Asymptotic analysis of atomic correlation energies and the generalized gradient approximation

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It has long been known that the non-relativistic ground-state energy in Thomas-Fermi theory becomes rel-atively 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 has improved our understanding of kinetic and exchange energies as functionals of the density, providing a unified approach to the explicit construction of these functionals. Recent benchmark cal-culations 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 coefficients roughly agree with those of the high-density limit of the numerical real-space construction (RSC) of the generalized gradient approximation. The PBE functional, which is de-rived from the RSC, 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. It reproduces the asymptotic trends in the atomic benchmark data, improving PBE atomic correlation energies for all but the smallest Z.