What is the range of electron correlation in density functionals?

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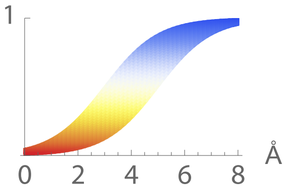
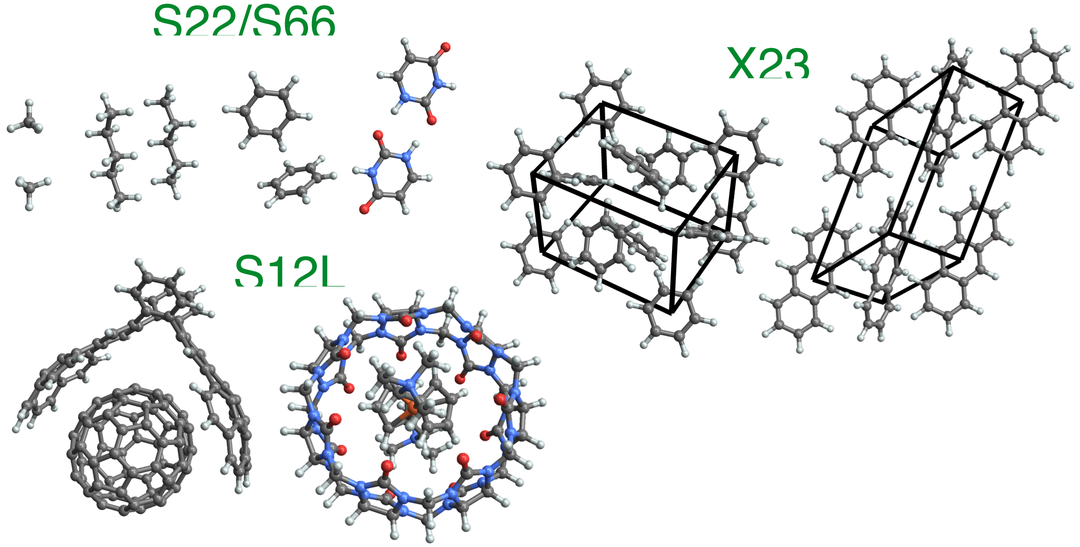
Range separation in DFT+vdW methods for noncovalent interactions

- Crossover from short-range (XC functionals) to long-range electron correlation (vdW models)[1]
- Fitting parameters on vdW benchmark

$$v(R) = v(R)(1 - f(R)) + v(R)f(R)$$

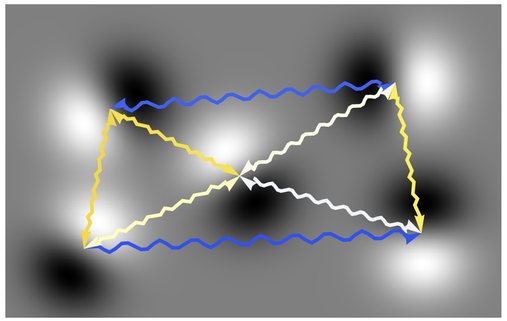


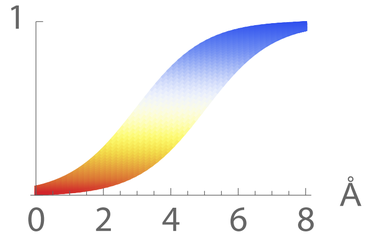


SCAN M06 XDM
D3 LDA TS
vdW–DF
B3LYP
VV10 PBE MBD
PBE0

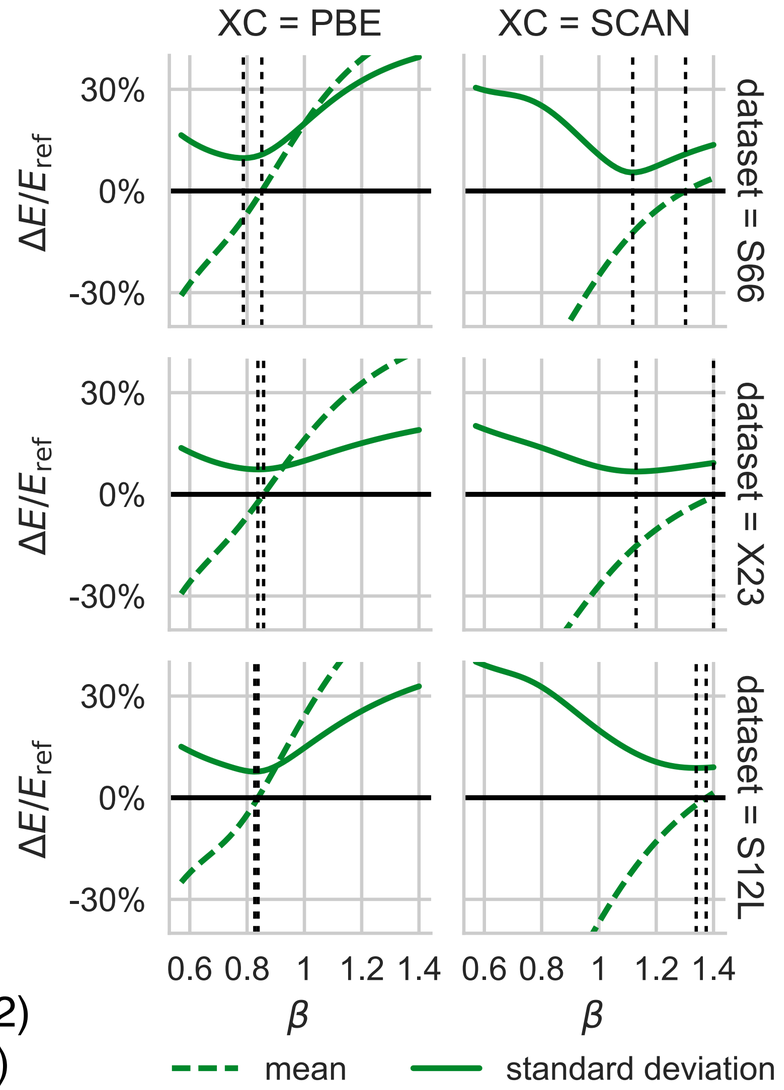
[1]Hermann, DiStasio & Tkatchenko, *Chem. Rev.* (2017), DOI: 10.1021/acs.chemrev.6b00446

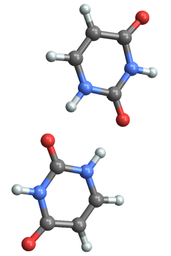
Optimal range separation on small dimers (S66), molecular crystals (X23) and supramolecular complexes (S12L)

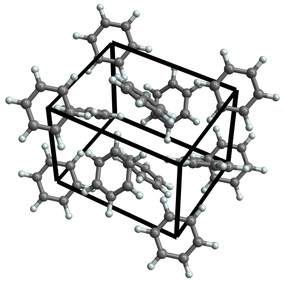


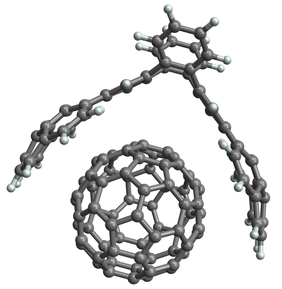


- Many-body dispersion[1,2] (MBD) as a probing vdW model
- Single fitted parameter β: $f(\beta R_{vdW}) = 0.5$
- PBE+MBD: $\beta = 0.83 \pm 0.03$
- SCAN+MBD: β from 1.1 to 1.4

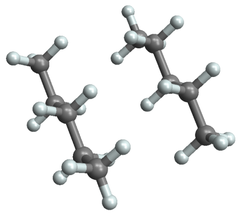




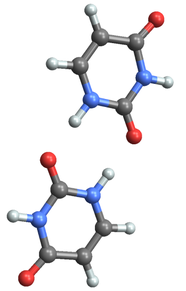


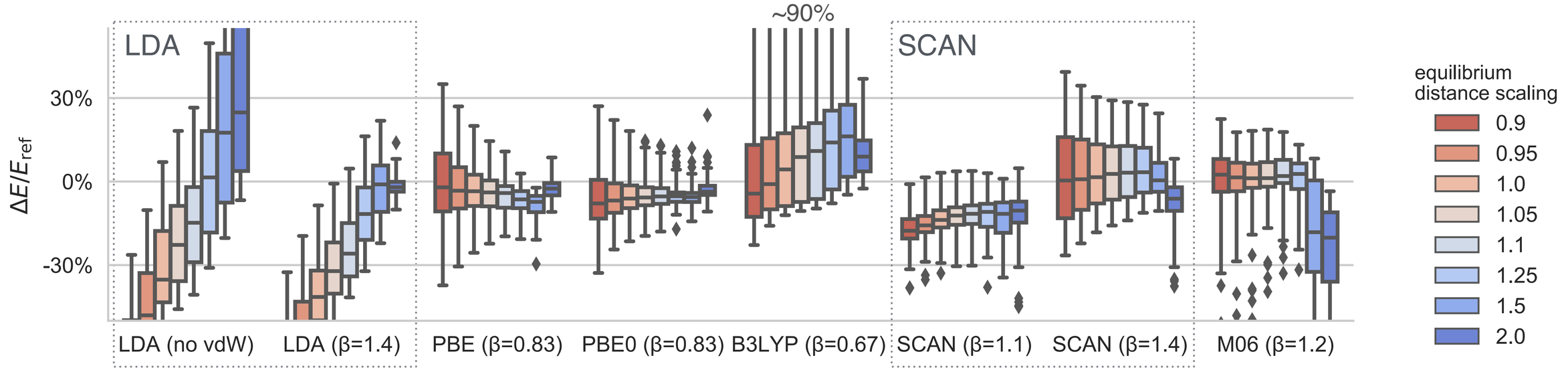


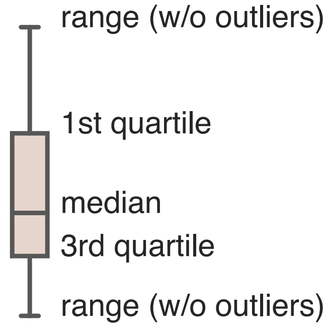
[1]Tkatchenko *et al.*, *Phys. Rev. Lett.* 108, 236402 (2012)
[2]Ambrosetti *et al.*, *J. Chem. Phys.* 140, 18A508 (2014)



Varying range-separation profiles over binding distances on S66 set



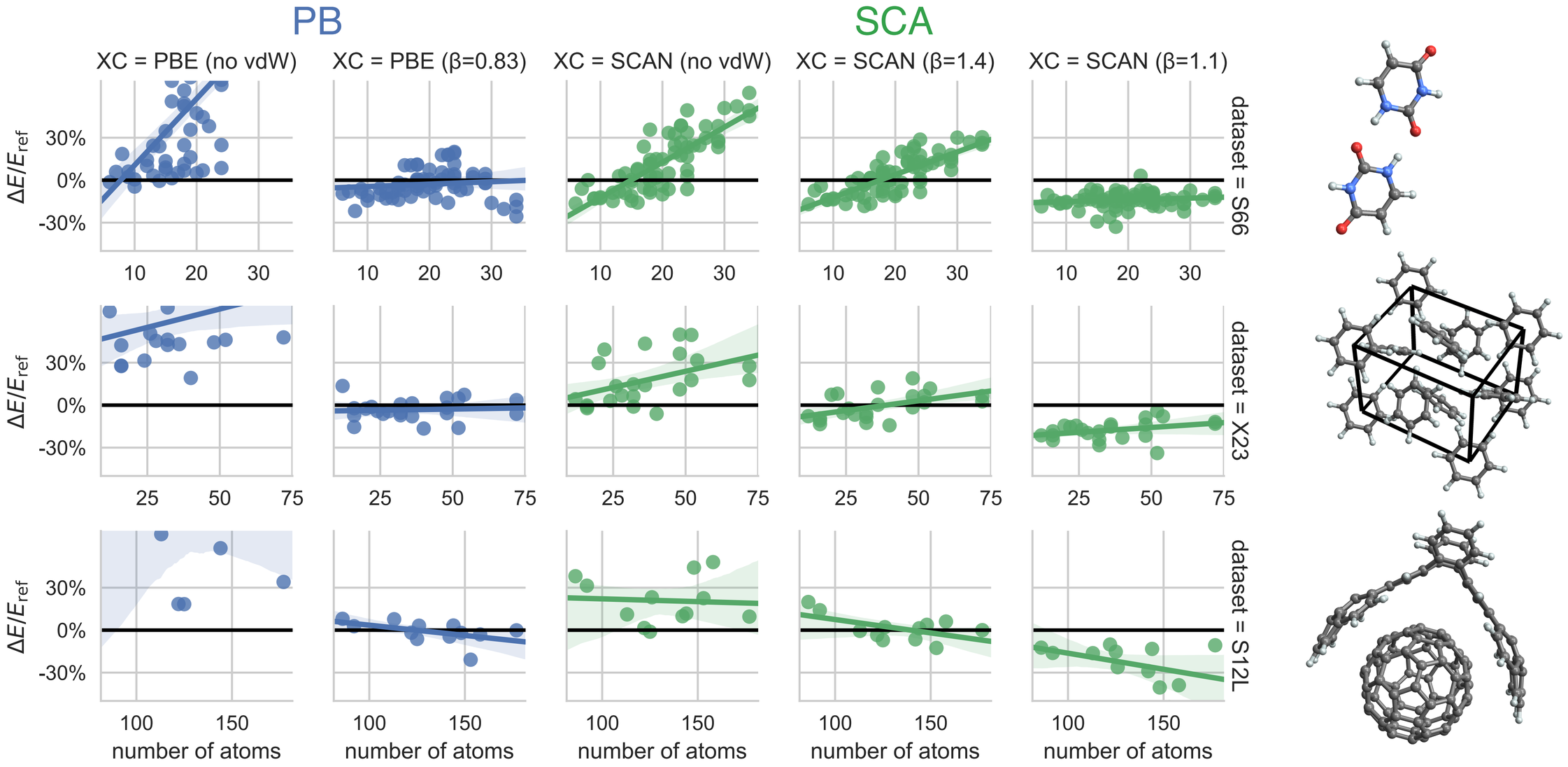




- LDA strongly imbalanced
- PBE well balanced, but larger deviations at short distances

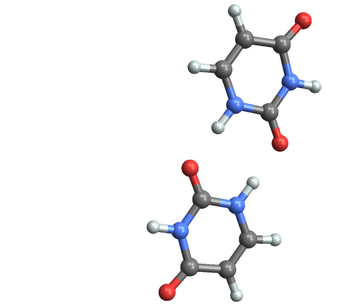
- Exact exchange in PBE0: no systematic shift, but smaller statistical errors
- SCAN: small statistical errors at short distances, but systematic overbinding

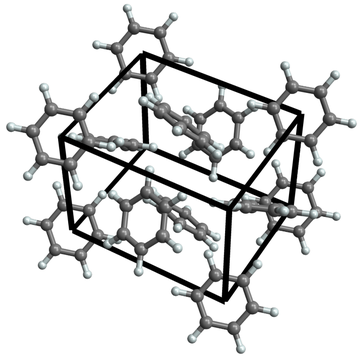
Dependence on system size

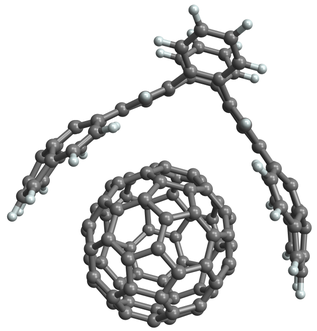


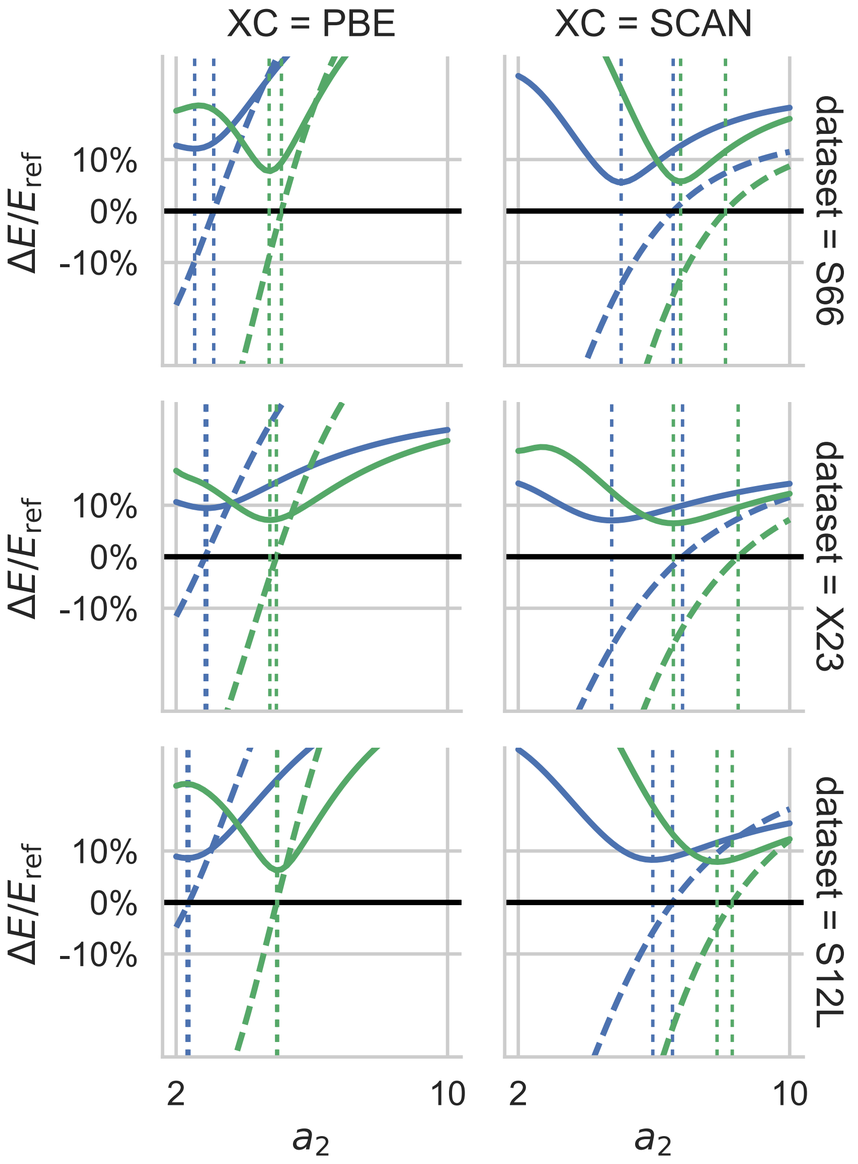
Optimal range separation with DFT-D3[1]

- Different form of damping
- Three fitting parameters instead of one in MBD
- Similar conclusions as with MBD



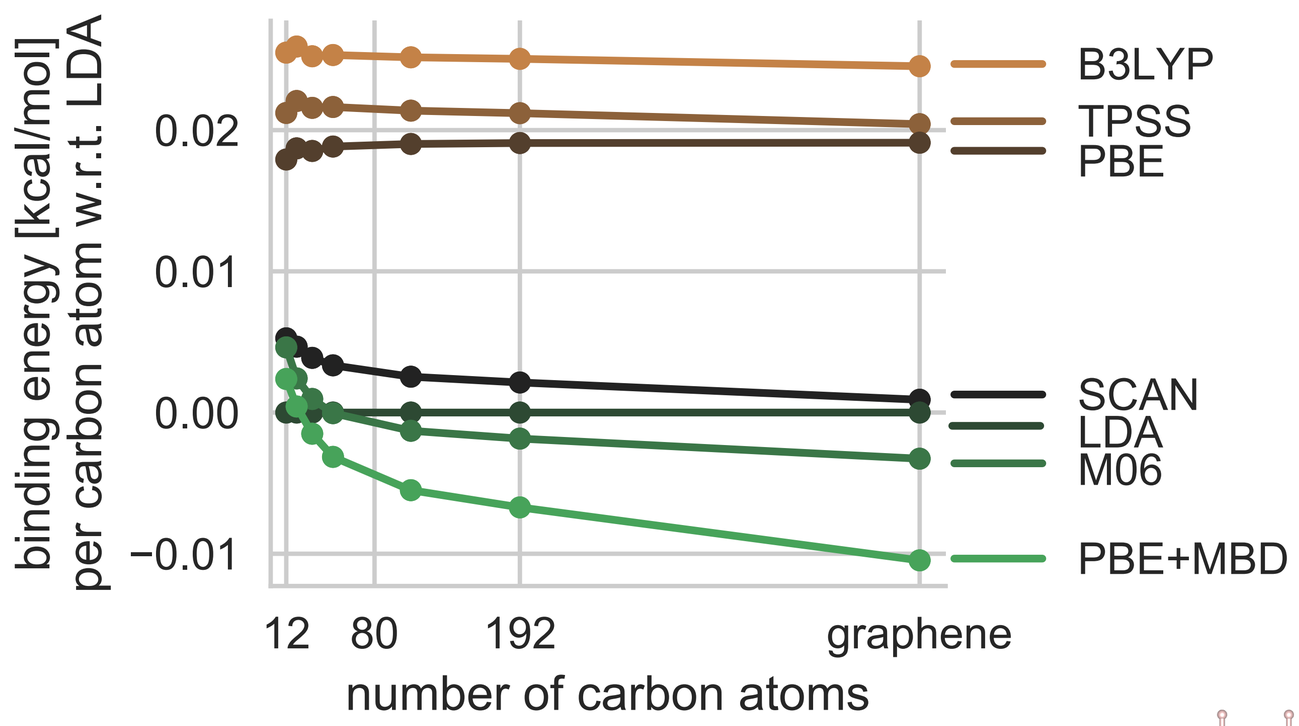


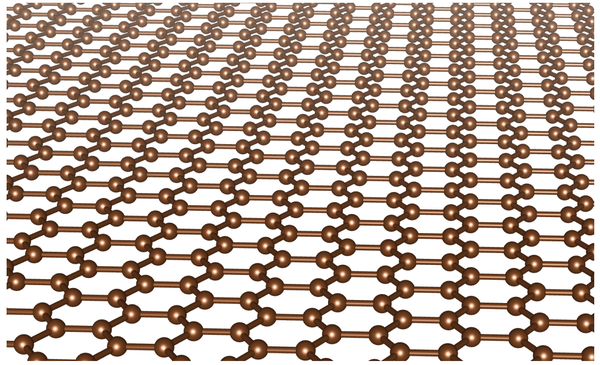


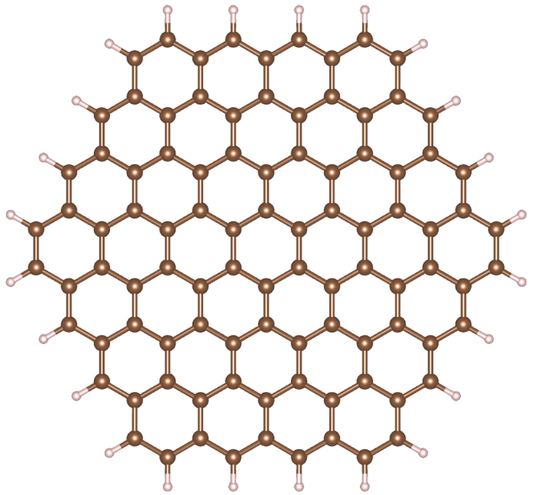


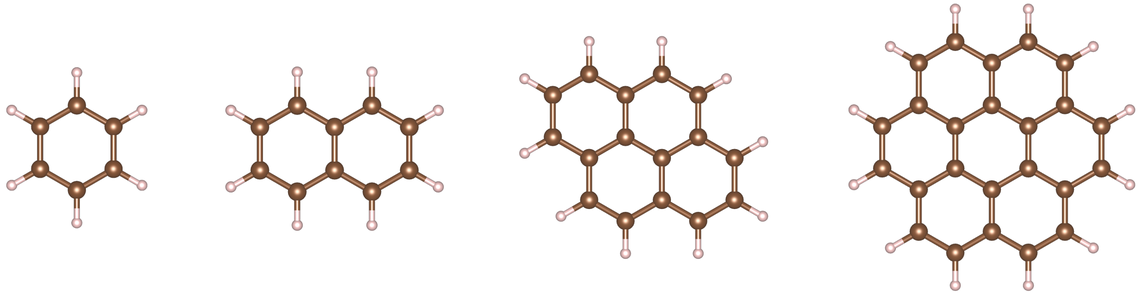
[1]Grimme *et al.*, *J. Chem. Phys.* 132, 154104 (2010)

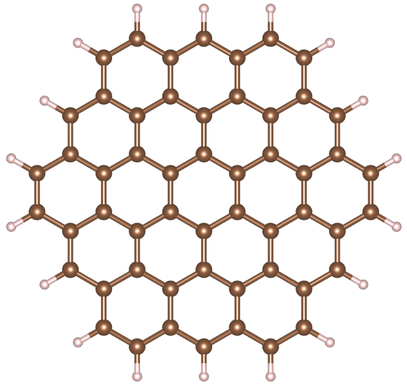
From benzene dimer to bilayer graphene — binding per carbon atom



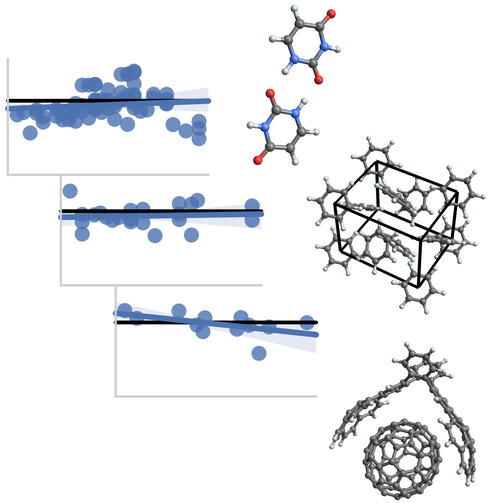




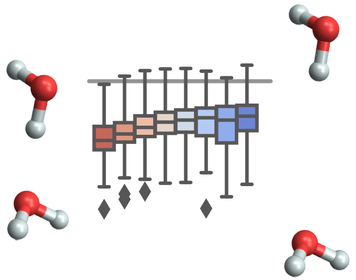




Summary & outlook



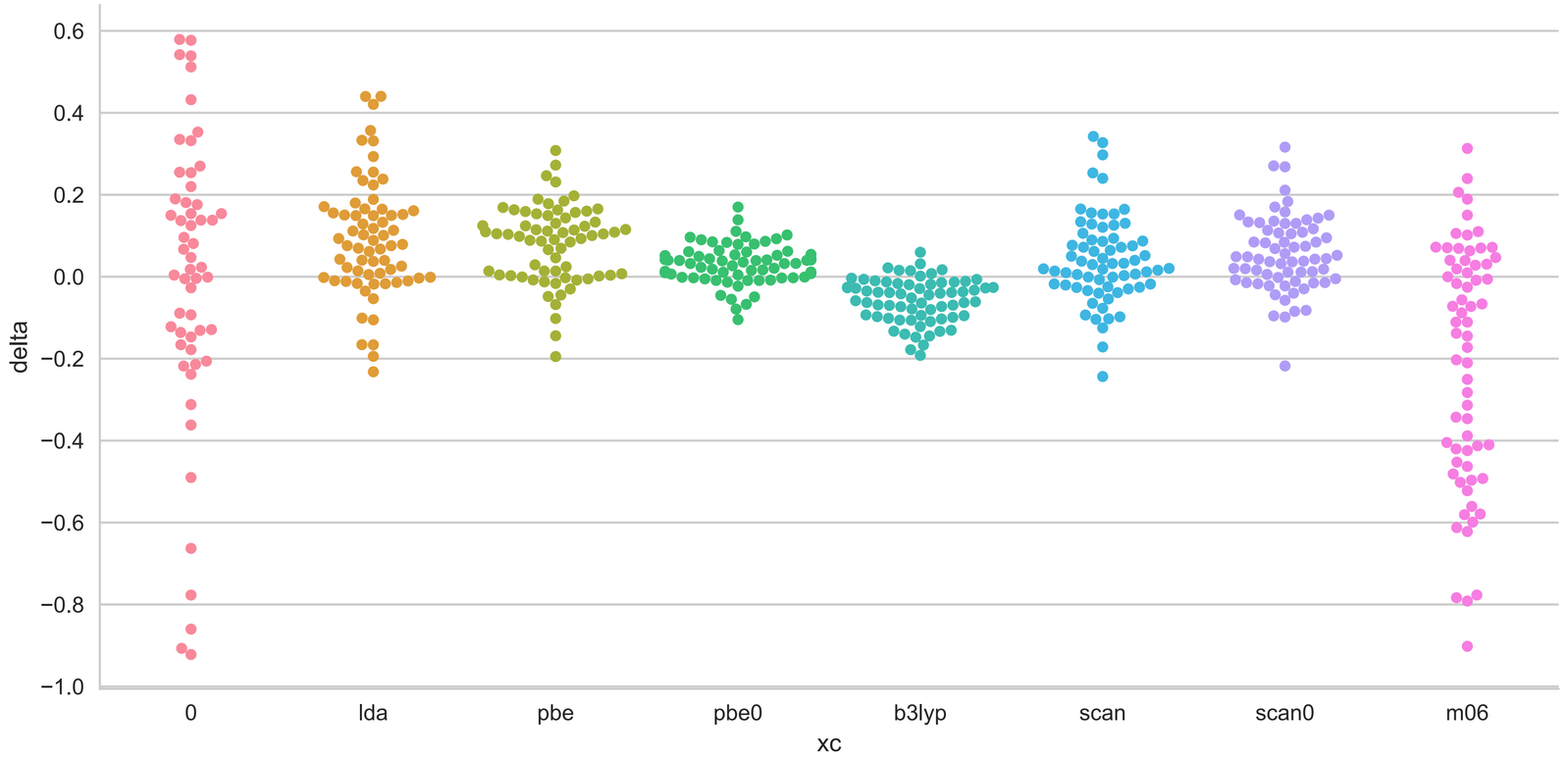
- Accurate and general DFT+vdW methods require a consistent range separation of electron correlation across system sizes and binding distances



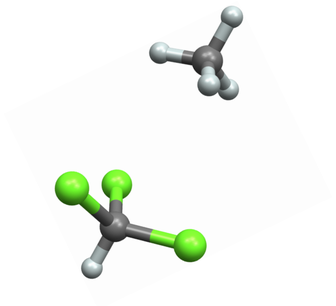
- More advanced functionals such as SCAN have a complex behaviour of the correlation range, which complicates combinations with long-range vdW models

- How does the density-based range separation in the VV10 nonlocal functional work?
- What functional ingredients are causing the increased sensitivity to density tail overlaps?

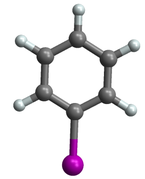
Errors in three-body interaction energies

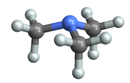


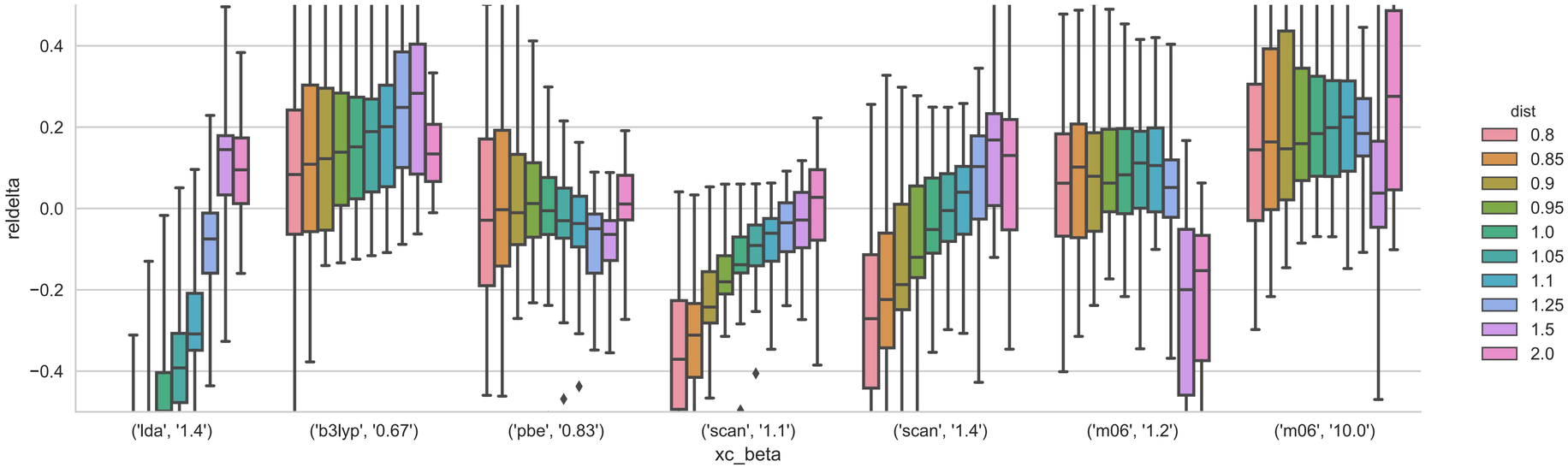
- 3B-69 dataset: 69 trimers of molecules taken from 23 molecular crystals



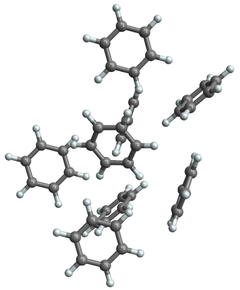
Errors on X40x10 with different functionals



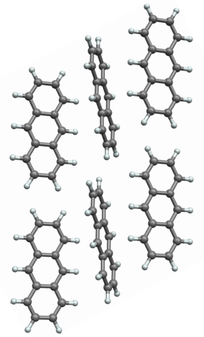


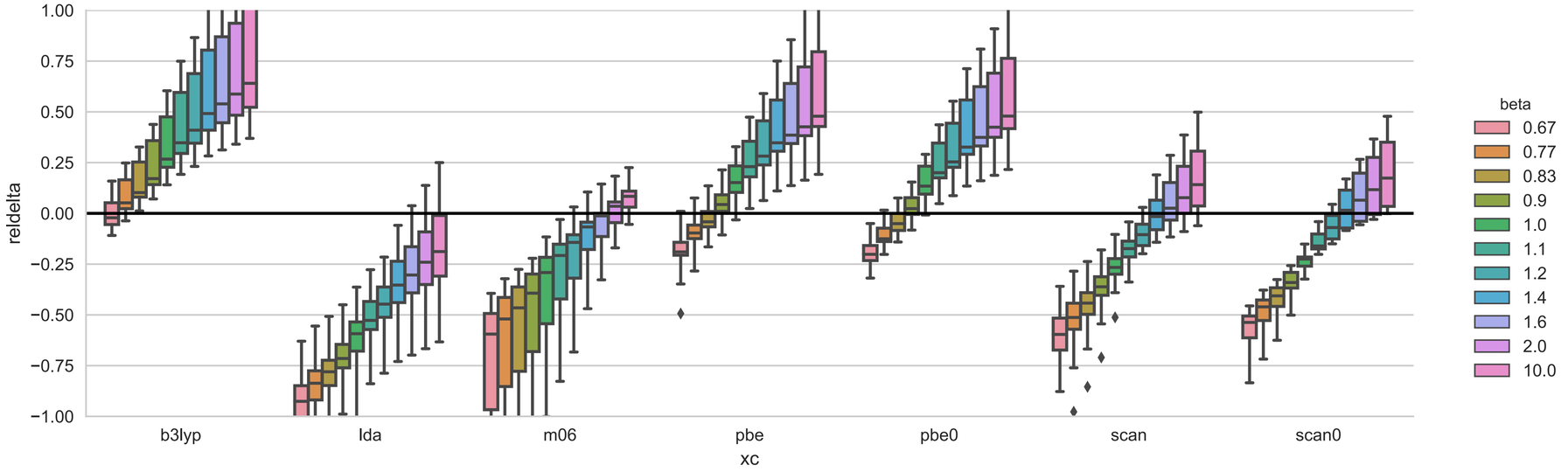


- X40 dataset targets compounds with strong ionic character
- Larger deviations than on S66



Effect of exact exchange: molecular crystals





- Adding exact exchange to GGAs reduces largest deviations, but overall effect is small