



Why does Basis Set Superposition Error (BSSE) matter for us?

BSSE in quantum-chemical calculations is due to finite basis sets. When two molecular fragments interact, each fragment can use basis functions centred on the other, artificially lowering the energy of the system. In isolated computations of the individual fragments, this additional flexibility is unavailable → overestimation of interaction energies

$$\Delta E_{Int} = E_{AB} - E_A - E_B$$

BSSE is (i) particularly critical when modelling the noncovalent interactions and (ii) scales extensively with system size. It can be remedied using complete basis set (CBS) approaches, however, these are computationally expensive.

CP correction should always be applied when using big systems

Boys–Bernardi “function counterpoise” (CP) correction^[1]

computes the energy of each monomer in the dimer basis set, meaning that the missing basis functions from the other fragment are included as ghost orbitals

$$E_{int}^{CP} = E_{AB} - (E_A^{ghost} + E_B^{ghost})$$

Controversy^[2]

A widespread belief that CP correction “overcorrects” BSSE emerged primarily from early studies using small basis sets, where CP-corrected energies sometimes appeared too weak compared to larger basis sets. These conclusions were often drawn without considering the *basis set incompleteness error* (BSIE), which results in underestimation of total and binding energies → error compensation. For small basis sets, uncorrected simulations severely overbind noncovalent interactions due to BSSE.

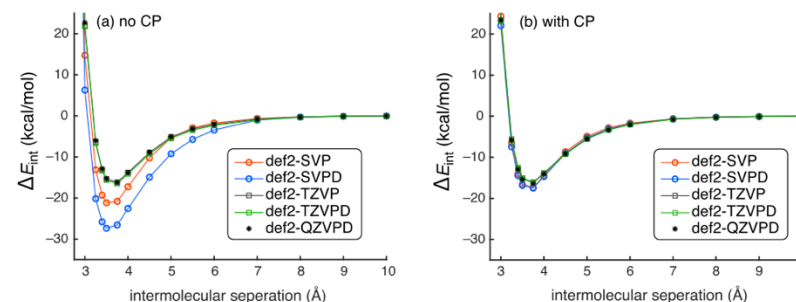
CP correction does not overcorrect BSSE

Methodology^[2]

Systematic evaluation of counterpoise correction in density functional theory

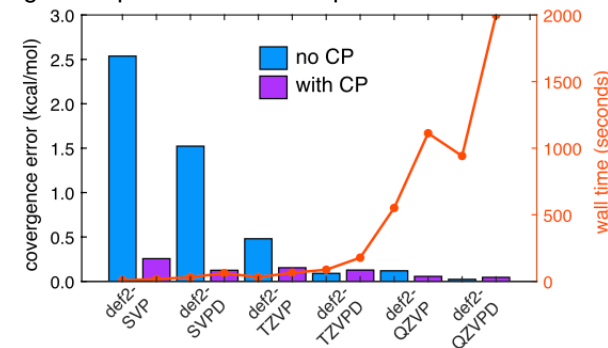
- Data set: small dimer complexes (S66 set) and large supramolecular systems such as protein-ligand complexes and graphene-oligothiophene complexes.
- Functionals: generalised gradient approximations to double-hybrid functionals.
- Basis sets: Dunning, Karlsruhe, and Pople.

[1] *Mol. Phys.* **1970**, *19*, 553-566.



Above: Potential energy profiles for the eclipsed-cofacial configuration of (coronene)₂, computed using ω B97M-V in various basis sets.^[2]

Below: Mean absolute convergence errors for BLYP+D3(BJ) calculations of the S66 complexes (bar graph, axis at left) vs. wall time required for pentane dimer (orange dots, axis at right). Calculations were performed on a single compute node with 14 processors.^[2]



→ CP-corrected double- ζ results can be as accurate as triple- ζ calculations but with significantly lower computational cost.

BSSE (i) reduces dependence on diffuse functions, (ii) increases the accuracy when using smaller basis sets, (iii) facilitates basis set convergence.

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Below: Convergence errors (with respect to the DFT/CBS limit) for the BLYP+D3(BJ) functional using (a) Dunning, (b) Karlsruhe, and (c) Pople basis sets. Gray rectangles delineate errors of ± 0.25 and ± 0.50 kcal/mol.^[2]

