ATOMIC COUTERPOISE CORRECTION FOR BSSE

Hard to believe but here's another approach to dealing with *intramolecular* basis set super position error (BSSE). Jensen's approach[1] is to define the atomic counterpoise correction as

$$\Delta E_{ACP} = \Sigma\, E_A(\text{basisSet}_A) - E_A(\text{basisSet}_{AS})$$

where this sum runs over all atoms in the molecule and $E_A(\text{basisSet}_A)$ is the energy of atom A using the basis set centered on atom A. The key definition is of the last term $E_A(\text{basisSet}_{AS})$, where this is the energy of atom A using the basis set consisting of those function centered on atom A and some subset of the basis functions centered on the other atoms in the molecule. The key assumption then is just how to select the subset of ghost functions to include in the calculation of the second term.

For intermolecular basis set superposition error, Jensen suggests using the orbitals on atom A along with all orbitals on the other fragment, but not include the orbitals on other atoms in the same fragment where atom A resides.

He demonstrates that this approach gives essentially identical superposition corrections as the traditional counterpoise correction for N_2, ethylene dimer and benzene dimer.

For intramolecular corrections, Jensen suggests keeping only the orbitals on atoms a certain bonded distance away from atom A. So for example, ACP(4) would indicate that the energy correction is made using all orbitals on atoms that are 4 or more bonds away from atom A. Jensen suggests in addition that orbitals on atoms that are farther than some cut-off distance away from atom A may also be omitted. He demonstrates the use of these ideas for the relative energies of tripeptide conformational energies.

So while the ACP method is conceptually simple, and also computationally efficient, it does require some playing around with the assumptions of which orbitals will comprise the appropriate subset. And it may be that one has to tune this selection for the individual system of interest.

Source: http://comporgchem.com/blog/?p=615