Density functional correlation theories based on the Unsöld approximation

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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

1. A. Unsöld, *Zeitschrift für Physik* **43** (1927), 563.
2. T. C. Wiles and F. R. Manby, *J. Chem. Theory Comput.* **14** *(2018), 4590.*