New advances in Density Functional Theory for intermolecular interactions

Maria M. Szczesniak

Abstract

Strategies of designing new meta-GGA functionals suitable for covalent and noncovalent interactions will be discussed. In contrast to the existing approaches involving fitting large numbers of adjustable parameters to benchmark sets, a strategy of constraint satisfaction is pursued. Most of the existing exchange and correlation functionals often depend on the mutual error cancellations. Thus, attempts to improve one of the components may result in worsening of the overall performance. The solution is to avoid the error cancellation in the first place. One idea involves designing a new scheme for converting existing exchange functionals into range-separated hybrids. The scheme is based on the underlying Becke-Roussel exchange hole that has the exact second-order expansion in the inter-electron distance. The resulting range-separated exchange functional depends on the kinetic energy density and Laplacian even if the base functional lacks the dependence on these variables. A very successful option will be presented that combines the range-separated PBE exchange elevated by this procedure to the meta-GGA rung with a meta-GGA TPSS correlation and Grimme's dispersion. The performance of this functional on a variety of test sets will be evaluated and the merits of each component will be discussed.