Perspectives on Dispersion in Density-Functional Theory

Marie Døvre Strømsheim[a)], Andrew M. Teale[a)] and Trygve Helgaker[a)]
a) *Centre for Theoretical and Computational Chemistry, University of Oslo, P. O. Box 1033, Blindern, N-0315, Oslo, Norway*

The failures of existing density functionals to describe the dispersion interaction are well documented in the literature. The helium dimer serves as a prototypical system to illustrate many aspects of this interaction and has been previously studied within Hartree-Fock-Kohn-Sham Density-Functional Theory (HF-KS-DFT) by Allen and Tozer [1] from the perspective of the Hellmann-Feynman electrostatic theorem. From this view point the dispersion force arises from subtle density distortions in the vicinity of each atom due to the presence of other distant atoms. The result being a net attractive force due to the nucleus being attracted towards the distorted density in its own vicinity.

In the present work the dispersion interaction has been studied within the usual KS-DFT formalism through Lieb maximization [2] at the CCSD(T) level [3, 4, 5]. When applied to the non-interacting system this procedure brings the calculations of Ref. [1] into the KS-DFT formalism, where the exchange contribution to the Kohn-Sham matrix is given by a multiplicative potential. Particular care has been taken in order to ensure that the Hellmann-Feynman electrostatic theorem holds and to this end floating centers [6] have been used in the wave-function optimization and subsequent BSSE correction of the potential energy curves presented here. Whilst calculations on the non-interacting system yield Kohn–Sham exchange–correlation potentials, orbitals and orbital energies, no information on the dispersion contribution to Kohn-Sham exchange–correlation energies is returned. To provide additional energetic information the Lieb maximization is generalized to arbitrary electronic interaction strengths, allowing the adiabatic connections (ACs) [7, 8, 9, 10] for the interaction energies to be calculated.

Recently, empirical dispersion DFT-D corrections constructed by Grimme [11] have proved popular to correct existing functionals to account for dispersion. The advantages and disadvantages of these methods are discussed in light of the presented adiabatic connection analysis. Prospects for "Double-Hybrid" approaches such as B2PLYP [12] and a self-consistent OEP(B2PLYP) implementation will also be discussed.

[1] M.J. Allen and D.J. Tozer, *J. Chem. Phys.* **117**, 11113 (2002)
[2] E.H. Lieb, *Int. J. Quantum. Chem.* **24**, 243 (1983)
[3] A.M. Teale, S. Coriani, T. Helgaker, *J. Chem. Phys.* **130**, 104111 (2009)
[4] F. Colonna and A. Savin, *J. Chem. Phys.* **110**, 2828 (1999)
[5] Q. Wu and W. Yang, *J. Chem. Phys.* **118**, 2498 (2003)
[6] T. Helgaker and J. Almlöf, *J. Chem. Phys.*, **89**, 4889 (1988)
[7] J. Harris and R. O. Jones, *J. Phys. F: Met. Phys.* **4**, 1170 (1974)
[8] D.C. Langreth and J.P. Perdew, *Sol. St. Comm.* **17**, 1425 (1975)
[9] O. Gunnarsson and B.I. Lundqvist, *Phys. Rev. B* **13**, 4274 (1976)
[10] D.C. Langreth and J.P. Perdew, *Phys. Rev. B* **15**, 2884 (1977)
[11] S. Grimme, *J. Comp. Chem.* **27**, 1787 (2006)
[12] S. Grimme, *J. Chem. Phys.* **124**, 034108 (2006)