

Calculation of the BSSE correction for a system consisting of more than 2 parts

April 26, 2012

Consider a molecule consisting of N parts. We are interested in the calculation of its binding (formation) energy:

$$\Delta E = E_{all}^{(\infty)} - \sum_{j=1}^N E_{j_0}^{(\infty)} \quad (1)$$

where the upper index (superscript) by the energy symbol corresponds to the basis set, while the lower one (subscript) to the system: j means the part j in the geometry of the whole molecule, j_0 - the same in the geometry at infinity (the relaxed isolated fragment). The superscript ∞ means that the complete basis set is to be used in order to compare these energies and calculate the binding energy.

This is in theory. In practice, we do not have luxury of using complete basis sets, no do we have identical basis sets in calculating different parts in the energy difference (1), and this is the source of a large error if the basis set is far from being complete, which is usually the case in the local basis set calculations.

We cannot calculate the energies $E_{j_0}^{(\infty)}$, but we can do $E_{j_0}^{(j)}$ which are obtained using the basis set of the fragment alone:

$$\Delta E = \left[E_{all}^{(\infty)} - \sum_{j=1}^N E_{j_0}^{(j)} \right] + \sum_{j=1}^N \left(E_{j_0}^{(j)} - E_{j_0}^{(\infty)} \right) = \Delta E_0 + \sum_j \Delta E_j^{BSSE} \quad (2)$$

Here

$$\Delta E_0 = E_{all}^{(\infty)} - \sum_{j=1}^N E_{j_0}^{(j)} \simeq E_{all}^{(\cup j)} - \sum_{j=1}^N E_{j_0}^{(j)}$$

is what is usually calculated as the first approximation to the binding energy: take the energy of the whole system consisting of all parts and with the combined basis set, $\cup j = \cup_{j=1}^N$, subtract from it the energy of each individual system, $E_{j_0}^{(j)}$, in its own local basis set and fully relaxed geometry. The problem is that each of these energies is calculated using different basis and since the latter is far from complete the energies are not very well compatible. That is why there is the 2nd term in (2):

$$\Delta E_j^{BSSE} = E_{j_0}^{(j)} - E_{j_0}^{(\infty)} \quad (3)$$

is the BSSE correction associated with the part j . Note that if the molecule is split into N fragments, N such corrections must be calculated! So, the correction is the energy difference for each fragment between it being calculated in the complete and actual bases. Since the complete basis is not accessible to us, and also the whole system also is not calculated in the complete basis (but its basis is better than for any individual system as it combined many orbitals from *all* fragments), a practical way of calculating the correction is needed.

It is the following, it is called counterpose correction and is due to Boys and Bernardy I think. By the 'infinite' basis set we assume the basis set of the whole molecule. Then, let us modify ΔE_j^{BSSE} as follows:

$$\begin{aligned} \Delta E_j^{BSSE} &\simeq E_{j_0}^{(j)} - E_{j_0}^{(all)} = \left(E_{j_0}^{(j)} - E_{j_0}^{(all)} \right) + \left(E_j^{(j)} - E_j^{(all)} \right) + \left(E_j^{(all)} - E_{j_0}^{(all)} \right) \\ &= \left(E_j^{(j)} - E_j^{(all)} \right) + \left[E_{j_0}^{(j)} - E_{j_0}^{(all)} - E_j^{(j)} + E_j^{(all)} \right] \end{aligned} \quad (4)$$

The expression in the square brackets can be rewritten as

$$E_{j_0}^{(j)} - E_{j_0}^{(all)} - E_j^{(j)} + E_j^{(all)} = \left(E_j^{(all)} - E_{j_0}^{(all)} \right) - \left(E_j^{(j)} - E_{j_0}^{(j)} \right) \quad (5)$$

In both round brackets we have the *relaxation energies* for species j between the configuration in the molecule and that at infinity, both quantities are positive (since the geometry of j in the molecule does not correspond to the energy minimum of an isolated fragment, j_0 , and hence the energy of an isolated fragment in the geometry j must be higher (less negative) than in the geometry j_0). The difference in the first bracket in (5) is calculated using the basis set of the whole molecule, while the

second one - using the basis set of the fragment j only. However, both terms mean the same: these are relaxation energies of the fragment j from its geometry in the molecule and when isolated. But these are calculated using different bases. In spite of this, differences of energies behave much better than the energies themselves with the increase of the basis set. That is why one may think that both relaxation energies must be very close to each other. But since in (5) these are subtracted from each other, the result can approximately be thought to be zero. Therefore, the term in the square brackets in Eq. (4) can be neglected and thus

$$\Delta E_j^{BSSE} \simeq E_j^{(j)} - E_j^{(all)} \quad (6)$$

This is the final result. Note that the correction is positive as an increase of the basis set should reduce the energy (make it more negative).

Thus, in order to calculate the BSSE correction to the binding energy of a molecule consisting of N fragments, one has to use Eq. (2):

$$\Delta E = \Delta E_0 + \sum_j \Delta E_j^{BSSE}$$

where

$$\Delta E_0 = E_{all}^{(all)} - \sum_{j=1}^N E_{j_0}^{(j)}$$

is the uncorrected binding energy and ΔE_j^{BSSE} is the correction for the fragment j that is given by Eq. (6). Altogether, for each fragment, 3 energies need to be calculated: $E_j^{(j)}$, $E_j^{(all)}$ and $E_{j_0}^{(j)}$; also, one needs to have the fully relaxed energy $E_{all}^{(all)}$ of the whole molecule. For instance, if the molecule consists of 4 fragments, apart from the single total energy of the whole molecule, one has to calculate in addition (single point calculations only) $4 \times 3 = 12$ energies.