

**Fitting a round peg into a round hole – a generalized gradient approximation based upon the asymptotic analysis of atomic correlation energies.**

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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  $Z \rightarrow \infty$  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.<sup>1</sup> 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 re-parameterize the high density limit of the PBE for finite levels of inhomogeneity to construct an asymptotically corrected GGA. This reparametrization captures much but not all of the asymptotic trend in atomic benchmark data, with remainder reflecting the density dependence of the gradient expansion for correlation at finite  $Z$ . The results compare favorably at all  $Z$  to empirical functionals.

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<sup>1</sup>K. Burke, A. Cancio, T. Gould, and S. Pittalis, *J. Chem. Phys.* **145**, 054112 (2016).