

# Counterpoise Correction and Basis Set Superposition Error

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## Introduction

In studies of weakly bound clusters, one often encounters an artificial shortening of intermolecular distances and concomitant artificial strengthening of the intermolecular interaction. Such problems are ascribed to “basis set superposition errors” (BSSEs),<sup>1,2</sup> and they are more pronounced for smaller basis sets. As monomer A approaches monomer B, the dimer can be artificially stabilized as monomer A utilizes the extra basis functions from monomer B to describe its electron distribution, and vice versa. As pointed out by van Duijneveldt *et al.*,<sup>3</sup> the improvement in the descriptions of monomers A and B through the addition of extra accessible basis functions is not an error in itself; the error arises from the inconsistent treatment of the monomers — they are able to access additional functions from the other monomer at shorter intermolecular distances, but at large intermolecular distances, the other monomer is too far away (the overlap integrals are too small) for its functions to provide stabilization. This inconsistent treatment of the basis set for each monomer as the intermolecular distance is varied is the source of the basis set superposition error. Of course, even if this inconsistency could be perfectly eliminated, there would remain errors due to the fact that the basis set is incomplete — these would be described as “basis set incompleteness errors” (BSIEs). In the limit of a complete basis set, both the BSSE and the BSIE would be reduced to zero.

The Boys and Bernardi counterpoise correction (CP)<sup>4</sup> is a prescription for removing BSSE. The typical, uncorrected interaction energy between monomers A and B would be computed as:

$$\Delta E_{\text{int}}(AB) = E_{AB}^{AB}(AB) - E_A^A(A) - E_B^B(B), \quad (1)$$

where the superscripts denote the basis used, the subscripts denote the geometry, and the symbol in parentheses denotes the chemical system considered. Thus,  $E_{AB}^{AB}(AB)$  represents the energy of the bimolecular complex AB evaluated in the dimer basis (the union of the basis sets on A and B), computed at the geometry of the dimer. Likewise, monomers A and B are each evaluated at their own geometries in their own basis sets. Note that this can be performed as three separate, standard computations: one on the dimer, one on monomer A, and one on monomer B. Alternatively, one could obtain the energy of the dissociation limit by a computation of the A+B supermolecule at

some very large intermolecular separation (where the distance between A and B would be so large that the basis functions of one monomer would not overlap with those of the other); this might be necessary for theoretical methods which are not size-extensive, such as truncated configuration interaction, for which the energy of A+B at infinite separation is not equal to the sum of the energies from separate computations on A and B.

We can attempt to correct Eq. (1) by estimating the amount by which monomer A is artificially stabilized by the extra basis functions from monomer B (and vice versa). This may be estimated as:

$$\begin{aligned} E_{\text{BSSE}}(A) &= E_A^{AB}(A) - E_A^A(A), \\ E_{\text{BSSE}}(B) &= E_B^{AB}(B) - E_B^B(B), \end{aligned} \quad (2)$$

where we have subtracted the energy of monomer A in its monomer basis from the energy of monomer A in the dimer basis (and likewise for monomer B). For the moment, we have assumed that the geometries of monomers A and B do not change as they approach each other and form the bimolecular complex. This is often a very good approximation and simplifies the procedure; below, we will consider the possibility that the monomer geometries are deformed as they join in the bimolecular complex. The energy of monomer A in the dimer basis must necessarily be lower (more stable) than the energy of monomer A in the monomer basis, so  $E_A^{AB}(A) < E_A^A(A)$ , and thus  $E_A^{\text{BSSE}} < 0$  as defined above (the error is stabilizing). If we subtract this error from the interaction energy defined in Eq. (1), the terms  $E_A^A(A)$  and  $E_B^B(B)$  cancel, yielding:

$$\Delta E_{\text{int}}^{\text{CP}}(AB) = E_{AB}^{AB} - E_A^{AB} - E_B^{AB}. \quad (3)$$

Practically speaking, to evaluate the energy of monomer A in the dimer basis, one places all the basis functions of monomer B on the atomic centers of monomer B while neglecting the electrons and the nuclear charges of monomer B. The functions on monomer B are thus referred to as “ghost functions,” or the atoms of B are referred to as “ghost atoms” in such a computation. It has been argued that such a procedure should “overcorrect” for BSSE, because some of the basis functions in monomer B are occupied and hence unavailable to monomer A because of the Pauli exclusion principle. Indeed, there do appear to be situations in which the counterpoise correction overcorrects, particularly for smaller basis sets.<sup>5,6</sup> This appears to happen in particular for hydrogen-bonded complexes (although the counterpoise corrected interaction energies approach the complete basis set more smoothly and are more suitable for extrapolation).<sup>7</sup> On the other hand, for dispersion-dominated systems it appears that the counterpoise corrected values are superior.<sup>8</sup> van Duijneveldt *et al.* have argued that the counterpoise correction does not overcorrect,<sup>3</sup> and that poorer agreement with experiment or higher-level theory after counterpoise correction is a reflection of BSIE or other errors. Some researchers prefer to use the average of the uncorrected and the counterpoise-corrected values;<sup>9</sup> this procedure appears to work quite well for hydrogen-bonded complexes,<sup>7</sup> among others.

## Counterpoise Correction in Clusters

So far, we have only considered dimers. It is also possible to define a counterpoise correction for trimers and larger clusters. The most unambiguous way to define this procedure is to use the trimer basis set for the counterpoise correction.<sup>3</sup>

$$\Delta E_{\text{int}}^{\text{CP}}(ABC) = E_{ABC}^{\text{ABC}}(ABC) - E_A^{\text{ABC}}(A) - E_B^{\text{ABC}}(B) - E_C^{\text{ABC}}(C) \quad (4)$$

These trimer interaction energies may be broken down into their two-body and three-body components, according to the definitions of Hankins, Moskowitz, and Stillinger.<sup>10</sup> The two-body interactions are defined as

$$\Delta^2 E_{\text{int},AB}^{\text{CP}} = E_{AB}^{\text{ABC}} - E_A^{\text{ABC}} - E_B^{\text{ABC}} \quad (5)$$

$$\Delta^2 E_{\text{int},AC}^{\text{CP}} = E_{AC}^{\text{ABC}} - E_A^{\text{ABC}} - E_C^{\text{ABC}} \quad (6)$$

$$\Delta^2 E_{\text{int},BC}^{\text{CP}} = E_{BC}^{\text{ABC}} - E_B^{\text{ABC}} - E_C^{\text{ABC}} \quad (7)$$

The total interaction energy is then written as a sum of these two-body interaction energies plus a three-body interaction energy,

$$\Delta E_{\text{int},ABC}^{\text{CP}} = \Delta^2 E_{\text{int},AB}^{\text{CP}} + \Delta^2 E_{\text{int},AC}^{\text{CP}} + \Delta^2 E_{\text{int},BC}^{\text{CP}} + \Delta^3 E_{\text{int},ABC}^{\text{CP}} \quad (8)$$

The total interaction energy can be computed according to equation 4 above, so that the three-body term is:

$$\Delta^3 E_{\text{int},ABC}^{\text{CP}} = E_{\text{int},ABC}^{\text{CP}} - \Delta^2 E_{\text{int},AB}^{\text{CP}} - \Delta^2 E_{\text{int},AC}^{\text{CP}} - \Delta^2 E_{\text{int},BC}^{\text{CP}} \quad (9)$$

## Counterpoise Correction Including Monomer Deformations

The equations so far have assumed that the monomer geometries do not change as a complex is formed. However, for strongly interacting molecules, the monomers may be significantly deformed upon complexation. As before, we can estimate the BSSE for monomer A as the difference in energy between monomer A in the monomer basis and monomer A in the dimer basis. However, if the geometry of A changes significantly upon complexation, then we need to use the geometry of A as it appears in the cluster, not the geometry of the isolated monomer. Hence, the BSSE is now estimated as:

$$E_{\text{BSSE}}(A) = E_A^{\text{AB}}(A) - E_A^{\text{AB}}(A), \quad (10)$$

$$E_{\text{BSSE}}(B) = E_B^{\text{AB}}(B) - E_B^{\text{AB}}(B).$$

Before, the interaction energy was defined as the energy change as two rigid monomers are brought together from infinite separation into a complex. Now let us define the energy difference between the complex and infinitely separated monomers as the *binding energy*:

$$\Delta E_{\text{bind}}(AB) = E_{AB}^{\text{AB}}(AB) - E_A^{\text{A}}(A) - E_B^{\text{B}}(B), \quad (11)$$

where the form of the equation is the same as for  $E_{int}(AB)$  in Eq. (1), but it is now understood that the geometries of A and B in the complex AB may be different than in the isolated monomers. (Note: this binding energy is defined as a negative number, like  $E_{int}(AB)$ , but it is often customary to report the negative of this quantity to make binding energies positive).

Now, when we subtract these BSSEs in Eq. (10) from the interaction energy, the monomer energies in the monomer basis no longer cancel, and we obtain

$$\Delta E_{bind}^{CP}(AB) = E_{AB}^{AB}(AB) - E_A^A(A) - E_B^B(B) - E_{AB}^{AB}(A) + E_{AB}^A(A) - E_{AB}^{AB}(B) + E_{AB}^B(B). \quad (12)$$

Note that if the monomer geometries were rigid, then  $E_{AB}^A(A) = E_A^A(A)$  and  $E_{AB}^B(B) = E_B^B(B)$ , leading to a cancellation of terms and  $\Delta E_{bind}(AB) = \Delta E_{int}(AB)$ .

It is convenient to rewrite the above result in this form:

$$\Delta E_{bind}^{CP}(AB) = [E_{AB}^{AB}(AB) - E_{AB}^{AB}(A) - E_{AB}^{AB}(B)] + [E_{AB}^A(A) - E_A^A(A)] + [E_{AB}^B(B) - E_B^B(B)], \quad (13)$$

or as

$$\Delta E_{bind}^{CP}(AB) = E_{int}^{CP}(AB) + E_{def}^A(A) + E_{def}^B(B), \quad (14)$$

where  $\Delta E_{int}^{CP}(AB)$  is the interaction energy defined in Eq. (1) for rigid monomers,  $E_{def}^A(A)$  is the ‘‘deformation energy’’ of monomer A (the energy required to deform monomer A from its equilibrium geometry to the geometry it has in the complex, or  $E_{AB}^A(A) - E_A^A(A)$ ), and likewise  $E_{def}^B(B)$  is the deformation energy of monomer B. As pointed out by van Duijneveldt *et al.*,<sup>3</sup> it may be advantageous to use different theoretical methods to compute  $E_{int}^{CP}(AB)$  and the deformation energies; the deformation energies will typically be much easier to compute, whereas  $\Delta E_{int}^{CP}(AB)$  is a more subtle quantity and may require large basis sets and/or elaborate descriptions of electron correlation.

## Counterpoise Corrected Total Energies

Above, we discussed how the counterpoise correction can be applied to yield interaction energies that are hopefully more accurate, because they subtract an estimate of the overbinding due to BSSE. A researcher may be interested not only in energetics at a given geometry, but also in the optimum geometry for a van der Waals dimer. In that case, if they use the usual dimer energy  $E_{AB}^{AB}$  and its gradient, then the resulting optimized geometry will be contaminated by BSSE, and the intermolecular distance will typically be underestimated.

Optimizers typically expect to work using *total energies*, like  $E_{AB}^{AB}$ , rather than interaction energies like Eq. (3). This is not a problem, because we can apply the counterpoise correction also to a total energy — we simply remove the BSSE from the dimer energy:

$$\begin{aligned} E_{tot,AB}^{CP} &= E_{AB}^{AB}(AB) - E_{BSSE}(A) - E_{BSSE}(B), \\ &= E_{AB}^{AB}(AB) - [E_A^{AB}(A) - E_A^A(A)] - [E_B^{AB}(B) - E_B^B(B)]. \end{aligned} \quad (15)$$

Optimizations proceed much more efficiently if one has analytic gradients of the energy with respect to nuclear perturbations. This is not a problem in principle, as one simply differentiates each term of the above equation, so that the CP-corrected gradient is just a sum of five individual gradients (although most quantum chemistry programs do not have built-in support to automatically compute such composite gradients).

Alternatively, one could also attempt to optimize the counterpoise-corrected interaction energy  $\Delta E_{\text{int}}^{\text{CP}}(AB)$ , Eq. (3), directly. This is apparently simpler, because Eq. (3) involves only three terms (and its overall gradient thus is a sum of three gradients). However, this will be appropriate only if the monomers are constrained to be rigid. Only in that case will the minimum of  $\Delta E_{\text{int}}^{\text{CP}}(AB)$  be the same as the minimum of  $E_{\text{tot},AB}^{\text{CP}}$ . Comparing the equations, one can see that they differ by  $E_A^A(A) + E_B^B(B)$ , i.e., by a constant shift that when subtracted from the CP-corrected total energy yields a CP-corrected interaction energy. If the monomers are allowed to deform when they approach each other in the dimer, then this equality does not hold, and optimizing  $\Delta E_{\text{int}}^{\text{CP}}(AB)$  could yield an unphysical geometry: the monomers could greatly deform to give the greatest possible stabilization of  $\Delta E_{\text{int}}^{\text{CP}}(AB)$ , but the geometry deformation penalty would not be accounted for.

## Intramolecular BSSE

Our discussion so far has considered complexes of discrete molecules. However, in principle, there is no reason why BSSE would not also affect single molecules; one part of the molecule may be stabilized by accessing basis functions from other parts of the molecule, and if these two parts can come in and out of contact, then there is a significant possibility of an imbalance in the effective size of the basis set as a function of intramolecular geometry. Asturiol, Duran, and Salvador showed that artificial puckering of aromatic rings like benzene at certain levels of theory (caused by imbalanced basis sets) can be alleviated by applying intramolecular counterpoise corrections.<sup>11</sup> Valdés *et al.* have shown<sup>12</sup> significant intramolecular BSSE effects in  $[n]$ Helicenes and in the Phe-GLy-Phe tripeptide; they argue that in systems where there can be significant noncovalent interactions between different parts of the molecule, then correlated electronic structure methods such as MP2 and CCSD(T) must be used with great caution unless some attempts to correct for intramolecular BSSE are made — such as using larger basis sets (larger than aug-cc-pVDZ, 6-311G, or TZVP) or using intramolecular counterpoise corrections.

One can apply the counterpoise correction to a single molecule by dividing the molecule into fragments; the BSSE error for each fragment in the presence of the ghost functions from the rest of the molecule can be evaluated and subtracted from the total energy. The only problem with this approach is that there is no unique way to define the fragments. Perhaps the most well-defined procedure is to break up the molecule into atoms and evaluate the BSSE for each atom; however, this leads to  $2N$  computations for molecules with  $N$  atoms, which seems excessive.

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