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Preconditioners and Electron Density Optimization in Orbital-Free Density Functional Theory

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Abstract. Orbital-free density functional theory (OFDFT) is a quantum mechanical method in which the energy of a material depends only on the electron density and ionic positions. We examine some popular algorithms for optimizing the electron density distribution in OFDFT, explaining their suitability, benchmarking their performance, and suggesting some improvements. We start by describing the constrained optimization problem that encompasses electron density optimization. Next, we discuss the line search (including Wolfe conditions) and the nonlinear conjugate gradient and truncated Newton algorithms, as implemented in our open source OFDFT code. We finally focus on preconditioners derived from OFDFT energy functionals. Newly-derived preconditioners are successful for simulation cells of all sizes without regions of low electron-density and for small simulation cells with such regions.

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1 Introduction

When modeling materials, a quantum mechanical theory's utility is limited by its computational cost. Part of the cost comes from the evaluation of energy functionals. In this respect, orbital-free density functional theory (OFDFT) [1] is relatively inexpensive

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compared to the more-popular Kohn-Sham density functional theory (KSDFT). OFDFT describes the electronic energy of a system solely using electron density and an ionic external potential; it does not use any wavefunctions and all energy functionals can be formulated to be quasilinear scaling ($\mathcal{O}(N\log(N))$ with a small prefactor [2, 3]. These computational advantages come as a trade-off with accuracy, such that materials with large spatial fluctuations in electron density are not yet well represented by kinetic energy density functionals (KEDFs) in OFDFT. However, main group metals such as aluminum (Al) can be modeled with energies reproducing KSDFT results to $\sim$10 meV [4, 5].

The second part of the computational cost in materials science simulations is due to the optimization method used to minimize the energy. Optimizations must be performed on several levels to fully minimize the total energy of the system. To optimize the cell lattice vectors, cell stresses are minimized. To optimize ion positions, the forces are minimized. And to evaluate the ground state energies, forces, or stresses for a fixed geometry, the electron density must be fully optimized. Princeton Orbital-Free Electronic Structure Software (PROFESS) [2, 6], which uses OFDFT to compute energies, optimizes the electron density, atomic configurations, and cell lattice vectors using iterative methods. In this work, we describe recent improvements to electron density optimization algorithms implemented within PROFESS and report benchmark results.

In Section 2, we introduce the specific OFDFT optimization problem and the treatment of constraints. Unlike wavefunction-based methods, there is no need to orthogonalize orbitals; only two physical conditions must be satisfied. First, the total number of electrons N_e must remain constant. Second, the electron density at any given point must be non-negative. These constraints are satisfied by a judicious choice of optimization variable and the use of a Lagrange multiplier.

Next, we describe our calculational details and benchmarking metrics in Section 3.

In Section 4, we detail the iterative line-search optimization methods implemented within PROFESS. We first describe a line search that conserves the total number of electrons in the simulation [8], and derive the line-search-termination criteria that are analogous to the Wolfe conditions for a standard line search. We then review the nonlinear conjugate gradient (CG) and the truncated Newton (TN) methods, which determine the descent direction to take during the line search. Some benchmarks comparing CG and TN performance for simulation cells containing Al are also included in this section.

In Section 5, we derive and test preconditioners for the inner CG loop of the TN method. In the past, a preconditioner based on the von Weizsäcker (vW) [9] KEDF was found to accelerate convergence in bulk crystals but caused optimization to fail in the presence of vacuum [10]. Here, we propose preconditioners based on Lindhard linear response and preconditioners that include both a Hartree energy term together with a kinetic energy term. The preconditioners are benchmarked with simulation cells of bulk material (no surfaces/vacuum) and with simulation cells containing vacuum.