Highly Accurate Estimates of Hydrogen-Bond Energies Relying on Basis Set Convergence Patterns

Klaus R. Liedl*,† and Romano T. Kroemer‡

Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria, and Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, England

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We introduce a method for the determination of highly accurate estimates of the electronic interaction energies in uncharged hydrogen-bonded clusters, using basis set convergence patterns (=BSCP) of the aug-cc-pVxZ series of basis sets at MP2(FC) level of theory. The method is characterized by its robustness toward systematic deficiencies of MP2(FC)/aug-cc-pVxZ description of hydrogen bonds. The achieved reliability is due to a one parameter scaling ansatz that transforms the disadvantages of the basis set superposition error into precious information. The method is applied to the trimer of hydrogen fluoride and the trimer of water which were both fully geometry optimized up to MP2(FC)/aug-cc-pVQZ level of theory. The electronic interaction energy is predicted to be −15.05 kcal/mol for the trimer of hydrogen fluoride and −15.91 kcal/mol for the trimer of water.

1. Introduction

The determination of accurate hydrogen-bond energies is considerably hindered by the so-called basis set superposition error.[1] Various procedures to reduce this error arising from the improved description of the individual hydrogen bond partners in the basis set of the complete hydrogen-bonded complex have been proposed and reviewed extensively.[2,3]

We do not want to propose yet another method to calculate basis set superposition error corrected electronic interaction energies at a specific level of theory, but we rather want to introduce a completely empirical procedure: Our target property is not the basis set limit of the electronic interaction energy within a specific method, but rather a best estimate of the electronic interaction energy itself. The proposed method uses both the full counterpoise corrected[1] (including monomer relaxation[4]) and the not-basis-set-superposition-corrected electronic interaction energy at MP2(FC)/aug-cc-pVxZ[5−7] level of theory to predict the electronic interaction energy at an accuracy that is normally only available by much more expensive methods such as CCSD(T) or MP2-R12 toward the basis set convergence limit.

The method was introduced to achieve an accurate estimate of the electronic interaction energy of the carbonic acid dimer and was validated for the formic acid dimer.[8] Here we want to give for the first time a more detailed description and discussion of this method. Further on, applications to the trimer of hydrogen fluoride and water are presented and benchmarked against the best estimates of the electronic interaction energy available for these systems.

2. Method

The major idea of the method proposed is to give very accurate estimates of electronic hydrogen bond interaction energies by relying on very similar basis set convergence behavior for different uncharged hydrogen bonded systems. The method, which we will call basis set convergence pattern (BSCP) method in the following, takes not only reference information from theoretically and experimentally very-well studied hydrogen bonded systems into account but also relies both on fully counterpoise corrected as well as on not-counterpoise-corrected electronic interaction energies at MP2(FC)/aug-cc-pVxZ level. In principal, the method is nothing but a trivial least square fit to scaled reference values as explained in the following in more detail.

The first step in the method is to take very-well-studied hydrogen bonded systems (in our case the water dimer and the dimer of hydrogen fluoride) and to divide their electronic interaction energies at MP2(FC)/aug-cc-pVxZ level, the fully counterpoise corrected results ($\Delta E^{\mathrm{R,aug-cc-pVxZ}}_{\mathrm{fcp-corrected}}$) as well as the not-counterpoise-corrected ones ($\Delta E^{\mathrm{R,aug-cc-pVxZ}}_{\mathrm{uncorrected}}$), by the best estimates for their electronic interaction energies ($\Delta E^{\mathrm{R}}_{\mathrm{best\ est}}$) resulting from combined experimental and theoretical efforts. For the water dimer and the dimer of hydrogen fluoride these best estimates are known with an error of less than it ±0.1 kcal/mol and they amount to −5.00[4,9] and −4.56 kcal/mol,[10] respectively. The resulting divided electronic interaction energies will be called scaled reference values in the following (the reference values were taken from the literature[4,9,10]).

The second step is to find a common scaling factor for the system under investigation that minimizes the sum of weighted square deviations of the fully counterpoise corrected electronic interaction energies ($\Delta E^{\mathrm{I,aug-cc-pVxZ}}_{\mathrm{fcp-corrected}}$) as well as not-counterpoise-corrected ones ($\Delta E^{\mathrm{I,aug-cc-pVxZ}}_{\mathrm{uncorrected}}$) from the scaled reference values at each MP2(FC)/aug-cc-pVxZ level at the same time (cf. Figures 1 and 3). (For convenience we use aug-cc-pVxZ ($x = 2-4$) as synonyms for aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ.) The weighting factors used in this study equal $(x-1)^2$ for MP2(FC)/aug-cc-pVxZ results (i.e., the

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* Corresponding author.

† University of Innsbruck.

‡ University of Oxford.

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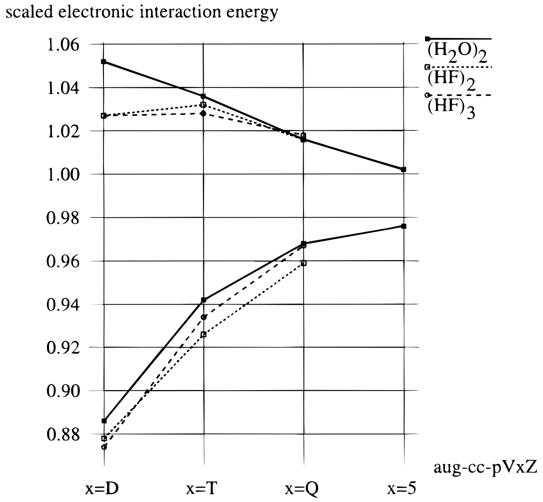

Figure 1. Interaction energies of the hydrogen fluoride trimer in its C_{3h} minimum structure at MP2(FC)/aug-cc-pVxZ level of theory scaled by the best estimate of $\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q} = -15.05$ kcal/mol resulting from full BSCP analysis performed up to MP2(FC)/aug-cc-pVQZ level compared to the scaled reference values (the lower lines correspond to the fully counterpoise corrected results, whereas the upper lines indicate the uncorrected results; additionally, MP2(FC)/aug-cc-pV5Z results of the water dimer are displayed).

MP2(FC)/aug-cc-pVTZ and the MP2(FC)/aug-cc-pVQZ results are weighted 4 times and 9 times more relative to the MP2(FC)/aug-cc-pVDZ results, respectively). The best estimate for the electronic interaction energy of the system under investigation ($\Delta E_{\mathrm{BSCP}}^{\mathrm{I},n}$) obviously is the best scaling factor itself (n indicates the largest basis set used: $D \equiv 2$, $T \equiv 3$, or $Q \equiv 4$).

In other words, to obtain this best scaling factor $\Delta E_{\mathrm{BSCP}}^{\mathrm{I},n}$ for a specific system under investigation a simple minimization of the function $F(\Delta E_{\mathrm{BSCP}}^{\mathrm{I},n})$ defined as

$$F(\Delta E_{\mathrm{BSCP}}^{\mathrm{I},n}) =$$

$$\sum_{R\in\{\mathrm{ref\ sys}\}} \sum_{x=2}^{n} \left[(x-1)^2 \left(\frac{\Delta E_{\mathrm{fcp-corrected}}^{\mathrm{I,aug-cc-pVxZ}}}{\Delta E_{\mathrm{BSCP}}^{\mathrm{I},n}} - \frac{\Delta E_{\mathrm{fcp-corrected}}^{\mathrm{R,aug-cc-pVxZ}}}{\Delta E_{\mathrm{best\ est}}^{\mathrm{R}}} \right)^2 \right] + \tag{1}$$

$$\sum_{R\in\{\mathrm{ref\ sys}\}} \sum_{x=2}^{n} \left[(x-1)^2 \left(\frac{\Delta E_{\mathrm{uncorrected}}^{\mathrm{I,aug-cc-pVxZ}}}{\Delta E_{\mathrm{BSCP}}^{\mathrm{I},n}} - \frac{\Delta E_{\mathrm{uncorrected}}^{\mathrm{R,aug-cc-pVxZ}}}{\Delta E_{\mathrm{best\ est}}^{\mathrm{R}}} \right)^2 \right] \tag{2}$$

has to be performed. The superscript I marks the system under investigation whereas the superscript R indicates the reference systems. $\Delta E_{\mathrm{fcp-corrected}}^{\mathrm{R,aug-cc-pVxZ}}/\Delta E_{\mathrm{best\ est}}^{\mathrm{R}}$ and $\Delta E_{\mathrm{uncorrected}}^{\mathrm{R,aug-cc-pVxZ}}/\Delta E_{\mathrm{best\ est}}^{\mathrm{R}}$ are the fully counterpoise corrected and uncorrected scaled reference values. $\Delta E_{\mathrm{fcp-corrected}}^{\mathrm{I,aug-cc-pVxZ}}/\Delta E_{\mathrm{BSCP}}^{\mathrm{I},n}$ and $\Delta E_{\mathrm{uncorrected}}^{\mathrm{I,aug-cc-pVxZ}}/\Delta E_{\mathrm{BSCP}}^{\mathrm{I},n}$ are the fully counterpoise corrected and uncorrected scaled interaction energies of the system under investigation. The only unknown $\Delta E_{\mathrm{BSCP}}^{\mathrm{I},n}$ is adapted to minimize the weighted square difference between scaled reference values and scaled interaction energies of the system under investigation.

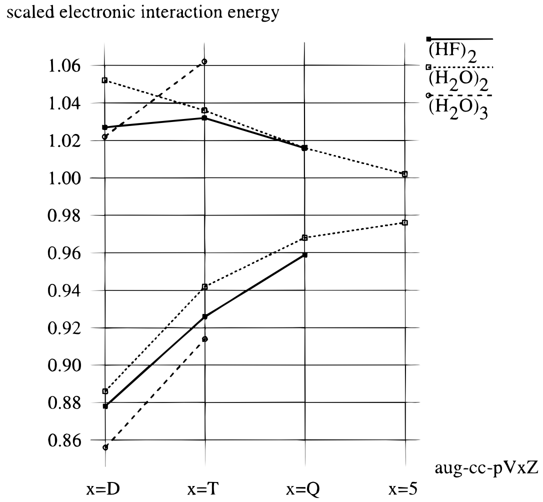

Figure 2. Interaction energies of the water trimer in its minimum structure at MP2(Full)/aug-cc-pVDZ and MP2(Full)/aug-cc-pVTZ//MP2(Full)/aug-cc-pVDZ level of theory scaled by the best estimate of $\Delta E_{\mathrm{BSCP}}^{(\mathrm{H_2O})_3,\mathrm{T(Full)//D(Full)}} = -16.21$ kcal/mol resulting from full BSCP analysis performed up to MP2(Full)/aug-cc-pVTZ//MP2(Full)/aug-cc-pVDZ level compared to the scaled reference values at MP2(FC)/aug-cc-pVxZ level.

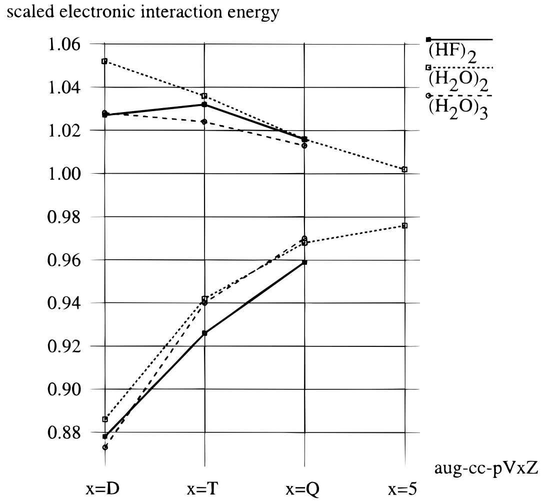

Figure 3. Interaction energies of the water trimer in its minimum structure at MP2(FC)/aug-cc-pVxZ level of theory scaled by the best estimate of $\Delta E_{\mathrm{BSCP}}^{(\mathrm{H_2O})_3,Q} = -15.91$ kcal/mol resulting from full BSCP analysis performed up to MP2(FC)/aug-cc-pVQZ level compared to the scaled reference values at MP2(FC)/aug-cc-pVxZ level.

TABLE 1: Electronic Interaction Energy of (HF)$_3$ (C_{3h}) with and without Counterpoise Correction[a]

MP2(FC)/aug-cc-pVxZ	$x = \mathrm{D}$	$x = \mathrm{T}$	$x = \mathrm{Q}$
$\Delta E_{\mathrm{fcp-corrected}}^{(\mathrm{HF})_3,\mathrm{aug-cc-pVxZ}}$	−13.15	−14.06	−14.55
$\Delta E_{\mathrm{uncorrected}}^{(\mathrm{HF})_3,\mathrm{aug-cc-pVxZ}}$	−15.46	−15.47	−15.33

[a] Energy in kcal/mol.

3. Applications

3.1. Hydrogen Fluoride Trimer. Table 1 summarizes the results for the electronic interaction energy of the hydrogen fluoride trimer (C_{3h} minimum) calculated at MP2(FC)/aug-cc-pVxZ level ($x = 2-4$) with and without counterpoise correction. The range of the obtained values spans more than 2.3 kcal/mol, which is about 15% of the total electronic interaction energy.

In Table 2 an overview of estimates resulting from the BSCP method for the hydrogen fluoride trimer is presented. The most reliable value ($\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q} = -15.05$ kcal/mol) results from minimization of the function:

TABLE 2: Estimates for the Electronic Interaction Energy of $(HF)_3$ (C_{3h}) from BSCP Method[a]

largest aug-cc-pVnZ basis set used	$n = \mathrm{D}$	$n = \mathrm{T}$	$n = \mathrm{Q}$
$\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,n}$ only from $\Delta E_{\mathrm{fcp-corrected}}^{R,\mathrm{aug-cc-pVxZ}}$	−14.91 (0.0040)	−15.03 (0.0081)	−15.08 (0.0064)
$\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,n}$ only from $\Delta E_{\mathrm{uncorrected}}^{R,\mathrm{aug-cc-pVxZ}}$	−14.87 (0.0125)	−14.94 (0.0064)	−15.04 (0.0061)
$\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,n}$ (from both)	−14.89 (0.0094)	−14.98 (0.0078)	**−15.05** (0.0064)

[a] Energy in kcal/mol. The first column was derived using only aug-cc-pVDZ results. The second column contains values relying on both aug-cc-pVDZ and aug-cc-pVTZ results, whereas the third one includes all results up to aug-cc-pVQZ level. The first row shows numbers derived from fully counterpoise corrected calculations only, the second one those resulting from not-counterpoise-corrected calculations. In the third row both approaches are included. (The numbers in parentheses indicate the root of the weighted mean-square deviations of the scaled interaction energies from the scaled reference values.)

$$
\begin{aligned}
F(\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q}) = {} & \left(\frac{-13.15}{\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q}} - \frac{-4.43}{-5.00}\right)^2 + 4\left(\frac{-14.06}{\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q}} - \frac{-4.71}{-5.00}\right)^2 + 9\left(\frac{-14.55}{\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q}} - \frac{-4.84}{-5.00}\right)^2 + \\
& \left(\frac{-13.15}{\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q}} - \frac{-4.01}{-4.56}\right)^2 + 4\left(\frac{-14.06}{\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q}} - \frac{-4.22}{-4.56}\right)^2 + 9\left(\frac{-14.55}{\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q}} - \frac{-4.37}{-4.56}\right)^2 + \\
& \left(\frac{-15.46}{\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q}} - \frac{-5.26}{-5.00}\right)^2 + 4\left(\frac{-15.47}{\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q}} - \frac{-5.18}{-5.00}\right)^2 + 9\left(\frac{-15.33}{\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q}} - \frac{-5.08}{-5.00}\right)^2 + \\
& \left(\frac{-15.46}{\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q}} - \frac{-4.68}{-4.56}\right)^2 + 4\left(\frac{-15.47}{\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q}} - \frac{-4.71}{-4.56}\right)^2 + 9\left(\frac{-15.33}{\Delta E_{\mathrm{BSCP}}^{(\mathrm{HF})_3,Q}} - \frac{-4.63}{-4.56}\right)^2
\end{aligned}
$$

(The first and second row in this formula correspond to fitting to the scaled counterpoise corrected reference values of water and hydrogen fluoride dimer, respectively. The third and fourth row correspond to fitting to the scaled uncorrected reference values of water and hydrogen fluoride dimer, respectively. The first, second, and third column correspond to fitting to scaled reference values at MP2(FC)/aug-cc-pVDZ, MP2(FC)/aug-cc-pVTZ and MP2(FC)/aug-cc-pVQZ level, respectively.)

To give an impression of the very high robustness of the method, not only the full BSCP results taking all calculations up to the MP2(FC)/aug-cc-pVQZ level of theory into account are given. Table 2 also contains the results that would emerge if only results up to the MP2(FC)/aug-cc-pVTZ or MP2(FC)/aug-cc-pVDZ level were available (this corresponds to skipping of columns in the previous formula) as well as the results only relying on the not-counterpoise-corrected electronic stabilization energies or only on the fully counterpoise corrected electronic stabilization energies, i.e., only relying on term 1 or only on term 2 in the definition of $F(\Delta E_{\mathrm{BSCP}}^{\mathrm{I},n})$ (this corresponds to skipping of the first two rows or rows three and four, respectively, in the previous formula). It is amazing that the largest discrepancy between the predictions is as small as 0.21 kcal/mol (or relatively seen below 1.5% of the total electronic interaction energy). This indicates that the BSCP method is also useful if it is impossible to do studies up to MP2(FC)/aug-cc-pVQZ level. The value of −15.05 kcal/mol resulting from a full BSCP analysis performed up to MP2(FC)/aug-cc-pVQZ level is in excellent agreement with experiment[11−14] and best estimates derived from both experiment and theory[15] suggesting a value of 15.1 kcal/mol. This result is also fully consistent with a CCSD(T)/aug-cc-pVTZ benchmark[16] yielding 14.36 kcal/mol with and 15.83 kcal/mol without counterpoise correction.

TABLE 3: Electronic Interaction Energy of $(H_2O)_3$ with and without Counterpoise Correction (all values taken from Xantheas[17])[a]

MP2(Full)/aug-cc-pVxZ	$x = \mathrm{D}$	$x = \mathrm{T/D}$
$\Delta E_{\mathrm{fcp-corrected}}^{(\mathrm{H_2O})_3,\mathrm{aug-cc-pVxZ}}$	−13.87	−14.81
$\Delta E_{\mathrm{uncorrected}}^{(\mathrm{H_2O})_3,\mathrm{aug-cc-pVxZ}}$	−16.56	−17.21

[a] Energy in kcal/mol.

The interaction energies of the hydrogen fluoride trimer in its C_{3h} minimum structure at MP2(FC)/aug-cc-pVQZ level of theory scaled by this value of −15.05 kcal/mol are shown in Figure 1 and compared to the scaled reference values. The striking similarity of basis set convergence behavior becomes obvious, especially considering that the scaled energy axis is divided by steps of only 2% of the electronic interaction energy. This finding is even more astonishing on considering that the hydrogen bonds in the trimer of hydrogen fluoride are in no way relaxed, but rather strained. Viewed in this way, the reliability of the BSCP method neither seems to be disturbed by very different hydrogen bond strengths (as shown for the dimer of formic acid[8]) nor by geometric distortions of the hydrogen bond or by strong cooperative effects as obvious from the calculations presented here.

3.2. Water Trimer. To present another test case we analyzed the results for the water trimer published by Xantheas[17] in 1994 with our BSCP method. Xantheas provides electronic interaction energies in his work with and without counterpoise correction at MP2 (Full) /aug-cc-pVDZ and MP2 (Full)/aug-cc-pVTZ//MP2 (Full)/aug-cc-pVDZ level of theory (cf. Table 3). The provided data actually do not fulfill our quality criteria (fully optimized geometries at each considered aug-cc-VxZ level), because they suffer obviously from the drawback of the missing geometry optimization at MP2(Full)/aug-cc-pVTZ level. Another disadvantage of these data is the fact that they include all electrons in the correlation calculation[18] without providing additional flexibility to the description of core−core and core−valence correlation as it would be the case in the aug-cc-pCVxZ series of basis sets.[7] Therefore it is not surprising that the obtained electronic interaction energies span a larger range of 3.34 kcal/mol (about 20% of the total interaction energy).

Table 4 shows the results obtained by application of the BSCP method. Due to the comparably higher discrepancy in the starting values, the scattering of the obtained estimates is worse than in the case of the hydrogen fluoride trimer. Still the improvement over the variance of Table 3 is striking. Even if the BSCP method is only performed at MP2(Full)/aug-cc-pVDZ level of theory, it is already close to a MP2-R12 benchmark studies yielding −16.5[19] and −16.32 kcal/mol[20] for the total interaction energy. Figure 2 displays the corresponding con-

TABLE 4: Estimates for the Electronic Interaction Energy of $(H_2O)_3$ from BSCP Method Resulting from Data in Table 3 (as Described In the Caption to Table 2)[a]

largest aug-cc-pVnZ basis set used	$n = D$	$n = T$
$\Delta E^{(H_2O)_3,n}_{BSCP}$ only from $\Delta E^{R,aug-cc-pVxZ}_{fcp-corrected}$	−15.73 (0.0040)	−15.83 (0.0079)
$\Delta E^{(H_2O)_3,n}_{BSCP}$ only from $\Delta E^{R,aug-cc-pVxZ}_{uncorrected}$	−15.93 (0.0125)	−16.51 (0.0189)
$\Delta E^{(H_2O)_3,n}_{BSCP}$ (from both)	−15.85 (0.0111)	−**16.21** (0.0249)

[a] Energy in kcal/mol.

TABLE 5: Electronic Interaction Energy of $(H_2O)_3$ with and without Counterpoise Correction[a]

MP2(FC)/aug-cc-pVxZ	$x = D$	$x = T$	$x = Q$
$\Delta E^{(H_2O)_3,aug-cc-pVxZ}_{fcp-corrected}$	−13.89	−14.96	−15.44
$\Delta E^{(H_2O)_3,aug-cc-pVxZ}_{uncorrected}$	−16.36	−16.29	−16.11

[a] Energy in kcal/mol.

vergence behavior. Nevertheless, both from the root of the weighted mean-square deviations of the scaled interaction energies given in Table 4 in parentheses as well as from Figure 2 it is quite obvious that the fit of the basis set convergence pattern is considerably worse than in the above demonstrated case of the hydrogen fluoride trimer.

To test our suspicion that the comparably worse agreement of basis set convergence patterns in the case of the water trimer arises from deficiency of underlying water trimer data we reinvestigated the water trimer. We performed full geometry optimizations at all MP2(FC)/aug-cc-pVxZ (x = D−Q) levels of theory. The resulting electronic interaction energies as well as the fully counterpoise corrected interaction energies are given in Table 5. A comparison of Table 3 and Table 5 reveals the importance of using the frozen core approximation in combination with the aug-cc-pVxZ series of basis sets. Whereas the basis set superposition error at MP2(Full)/aug-cc-pVTZ//MP2-(Full)/aug-cc-pVDZ level arises to 2.40 kcal/mol, it is reduced to 1.33 kcal/mol at MP2(FC)/aug-cc-pVTZ level. (This difference is not due to the missing geometry optimization at MP2-(Full)/aug-cc-pVTZ//MP2(Full)/aug-cc-pVDZ level, as a test calculation at MP2(FC)/aug-cc-pVTZ//MP2(FC)/aug-cc-pVDZ level equally yielded an uncorrected electronic interaction energy of −16.29 kcal/mol.)

The obtained values span a range of 2.5 kcal/mol, which is just like in the case of the hydrogen fluoride trimer about 15% of the total electronic interaction energy. The application of the BSCP method narrows down this insecurity by an order of magnitude as shown in Table 6. Figure 3 displays the interaction energies of the trimer of water at MP2(FC)/aug-cc-pVxZ (x = D−Q) level of theory scaled by the best estimate of −15.91 kcal/mol resulting from the BSCP method up to MP2-(FC)/aug-cc-pVQZ level relying both on fully counterpoise corrected as well as on not counterpoise corrected electronic interaction energies. This figure as well as the root of the weighted mean-square deviations of the scaled interaction energies from the scaled reference values indicate that the fit is indeed highly improved. Most strikingly the basis set convergence patterns of the water trimer in Figure 3 are nearly identical to the ones of the hydrogen fluoride trimer in Figure 1 confirming our above-mentioned suspicion concerning the data of Xantheas. This again underlines that it is possible to predict the further basis set convergence behavior of the electronic interaction energy within the MP2(FC)/aug-cc-pVxZ series very reliably already from the mere knowledge of the fully counterpoise corrected as well as uncorrected electronic interaction energy at MP2(FC)/aug-cc-pVDZ level.

4. Discussion

There are several advantages of the BSCP method over other basis set convergence considerations: First of all, the BSCP method does not need any analytical form for the basis set convergence behavior. It has only one parameter, namely, the electronic interaction energy of the system itself. It takes at the same time the information gained from fully counterpoise corrected as well as from not-counterpoise-corrected electronic interaction energies into account.

If it is not reasonably possible to fit all energy values at the same time to the reference values, the BSCP method is obviously inappropriate (e.g., hydrogen bonds that involve charged species are obviously dominated by ion−dipole interactions that are quite different to the uncharged hydrogen bonds investigated here and can not be expected to follow the same basis set convergence patterns due to the prevalent ion−dipole interaction). Therefore, an application of the BSCP method using the reference systems employed here would not be appropriate for such charged hydrogen-bonded systems. The root of the weighted mean-square deviations should help to detect such cases of inappropriate application.

Finally, the accuracy of the method can easily be adapted to the resources available by adding reference systems and by choosing the basis set level up to which the BSCP method is performed.

5. Conclusions

The proposed BSCP method provides a rather inexpensive possibility to systematically estimate total interaction energies in hydrogen bonded complexes. It is capable of providing highly accurate estimates already basing only on MP2(FC)/aug-cc-pVDZ level of theory. The method overcomes systematic errors like BSSE inherently by scaling them out reliably.

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Appendix

As the calculations presented here involve full geometry optimizations of the trimer of hydrogen fluoride and water up to MP2(FC)/aug-cc-pVQZ level we finally want to give the resulting geometries at this highest level.

TABLE 6: Estimates for the Electronic Interaction Energy of $(H_2O)_3$ from BSCP Method from Data in Table 5 (as Described in the Caption to Table 2)[a]

largest aug-cc-pVnZ basis set used	$n = D$	$n = T$	$n = Q$
$\Delta E^{(H_2O)_3,n}_{BSCP}$ only from $\Delta E^{R,aug-cc-pVxZ}_{fcp-corrected}$	−15.75 (0.0040)	−15.97 (0.0095)	−16.01 (0.0069)
$\Delta E^{(H_2O)_3,n}_{BSCP}$ only from $\Delta E^{R,aug-cc-pVxZ}_{uncorrected}$	−15.74 (0.0125)	−15.75 (0.0059)	−15.82 (0.0048)
$\Delta E^{(H_2O)_3,n}_{BSCP}$ (from both)	−15.74 (0.0093)	−15.85 (0.0104)	−**15.91** (0.0083)

[a] Energy in kcal/mol.

TABLE 7: Cartesian Coordinates of Water Trimer in Standard Orientation Optimized at MP2(FC)/aug-cc-pVQZ level[a]

atom	*X*	*Y*	*Z*
O	1.293 931	−0.948 392	−0.091 579
O	0.177 716	1.591 525	0.108 248
O	−1.472 493	−0.636 750	−0.081 757
H	1.217 907	0.018 563	−0.021 687
H	−0.625 150	1.045 633	0.056 258
H	−0.609 743	−1.080 345	−0.026 906
H	1.966 189	−1.201 029	0.542 670
H	0.089 451	2.242 373	−0.589 743
H	−2.031 884	−1.076 263	0.560 113

[a] Coordinates in angstroms.

For the trimer of hydrogen fluoride (C_{3h}) we find a F−F distance of 2.601 Å and F−H distances of 0.936 and 1.765 Å within the hydrogen bonds. Table 7 contains the Cartesian coordinates of the water trimer (C_1) in its standard orientation corresponding to O−O distances of 2.779−2.784 and O−H distances of 0.972 Å and 1.889−1.909 Å within the hydrogen bonds.

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