Local effective potentials with correct asymptotic behavior in dft and reduced-density-matrix-functional theory

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We propose to minimize orbital functionals in terms of a local effective potential under two subsidiary conditions, in terms of the electronic effective repulsive density [1] that corresponds to the repulsion part of the effective Kohn-Sham potential. The first of these conditions is that the total effective repulsive charge is N-1 electrons, a property of the exact Kohn-Sham potential. The second is the effective repulsive density is nonnegative and thus can be taken to represent the density of N-1 electrons. These conditions can be easily applied when the total energy functional is minimized in terms of the effective repulsive density. By employing the first of these conditions, the asymptotic behavior of the effective potential is corrected, thus the errors of self-interactions in the Kohn Sham potential are corrected. This idea is applied to standard DFT approximations, like LDA, leading to correct ionization potentials[1]. It is also applied to the minimization of reduced density matrix functionals in terms of the natural orbitals[2]. In this way natural orbitals are assumed to correspond to a local potential. Although it is an approximate minimization, we demonstrate that it has certain advantages. One such an advantage is computational efficiency. Most importantly, it leads to the definition of a single

electron spectra in reduced density functional theory. We show numerically [2] that one can get

single electron properties close to experiment while other quality features of reduced density

matrix functionals like the correct dissociation of molecules is not affected by the additional local

potential approximation.

[1] N. I. Gidopoulos, and N. N. Lathiotakis, J. Chem. Phys. 136 , 224109 (2012).

[2] N. N. Lathiotakis, N. Helbig, A. Rubio, N.I. Gidopoulos (to be submitted