Machine learning of kinetic energy density functionals for large-scale ab initio modeling

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Large-scale ab initio modeling is required to model properties of materials at realistic time and length scales. Today's workhorse ab initio method for materials modeling, Kohn-Sham Density Functional Theory (KS-DFT), suffers from a near-cubic scaling with system size, which limits *routine* modeling to systems on the order of 100 atoms. For much larger systems, one typically has to rely on force fields which themselves have to be fitted to reference data (such as ab initio) and in principle cannot provide electronic properties. This scaling of KS-DFT is due to reliance on orbitals. Orbital-Free DFT (OF-DFT) avoids orbitals and allows for near-linear scaling; up to 10^5 atoms can be routinely modeled on a desktop. The Achilles' heel of OF-DFT is the poor quality of available kinetic energy functionals (KEF) which replace the non-interacting kinetic energy T or kinetic energy density (KED) $t(\mathbf{r})$ based on orbitals ψ_i with a functional of electron density only: $T = \int t(\boldsymbol{r})d\boldsymbol{r} = \int \left(-\frac{1}{2}\sum \psi_i \Delta\psi_i\right) d\boldsymbol{r} \approx T'[\rho(\boldsymbol{r})] = \int t'[\rho(\boldsymbol{r})]d\boldsymbol{r}$, where $\rho(\boldsymbol{r}) = \sum|\psi_i|^2$. This problem is so bad that as of today, OF-DFT cannot be used in applications beyond light metals. We present the results of applying machine learning using neural networks (NN) to learn the KS KED of bulk light metals (Li, Mg, Al), a bulk semiconductor (Si) and molecules (H_2O and C_6H_6). We train the NN using terms of the 4th order gradient expansion (T^4) as inputs. We achieve ultra-low fit errors with *no NN overfitting* (contrary to other works). KS KED can be reproduced very accurately for Li, Mg, and Al; most importantly, a very good fit was also achieved for Si – a much more difficult case. A decent fit was achieved for H_2O KED, but not for C_6H_6. We also highlight the critical role played by the type of pseudopotential as well as by KED data distribution, suggesting directions of further research. (read more: arXiv:1805.10855)

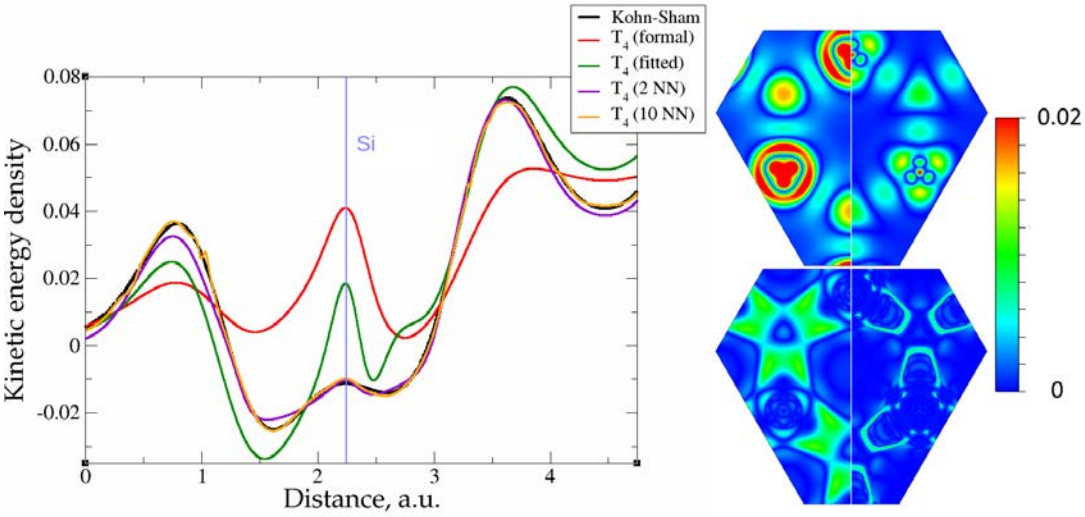

Fig. 1. KED for silicon: KS KED, 4th order gradient expansions T^4 (as published and with fitted coefficients) and NN fits. On the left – the line along direction {1 1 1}; on the right – the projection of plane {1 1 1} with absolute differences from the KS KED for: upper left quadrant – formal T^4, upper right quadrant – fitted T^4, bottom left/right quadrants - NN fits with 2/10 hidden neurons.