Angular Momentum Dependent Orbital Free Density Functional Theory

Youqi Ke, Florian Libisch, Junchao Xia, and Emily A. Carter

Department of Mechanical and Aerospace Engineering, Program in Applied and Computational Mathematics, and Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ 08544-5263, USA

Abstract

Orbital-free density functional theory (OFDFT) directly solves for the ground state electron density. It scales linearly with respect to system size, providing a promising tool for large scale material simulations. Unfortunately, the lack of orbitals requires the use of approximate kinetic energy density functionals and local pseudopotentials to represent the interaction with ionic cores, severely limiting the capability of conventional OFDFT. While main group elements are often well-described within conventional OFDFT, transition metals remain an enormous challenge due to their localized d-electrons. To advance the accuracy and general applicability of OFDFT, we propose a general angular momentum dependent formulation of OFDFT as a next-generation OFDFT [1]. The explicit treatment of the angular momenta of electrons provides an important basis for accurately describing the important ionic core region, which is not possible in conventional OFDFT. We introduce an additional nonlocal energy term containing a set of angular momentum dependent energies, which corrects the errors due to the approximate kinetic energy density functional and local pseudopotentials. We discuss implementation details of our approach, including force formulas required for geometry relaxation. We calculate a diverse set of properties of the transition metal Ti, including mechanical properties of different phases, and compare with different levels of DFT. Our approach greatly increases the accuracy of OFDFT while largely preserving its numerical simplicity. The results suggest that angular momentum dependent OFDFT ultimately will extend the reliable reach of OFDFT to the rest of the periodic table.

References

[1] Y. Ke, F. Libisch, J. Xia, L.-W. Wang, and E. A. Carter, *Phys. Rev. Lett.*, **111**, 066402 (2013); Y. Ke, F. Libisch, J. Xia, and E. A. Carter, *Phys. Rev. B,* submitted (2013).