Pitfalls in the accurate determination of non-covalent interaction energies in large systems using the example of the C_{60} dimer

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Fullerene-fullerene interactions dominate the behavior of all supramolecular systems containing fullerenes. Many methods for describing the van der Waals interaction have been proposed in the last 30 years, but until recent only DFT with Grimme's corrections was possible for such large systems. Ruzsinszky [1] questioned this approach. We have now performed rigid scans of the C_{60}-C_{60} interaction (following methodology used in Hobza's S66 dataset) at different levels of theory: DFT-functionals from different rungs of Jaccob's ladder, including double hybrids, MP2 and finally DLPNO-CCSD(T) and DLPNO-CEPA/1 methods.

For DFT - influences of D3BJ and nonlocal (NL) corrections were checked and compared.

For double hybrids and MP2 methods with varied spin-same and spin opposite coefficients were examined (DSD-DH, DOD-DH and SCS-MP2, SOS-MP2). While overestimation of dispersion by MP2 is well known, usage of SCS- and especially SOS-schemes improves the results significantly, but MP2-schemes modified for molecular interaction (SCS- and SOS-MI-MP2) unexpectedly give the wrong answers.

A strong effect of basis set was found for DLPNO-CoupledCluster and CEPA methods: TZV and def2-TZVP(-f) basis sets gives results nearly twice as high as cc-pVDZ and cc-pVTZ. The results obtained with Dunning basis sets seemed to be more correct for the following reasons: 1) CBS extrapolation is possible and the extrapolated result is relatively close to cc-pVTZ 2) the results obtained with this basis sets are much closer to an estimation based on the heat of sublimation (known from experiment) 3) strong overestimation of dispersion interaction by the TZV basis set also was observed for the anthracene dimer – a system that is much better described in the literature.

The results obtained have both methodological and practical relevance: some methods that have been claimed to describe noncovalent interactions well were shown to give large errors, the effect of basis sets on DLPNO calculations was explored, and the curve obtained allows us to parametrize a semiempirical correction for the correct description of large fullerene ensembles by computationally efficient methods.

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[1] **A.** Ruzsinszky, J.P. Perdew, J. Tao, G.I. Csonka, and J. M. Pitarke Van der Waals Coefficients for Nanostructures: Fullerenes Defy Conventional Wisdom, *Phys. Rev. Lett.*, **2012**, *109*, 233203