On the transferability of a parametrized kinetic functional for orbital-free density functional theory calculations

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Because of issues with accuracy and transferability of existing orbital-free (OF) density functionals, OF functional development remains an active research area. However, due to numerical difficulties, all-electron self-consistent assesment of OF functionals is limited. Using projector augmented wave method transformation, we compute OFDFT all-electron values [1] and we evaluate the performance of parametrized OF functionals for a wide range of parameter space for atoms and molecules.

Specifically we investigate Thomas-Fermi-Weizsäcker model for kinetic functional where fractions of Thomas-Fermi and Weizsäcker are parametrized as (γ, λ), respectively, in atoms [2]. Our interest lies in total energy and Euler equation eigenvalue. The optimum (γ, λ) with respect to Kohn-Sham values is however different for each property and atom investigated. Recently these results have been combined to investigate the transferrability of these parameters from atoms to molecules [3]. We also present some findings on limitations of describing charged particles with Thomas-Fermi-Weizsäcker model and limitations on parametrized approach similar to Deb and Gosh[4] when applied to small molecules.

[1]Lehtomäki J., Makkonen I., Caro, M., Harju, A., Lòpez-Acevedo O., J. Chem. Phys. 141, 234102 (2014).
[2]Espinosa Leal L., Karpenko A., Caro M., Lòpez-Acevedo O., Phys. Chem. Chem. Phys., DOI: 10.1039/C5CP01211B (2015).
[3]Karpenko A., Espinosa Leal L., Caro M., Lehtomäki J., Lòpez-Acevedo O. (in preparation).
[4]Deb, B. M. and Ghosh, S. K., Int. J. of Quantum Chem., DOI:10.1002/qua.560230104 (1983)