Evaluation of non-covalent interactions with double-hybrid functionals

MASSAFRA Davide;[A] **TURELLI Michele**;[A] **TOGNETTI Vincent**;[B] **JOUBERT Laurent**;[B] **ADAMO Carlo**;[A]

A) Institute of Chemistry for Life and Health Sciences (i-CLeHS), 11, rue Pierre et Marie Curie, Paris
B) Laboratoire COBRA - Université de Rouen, 1 rue Tesnière, 76821 Mont-Saint-Aignan Cedex, Rouen

davide.massafra@chimieparistech.psl.eu

Weak non-covalent intermolecular forces play a pivotal role in the behaviour of organic systems. However, the theoretical simulation of these interactions is difficult and requires models like density functional theory (DFT) combined with heavily parameterised empirical dispersion corrections.

In this work we illustrate how double hybrid functionals can provide an improved description of weak non-covalent interactions between small organic molecules, even without employing large basis sets and empirical corrections. The study focuses on systems extracted from the GMTKN30 database[1], specifically from the S66x8 subset, which contains high-level reference structures and energies for small organic molecular pairs at different intermolecular distances.

By comparing the results of single-point calculations employing Perdew–Burke–Ernzerhof Quadratic Integrated Double-Hybrid (PBE-QIDH)[2], hybrid functional (PBE0), and the simple generalized gradient approximation functional (PBE), we demonstrate the efficacy of our computational protocol.

The DFT approaches are combined with small basis sets such as def2-SVPD and DHSVP[3], as well as larger ones like def2-TZVPP. The further addition of an empirical dispersion correction D3(BJ)[4] for all functionals in combination with TZ and DHSVP basis sets completes the set of levels of theory across which we perform our comparative study.

Results, reveal that, for the PBEQIDH/DHSVP level of theory, dispersion energy does not necessarily improve the evaluation of weak interactions, thus reinforcing the idea that the combination between double hybrid functionals and small basis sets provides alone an accurate-enough description of these interactions at reduced cost.

Keywords: DFT, double-hybrid functional, non-covalent interactions.

---

[1] L. Goerigk, S. Grimme, *Journal of Chemical Theory and Computation* 7(2) (2011) 291-309.
[2] E. Bremond, I. Ciofini, J.C. Sancho-García, C. Adamo, *Accounts of Chemical research* 49(8) 2016 1503-1513.
[3] J.S. García, E. Bremond, M. Campetella, I. Ciofini, C. Adamo, *Journal of Chemical Theory and Computation 15(5) 2019 2944-2953.*
[4] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *The Journal of chemical physics* 132(15) 2010.