A Laplacian-based model for the exchange energy – applications to atoms and jellium droplets.[1]
ANTONIO C. CANCIO, CHRISTOPHER E. WAGNER[2], Ball State University — We report recent work in developing a GGA-level density functional that exploits the "gauge" invariance of the gradient expansion of density functional theory – the freedom to use either the gradient-squared of the density or its Laplacian to describe the lowest-order gradient correction to the local density approximation. The functional, which uses a linear combination of the two, has an exchange potential which is finite and well-behaved at the atomic nucleus, where those of normal GGA's (i.e. gradient-only models) become singular, and which avoids the unphysical oscillations that can plague functionals built with the Laplacian. In addition, we can show that all constraints of the GGA that are "gauge invariant" – such as scaling laws – can be satisfied by our formulation of DFT. The local Lieb-Oxford bound, which is not, is replaced by the constraint that the model fit the exchange energy of low-Z atoms, a natural complement to the high-Z limit of the exchange energy which may be used to determine the gradient expansion of this quantity, as has been done in the recent APBE variant of the GGA. Doing so reproduces the behavior of the APBE vis-a-vis the exchange energy of atoms. Our formulation at the same time can be made to satisfy partially the fourth-order gradient expansion of exchange, although it is perhaps uncertain what that expansion should be for atoms in light of the redefinition of the gradient expansion in terms of the extended Thomas-Fermi model of the atom. Finally we apply our model to recent nearly exact calculations of the density and exchange potential of jellium droplets. In this case, we particularly notice beneficial effects from the fourth-order terms in the gradient expansion about the homogeneous electron gas.

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