Efficient self-consistent implementation of a non-local van der Waals density functional with a Gaussian basis set

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The vast majority of density functional approximations fail to properly describe van der Waals interactions. Van der Waals potentials predicted by common functionals can be either repulsive or attractive at short range but always fail to reproduce the correct asymptotics. Empirical corrections cannot fully grasp the complex physics and are only reliable for the systems similar to the ones they were fitted for. In sharp contrast, the non-local van der Waals density functional (vdW-DF) proposed in Ref. [1] was derived from first principles, describes dispersion interactions in a seamless fashion, and yields the correct asymptotics. Non-local dependence on the electron density makes implementation of this functional cumbersome. A self-consistent implementation within a plane-wave code has been reported only very recently [2]. We have implemented vdW-DF self-consistently with Gaussian basis functions. We have also derived and coded the gradients of the energy with respect to nuclear displacements, enabling efficient geometry optimizations. We propose and test several improvements to the methodology, including better approximations to the exchange part of the functional and more robust forms of the non-local correlation kernel. With these changes, it is possible to enhance both computational efficiency and accuracy of the method.

[1] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, Phys.Rev.Lett. **92**, 246401 (2004); Phys.Rev.Lett. **95**, 109902(E) (2005).

[2] T. Thonhauser, V. R. Cooper, S. Li, A. Puzder, P. Hyldgaard, and D. C. Langreth, Phys.Rev.B, **76**, 125112 (2007).