

Predicting both dispersion interactions and electronic structure using density functional theory

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Abstract

Noncovalent, dispersive interactions are essential to many fields of materials physics and chemistry. However, treatment of dispersion is inherently outside the reach of (semi)-local approximations to the exchange-correlation functional of density functional theory, as well as of conventional hybrid density functionals based on semi-local correlation. Here, we offer an approach that provides a treatment of both dispersive interactions and the electronic structure within a computationally tractable scheme. The approach is based on adding the leading interatomic dispersion term via pairwise ion-ion interactions to a suitably chosen non-empirical functional that is best suited for capturing the electronic structure, with the dispersion coefficients and van der Waals radii determined from first-principles using the recently proposed “TS-vdW” scheme.¹ Here, we demonstrate the strength of this approach using two recent studies.

In the first study, weakly bound metal-phthalocyanine dimers have been studied as a prototypical organic electronic system.² We show that semi-local functionals can fail qualitatively, primarily because of under-binding of localized orbitals due to self-interaction errors.³ We find that the dispersion-corrected PBE-hybrid functional predicts both the electronic structure and the equilibrium geometry well. The performance of our approach is additionally compared to that of the semi-empirical M06 functional. The latter also predicts the electronic structure and the equilibrium geometry well, but with significant differences in binding energy and in asymptotic behavior compared to the dispersion-corrected PBE-hybrid functional.

In the second study, the interlayer sliding energy landscape of hexagonal boron nitride (h-BN) was investigated using dispersion-corrected DFT calculations.⁴ We find that the main role of the van der Waals forces is to “anchor” the layers at a fixed distance, whereas the electrostatic forces dictate the optimal stacking mode and the interlayer sliding energy. A nearly free-sliding path is identified, along which bandgap modulations of 0.6 eV are obtained. We propose a simple geometrical model that quantifies the registry matching between the layers and captures the essence of the corrugated h-BN interlayer energy landscape.

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