Density functional correlation theories based on the Unsöld approximation

Zack M. Williams, a Timothy C. Wiles a and Frederick R. Manby a

a Centre for Computational Chemistry, School of Chemistry, University of Bristol, Bristol, BS8 1TS, United Kingdom
zack.williams@bristol.ac.uk

We present Unsöld-W12 (UW12) an approximate method for including explicit correlation in density functional theory [1, 2]. The approximation has a similar form to second-order Møller–Plesset (MP2) theory, without the dependence on virtual orbitals. Therefore, unlike double hybrid functionals, the approximation does not suffer from poor basis set convergence and is fully self-consistent.

We showcase two exchange—correlation functionals based on this approach; XCH-BLYP-UW12 and fB-LYP-osUW12, demonstrating their performance for small systems. These functionals, among other advantages contain an exceptionally small amount of self-interaction error; the cause of many problems in density functional theory.

We also consider possible new functional forms for the approximation.

References