Visualizing the Kohn-Sham kinetic energy density in molecules [1] ANTONIO C. CANCIO, AERYK KUNA, Department of Physics and Astronomy, Ball State University — In recent years interest has grown in the construction of orbital-free density functionals, and thus orbital-free models of the Kohn-Sham kinetic energy density (KED), driven by the demands of applications at high temperature and large system size. We visualize the Kohn-Sham KED and several orbital-free KED models for the AE6 test set of molecules commonly used to test density functional performance for atomization energies. Calculations are performed using the ABINIT plane-wave code with over-converged cutoffs and simulation cell sizes to produce as accurate results as possible within a pseudopotential approximation. The orbital-dependent KED is compared to the simple gradient expansion and von-Weiszacker KED's and to a sophisticated metaGGA-level functional proposed by Perdew and Constantin (PC). All models fail to reproduce the Kohn-Sham KED reasonably in high density regions characterized by covalent and polar bonds and valence lone-pairs. In particular, the PC model actually disimproves on the gradient expansion in these regions. A simple fix is proposed for the PC functional, substantially modifying its behavior for regions of high values of the Laplacian of the density and low density gradient.

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