Non-empirical Constraint-based Parameterization of a Generalized Gradient Approximation for the Orbital-Free Kinetic Energy

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To develop the constraint-based "modified conjoint" Generalized Gradient Approximation(GGA) forms for the orbital-free Kohn-Sham kinetic energy, empirical parameterization with respect to a very small training set has been unavoidable up to now. Making this parameterization non-empirical is rather difficult [1]. Here we explore one possible way to do so. We consider the reparameterized Perdew-Burke-Ernzerhof exchange functional PBEmol [2], which is self-interaction free for the Hydrogen atom density n_1. One then can constrain the Pauli kinetic energy (T_θ in $T_s = T_W + T_\theta$, with T_W the von Weizsäcker KE) to cancel the remaining spurious correlation energy, *i.e.* $T_\theta[n_1] + E_{c,PBE}[n_1] = 0$. Bounding the functional by $T_W + T_{TF}$, with T_{TF} the Thomas-Fermi KE and retaining the original constraint that $T_\theta > 0$ assures a non-empirical estimate of the parameters. We report initial numerical results and findings of this procedure here.

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[1] Phys. Rev. B **80**, 245120 (2009)

[2] J. Chem. Phys. **136**, 104108 (2012)