Basis set superposition error

In the systems treated in this report, two atoms approach each other. This means that their basis sets are going to overlap. Now a situation arises where each atom 'borrows' basis set functions of the other atom, effectively improving its basis set and therefore its energy. This effect increases as the atoms orientate themselves closer, thereby creating an effectively varying basis set against the interatomic distance. This effect is called the basis set superposition error (BSSE).

The interaction energy between two atoms A and B is

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

where, at the right hand side of the equation, the subscript denotes the geometry of the system and the superscript the used basis sets. ΔE_{int} denotes the interaction energy of the system. The energy of the separate atoms does not depend on the interatomic distance, while the basis set superposition error varies with the interatomic distance. The interaction energy in Eq. (1) is in need for a correction on the BSSE.

Boys and Bernardi introduced the counterpoise correction to correct for the BSSE. In the counterpoise correction, the artificial stabilization is countered by letting the separate atoms improve their basis sets by borrowing functions of an empty basis set. To realize such an empty basis set, a ghost atom is used. The ghost atom has the basis set of the according atom, but no electrons to fill it. Performing this procedure for both atoms on the grid will correct for the BSSE. Hence, the interaction energy with counterpoise correction is

$$\Delta E_{\text{int}}^{\text{CP}}(r_{AB}) = E_{AB}^{AB}(r_{AB}) - E_A^{AB}(r_{AB}) - E_B^{AB}(r_{AB}). \tag{2}$$

Note that in Eq. 2 the energy of the seperate atoms depend on a inter'nuclear' distance – the distance between the atom and the ghost atom.