A Variational Approach to London Dispersion Interactions Without Density Distortion

Derk P. Kooi[a] and Paola Gori-Giorgi[a]

[a]*Department of Theoretical Chemistry and Amsterdam Center for Multiscale Modeling, Faculty of Science, Vrije Universiteit Amsterdam, 1081 HV Amsterdam, The Netherlands.*
d.p.kooi@vu.nl

London dispersion interactions play a crucial role in physical, chemical and biological processes. Despite their nature being elucidated already in the 1930s, calculating accurately the strength of these interactions remains a computational challenge and is one of the main challenges for Density Functional Theory (DFT) today. In our work [1] we have introduced a class of variational wavefunctions that capture the long-range interaction between systems (atoms and molecules) without changing the diagonal of the density matrix of each monomer. As the individual monomer densities are kept fixed, we can also unambiguously assess the effect of the density distortion on London dispersion interactions: for example, we obtain virtually exact dispersion coefficients between two hydrogen atoms up to C_{10}, and relative errors below 0.2% in other simple cases. We are now assessing the method for larger systems and studying the effect of using different approximations for the monomers.
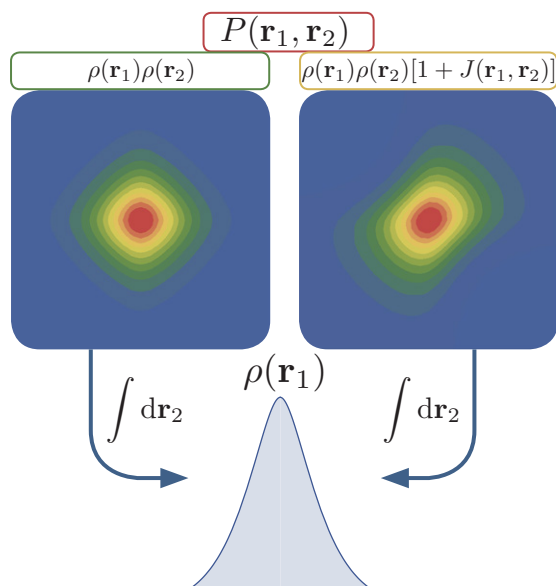

Figure 1: illustration of the basic principle used in the paper: the intermonomer pair density can be distorted to produce attraction, while keeping the individual monomer densities constant.

References
1. D.P. Kooi, P Gori-Giorgi, A Variational Approach to London Dispersion Interactions Without Density Distortion, *J. Phys. Chem. Lett.* **10**, 7 (2019). DOI: 10.1021/acs.jpclett.9b00469.