Modeling the Kohn-Sham kinetic energy density in atoms and molecules [1] <u>ANTONIO C. CANCIO</u>, DANE STEWART, JEREMY REDD, Department of Physics and Astronomy, Ball State University — In recent years, driven by applications at high temperature and large system size, interest has turned to the construction of orbital-free density functionals, modeling the Kohn-Sham kinetic energy solely as a functional of the electron density and its derivatives. We report work on a meta-GGA level orbital-free kinetic energy functional parametrized in terms of the local Laplacian and gradient of the density, and based on insights gained in the visualization of the kinetic energy density (KED) for atoms and the AE6 test set of molecules. This visualization points out significant flaws in an earlier meta-GGA proposed by Perdew and Constantin, particularly to describe the region of localized electron pairs, such as atomic lone pairs and covalent bonds. We find that these can be substantially fixed by revising an implicit constraint built into the prior model in the limit of strong electron localization – when the Kohn-Sham KED approaches the bosonic limit. A first attempt at an improved model dramatically improves atomization energies for the AE6 test set, but remains an order of magnitude worse than a conventional Kohn-Sham GGA. The model consistently overestimates total energies, probably due to an overcorrection for systems with localized electrons; we address attempts to correct this issue.