Delocalization, N-representability and Jacob's ladder

Alberto Vela,[1] Angel M. Albavera-Mata,[1] Daniel Mejía-Rodríguez[2] and José L. Gázquez[3]

[1]Departamento de Química, Cinvestav, Av. Instituto Politécnico Nacional 2508, San Pedro Zacatenco, Ciudad de México, 07360, México.
[2]Quantum Theory Project, Department of Physics, P. O. Box 118435, University of Florida, Gainesville, Florida 32611-8435, USA.
[3]Departamento de Química, Universidad Autónoma Metropolitana Iztapalapa, Av. San Rafael Atlixco 186, Ciudad de México, 09340, México.

The behavior of the delocalization, or fractional charge, error as defined by Yang et al.[1-3] and the fulfillment of the bound required to satisfy N-representability by a density functional approximation (DFA) to the exchange-correlation energy (E_{xc}) functional are explored for a set of over two hundred E_{xc}-functionals available in the Libxc[4] library. We show that the fractional charge error orders the DFAs essentially in accord with the categorization of the famous Perdew-Schmidt Jacob's ladder[5] of functional complexity. As expected, we also show that adding exact exchange reduces the fractional charge error. The N-representability bound for E_{xc} established by Ayers and Liu[6] is also tested for the same set of DFAs on a training set that includes the atomic species recently used to study the quality of the density obtained with different DFAs,[7] which was extended to include ten small molecules. We found that about 20% of the tested E_{xc} DFAs satisfy the N-representability bound, including GGAs whose coefficient corresponding to the quadratic term in the dimensionless exchange gradient has the value obtained from that expansion, namely 10/81. The possible implications of these results in E_{xc} design are discussed.

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