P4

Fitting a round peg into a round hole – constructing an asymptotically correct generalized gradient approximation.

Antonio C. Cancio, Dept. of Physics and Astronomy, Ball State University
Kieron Burke, Department of Chemistry, UC Irvine
Tim Gould, Qld Micro- and Nanotechnology Centre, Griffith University, Qld, Australia

It has long been known that the non-relativistic ground-state energy in Thomas-Fermi theory becomes relatively exact in the high-density, large particle number limit typified by the atomic number $Z \to \infty$ limit of neutral atoms. The analysis of this limit provides a unified approach to the explicit construction of density functionals, inspiring advances in understanding kinetic and exchange energy functionals, and giving a better sense of what a functional at any given level of approximation should achieve. Recent benchmark calculations of atomic correlation energies allow us to extend this analysis to correlation.[1] Asymptotic extrapolation gives a correlation energy of the form $-AZ\log Z + BZ$ with A a known universal quantity, and B about 37 millihartrees. The PBE functional, derived in part from an analysis of the high density limit, has remarkably good scaling behavior with Z, but fails to predict this limit quantitatively. We re-parameterize the high density limit of the PBE to construct an asymptotically corrected GGA. With the additional inclusion of the density dependence of the gradient expansion for correlation, we nearly recapture the asymptotic trend of atomic benchmark data down to the lowest values of Z.

[1] K. Burke, A. Cancio, T. Gould, and S. Pittalis, J. Chem. Phys. **145**, 054112 (2016).