1,2} (DFT-SAPT) is a powerful method for the decomposition of intermolecular interaction energy into physically meaningful components. The use of density functional theory as a basis for a SAPT analysis allows for an investigation of larger systems than is possible with SAPT based on the Hartree–Fock method³ or the post-HF methods. DFT-SAPT converges with the basis set size faster than the wave function theory (WFT) methods, and already the aug-cc-pVDZ basis set provides reasonable energy terms. The only exception represents the London dispersion energy, whose convergence is much slower. Furthermore, it is the most computationally intensive part of the calculation.

Problems with convergence are characteristic for the correlated WFT methods and are often addressed by an extrapolation of the energy to the complete basis set (CBS) limit from calculations in smaller basis sets. Some authors apply the extrapolation schemes developed for the WFT methods to DFT-SAPT^{4,5} without comparing the extrapolated values to a reliable estimate of the DFT-SAPT CBS limit. It has also been suggested that scaling the DFT-SAPT dispersion energy obtained in a small basis set by 10–15% could estimate the CBS limit,⁶ but this hypothesis has not been tested further. Therefore, there are no reliable data on what scaling factor should be used and how robust this approach is when applied to complexes of a different nature. The development of such a scaling is important not only as a tool for interaction energy decomposition but also as an efficient method to estimate the DFT-SAPT/CBS interaction energy from a calculation in a smaller basis set applicable to large complexes. Despite the approximations used, the DFT-SAPT/CBS interaction energies are very close (within 5%) to the benchmark CCSD(T)/CBS values.⁷

In this work, we have investigated 10 small complexes where we can use multipoint regression to obtain accurate DFT-SAPT dispersion energies at the CBS limit. From these calculations, we have obtained information that addresses both of the issues introduced above. The parameters in the fitting function can be used to design an optimal two-point extrapolation scheme that is more practical for calculations of larger systems. The ratio of the dispersion energy in a given basis set compared to the CBS limit can also be used to estimate the CBS value from just a single calculation. We present average scaling factors that can be used for complexes with a varying amount of dispersion contribution. The DFT-SAPT calculations are also compared to benchmark CCSD(T)/CBS interaction energies in order to discuss the overall accuracy of DFT-SAPT. Finally, the scaling of the dispersion term is tested on a larger set of medium-sized complexes.

For a reliable description of the dispersion, diffuse functions improve the performance of a basis set significantly. In this study, we have used the series of correlation-consistent basis sets of Dunning⁸ with diffuse functions,⁹ labeled aug-cc-pVXZ, where X = D, T, Q, and 5. The quintuple ζ aug-cc-pV5Z is the largest basis set practically usable for our model systems, and the findings indicate that it yields results close to the CBS limit.

METHODS

DFT-SAPT Calculations. All of the calculations at the DFT-SAPT level were performed using the MOLPRO 2009 package,¹⁰ employing the density fitting procedure.¹¹ We have used the PBE0AC functional recommended by the authors of the

Received: January 4, 2011

Published: February 10, 2011

Table 1. Interaction Energies (kcal/mol) from the DFT-SAPT Calculations in the aug-cc-pVXZ (X = D,T,Q,5) Basis Set, Combined into an Uncorrelated Component (E_{noD}) and the Dispersion Part (E_{D}), and Their Sum, the Total DFT-SAPT Interaction Energy^a

	E_{noD}				E_{D}				$E_{\text{noD}} + E_{\text{D}}$				CCSD(T) CBS
	D	T	Q	5	D	T	Q	5	D	T	Q	5	
water dimer	−2.276	−2.333	−2.367	−2.363	−1.988	−2.332	−2.421	−2.448	−4.264	−4.664	−4.788	−4.811	−4.996
methane dimer	0.442	0.453	0.452	0.451	−0.889	−0.976	−0.999	−1.007	−0.447	−0.523	−0.547	−0.556	−0.530
methane····water	0.113	0.041	0.042	0.042	−0.892	−1.025	−1.049	−1.055	−0.779	−0.984	−1.007	−1.012	−0.971
ammonia dimer	−0.945	−1.012	−1.018	−1.018	−1.821	−2.098	−2.163	−2.184	−2.766	−3.110	−3.181	−3.202	−3.147
ethyne dimer	−0.352	−0.368	−0.372	−0.372	−1.168	−1.302	−1.331	−1.338	−1.520	−1.671	−1.703	−1.710	−1.539
ammonia····water	−3.540	−3.646	−3.661	−3.659	−2.309	−2.700	−2.787	−2.814	−5.849	−6.346	−6.447	−6.473	−6.432
ammonia····N ₂	0.043	0.042	0.034	0.032	−0.615	−0.680	−0.697	−0.702	−0.571	−0.638	−0.663	−0.669	−0.686
formic acid····water	−4.193	−4.367	−4.425	−4.423	−4.775	−5.534	−5.752	−5.821	−8.968	−9.901	−10.177	−10.243	−10.779
methane····N ₂	0.194	0.194	0.193	0.193	−0.492	−0.540	−0.554	−0.559	−0.298	−0.346	−0.361	−0.367	−0.352
water····N ₂	−0.159	−0.174	−0.188	−0.193	−0.798	−0.899	−0.923	−0.929	−0.957	−1.073	−1.111	−1.122	−1.189
RMSE ^a									0.549	0.164	0.059	0.035	

^aThe CCSD(T)/CBS interaction energy is provided as a reference to the DFT-SAPT/CBS results.

method;¹² the calculations of the monomers have been performed in the basis set of the dimer. The shift needed to correct the asymptotic behavior of the functional¹³ was calculated as the difference between the HOMO energy of each monomer and the true ionization potential obtained from the calculation of its neutral and ionized forms. The shifts have been calculated using the same functional in the aug-cc-pVTZ basis set.

Extrapolation Scheme. Little is known on how exactly the dispersion term of DFT-SAPT changes with basis set size and therefore what function should be used for its extrapolation. A good starting point is the extrapolation schemes developed for the correlated WFT methods. We have found that both the exponential- and power-law-based schemes proposed by Helgaker et al.¹⁴ provide good results, but the best fit can be achieved with Schwenke's power-law formula¹⁵ with a variable exponent:

$$E_{\text{corr},X} = E_{\text{corr,CBS}} + A X^{-p} \quad (1)$$

where A is a constant, X is the cardinal number of the basis set, and p is the optimized parameter. This scheme is a variation of Helgaker's scheme, but the fixed exponent ($p = 3$) is replaced by an optimized parameter to achieve better fit. This additional degree of freedom can compensate for the nonideal behavior of the series of the basis set and method. Equation 1 can be easily transformed into a formula for a two-point extrapolation using the basis sets X and $X + 1$, eliminating the constant A :

$$E_{\text{corr,CBS}} = \frac{(E_{\text{corr},X+1}(X+1)^p - E_{\text{corr},X} \times X^p)}{((X+1)^p - X^p)} \quad (2)$$

CCSD(T)/CBS Calculations. The benchmark interaction energies of the complexes were calculated from the MP2/CBS value obtained with Helgaker's extrapolation scheme¹⁴ and the difference between the CCSD(T) and MP2 correlation energy (the so-called CCSD(T) correction term) calculated in a suitable basis set.¹⁶ For the 10 model complexes, the aug-cc-pVQZ and aug-cc-pVSZ basis sets were used for the MP2 calculations and the aug-cc-pVTZ for the CCSD(T) correction term; such a setup ensured results close to the CBS limit. All of those calculations have been performed using the MOLPRO 2009 package.¹⁰

Model Complexes. A set of 10 complexes of small molecules has been prepared for this study. These complexes contain up to four first-row atoms, which makes it possible to calculate the DFT-SAPT interaction energy with large basis sets. An important feature of this set is to include different types of interactions in a balanced way. Therefore, the set contains both polar and nonpolar molecules in all of the possible combinations. These complexes are water, ammonia, methane, and ethyne (T-shape) homodimers and ammonia····water, ammonia····N₂, water····N₂, water····methane, methane····N₂, and formic acid····water complexes (geometries provided in the Supporting Information). The average interaction energy in this set is −3.0 kcal/mol. The structure of these complexes was optimized at the MP2/cc-pVTZ level with the counterpoise correction. It was shown that these geometries are close to those obtained at the CCSD(T) level.¹⁷

Validation Complexes. The proposed schemes using a smaller basis set have been tested on a set of 31 larger complexes (up to nine first-row atoms). The list of these complexes and their geometries are provided in the Supporting Information. The geometry of these complexes has been optimized using the same method as used with the model complexes. The DFT-SAPT calculations in the aug-cc-pVDZ and aug-cc-pVTZ basis set have been performed for all of these complexes; aug-cc-pVQZ had been used for the first 11 of them.

RESULTS AND DISCUSSION

Multipoint Fits. For each of the model complexes, a series of DFT-SAP interaction energies in the aug-cc-pVXZ (X = D, T, Q, 5) basis set has been calculated. All of the terms were divided into two groups and summed into the dispersion component and the remaining, nondispersion part of the energy:

$$E_{\text{D}} = E_{\text{disp}}^2 + E_{\text{exch-disp}}^2 \quad (3)$$

$$E_{\text{noD}} = E_{\text{pol}}^1 + E_{\text{exch}}^1 + E_{\text{ind}}^2 + E_{\text{exch-ind}}^2 + \delta\text{HF} \quad (4)$$

These results, along with the reference CCSD(T)/CBS calculations, are listed in Table 1. It should be noted that even

Table 2. RMSE (in kcal/mol) of the Two-Point Extrapolation Schemes As against the DFT-SAPT/CBS Values

basis sets	p	RMSE (E_D)	RMSE (E_{tot})
D→T	2.868	0.009	0.036
	3	0.015	0.065
	3.489	0.044	0.009
T→Q	2.868	0.008	0.006
	3	0.006	0.012
	3.489	0.013	0.015
Q→5	2.868	0.015	0.016
	3	0.016	0.020
	3.489	0.020	0.000

the best (in terms of basis set used) DFT-SAPT only approximates the interaction energy when compared to the CCSD(T) results. The first reason might be the difference in the underlying theory, because the DFT-SAPT treats the interaction as a perturbation only up to the second order; higher-order contributions are included only in the $\delta(\text{HF})$ term, which does not contain correlation energy. Second, the results of the DFT-SAPT are affected by the functional used. Our findings are consistent with the previously reported comparison of the DFT-SAPT and CCSD(T) interaction energies.^{4,7,18}

As mentioned above, the nondispersion part of the interaction energy converges faster with the basis set size, and the value calculated with a rather large basis set is close enough to the CBS limit. We, therefore, do not extrapolate this component as recommended in the literature.¹⁹ The DFT-SAPT/CBS energy is built from the E_{noD} calculated in the aug-cc-pVSZ basis set, and only the E_D is extrapolated to the CBS.

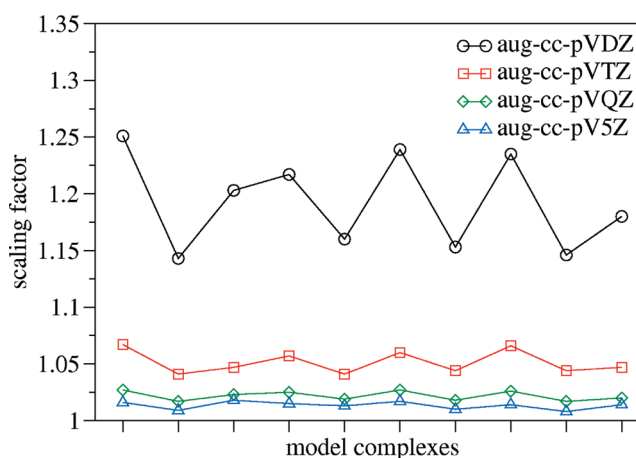
The complete series of basis sets is used to optimize the fitting function in order to find the value of the exponent p that minimizes the error between the actual E_D and the value obtained from eq 1 for each basis set. In order to build a transferable fitting function, we looked for a single value of p for the whole set of complexes. In such an optimization, the factor A and the $E_{D,\text{CBS}}$ of each system act as variable parameters. The target variable to be minimized is the sum of the squares of the residual errors.

It is known that the largest nonsystematic error is observed for the small basis sets. Therefore, a better fit can be achieved when the augmented double- ζ basis is not included in the series (the error is reduced also because the fitted set is smaller). However, for larger systems, we would like to use the smallest basis sets possible for the extrapolation, which means extrapolation from the double- and triple- ζ basis sets. We performed the fitting both on the full series (D, T, Q, 5) and on truncated series of just T, Q, and 5, but we will focus on the first one in the discussion below. For the full series, the value of $p = 2.868$ and the root-mean-square (RMS) of the residual error is 0.0039 kcal/mol. For the truncated series, we obtained $p = 3.489$ with an RMS error of 0.0003 kcal/mol. It is worth noting that both values of p are close to the theoretically predicted value of 3. The resulting $E_{D,\text{CBS}}$ values from all of these fits ($p = 2.868$, 3.489, and 3) are very similar (the RMS difference between them being ≤ 0.01 kcal/mol). Such a difference is negligible when compared to the error with respect to the CCSD(T)/CBS reference (RMSE = 0.17 kcal/mol, which is about 6%).

Two-Point Extrapolation. Knowing the exponent p , we can use eq 2 for an extrapolation to the CBS limit from two calculations. Table 2 lists the results of the two-point

Table 3. Ratios of the Dispersion Part of the Interaction Energy (E_D) at the CBS Limit to E_D Calculated in the Finite Basis Set aug-cc-pVXZ (X = D, T, Q, 5)

	$f(\text{D})$	$f(\text{T})$	$f(\text{Q})$	$f(5)$
water dimer	1.251	1.067	1.027	1.016
methane dimer	1.143	1.041	1.017	1.009
methane...water	1.203	1.047	1.023	1.018
ammonia dimer	1.217	1.057	1.025	1.015
ethyne dimer	1.160	1.041	1.019	1.013
ammonia...water	1.239	1.060	1.027	1.017
ammonia...N ₂	1.153	1.044	1.018	1.010
formic acid...water	1.235	1.066	1.026	1.014
methane...N ₂	1.146	1.044	1.017	1.008
water...N ₂	1.180	1.047	1.020	1.014
average	1.193	1.051	1.022	1.013

**Figure 1.** Ratios of the dispersion part of the interaction energy E_D at the CBS limit to E_D calculated in the finite basis set aug-cc-pVXZ (X = D, T, Q, 5) for the model complexes considered in this work.

extrapolations using various combinations of basis sets and exponents p as the RMSE to the DFT-SAPT/CBS value obtained using $p = 2.868$. Both the dispersion part and the total interaction energy are considered.

The extrapolated values are very close to the DFT-SAPT/CBS limit, and all of them are of a quality at least comparable to DFT-SAPT/aug-cc-pVSZ. All of these errors are an order of magnitude smaller than the difference between the DFT-SAPT and CCSD(T); therefore, any extrapolation yields an estimate of the CBS limit accurate enough for practical purposes.

Scaling of the Dispersion Term. By comparing the dispersion term E_D obtained with each basis set with its CBS limit, we can obtain the scaling factor (f) needed to estimate the CBS value from just a single calculation. These factors, and their average over the set, are listed in Table 3 and plotted in Figure 1. It is clear that these factors depend on the character of the interaction, but this dependence diminishes with the increasing size of the basis set. However, even for the double- ζ basis set, the absolute deviations from the average scaling factors are always lower than $f - 1$, which means that such a scaling only improves the result when compared to the CBS limit. Our accurate estimate of the CBS limit allows us to calculate the scaling factors, which are

Table 4. Comparison of the One-Point Scaling Schemes for 10 Model Complexes^a

scaled E_D	E_{noD}	f	RMSE
aug-cc-pVDZ	aug-cc-pVDZ	1.193	0.174
aug-cc-pVDZ	aug-cc-pVTZ	1.193	0.104
aug-cc-pVTZ	aug-cc-pVTZ	1.051	0.050

^a The dispersion part of the interaction energy is scaled by the factor f in order to get closer to the CBS limit. The errors (in kcal/mol) are relative to an accurate estimate of the CBS limit.

larger than those previously used in the literature, where a scaling of 1.1 or 1.15 was suggested for the aug-cc-pVDZ basis set⁶ without a rigorous derivation.

The most practical estimates of the E_D CBS limit obtained by such a scaling are those from smaller basis sets. If it is possible to perform the calculation in a larger basis set, another calculation in a smaller one makes it possible to use the more accurate two-point extrapolation. Here, we consider three scaling schemes: The scaling of E_D in an aug-cc-pVDZ calculation (labeled D*/D), the scaling of E_D in the aug-cc-pVTZ (labeled T*/T), and the combination of the scaled E_D from the aug-cc-pVDZ with the E_{noD} from the aug-cc-pVTZ (labeled D*/T). Since the calculation of the dispersion term is the limiting factor, the latter scheme allows us to improve the nondispersion part at a little extra expense.

The results of such calculations are summarized in Table 4 as the RMSE relative to the CBS limit. With the D*/D scheme (first line), this error is 0.17 kcal/mol, as compared to 0.55 kcal/mol in the aug-cc-pVDZ calculation without scaling. The D*/T scheme (second line) is the optimum between the computational cost and accuracy. Here, the error is 0.1 kcal/mol when compared to 0.48 kcal/mol in the same calculation without the scaling. Finally, the T*/T scheme (third line) is the most accurate one with an error of 0.05 kcal/mol. Better accuracy (0.04 kcal/mol) can be achieved with two-point extrapolation at a similar cost, but the difference is surprisingly small.

We have also tested separate scaling of the dispersion and dispersion-exchange terms of the SAPT decomposition. This approach yields worse results than scaling their sum as described before.

Validation of One-Point Scaling. In order to test the scaling schemes outside the training set, we calculated a set of 31 larger complexes in the aug-cc-pVDZ and aug-cc-pVTZ basis sets. The average interaction energy in this set is -5.5 kcal/mol. Here, the two-point extrapolation serves as a reference for the scaled calculation. We validated this reference against the aug-cc-pVTZ to aug-cc-pVQZ extrapolation for the 11 smallest complexes from this set; the RMSE is 0.027 kcal/mol. This is an order of magnitude smaller than the error of the scaling schemes we have investigated here. We therefore consider even the aug-cc-pVDZ to aug-cc-pVTZ extrapolation as a reasonable estimate of the CBS limit for this purpose. The errors, summarized in Table 5, are very similar to those observed in the validation set. The scaled double- ζ calculations are slightly more accurate than the unscaled triple- ζ ones, and the scaled triple- ζ results are very close to the CBS limit. These results confirm that the scaling factors presented here are transferable and provide a significant improvement in accuracy without any extra expense (a 4-fold improvement with the simplest scaling scheme using just the aug-cc-pVDZ calculation).

Table 5. Evaluation of the One-Point Scaling Schemes for the Validation Set of 31 Complexes As Compared to the Unscaled Results^a

scaled E_D	E_{noD}	f	RMSE (kcal/mol)
aug-cc-pVDZ	aug-cc-pVDZ	no scaling	0.684
aug-cc-pVTZ	aug-cc-pVTZ	no scaling	0.196
aug-cc-pVDZ	aug-cc-pVDZ	1.193	0.169
aug-cc-pVDZ	aug-cc-pVTZ	1.193	0.156
aug-cc-pVTZ	aug-cc-pVTZ	1.051	0.044

^a The errors are relative to the CBS estimate extrapolated from calculations in the aug-cc-pVDZ and aug-cc-pVTZ basis sets.

CONCLUSIONS

Using accurate DFT-SAPT calculations in up to the aug-cc-pV5Z basis set, we have constructed a fitting function that can be used for the extrapolation of the DFT-SAPT dispersion energy to the CBS limit. The remaining part of the interaction energy converges faster with basis set size and is not extrapolated.

A power-law-based formula (eq 1) with the exponent $p = 2.868$ yields the best results for any pair of basis sets. The interaction energies obtained with this extrapolation are very close to the CBS limit, and the difference from the more accurate CBS estimate is an order of magnitude smaller than the accuracy of the DFT-SAPT when compared to the CCSD(T) results. Therefore, even an extrapolation using the aug-cc-pVDZ and aug-cc-pVTZ basis sets should yield results that can be safely used as a DFT-SAPT/CBS estimate.

The most affordable way of improving the DFT-SAPT calculation toward the CBS limit is a simple scaling of the dispersion. When the dispersion energy is calculated with the smallest basis set in the series, aug-cc-pVDZ, the results vary with the type of the interaction, but even this simple approach yields results better than the unscaled calculation in all of the cases we have tested. Moreover, this scheme can be improved at little extra expense by calculating the nondispersion part in a larger basis set. The resulting computational scheme offers a very efficient way of obtaining accurate total interaction energies and their components for extended complexes^{20,21} on the basis of “cheap” DFT-SAPT/aug-cc-pVDZ calculations. It should be stressed again that the DFT-SAPT/CBS interaction energies are very close to the benchmark CCSD(T)/CBS ones.

ASSOCIATED CONTENT

S Supporting Information. Geometries of the model complexes, list and geometries of validation complexes, all of the components of the DFT-SAPT decomposition for each system and basis set. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT

This work was a part of Research Project No. Z40550506 of the Institute of Organic Chemistry and Biochemistry, Academy

of Sciences of the Czech Republic, and was supported by Grants No. LC512 and MSM6198959216 from the Ministry of Education, Youth and Sports of the Czech Republic. The support of Praemium Academiae, Academy of Sciences of the Czech Republic, awarded to P.H. in 2007, is also acknowledged.

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