JCTC Journal of Chemical Theory and Computation

An Atomic Counterpoise Method for Estimating Inter- and Intramolecular Basis Set Superposition Errors

Frank Jensen

Department of Chemistry, University of Aarhus Langelandsgade 140, DK-8000 Aarhus, Denmark

Received August 16, 2009

Abstract: An atomic counterpoise method is proposed to calculate estimates of inter- and intramolecular basis set superposition errors. The method estimates the basis set superposition error as a sum of atomic contributions and can be applied for both independent particle and electron correlation models. It is shown that the atomic counterpoise method provides results very similar to the molecular counterpoise method for intermolecular basis set superposition errors at both the HF and MP2 levels of theory with a sequence of increasingly larger basis sets. The advantage of the atomic counterpoise method is that it can be applied with equal ease to estimate intramolecular basis set superposition errors, for which few other methods exist. The atomic counterpoise method is computationally quite efficient, requiring typically double the amount of computer time as required for calculating the uncorrected energy.

Introduction

The calculation of weak intermolecular interactions by electronic structure methods has long been known to suffer from a systematic overestimation due to the incomplete basis sets used in practical calculations.[1−3] The reason for the overestimation is that each fragment in a complex can partly compensate for basis set incompleteness by utilizing basis functions on the other fragment(s), which commonly is denoted as basis set superposition error (BSSE). The counterpoise (CP) correction[4−8] is the most common method for estimating BSSE, while other approaches,[9,10] such as the chemical Hamiltonian approach,[11−14] has been less used.

For a complex consisting of two fragments, the CP correction is calculated by subtracting the fragment energy calculated in the regular basis set from the fragment energy calculated in the full basis set for the whole complex. While it is recognized that this is only an estimate of the BSSE, it has been demonstrated that the CP-corrected complexation energy converges more regular toward the basis set limiting value than the directly calculated value.[15−17]

While BSSE primarily has been associated with the systematic overestimation of the stability of intermolecular complexes, it has been recognized that intramolecular BSSE is a component of the change in, for example, relative conformational energies of a single molecule with respect to changes in basis set.[18−20] The CP method has, in a few cases, been used to estimate intramolecular BSSE by dividing the molecule into nonbonded fragments and saturating dangling bonds, but the partitioning into fragments is nonunique, neglects the BSSE from the removed moiety, and requires involvement of the user.[21−24] Recently Asturiol et al. have attributed the artificial nonplanarity of aromatic systems at the MP2 level with certain Pople-type basis sets to intramolecular BSSE and have used a fragment approach to perform a CP correction.[25,26] Balabin has also used a fragment-based approach for estimating intramolecular BSSE in different conformations of small alkanes.[27]

The accurate calculation of conformational energies of systems with up to a few hundred atoms, like small peptides, is important for understanding, for example, biological recognition and for calibration of force field methods.[28] The relative energies of conformations with different degrees of compactness are very sensitive to intramolecular BSSE,[29−33] and there is clearly a need for methods capable of reducing this effect. The developments of explicitly correlated (F12) methods has the promise of calculating accurate correlation energies with basis sets of only triple-ζ quality,[34,35] and developments in linear scaling techniques will allow these methods to be applied to reasonably large system in the near future.[36] In such cases, the BSSE is likely to become a limiting factor for calculating accurate energies. In the present

10.1021/ct900436f
Published on Web 11/06/2009

paper, we show that it is possible to define an atomic version of the CP correction that provides results similar to the well-known molecular CP for nonbonded fragments and that it can be used also for estimating intramolecular BSSE.

Computational Details

For a bimolecular complex A−B, the molecular counterpoise (MCP) correction is defined in eq 1.

$$\Delta E_{\mathrm{MCP}} = E_{\mathrm{A}}(\mathrm{Bas}_{\mathrm{A}}) - E_{\mathrm{A}}(\mathrm{Bas}_{\mathrm{AB}}) + E_{\mathrm{B}}(\mathrm{Bas}_{\mathrm{B}}) - E_{\mathrm{B}}(\mathrm{Bas}_{\mathrm{AB}}) \quad (1)$$

Here $E_{\mathrm{A}}(\mathrm{Bas}_{\mathrm{A}})$ indicates the energy of fragment A in the regular basis set $\mathrm{Bas}_{\mathrm{A}}$, while $E_{\mathrm{A}}(\mathrm{Bas}_{\mathrm{AB}})$ indicates the energy of fragment A in the combined basis set for both fragments and similar for fragment B.

The atomic counterpoise (ACP) correction is defined in eq 2:

$$\Delta E_{\mathrm{ACP}} = \sum_{\mathrm{A}}^{\mathrm{atoms}} E_{\mathrm{A}}(\mathrm{Bas}_{\mathrm{A}}) - E_{\mathrm{A}}(\mathrm{Bas}_{\mathrm{AS}}) \quad (2)$$

Here $E_{\mathrm{A}}(\mathrm{Bas}_{\mathrm{A}})$ indicates the energy of atom A in the regular basis set $\mathrm{Bas}_{\mathrm{A}}$, while $E_{\mathrm{A}}(\mathrm{Bas}_{\mathrm{AS}})$ indicates the energy of atom A in a subset of the full basis set, which always includes the regular basis function on A, and the subscript S indicates the additional subset of basis functions for atom A. In the intermolecular case, where the two fragments are not covalently bonded, the subset includes basis functions on all the atoms in the *other* fragment, but basis functions on atoms within the *same* fragment are excluded. In the intramolecular case, the subset includes basis functions on atoms separated from atom A in terms of bonding and distance, as discussed in the next sections. For the intermolecular case with fragments beyond a certain size, the ACP can be used to include both intra- and intermolecular BSSE. Galano and Alvarez-Idaboy have reported a very similar method denoted $\mathrm{CP}^{\mathrm{aa}}$ where $\mathrm{Bas}_{\mathrm{AS}}$ includes all basis functions for the whole system,[37] and this is a special case of the current ACP. They used it for calculating intermolecular BSSE where the $\mathrm{CP}^{\mathrm{aa}}$ for the fragments were subtracted from the $\mathrm{CP}^{\mathrm{aa}}$ of the complex to provide an alternative to the conventional MCP that includes differences in intramolecular BSSE in each of the fragments. For calculating intramolecular BSSE, they partition the molecule into fragments and treat these as in the intermolecular case.

All calculations have been done using the Gaussian-03 program package[38] using unrestricted wave functions for open-shell species. The spin contamination for all atomic calculations is completely negligible. The geometries of all the systems are provided as Supporting Information.

Results and Discussion

Table 1 shows the molecular and ACP corrections for a T-shaped complex of two N_2 molecules (shortest intermolecular distance between atoms is 3.55 Å) as a function of increasingly larger basis sets of the correlation consistent type[39,40] at the HF and MP2 levels of theory. The MCP correction is a sum of two contributions for each of the two N_2 fragments, each employing all the basis functions. The ACP correction is a sum of four contributions for each of the four N atoms, each employing basis functions for three atoms, i.e., neglecting the basis functions on the directly bonded atom. It is seen that the two different methods of estimating the BSSE provide similar results and that they reduce to zero as the basis set approaches completeness. Table 2 shows similar results for two ethylene molecules in a face-to-face parallel displaced geometry with a shortest intermolecular distance between carbon atoms of 3.74 Å.

Table 1. Molecular and ACP Corrections for a T-Shaped Complex between Two N_2 Molecules (kJ/mol)

basis set	HF		MP2	
	MCP	ACP	MCP	ACP
cc-pVDZ	1.32	1.18	1.71	1.55
cc-pVTZ	0.54	0.43	1.10	0.69
cc-pVQZ	0.25	0.15	0.56	0.28
cc-pV5Z	0.15	0.06	0.36	0.11
aug-cc-pVDZ	0.32	0.47	1.12	0.88
aug-cc-pVTZ	0.22	0.21	0.75	0.57
aug-cc-pVQZ	0.07	0.09	0.37	0.33
aug-cc-pV5Z	0.01	0.01	0.12	0.12

Table 2. Molecular and ACP Corrections for a Parallel Displaced Complex between Two Ethylene Molecules (kJ/mol)

Basis set	HF		MP2	
	MCP	ACP	MCP	ACP
cc-pVDZ	1.68	1.64	2.66	2.54
cc-pVTZ	0.60	0.48	1.20	0.97
cc-pVQZ	0.24	0.14	0.53	0.39
aug-cc-pVDZ	0.93	0.92	3.25	2.15
aug-cc-pVTZ	0.18	0.41	1.11	1.33
aug-cc-pVQZ	0.06	0.14	0.49	0.66

The benzene dimer has been a popular test case for evaluating the performance of different theoretical methods.[41,42] Table 3 shows the MCP and ACP corrections for a sandwich (S) and a T-shaped benzene−dimer complex, where the distance between the centers of the two ring systems is 3.6 and 5.0 Å, respectively. It is again seen that the ACP mirrors the MCP results quite closely at both the HF and MP2 levels of theory. The results in Tables 1−3, thus, show that the familiar MCP estimate of the BSSE can be reproduced quite accurately as a sum of atomic contributions, with the exact difference between the two estimates depending on the system and the basis set.

The results in Tables 1−3 have been obtained using atomic ground states for the ACP calculations, i.e., a triplet state for carbon and a quartet state for nitrogen. We have tested the sensitivity of the results to other choices, like a singlet state for carbon and a doublet state for nitrogen. For the N_2−dimer system (Table 1), the MP2 ACP result with the cc-pVDZ basis set changes from 1.55 to 1.74 kJ/mol when using the lowest energy doublet state as the atomic reference state instead of a quartet state, and both values can be compared to the MCP result of 1.71 kJ/mol. A significantly larger value of 4.95 kJ/mol is obtained if an excited doublet state corresponding to a $(2p_x)^2(2p_y)^1$ electron configuration is employed.

Table 3. Molecular and ACP corrections for a Sandwich (S) and a T-shaped Complex of Two Benzene Molecules (kJ/mol)

	HF				MP2			
	S-complex		T-complex		S-complex		T-complex	
basis set	MCP	ACP	MCP	ACP	MCP	ACP	MCP	ACP
6-31G**	9.3	13.5	3.3	9.7	11.6	16.4	7.3	13.1
cc-pVDZ	5.0	7.0	2.7	4.3	8.7	10.4	6.8	7.4
cc-pVTZ	1.9	2.2	1.1	1.4	4.9	4.6	3.3	2.9
cc-pVQZ	0.8	0.7	0.5	0.4	2.2	2.1	1.6	1.3
6-31++G**	2.4	4.9	1.5	3.6	15.6	21.3	13.2	14.3
aug-cc-pVDZ	4.9	4.3	4.7	3.6	13.5	10.2	13.0	9.3
aug-cc-pVTZ	0.9	2.1	0.8	1.5	5.5	6.8	5.2	5.3
aug-cc-pVQZ	0.2	0.7	0.2	0.5	1.9	3.5	1.7	2.5

For the S-shaped benzene−dimer complex, the MP2 ACP results with the cc-pVDZ basis set change from 10.4 to 12.6 kJ/mol, if the lowest (open-shell) singlet state is used as the atomic reference state for carbon instead of a triplet state, while the corresponding results for the T-shaped complex are 7.4 and 8.5 kJ/mol. These values can be compared to the MCP results of 8.7 and 6.8 kJ/mol, respectively, for the two complexes. The ACP differences, due to using a singlet rather than a triplet atomic reference state, diminish for larger basis sets, and for the aug-cc-pVTZ basis set, for example, the values for the S- and T-shaped complexes change from 6.8 to 7.1 kJ/mol and from 5.3 to 5.5 kJ/mol, respectively.

These results show, as expected, that the ACP estimate of the BSSE increases as the electronic distribution of the atomic reference state becomes more and more diffuse. The premise of the ACP method is, thus, that the (local) electron distribution in the molecule resembles the distribution in the atomic reference state in terms of spatially diffuseness.

For estimating intermolecular BSSE, the ACP procedure offers little advantage over the corresponding molecular version, although the ACP method may be computationally less demanding for large fragments (see the Computational Considerations Section). For estimating intramolecular BSSE, however, the MCP procedure requires an ad hoc definition of an equivalent intermolecular reference system, which requires user involvement, is nonunique, and only recovers part of the BSSE.[21−24] The ACP method provides a common reference system for all molecules but requires the definition of atomic reference states and the subset of basis functions to be included in the CP calculations. The interpretation of BSSE in an intermolecular complex, as an artifact due to basis functions nearby in space but not directly bonded, suggests that the subspace in an intramolecular case should be limited to atoms sufficiently far removed in terms of bonding to effectively be considered as nonbonded atoms. This is in analogy to the situation in force field methods, where the nonbonded energy is only calculated for atoms that are at least three bonds apart, and contributions from atom pairs that are separated by exactly three bonds are sometimes reduced.[43] The number of bonds between atoms, which in an ACP sense is considered nonbonded, is therefore a free parameter which can be used to tune the performance.

While the magnitude of the intermolecular BSSE can be assessed by a MCP calculation, the magnitude of the corresponding intramolecular BSSE is more difficult to quantify. The commonly employed method consists of evaluating the MCP for a suitable intermolecular model system.[21−24] Valdez et al. have estimated the intramolecular BSSE in folded and extended conformations of the phenylalanine−glycine−phenylalanine (FGF) tripeptide by partitioning the system into two benzene molecules with the same geometries, as shown in Figure 1.[23] The aug′-cc-pVDZ (aug′ indicates that diffuse functions are omitted for hydrogen) HF and MP2 MCP and ACP results using one to eight bonds for defining the subspace in eq 2 are shown in Table 4. As the model system neglects all atoms in the peptide backbone, the true intramolecular BSSE for each conformation will be significantly larger than that of the MCP estimate. However, the backbone structure of the two conformations is similar, and the difference in the MCP between the two conformations is, thus, expected to provide a reasonably accurate estimate of the difference in the intramolecular BSSE. The results in Table 4 show that the ACP estimate of the difference in intramolecular BSSE is relatively insensitive to the exact value of the number of bonds for defining the subspace in eq 2. The ACP(1) method is equivalent to the CP^{aa} method of Galano and Alvarez-Idaboy[37] and appears to underestimate the BSSE difference, but all of the ACP(2)-ACP(8) results provide useful estimates of the difference in intramolecular BSSE between the two conformations. Given the uncertainty in the MCP estimate

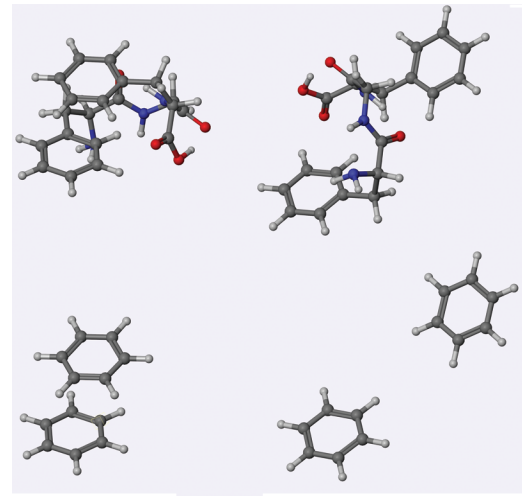

Figure 1. Folded and extended conformations of the FGF tripeptide and of the corresponding benzene dimer model systems used for calculating the results shown in Table 4.

Table 4. Molecular and ACP Corrections for the Di-Benzene Complexes and the FGF Tripeptide Conformations in Figure 1 with the aug′-cc-pVDZ Basis Set (kJ/mol)[a]

	HF			MP2		
	folded	extended	Δ	folded	extended	Δ
MCP	4.3	0.2	4.1	13.7	0.8	12.9
ACP(1)	88.5	86.9	1.6	446.9	440.3	6.6
ACP(2)	58.0	54.8	3.2	176.1	164.4	11.7
ACP(3)	39.5	34.5	5.0	96.5	80.9	15.6
ACP(4)	26.6	20.1	6.5	59.6	42.3	17.3
ACP(5)	20.6	14.1	6.5	44.9	28.7	16.2
ACP(6)	16.3	10.3	6.0	35.2	20.3	14.9
ACP(7)	13.5	7.6	5.9	29.6	15.1	14.5
ACP(8)	12.2	6.4	5.8	26.7	12.8	13.9

[a] In the ACP(*n*) notation, *n* indicates the number of bonds between atoms for defining the basis set subspace in eq 2.

of the intramolecular BSSE, it is difficult to objectively select a unique lower bonded criterion based on the results in Table 4.

Another method for estimating the intramolecular BSSE is to compare the result with a given basis set to the basis set limiting result, but data for systems containing 50−100 atoms, where intramolecular BSSE can be significant, is scarce. We have, in recent work, investigated the performance of conventional and local MP2 methods for predicting the energy difference between peptide conformations, including helical and extended structures of polyalanines with four, six, and eight amino acids (42, 62, and 82 atoms, respectively), as shown in Figure 2.[44] The local MP2 method calculates electron correlation using localized occupied orbitals, and a restricted set of virtual orbitals which significantly reduces the intramolecular BSSE compared to canonical MP2.[45−47] Table 5 shows the energy differences between the two conformations for the three peptides with the aug′-cc-pVDZ and aug′-cc-pVTZ basis sets. The basis set limiting value obtained by extrapolating aug′-cc-pVTZ and aug′-cc-pVQZ results[44] for the octaalanine peptide is 60−64 kJ/mol, which the LMP2 method mirrors closely with both the aug′-cc-pVDZ and aug′-cc-pVTZ basis sets. The canonical MP2 method, on the other hand, overestimates the stability of the helical structure by ∼30 and ∼20 kJ/mol, respectively, which was attributed to differences in intramolecular BSSE. For the tetra- and hexa-alanine peptides, the MP2 and LMP2 results are much closer, which suggests that the BSSE almost cancels between the two conformations for these systems.

If the difference between the results from the local and canonical MP2 methods is taken as a measure of the difference in intramolecular BSSE, then this allows another probe of how many bonds atoms must be separated in order to be considered nonbonded in an ACP sense. Table 5 shows the difference in ACP calculated for the two conformations of the polyalanine peptides using different bond separations for defining the subspace in eq 2. The ΔACP values do not depend strongly on which bond criterion is used, but the best agreement is obtained using a four-bond criterion. The ACP(1) result, which is equivalent to the CP^{aa} method, again appears to underestimate the difference in BSSE. It is worth noting that the ACP(4) results mirror closely the LMP2−MP2 differences for all three systems, including the small positive and negative values for the tetra- and hexa-alanines, and for both basis sets.

The two different independent methods for calibration, using either a suitable intermolecular model system or using the difference between local and canonical MP2 results, suggest that an ACP-type correction using a lower bonded criterion for defining the nonbonded subspace in eq 2 can provide a useful estimate of the intramolecular BSSE. From the limited results in the present paper, a value around four bonds appears to be a heuristic choice, at least for estimating differential BSSE between different conformations, but further studies may reveal a different optimum choice. The atomic reference state is another possible variable, but the results in Tables 1−5 suggest that ground atomic reference states can provide useful estimates of the BSSE for even quite polar systems, like poly peptides. The optimum choice of atomic reference states for charged systems, especially with strongly localized charges, will require careful calibration studies.

Computational Considerations

The MCP method requires calculations for each of the two fragments in a dimolecular complex, using all the basis functions for the whole complex, typically doubles the computational effort compared to calculating the energy of the complex and the two fragments. The ACP method requires N_{atom} calculations, each using a large fraction of all the basis functions for the whole system, which taken at face value would indicate a large computational overhead, especially if correlated methods are used. There are, however, a number of features that significantly reduce the computational cost:

1. Each calculation has only one atom and, thus, only a small number of occupied orbitals.
2. Hydrogen has only one electron and, therefore, no electron correlation energy.
3. If only the valence electrons are correlated, as is often the case, then the number of correlating electrons for non-hydrogen atoms is small.
4. Although each calculation has a large number of basis functions, many contribute only very little to the final results.

The latter point will automatically reduce the computational effort, if efficient integral-screening techniques are employed.[48] The computational time may also be reduced by a priori truncating the basis set based on a distance criterion. Figure 3 shows the magnitude of the HF and the MP2 ACP(4) corrections for the helical and the extended conformations of the octa-alanine peptide, as a function of a cutoff distance beyond which basis functions are excluded in the ACP calculations. With the aug′-cc-pVDZ basis set, the MP2 ACP(4) correction is calculated to within 0.5 kJ/mol of the limiting value with a cutoff distance of 10 Å (the dimensions of the two conformations are ∼20 and ∼30 Å, respectively). Given that the ACP only provides an estimate of the BSSE, there is little reason to refine the numerical value to an accuracy better than ∼0.5 kJ/mol. The 10 Å cutoff limit corresponds qualitatively to a distance where the maximum overlap between basis functions on different atoms

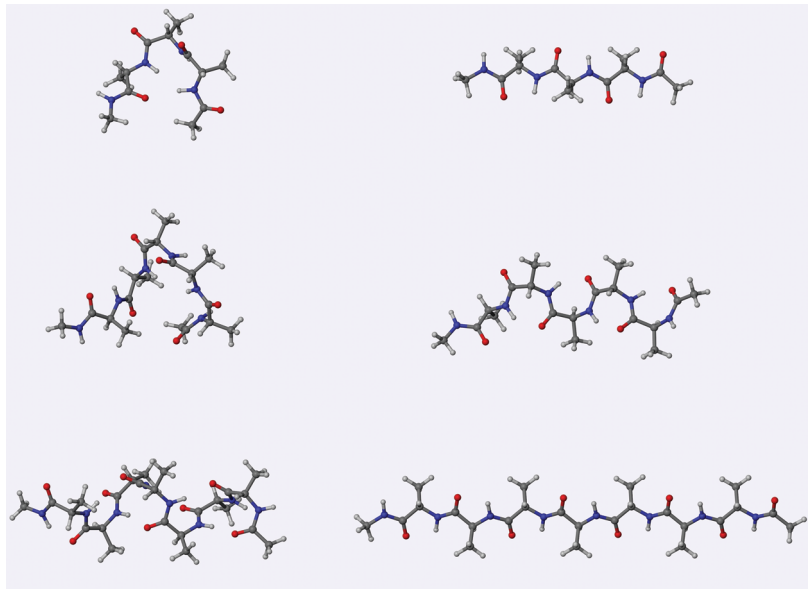

Figure 2. Helical and extended conformations of the tetra-, hexa-, and octa-alanine peptides used for calculating the results in Table 5.

Table 5. MP2 Energy Differences between the Extended and Helical Conformations of Tetra-, Hexa-, and Octa-Alanine Peptides Shown in Figure 2 as a Function of Basis Set (kJ/mol)[a]

		aug′-cc-pVDZ	aug′-cc-pVTZ	extrapolated
tetra-alanine	MP2	12.6	15.7	18.0
	LMP2	18.2	18.6	19.1
	LMP2−MP2	5.6	2.9	1.1
	ΔACP(1)	2.0	2.7	
	ΔACP(2)	3.1	1.4	
	ΔACP(3)	3.5	2.1	
	ΔACP(4)	4.3	3.0	
	ΔACP(5)	3.9	3.3	
	ΔACP(6)	4.4	3.1	
hexa-alanine	MP2	47.3	45.6	45.6
	LMP2	46.2	44.3	45.8
	LMP2−MP2	−1.1	−1.3	0.2
	ΔACP(1)	−0.4		
	ΔACP(2)	0.4		
	ΔACP(3)	1.3	−0.3	
	ΔACP(4)	−1.8	−1.4	
	ΔACP(5)	−0.6	−1.6	
	ΔACP(6)	2.0	1.1	
octa-alanine	MP2	−94.5	−84.0	−64.0
	LMP2	−60.1	−63.2	−60.2
	LMP2−MP2	34.4	20.8	3.8
	ΔACP(1)	17.5		
	ΔACP(2)	26.9		
	ΔACP(3)	32.0	15.4	
	ΔACP(4)	33.8	20.4	
	ΔACP(5)	27.1	20.3	
	ΔACP(6)	25.1	17.3	

[a] ΔACP(*n*) indicates the difference in ACP corrections between the helical and extended conformations, where *n* is the number of bonds between atoms for defining the basis set subspace in eq 2. Extrapolated indicates results extrapolated to the basis set limit from aug′-cc-pVTZ and aug′-cc-pVQZ results.[44]

drops below a certain critical value and will, thus, be smaller for basis sets without diffuse functions. For the cc-pVDZ basis set, the ACP(4) results (not shown) stabilize to the same level of accuracy at a cutoff distance of 7 Å, while basis sets employing multiple diffuse functions may require a cutoff distance larger than 10 Å.

The use of a lower bonded and an upper distance criterion reduces the number of basis functions for each ACP calculation, and the latter is especially effective for large systems. The distance criterion means that the overall computational effort for calculating the ACP scales linearly with the number of atoms in the system and is, of course, trivially parallelizable. For the benzene dimer, the computational time for an ACP calculation is slightly less than the time required for the MCP calculation. For the helical conformation of the octa-alanine peptide, the total computational time for the MP2 ACP(4) calculations is roughly twice that of the time for calculating the MP2 energy with

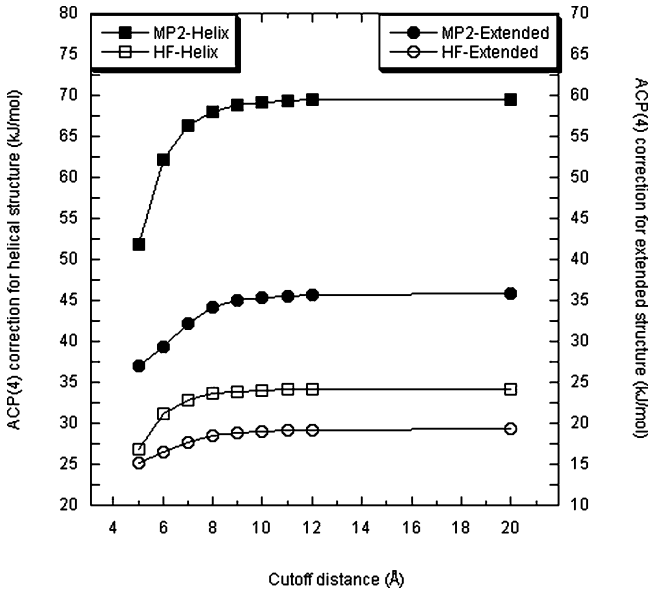

Figure 3. HF and MP2 ACP(4) results (kJ/mol) for the helical and the extended conformations of the octa-alanine peptide as a functions of cutoff distance (Å).

the aug′-cc-pVDZ basis set, while the ACP(4) calculations only require one-third of the time for the MP2 energy for the extended conformation, due to the larger number of basis functions discarded by the distance criterion. For typical applications, the computational time for performing such a posterori ACP calculations is, thus, comparable to the time required for generating the BSSE uncorrected results.

We note that it is possible to improve the computational efficiency if the ACP corrections are generated as an integral part of the molecular energy calculation, rather than as an a posterori correction. In the current ACP procedure, a significant fraction of all the integrals over basis functions is regenerated for each atomic calculation, however, all of these integrals are also required for the molecular energy calculation. If the ACP calculations are performed at the same time as the molecular energy is calculated, then the overhead due to recalculating integrals N_{atom} times will be removed. This suggests that the ACP method provides a cost-efficient way of estimating BSSE, especially for intramolecular systems where few other methods are available.

Summary

We propose an atomic counterpoise (ACP) method, where the BSSE is estimated as a sum of atomic contributions, calculated as differences in energy in a regular basis set and in a subset consisting of basis functions on atoms separated by a minimum number of bonds. The computational efficiency can be improved by omitting functions on atoms separated by more than ∼7 or ∼10 Å for regular and augmented basis sets, respectively, without affecting the final results. Atomic ground states are used for all ACP calculations, but the results are not overly sensitive to using alternative atomic reference states. Differences in ACP values are also relatively insensitive to the exact value of the lower bonded criterion used, which indicates that the majority of the difference in intramolecular BSSE between conformations is due to atoms remote in terms of bonding but close in physical space. From the (limited) results in the present paper, a value of four as the minimum bond criterion for including basis functions in the CP correction appears to be a heuristic choice, but further work may yield a different optimum value.

The ACP provides a method for estimating BSSE, which for intermolecular systems mirrors the results obtained with the molecular counterpoise method but can be applied with equal ease to estimate intramolecular BSSE as well. The ACP method is shown to work at both the HF and MP2 levels of theory, and it is likely that it will be equally useful for density functional and higher level electron correlation methods. The calibration has been done by comparing the intermolecular model systems and to the local MP2 results, which reduces the BSSE compared to canonical MP2. The use of local correlation methods for estimating BSSE requires a careful consideration of the parameters used for defining the local correlation space, while the ACP method can be used for both correlated and independent particle models. The ACP may, thus, be useful for estimating intramolecular BSSE for systems where elimination of the BSSE by enlarging the basis set is infeasible.

The ACP method, except ACP(1), will require ad hoc adjustments for systems where the bonding pattern is ambiguous, like transition structures and perhaps hydrogen-bonded systems, a feature it shares with the molecular counterpoise method. For charged systems, the ACP method may need to be modified by utilizing alternative atomic reference states for at least some of the atoms, and this will need to be investigated by careful calibration studies. Finally, we note that it is straightforward to define derivatives of the ACP corrected energy,[49] which should be useful for reducing artifacts in molecular structures due to intramolecular BSSE.

Acknowledgment. This work was supported by grants from the Danish Center for Scientific Computation and the Danish Natural Science Research Council.

Supporting Information Available: Tables showing the molecular geometries used. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Chen, F.; Davidson, E. R. *Chem. Phys. Lett.* **2002**, *360*, 99.

(2) Tzeli, D.; Mavridis, A.; Xantheas, S. S. *J. Phys. Chem. A* **2002**, *106*, 11327.

(3) van Mourik, T. *J. Phys. Chem. A* **2008**, *112*, 11017.

(4) Jansen, H. B.; Ros, P. *Chem. Phys. Lett.* **1969**, *3*, 140.

(5) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(6) Meunier, A.; Levy, B.; Berthier, G. *Theor. Chim. Acta* **1973**, *29*, 49.

(7) Van Duijneveldt, F. B.; van Duijneveldt-van der Rijdt, J. G. C. M.; van Lenthe, J. H *Chem. Rev.* **1994**, *94*, 1873.

(8) Valiron, P.; Mayer, I. *Chem. Phys. Lett.* **1997**, *275*, 46–55.

(9) Sadley, A. D. *J. Chem. Phys.* **1991**, *95*, 6706.

(10) Famulari, A.; Specchio, R.; Sironi, M.; Raimondi, M. *J. Chem. Phys.* **1998**, *108*, 3296.

(11) Mayer, I.; Vibok, A. *Mol. Phys.* **1997**, *92*, 503.

(12) Mayer, I. *Int. J. Quantum Chem.* **1998**, *70*, 41.

(13) Mayer, I.; Valiron, P. *J. Chem. Phys.* **1998**, *109*, 3360.

(14) Salvador, P.; Paizs, B.; Duran, M.; Suhai, S. *J. Comput. Chem.* **2000**, *22*, 765.

(15) Peterson, K. A.; Dunning, T. H. *J. Chem. Phys.* **1995**, *105*, 2032.

(16) Halkier, A.; Koch, H.; Jørgensen, P.; Christiansen, O.; Nielsen, I. M. B.; Helgaker, T. *Theor. Chem. Acc.* **1997**, *97*, 150.

(17) van Mourik, T.; Wilson, A. K.; Peterson, K. A.; Woon, D. E.; Dunning, T. H. *Adv. Quantum Chem.* **1999**, *31*, 105–135.

(18) Sellers, H.; Almlof, J. *J. Phys. Chem.* **1989**, *93*, 5136.

(19) Jensen, F. *Chem. Phys. Lett.* **1996**, *261*, 633.

(20) Senent, M. L.; Wilson, S. *Int. J. Quantum Chem.* **2001**, *82*, 282.

(21) Holroyd, L. F.; van Mourik, T. *Chem. Phys. Lett.* **2007**, *442*, 42.

(22) (a) Palermo, N. Y.; Csontos, J.; Owen, M. C.; Murphy, R. F.; Lovas, S. *J. Comput. Chem.* **2007**, *28*, 1208. (b) van Mourik, T. *J. Comput. Chem.* **2008**, *29*, 1. (c) Csontos, J.; Palermo, N. Y.; Owen, M. C.; Murphy, R. F.; Lovas, S. *J. Comput. Chem.* **2008**, *29*, 4.

(23) Valdes, H.; Klusak, V.; Pitonak, M.; Exner, O.; Stary, I.; Hobza, P.; Rulisek, L. *J. Comput. Chem.* **2008**, *29*, 861.

(24) Suarez, E.; Diaz, N.; Suarez, D. *J. Chem. Theory Comp.* **2009**, *5*, 1667.

(25) Asturiol, D.; Duran, M.; Salvador, P. *J. Chem. Phys.* **2008**, *128*, 144108.

(26) Asturiol, D.; Duran, M.; Salvador, P. *J. Chem. Theory Comp.* **2009**, *5*, 2574.

(27) Balabin, R. M. *J. Chem. Phys.* **2008**, *129*, 164101.

(28) Kaminsky, J.; Jensen, F. *J. Chem. Theo. Comp.* **2007**, *3*, 1774.

(29) van Mourik, T.; Karamertzanis, P. G.; Price, S. L. *J. Phys. Chem. A* **2006**, *110*, 8.

(30) Toroz, D.; van Mourik, T. *Mol. Phys.* **2007**, *105*, 209.

(31) Shields, A. E.; van Mourik, T. *J. Phys. Chem. A* **2007**, *111*, 13272.

(32) van Mourik, T. *J. Chem. Theory Comput.* **2008**, *4*, 1610.

(33) Valdes, H.; Pluhackova, K.; Hobza, P. *J. Chem. Theory Comp.* **2009**, *5*, 2248.

(34) Tew, D. P.; Klopper, W.; Neiss, C.; Hattig, C. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1921.

(35) Knizia, G.; Adler, T. B.; Werner, H.-J. *J. Chem. Phys.* **2009**, *130*, 054104.

(36) Adler, T. B.; Werner, H.-J. *J. Chem. Phys.* **2009**, *130*, 241101.

(37) Galano, A.; Alvarez-Idaboy, J. R. *J. Comput. Chem.* **2006**, *27*, 1203.

(38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N. ; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian*, Revision 03; Gaussian, Inc.: Wallingford, CT, 2004.

(39) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(40) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J *J. Chem. Phys.* **1992**, *96*, 6796.

(41) Sinnokrot, M. O.; Sherrill, C. D. *J. Phys. Chem. A* **2006**, *110*, 10656.

(42) Pitonak, M.; Neogrady, P.; Rezac, J.; Jurecka, P.; Urban, M.; Hobza, P. *J. Chem. Theory Comp.* **2008**, *4*, 1829.

(43) Jensen, F. *Introduction to Computational Chemistry*, 2nd ed.; Wiley: West Sussex, U.K.,2006, p 41−42.

(44) Kaminsky, J.; Mata, R. A.; Werner, H.-J.; Jensen, F. *Mol. Phys.* **2008**, *106*, 1899.

(45) Pulay, P. *Chem. Phys. Lett.* **1983**, *100*, 151.

(46) Schutz, M.; Hetzer, G.; Werner, H.-J. *J. Chem. Phys.* **1999**, *111*, 5691.

(47) Saebo, S.; Pulay, P. *J. Chem. Phys.* **2001**, *115*, 3975.

(48) Doser, B.; Lambrecht, D. S.; Kussmann, J.; Ochsenfeld, C. *J. Chem. Phys.* **2009**, *130*, 064107.

(49) Simon, S.; Duran, M.; Dannenberg, J. J. *J. Chem. Phys.* **1996**, *105*, 11024.

CT900436F