Estimating dispersion energies using the BH-DFT-D method

Alisa Krishtal[1], Christian Van Alsenoy[2] and Paul Geerlings[3]

[1] *Fachbereich Chemie, Technische Universität Kaiserslautern, Erwin Schrödinger Straße, D-67663 Kaiserslautern, Germany*
[2] *Department of Chemistry, University of Antwerp, Universiteitsplein 1, B2610 Antwerp, Belgium*
[4] *Algemene Chemie, Vrije Universiteit Brussel, Pleinlaan 2, B-1050, Brussels, Belgium*

Abstract

Since Density Functional Theory (DFT) had been originally introduced into the world of quantum chemistry, it has become immensely popular for applications on a broad variety of systems. Among these are also systems containing dispersion interactions, which are usually unaccounted for in DFT due to the approximate nature of the exchange-correlation functional. The Buckingham-Hirshfeld method (BH-DFT-D)[1–4] allows to correct the description of dispersion interactions obtained using (semi)-local exchange-correlation functionals by evaluating the missing term in the interaction energy from the ab initio multipole polarizabilities of the interacting entities.

In the present form of the BH-DFT-D method, the dispersion energy is calculated for a dimer through a four-centered, fully anisotropic correction term that depends on the atomic polarizability tensors. The atomic polarizabilities are obtained by partitioning the molecular polarizabilities using the Hirshfeld method.[5] A four-centered damping function is introduced to compensate for the penetration effects at shorter distances and the partial recovery of dispersion energy by the functionals from the overlap density. The damping function is fitted to reproduce optimal interaction energies and geometries of 21 dispersion bonded dimers. Results for the interaction energies of the S22 and S66 data sets are presented, showing the BH-DFT-D method allows to reproduce interaction energies at the chemical accuracy level.

References:

[1] Olasz, A.; Vanommeslaeghe, K.; Krishtal, A.; Veszprémi, T.; Van Alsenoy, C.; Geerlings, P. *J. Chem. Phys.* 127, (2007) 224105.

[2] Krishtal, A.; Vanommeslaeghe, K.; Olasz, A.; Veszprémi, T.; Van Alsenoy, C.; Geerlings, P. *J. Chem. Phys.* 130 (2009), 174101.

[3] Krishtal, A.; Vannomeslaeghe, K.; Geldof, D.; Van Alsenoy, C.; Geerlings, P. *Phys. Rev. A* 83 (2001), 024501.

[4] Krishtal, A.; Geldof, D.; Vannomeslaeghe, K.; Van Alsenoy, C.; Geerlings, P. *J. Chem. Theory Comput.* 8 (2012), 125-134,

[5] Geldof, D.; Krishtal, A.; Geerlings, P.; Van Alsenoy, C. *J. Phys. Chem. A* 115 (2011), 13096-13103.