Recent advances in developing orbital-free kinetic energy functionals

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The main ingredient needed for a successful orbital-free (OF) DFT approach is a reliable density functional for the Kohn-Sham kinetic energy (KE). Existing KE functionals of the gradient expansion or generalized gradient approximation (GGA) types do not yield acceptable interatomic forces even for simple diatomic and polyatomic molecules. In previous work [1], we traced this poor performance primarily to the violation of the non-negativity condition that must be satisfied by the Pauli potential. In [1] we then proposed the use of modified conjoint functionals parameterized on very small training sets so as to reproduce interatomic forces without requiring that they also yield accurate total energy values. The modified functionals, in common with GGA-type functionals, are singular at the nuclei, but the singularity is positive, leading to semi-quantitatively correct interatomic forces. Here we present recent advances in developing simple semi-local KE functionals. Complete removal of the unphysical singularities from the Pauli potential by is achieved by introducing quantities we call reduced density derivatives. Based on an analysis of the Pauli potential in regions close to the nuclei, we define a reduced derivative approximation (RDA) kinetic-energy functional.

Calculations showing the potential capability of RDA functionals to predict forces and total energies simultaneously are presented.

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