Effect of the orbital-overlap dependence on Meta Generalized Gradient Approximation

Jianwei Sun, John P. Perdew, Bing Xiao, and Adrienn Ruzsinszky
Department of Physics and Quantum Theory Group,
Tulane University, New Orleans, Louisiana 70118, USA
(Dated: January 31, 2012)

The dimensionless inhomogeneity parameter, α, characterizing the extent of orbital overlap, is disentangled for the first time, by the means of separability assumption, from the other dimensionless inhomogeneity parameter, s, the reduced density gradient, in terms of constructing a meta generalized gradient approximation (MGGA) for the exchange functional. We show that the formation of the intershell region in an atom is associated with increase of α. This observation leads to a simple nonempirical MGGA exchange functional, which interpolates between the single-orbital regime for confinement systems, where $\alpha = 0$, and the slowly varying density regime, where $\alpha \approx 1$, and then extrapolates to $\alpha \to \infty$. The simple MGGA exchange functional penalizes the formation of the intershell region by having monotonically increasing s-dependence and monotonically decreasing α-dependence. When it is combined with the variant of the Perdew-Burke-Erzerhof (PBE) GGA correlation as used in the revised Tao-Perdew-Staroverov-Scuseria (revTPSS) MGGA, the resulted MGGA performs equally well for atoms, molecules, surfaces, and solids, with an implication of a tight Lieb-Oxford bound.