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Asymptotic analysis of atomic correlation energies and the generalized gradient approximation[1] ANTONIO CANCIO, Ball State University, KIERON BURKE, University of California, 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. Recent benchmark calculations of atomic correlation energies allow us to extend this analysis to correlation. Asymptotic extrapolation gives a correlation energy of the form $-AZ \log Z + BZ$ with A a known universal quantity, and B about 38 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 reparametrize the high density limit of the PBE for finite levels of inhomogeneity to construct an asymptotically corrected GGA. This reparametrization captures most but not all of the asymptotic trend in atomic benchmark data with the remainder mostly captured by the correct treatment of the density dependence of the gradient expansion for correlation. The results compare favorably at all Z to empirical functionals.

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