

Orbital-free DFT is becoming practical

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In 1964, Hohenberg and Kohn proved that the ground state of an interacting electron system is completely determined by its electron density. In principle, this result promises a dramatic simplification of electronic structure theory: instead of solving for a many-electron wave function in a 3N-dimensional space, one could obtain the ground state by minimizing an energy functional of the three-dimensional electron density. In practice, this vision has remained unrealized, because the key ingredient—the kinetic-energy functional of the density—is unknown for real molecular systems. Modern Kohn-Sham density functional theory circumvents this obstacle by introducing auxiliary orbitals, but at the price of cubic scaling with system size.

In this talk I will show that the missing functional can be learned to sufficient accuracy for increasingly complex chemistry using rotation equivariant machine learning models. After reaching chemical accuracy relative to KS-GGA functionals on relaxed geometries, I will give an update on speedups and show latest results on non-equilibrium geometries, open shell systems and for much of the periodic table.

These results suggest that machine learning may finally enable a practical realization of the Hohenberg–Kohn program, opening an orbital-free density functional theory route to chemically accurate electronic-structure calculations for large systems, complementing both linear-scaling density functional theory and machine-learned interatomic potentials.