

An Empirical Correction to Density Functional Theory for van der Waals Interactions

Qin Wu and Weitao Yang

Department of Chemistry, Duke University

Durham, North Carolina 27708

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Abstract

An empirical method has been designed to account for the van der Waals interactions in practical molecular calculations with density functional theory. For each atom pair separated at a distance R , the method adds to the density functional electronic structure calculations an additional attraction energy $E_{vdW} = -f_d(R)C_6R^{-6}$, where $f_d(R)$ is the damping function which equals to one at large value of R and zero at small value of R . The coefficients C_6 for pair interactions between hydrogen, carbon, nitrogen and oxygen atoms have been developed in this work by a least-square fitting to the molecular C_6 coefficients obtained from dipole oscillator strength distributions method by Meath and coworkers. Two forms of the damping functions have been studied, with one dropping to zero at short distances much faster than the other. Four density functionals have been examined: Becke's three parameter hybrid functional with the Lee-Yang-Parr correlation functional, Becke's 1988 exchange functional with the LYP correlation functional, Becke's 1988 exchange functional with Perdew and Wang's 1991 (PW91) correlation functional, and PW91 exchange and correlation functional. The method has been applied to three systems where the van der Waals attractions are known to be important: rare-gas diatomic molecules, stacking of base pairs and polyala-

nines' conformation stabilities. The results show that this empirical method, with the damping function dropping to zero smoothly, provides a significant correction to both of the Becke's hybrid functional and the PW91 exchange and correlation functional. Results are comparable to the corresponding second order Møller-Plesset calculations in many cases.