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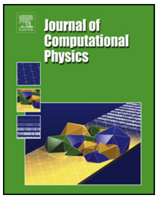

Augmented Lagrangian formulation of orbital-free density functional theory

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ABSTRACT

We present an Augmented Lagrangian formulation and its real-space implementation for non-periodic Orbital-Free Density Functional Theory (OF-DFT) calculations. In particular, we rewrite the constrained minimization problem of OF-DFT as a sequence of minimization problems without any constraint, thereby making it amenable to powerful unconstrained optimization algorithms. Further, we develop a parallel implementation of this approach for the Thomas–Fermi–von Weizsacker (TFW) kinetic energy functional in the framework of higher-order finite-differences and the conjugate gradient method. With this implementation, we establish that the Augmented Lagrangian approach is highly competitive compared to the penalty and Lagrange multiplier methods. Additionally, we show that higher-order finite-differences represent a computationally efficient discretization for performing OF-DFT simulations. Overall, we demonstrate that the proposed formulation and implementation are both efficient and robust by studying selected examples, including systems consisting of thousands of atoms. We validate the accuracy of the computed energies and forces by comparing them with those obtained by existing plane-wave methods.

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1. Introduction

Electronic structure calculations based on Kohn–Sham Density Functional Theory (DFT) [1,2] have been remarkably successful in describing material properties and behavior. In DFT, the system of interacting electrons is replaced with a system of non-interacting electrons moving in an effective potential. As a result, the problem of determining a single many-electron wavefunction reduces to the calculation of multiple single-electron wavefunctions/orbitals, the number of which commensurates with size of the system [3–5]. Solving for these orbitals using traditional approaches like diagonalization results in a cubic-scaling with respect to the number of atoms [4,5]. To overcome this restrictive scaling, substantial effort has been directed towards the development of linear-scaling methods [6,7]. However, an efficient linear-scaling method for metallic systems still remains an open problem [8]. Orbital-Free DFT (OF-DFT) represents a simpler linear-scaling version of DFT wherein the electronic kinetic energy is modeled using a functional of the electron density [9–13]. Detailed studies have shown that such a theory can provide an accurate description of systems whose electronic structure resembles a free-electron gas e.g. Aluminum [14–16]. Current efforts include extending the applicability of OF-DFT to covalently bonded materials [17] as well as molecular systems [18].

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OF-DFT calculations have traditionally employed the plane-wave basis [12,19,20], which is attractive because of the associated spectral convergence and the efficient evaluation of convolutions through the Fast Fourier Transform (FFT) [21]. However, the need for periodic boundary conditions limits the effectiveness of plane-waves in the study of isolated clusters and crystallographic defects. Further, the development of implementations which can efficiently utilize modern large-scale, distributed-memory computer architectures is particularly challenging. In view of this, recent efforts have been directed towards developing real-space approaches for OF-DFT, including finite-differences [22] and finite-elements [23,24]. Amongst these, the finite-element method provides the flexibility of an adaptive discretization. This attribute has been employed to perform all-electron calculations [23,24] and to develop a coarse-grained formulation of OF-DFT for studying crystal defects [25]. Notably, it has been demonstrated that higher-order finite-elements provide tremendous computational savings relative to their linear counterparts, especially for achieving chemical accuracies [24]. However, higher-order finite-differences — which have been particularly successful in DFT [26–29] due to their simplicity, efficiency and the ease with which the order of approximation can be changed — remain unexplored in the context of OF-DFT.

The electronic ground state in OF-DFT can be expressed as the solution of a non-linear, constrained minimization problem [22,30–32,23]. Approaches that have been employed to solve this problem include steepest descents [19], conjugate-gradients [19,23,33], truncated Newton [19,22] and multigrid methods [19]. Amongst these, the truncated Newton method has been found to be particularly effective, subject to the availability of a good starting guess [19,22]. In these aforementioned approaches, the techniques utilized to enforce the constraint include the penalty method [23], the Lagrange multiplier method [34,24] and its variant in terms of the projected gradient and Hessian [22]. In this work, we develop an Augmented Lagrangian [35] formulation for OF-DFT which inherits the advantages of both the Lagrange multiplier and penalty methods. Specifically, we rewrite OF-DFT's constrained minimization problem as a sequence of unconstrained minimization problems which can be solved using efficient optimization algorithms like conjugate gradients. We develop a parallel implementation of the proposed method in the framework of higher-order finite-differences. We demonstrate the robustness, efficiency and accuracy of the proposed approach through selected examples, the results of which are compared against the existing plane-wave methods.

The remainder of this paper is organized as follows. We introduce OF-DFT in Section 2 and discuss its solution using the Augmented Lagrangian method in Section 3. Subsequently, we describe the numerical implementation of the proposed method in Section 4, and validate it through examples in Section 5. Finally, we conclude in Section 6.

2. Orbital-free density functional theory

Consider a charge neutral system with M atoms and N electrons. Let $\mathbf{R} = \{\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_M\}$ denote the positions of the nuclei with charges $\mathbf{Z} = \{Z_1, Z_2, \ldots, Z_M\}$ respectively. The energy of this system as described by OF-DFT is [3]

$$\mathcal{E}(u, \mathbf{R}) = T_s(u) + E_{xc}(u) + E_H(u) + E_{ext}(u, \mathbf{R}) + E_{zz}(\mathbf{R}), \tag{1}$$

where $u = \sqrt{\rho}$, ρ being the electron density. The electronic kinetic energy $T_s(u)$ is typically modeled using the Thomas–Fermi–von Weizsacker (TFW) functional [3] with or without additional terms that account for the linear-response of a uniform electron gas [13]. Examples include the Wang and Teter (WT) [12] and Wang, Govind and Carter (WGC) [36,37] kinetic energy functionals. For the non-periodic setting considered here, we restrict ourselves to the TFW family of functionals

$$T_s(u) = C_F \int u^{10/3}(\mathbf{x})\,d\mathbf{x} + \frac{\lambda}{2}\int \left|\nabla u(\mathbf{x})\right|^2 d\mathbf{x}, \tag{2}$$

where λ is an adjustable parameter and the constant $C_F = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}$.

The second term in Eq. (1) is referred to as the exchange-correlation energy. In OF-DFT, it is generally modeled using the local density approximation (LDA) [2]:

$$E_{xc}(u) = \int \varepsilon_{xc}\big(u(\mathbf{x})\big)u^2(\mathbf{x})\,d\mathbf{x}, \tag{3}$$

where $\varepsilon_{xc}(u) = \varepsilon_x(u) + \varepsilon_c(u)$ is the sum of the exchange and correlation per particle of a uniform electron gas of density $\rho = u^2$. Within the Ceperley–Alder parametrization [38,39], the exchange and correlation functionals have the following representation

$$\varepsilon_x(u) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} u^{2/3}, \tag{4}$$

$$\varepsilon_c(u) = \begin{cases} \frac{\gamma_1}{1+\beta_1\sqrt{r_s}+\beta_2 r_s} & r_s \geq 1 \\ A_1 \log r_s + B_1 + C_1 r_s \log r_s + D_1 r_s & r_s < 1 \end{cases} \tag{5}$$

where $r_s = (\frac{3}{4\pi u^2})^{1/3}$, and the constants $\gamma_1 = -0.1423$, $\beta_1 = 1.0529$, $\beta_2 = 0.3334$, $A_1 = 0.0311$, $B_1 = -0.048$, $C_1 = 0.002$ and $D_1 = -0.0116$.

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