Using visualization to build intuition about kinetic-energy density functional theory

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One tool in the development and assessment of density functional theory is the visualization of related quantities, especially helpful in absence of any way to improve density functionals systematically. A classic example is the exchange-correlation hole, the fluctuation in density about the position of an electron, which determines the exchange-correlation energy, the unknown at the heart of Kohn-Sham method.

Recently, because of applications at high temperature and large system size, interest has turned to the construction of orbital-free density functionals, requiring knowledge the Kohn-Sham kinetic energy solely as a functional of the electron density and its derivatives. Although the kinetic energy lacks an equivalent to the exchange-correlation hole, the kinetic energy density (KED), taken in its positive-definite formulation, is a means to apply a visualization strategy to KE functional development.

We discuss recent work where this approach has provided useful insights: First of all, the AE6 test-set of molecules, a compact benchmark for testing DFT atomization energies, yet one that provides a wide survey of bonding types. Secondly, the scaling properties of single-atom KED's as nuclear charge Z varies from the Thomas-Fermi limit ($Z \to \infty$) down to real atoms. This gives us a semi-systematic way to visualize climbing the Jacob's ladder of DFT – how ever more nonlocal contributions to the energy are turned on as the number of electrons decreases and shell structure becomes more prominent. One notable lesson learned has been the surprising ways how the gradient expansion works (or doesn't) in each case.