

Dispersion Energy in Density- Functional Theory

Muhammad Shahbaz, Krzysztof Szalewicz

Department of Physics and Astronomy, University of Delaware,
Newark, DE 19716, USA

The standard functionals used in DFT model the correlations between electrons within a separation of the order of 1 angstrom and ignore those beyond it. The ignored nonlocal correlation effects are the source of dispersion interactions and form a large part of interaction energy for many technologically and biologically important materials. The so-called nonlocal correlation functionals are constructed to compliment the DFT energy by adding a correction resulting from long-range correlation effects in a seamless fashion. An example of such an approach are the Van der Waals density functionals (vdW-DF's) proposed by Langreth, Lundqvist and collaborators [1, 2] which are based on the adiabatic-connection-fluctuation dissipation theorem [3]. The performance of various nonlocal functionals will be discussed relative to the dispersion energy from symmetry-adapted perturbation theory (SAPT) [4, 5, 6, 7, 8]. Also, a new functional resulting from a simplification of the vdW-DF model will be presented. This new functional gives very accurate dispersion energies compared to other methods with low computational costs.

-
- [1] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist. Van der Waals density functional for general geometries. *Phys. Rev. Lett.*, 92:246401–(1:4), 2004.
 - [2] K. Lee, E. D. Murray, L. Kong, B. I. Lundqvist, and D. C. Langreth. Higher-accuracy van der Waals density functional. *Phys. Rev. B*, 82:081101–(1:4), 2010.
 - [3] O. Gunnarsson and B. I. Lundqvist. Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism. *Phys. Rev. B*, 13:4274–4298, 1976.
 - [4] A. J. Misquitta, B. Jeziorski, and K. Szalewicz. Dispersion energy from density-functional theory description of monomers. *Phys. Rev. Lett.*, 91:033201–(1:4), 2003.
 - [5] A. Hesselmann and G. Jansen. Intermolecular dispersion energies from time-dependent density functional theory. *Chem. Phys. Lett.*, 367:778–784, 2003.
 - [6] R. Podesszwa, C. Wojciech, and K. Szalewicz. Efficient calculations of dispersion energies for nanoscale systems from coupled density response functions. *J. Chem. Phys.*, (6):1963–1969, 2012.