Reduced-Gradient Analysis of van der Waals Complexes

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Several methods to describe dispersion interactions within density functional theory have been developed, which is critical to describe binding in van der Waals complexes. However, several key aspects of such complexes—such as binding energies, lattice constants, and binding distances—also depend on the exchange description that is paired with the description of dispersion interactions. Here, we present a systematic analysis of the reduced-gradient values that determine the semi-local exchange for different classes of van der Waals complexes [1]. In particular, we analyze molecular dimers, layered structures, surface adsorption, and molecular crystals. We find that reduced-gradient values of less than 1.25 contribute attractively to the exchange binding, while reduced gradients above those values are repulsive. We show that these attractive contributions are associated with low-density regions between the constituents with disk-like iso-surfaces. We further identify a mechanism wherein the surface area of these disks decreases through merging with other iso-surfaces and switches the gradient-correction to exchange from attractive to repulsive. This finding allows us to develop a generalized picture of the bond formation in weakly bonded materials in terms of the size and topology of their reduced-gradient iso-surfaces. This picture also initiates a discussion of desirable features of the exchange enhancement factor. While our analysis is focused on non-local density functional theory [2], it also casts light on van der Waals binding in a broader context and can be used to understand why methods perform differently for different classes of van der Waals systems.

[1] T. Jenkins, K. Berland, and T. Thonhauser, *Reduced-gradient analysis of van der Waals complexes*, Electron. Struct. **3**, 34 009 (2021), DOI: 10.1088/2516-1075/ac25d7.

[2] K. Berland, V. R. Cooper, K. Lee, E. Schröder, T. Thonhauser, P. Hyldgaard, and B. I. Lundqvist, *van der Waals forces in density functional theory: a review of the vdW-DF method*, Rep. Prog. Phys. **78**, 66 501 (2015), DOI: 10.1088/0034-4885/78/6/066501.