

Large-scale Ab Initio Simulations with Orbital-free Density Functional Theory

Beatriz Gonzalez del Rio,^a William C. Witt,^a Kaili Jiang,^a and Emily A. Carter^b

^a *Department of Mechanical and Aerospace Engineering,* ^b *School of Engineering and Applied Science, Princeton University, Princeton, New Jersey 08544-5263, USA*
eac@princeton.edu

Orbital-free (OF) density functional theory (DFT), rooted in quantum mechanics but involving only the non-interacting electron density, is an especially promising tool for large-scale electronic structure calculations. Achieved by circumventing the wavefunction operations required for conventional Kohn-Sham (KS) DFT, the two main advantages of OFDFT are speed and (quasi-)linear computational scaling with increasing system size. However, these advantages come at a cost in accuracy in the calculation of: i) the non-interacting electron kinetic energy, T_s ; and ii) the electron-ion (screened nucleus) interaction term, E_{ext} , in the form of local pseudopotentials (LPSs). Significant efforts have been made over the years to overcome both obstacles with meaningful success.

We discuss various approaches for improving approximations to T_s , which include recent work on the local, gradient-based kinetic energy density of nearly free electrons by the derivation of new response functions, as well as the use of hybrid techniques that include localized atom-centered density matrices within the usual OF formalism. We also report advances in constructing accurate LPSs employed in E_{ext} using global optimization techniques based on genetic algorithms.

We conclude by presenting a recent application of our OFDFT-code, PROFESS, in a molecular dynamics study of liquid Sn that confirms the existence of a second excitation mode in the collective dynamics, as well as its theoretical explanation through mode coupling.