Higher-order finite-difference formulation of periodic Orbital-free Density Functional Theory

Swarnava Ghosh, Phanish Suryanarayana

College of Engineering, Georgia Institute of Technology, GA 30332, USA

Abstract

We present a real-space formulation and higher-order finite-difference implementation of periodic Orbital-free Density Functional Theory (OF-DFT). Specifically, utilizing a local reformulation of the electrostatic and kernel terms, we develop a generalized framework suitable for performing OF-DFT simulations with different variants of the electronic kinetic energy. In particular, we develop a self-consistent field (SCF) type fixed-point method for calculations involving linear-response kinetic energy functionals. In doing so, we make the calculation of the electronic ground-state and forces on the nuclei amenable to computations that altogether scale linearly with the number of atoms. We develop a parallel implementation of this formulation using the finite-difference discretization, using which we demonstrate that higher-order finite-differences can achieve relatively large convergence rates with respect to mesh-size in both the energies and forces. Additionally, we establish that the fixed-point iteration converges rapidly, and that it can be further accelerated using extrapolation techniques like Anderson’s mixing. We validate the accuracy of our results by comparing the energies and forces with plane-wave methods for selected examples, one of which is the vacancy formation energy in Aluminum. Overall, we demonstrate that the proposed formulation and implementation is an attractive choice for performing OF-DFT calculations.

Key words: Finite-differences, Real-space, Fixed-point, Anderson mixing, Conjugate gradient, Electronic structure.

1. Introduction

Kohn-Sham Density Functional Theory (DFT) [1, 2] has a relatively high accuracy/cost ratio, which makes it a popular electronic structure theory for predicting 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 [3, 4]. The electronic ground-state in DFT is typically determined by solving for the Kohn-Sham orbitals, the number of which is commensurate with the size of the system, i.e. number of electrons [4, 5]. Since these orbitals need to be orthonormal, the overall solution procedure scales cubically with the number of atoms [4, 5]. In order to overcome this restrictive scaling, significant research has focused on the development of linear-scaling methods [6, 7]. Nearly all of these approaches, in one form or the other, employ the decay of the density matrix [8] in conjunction with truncation to achieve linear-scaling [6, 7]. However, an efficient linear-scaling algorithm for metallic systems still remains an open problem [9].

Orbital-free DFT (OF-DFT) represents a simplified version of DFT, wherein the electronic kinetic energy is modeled using a functional of the electron density [10]. Commonly used kinetic energy functionals
include the Thomas-Fermi-von Weizsacker (TFW) [11, 12, 13], Wang-Teter (WT) [14] and Wang, Govind & Carter (WGC) [15, 16] functionals. Amongst these, the WT and WGC energies are designed so as to match the linear-response of a homogeneous electron gas [10]. Previous studies have shown that OF-DFT is able to provide an accurate description of systems whose electronic structure resembles a free-electron gas e.g. Aluminum and Magnesium [17, 18, 19]. There have been recent efforts to extend the applicability of OF-DFT to covalently bonded materials [20] as well as molecular systems [21]. In essence, OF-DFT can be viewed as a ‘single-orbital’ version of DFT, wherein the cubic-scaling bottleneck arising from orthogonalization is no longer applicable. In addition to this, OF-DFT possesses an extremely favorable scaling with respect to temperature compared to DFT [22, 23]. Overall, OF-DFT has the potential to enable electronic structure calculations for system sizes that are intractable for DFT.

The plane-wave basis is attractive for performing OF-DFT calculations [14, 24, 25] because of the spectral convergence with increasing basis size and the efficient evaluation of convolutions using the Fast Fourier Transform (FFT) [26]. However, the development of implementations which can efficiently utilize modern large-scale, distributed-memory computer architectures is particularly challenging. Further, evaluation of the electrostatic terms within the plane-wave basis typically scales quadratically with the number of atoms [27]. In view of this, recent efforts have been directed towards developing real-space approaches for OF-DFT, including finite-differences [28] and finite-elements [29, 30]. Amongst these, the finite-element method provides the flexibility of an adaptive discretization. This attribute has been employed to perform all-electron calculations [29, 30] and to develop a coarse-grained formulation of OF-DFT for studying crystal defects [31]. However, higher-order finite-differences — which have been shown to be extremely efficient in non-periodic OF-DFT with the TFW kinetic energy functional [28] — remain unexplored in the context of periodic OF-DFT simulations, particularly when linear-response kinetic energy functionals like WT and WGC are employed.

The electronic ground state in OF-DFT can be expressed as the solution of a non-linear, constrained minimization problem [32, 33, 34, 35, 29, 28]. The approaches which have previously been employed to solve this problem include variants of conjugate-gradient [24, 29, 36, 28] and Newton [24, 32, 30] methods. In these approaches, the techniques used to enforce the constraints include Lagrange multipliers [37, 30], the penalty method [29] and the Augmented-Lagrangian method [28]. In this work, we present a local real-space formulation and implementation of periodic OF-DFT. In particular, we develop a fixed-point iteration with respect to the kernel potential for simulations involving linear-response kinetic energy functionals. 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 existing plane-wave methods. The remainder of this paper is organized as follows. We introduce OF-DFT in Section 2 and discuss its real-space formulation in Section 3. Subsequently, we describe the numerical implementation in Section 4, which we validate through examples in Section 5. Finally, we conclude in Section 6.

2. Orbital-free Density Functional Theory

Consider a charge neutral system of \( M_a \) atoms and \( N_e \) electrons in a cuboidal domain \( \Omega \) under periodic boundary conditions. Let \( \mathbf{R} = \{ \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_{M_a} \} \) denote the positions of the nuclei with charges \( \mathbf{Z} = \{ Z_1, Z_2, \ldots, Z_{M_a} \} \) respectively. The energy of this system as described by OF-DFT is [3]

\[
\mathcal{E}(u, \mathbf{R}) = T_s(u) + E_{xc}(u) + E_H(u) + E_{ext}(u, \mathbf{R}) + E_{zz}(\mathbf{R}),
\]

(1)
where \( u = \sqrt{\rho} \), \( \rho \) being the electron density. Introducing the parameters \( \lambda \) and \( \mu \in \{0, 1\} \) so that different variants of the electronic kinetic energy \( T_s(u) \) can be encompassed within a single expression, we can write

\[
T_s(u) = T_{TF}(u) + \lambda T_{vW}(u) + \mu T_{LR}(u),
\]

(2)

where \( T_{TF}(u) \) is the Thomas-Fermi energy \([11, 12]\), \( T_{vW}(u) \) is the von Weizsacker \([13]\) term and \( T_{LR}(u) \) is a non-local kernel energy incorporated to make the kinetic energy satisfy the linear-response of a homogeneous electron gas \([10]\). They can be represented as

\[
T_{TF}(u) = C_F \int_\Omega u^{10/3}(x) \, dx,
\]

(3)

\[
T_{vW}(u) = \frac{1}{2} \int_\Omega |\nabla u(x)|^2 \, dx,
\]

(4)

\[
T_{LR}(u) = C_F \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} u^{2\alpha}(x) K(|x - x'|, \rho(x), \rho(x')) u^{2\beta}(x') \, dx \, dx',
\]

(5)

where \( \alpha \) and \( \beta \) are parameters, and the constant \( C_F = \frac{2}{15}(3\pi^2)^{1/3} \). On the other hand, the Thomas-Fermi-von Weizsacker (TFW) family of functionals with the adjustable parameter \( \lambda \) is obtained by setting \( \mu = 0 \) \([3]\).

On the other hand, kinetic energy functionals which satisfy the Lindhard susceptibility function are obtained by setting \( \mu = \lambda = 1 \) with appropriate choices of \( \alpha \), \( \beta \) and the kernel \( K(|x - x'|, \rho(x), \rho(x')) \) \([10]\). In particular, the Wang & Teter (WT) functional \([14]\) utilizes a density independent kernel, whereas the Wang, Govind & Carter (WGC) functional \([15, 16]\) employs a density dependent kernel. It is common to perform a Taylor series expansion of the density dependent kernel \( K(|x - x'|, \rho(x), \rho(x')) \) about the average electron density \( \bar{\rho} \) \([16]\). On doing so, we arrive at

\[
T_{LR}(u) = C_F \sum_{m=0}^L \sum_{n=0}^L \sum_{p=0}^m \sum_{q=0}^n C_{mnpq} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} u^{2(m-p+\alpha)}(x) K_{mn}(|x - x'|) u^{2(n-q+\beta)}(x') \, dx \, dx',
\]

(6)

where \( L \) is the order of the expansion, the coefficients

\[
C_{mnpq} = \frac{(-1)^{p+q}}{m! \, n!} \binom{m}{p} \binom{n}{q} \bar{\rho}^{p+q-m-n},
\]

(7)

and the kernels

\[
K_{mn}(|x - x'|) = \bar{\rho}^{m+n} \left( \frac{\partial^{m+n} K(|x - x'|, \rho(x), \rho(x'))}{\partial \rho^m(x) \partial \rho^n(x')} \right) \bigg|_{\rho = \bar{\rho}}.
\]

(8)

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

\[
E_{xc}(u) = \int_\Omega \varepsilon_{xc}(u(x)) u^2(x) \, dx,
\]

(9)

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 \( \rho = u^2 \). Employing the Perdew-Zunger \([38]\) parameterization of the correlation energy calculated by Ceperley-Alder \([39]\), the exchange and correlation functionals can be represented as

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

(10)

\[
\varepsilon_c(u) = \begin{cases} \frac{2}{1 + p_1 r_s + p_2 r_s^2} & r_s \geq 1 \\ A_1 \log r_s + B_1 + C_1 r_s \log r_s + D_1 r_s^2 & r_s < 1 \end{cases}
\]

(11)
where \( r_s = \left( \frac{3}{4 \pi \varepsilon_0} \right)^{1/3} \), 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 \( D_1 = -0.0116 \).

The final three terms in Eqn. 1 represent electrostatic energies [5]. In periodic systems, they can be expressed as

\[
E_H(u) = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\Omega} \frac{u^2(x)u^2(x')}{|x - x'|} \, dx \, dx',
\]

\[
E_{ext}(u, \mathbf{R}) = \sum_I \int_{\Omega} u^2(x)V_I(x, \mathbf{R}_I) \, dx,
\]

\[
E_{zz}(\mathbf{R}) = \frac{1}{2} \sum_I \sum_{J \neq I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|},
\]

where the summation over \( I \) and \( J \) signifies all atoms in \( \mathbb{R}^3 \) and \( \Omega \) respectively. The Hartree energy \( E_H(u) \) is the classical interaction energy of the electron density, \( V_I(x, \mathbf{R}_I) \) is the potential due to the nucleus positioned at \( \mathbf{R}_I \), \( E_{ext}(u, \mathbf{R}) \) is the interaction energy between the electron density and the nuclei, and \( E_{zz}(\mathbf{R}) \) is the repulsion energy between the nuclei.

The ground state of the system in OF-DFT is given by the variational problem [33, 29, 32, 35, 28]

\[
\mathcal{E}_0 = \inf_{\mathbf{R} \in \mathbb{R}^{3M_a}} \inf_{u \in \mathcal{A}} \mathcal{E}(u, \mathbf{R}), \quad \mathcal{X} = \{ u : u \in \mathcal{X}, u \geq 0, C(u) = 0 \},
\]

where \( \mathcal{X} \) is some appropriate space of periodic functions and

\[
C(u) = \int_{\Omega} u^2(x) \, dx - N_e
\]

represents the constraint on the total number of electrons. The inequality constraint \( u \geq 0 \) is to ensure that \( u \) is nodeless, i.e. does not possess a zero crossing. In this work, we focus on developing a local formulation and higher-order finite-difference implementation for determining the ground-state in periodic OF-DFT simulations.

### 3. Real-space formulation

In this section, we develop a periodic OF-DFT formulation that is amenable to a linear-scaling real-space implementation. First, we present a local description of the kernel energy and potential in Section 3.1. Next, we discuss rewriting of the electrostatic terms into a local form in Section 3.2. Finally, we incorporate these local representations into a framework for determining the OF-DFT ground-state in Section 3.3.

#### 3.1. Local reformulation of the kernel energy and potential

In simulations where linear-response kinetic energy functionals are employed, the kernel energy \( T_{LR}(u) \) as well as the kernel potential

\[
V_{LR}(x) = \frac{\delta T_{LR}(u)}{\delta u^2}
\]

\[
= C_F \sum_{m=0}^{L} \sum_{n=0}^{L} \sum_{p=0}^{m} \sum_{q=0}^{n} C_{mnpq} \left[ (m - p + \alpha)u^{2(m-p+\alpha-1)}(x) \int_{\mathbb{R}^3} K_{mn}(|x - x'|)u^{2(n-q+\beta)}(x') \, dx' \right] + (n - q + \beta)u^{2(n-q+\beta-1)}(x) \int_{\mathbb{R}^3} K_{mn}(|x - x'|)u^{2(m-p+\alpha)}(x') \, dx',
\]

(17)
are inherently non-local in real-space. In order to enable a linear-scaling implementation, we start by defining

\[ V_{mnq\beta}(\mathbf{x}) = \int_{\mathbb{R}^3} K_{mn}(|\mathbf{x} - \mathbf{x}'|)u^{2(n-q+\beta)}(\mathbf{x}') \, d\mathbf{x}', \quad (18) \]

\[ V_{mn\alpha\rho}(\mathbf{x}) = \int_{\mathbb{R}^3} K_{mn}(|\mathbf{x} - \mathbf{x}'|)u^{2(m-p+\alpha)}(\mathbf{x}') \, d\mathbf{x}'. \quad (19) \]

After approximating the kernels \( K_{mn}(|\mathbf{x} - \mathbf{x}'|) \) in Fourier space using rational functions [40], we arrive at

\[ V_{mnq\beta}(\mathbf{x}) = \sum_{r=1}^{R} V_{mnq\beta r}(\mathbf{x}), \quad (20) \]

\[ V_{mn\alpha\rho}(\mathbf{x}) = \sum_{r=1}^{R} V_{mn\alpha\rho r}(\mathbf{x}), \quad (21) \]

where \( V_{mnq\beta r}(\mathbf{x}) \) and \( V_{mn\alpha\rho r}(\mathbf{x}) \) are solutions of the Helmholtz equations

\[ \frac{1}{(2\tilde{k}_F)^2} \nabla^2 V_{mnq\beta r}(\mathbf{x}) + Q_{mn} V_{mnq\beta r}(\mathbf{x}) = P_{mnr} f_{m\rho}(\mathbf{x}), \quad (22) \]

\[ \frac{1}{(2\tilde{k}_F)^2} \nabla^2 V_{mn\alpha\rho r}(\mathbf{x}) + Q_{mn} V_{mn\alpha\rho r}(\mathbf{x}) = P_{mn\alpha\rho r} f_{nq\beta}(\mathbf{x}), \quad (23) \]

under periodic boundary conditions and appropriate choice of complex constants \( P_{mnr} \) and \( Q_{mn} \). Above, \( \tilde{k}_F = (3\pi^2 \tilde{\rho})^{1/3} \) and

\[ f_{m\rho}(\mathbf{x}) = \begin{cases} \frac{1}{(2\tilde{k}_F)^2} \nabla^2 u^{2(m-p+\alpha)}(\mathbf{x}) & \text{if } m = n = 0, \\ u^{2(m-p+\alpha)}(\mathbf{x}) & \text{otherwise}, \end{cases} \quad (24) \]

\[ f_{nq\beta}(\mathbf{x}) = \begin{cases} \frac{1}{(2\tilde{k}_F)^2} \nabla^2 u^{2(n-q+\beta)}(\mathbf{x}) & \text{if } m = n = 0, \\ u^{2(n-q+\beta)}(\mathbf{x}) & \text{otherwise}. \end{cases} \quad (25) \]

Thereafter, the kernel potential \( V_{LR}(\mathbf{x}) \) and the corresponding kernel energy \( T_{LR}(u) \) can be calculated in linear-scaling fashion using the expressions

\[ V_{LR}(\mathbf{x}) = C_F \sum_{m=0}^{L} \sum_{n=0}^{L} \sum_{p=0}^{m} \sum_{q=0}^{n} \sum_{r=1}^{R} C_{mnpq} \left[ (m - p + \alpha)u^{2(m-p+\alpha-1)}(\mathbf{x})V_{mnq\beta r}(\mathbf{x}) + (n - q + \beta)u^{2(n-q+\beta-1)}(\mathbf{x})V_{mn\alpha\rho r}(\mathbf{x}) \right], \quad (26) \]

\[ T_{LR}(u) = \frac{1}{2} C_F \sum_{m=0}^{L} \sum_{n=0}^{L} \sum_{p=0}^{m} \sum_{q=0}^{n} \sum_{r=1}^{R} C_{mnpq} \int_{\Omega} \left[ u^{2(m-p+\alpha)}(\mathbf{x})V_{mnq\beta r}(\mathbf{x}) + u^{2(n-q+\beta)}(\mathbf{x})V_{mn\alpha\rho r}(\mathbf{x}) \right] \, d\mathbf{x}, \quad (27) \]

where \( V_{mnq\beta r}(\mathbf{x}) \) and \( V_{mn\alpha\rho r}(\mathbf{x}) \) are solutions of the Helmholtz equations given in Eqns. 22 and 23 respectively.
3.2. Local reformulation of the electrostatics

The electrostatic terms given in Eqns. 12, 13 and 14 are non-local in real-space. Further, they are individually divergent in periodic systems. To overcome this, we introduce the charge density of the nuclei [41, 29, 42, 43, 44, 28]:

\[ b(x, R) = \sum_J b_J(x, R_J), \quad b_J(x, R_J) = -\frac{1}{4\pi} \nabla^2 V_J(x, R_J), \]  

where \( b_J(x, R_J) \) is the charge density of the \( J^{th} \) nucleus, and the summation over \( J \) extends to all atoms in \( \mathbb{R}^3 \). In OF-DFT calculations, it is common to remove the core electrons and replace the singular Coulomb potential with an effective potential \( V_J(x, R_J) \), referred to as the pseudopotential approximation [45]. The absence of orbitals in OF-DFT requires that the pseudopotential be local, i.e. \( V_J(x, R_J) \) depends only on the distance from the nucleus. Since the pseudopotential replicates the Coulomb potential outside the core cutoff radius \( r_c \), \( b_J(x, R_J) \) has a compact support within a ball of radius \( r_c \) centered at \( R_J \) [41, 28]. In this framework, it follows that

\[ \int_{\mathbb{R}^3} b_J(x, R_J) \, dx = Z_J, \quad \int_{\Omega} b(x, R) \, dx = N_e. \]  

Using the above definition for the charge density of the nuclei, we can rewrite the total electrostatic energy as the following variational problem

\[ E_{H}(u) + E_{ext}(u, R) + E_{zz}(R) = \sup_{\phi \in Y} \left\{ -\frac{1}{8\pi} \int_{\Omega} |\nabla \phi(x)|^2 \, dx + \int_{\Omega} (u^2(x) + b(x, R)) \phi(x) \, dx \right\} - \frac{1}{2} \sum_J \int_{\Omega} b_J(x, R_J) V_J(x, R_J) \, dx + \mathcal{E}^*_{c}(R), \]  

where \( \phi(x) \) is the electrostatic potential, \( Y \) is some appropriate space of periodic functions, the second last term accounts for the self energy of the nuclei and the last term corrects for overlapping charge density of nuclei. A detailed discussion on the nature of \( \mathcal{E}^*_{c}(R) \) and its evaluation can be found in Appendix B. With this reformulation of the total electrostatic energy, we arrive at the variational problem

\[ \mathcal{E}(u, R) = \left\{ \sup_{\phi \in Y} J(u, R, \phi) + \mu T_{LR}(u) \right\}, \]  

where the functional

\[ J(u, R, \phi) = C_F \int_{\Omega} u^{10/3} \, dx + \frac{\lambda}{2} \int_{\Omega} |\nabla u(x)|^2 \, dx + \int_{\Omega} \varepsilon_{xc}(u(x)) u^2(x) \, dx - \frac{1}{8\pi} \int_{\Omega} |\nabla \phi(x)|^2 \, dx + \int_{\Omega} (u^2(x) + b(x, R)) \phi(x) \, dx - \frac{1}{2} \sum_J \int_{\Omega} b_J(x, R_J) V_J(x, R_J) \, dx + \mathcal{E}^*_{c}(R). \]  

3.3. OF-DFT ground-state

In the above described framework, the variational problem for determining the ground-state in OF-DFT can be written as

\[ \mathcal{E}_0 = \inf_{R \in \mathbb{R}^{3M_a}} \mathcal{E}^{\ast}(R), \]
Through this decomposition, the ground-state can be ascertained by solving the electronic structure problem in Eqn. 34 for every configuration of the nuclei encountered during the geometry optimization described by Eqn. 33. Below, we discuss local real-space approaches for each of these variational problems.

3.3.1. Electronic structure problem

Consider the variational problem in Eqn. 34 for determining the electronic ground-state. On taking the first variation, we arrive at the Euler-Lagrange equation

\[
\mathcal{H} u(x) = \eta u(x), \quad \mathcal{H} = -\frac{\lambda}{2} \nabla^2 + \left( V_{TF}(x) + \mu V_{LR}(x) + V_{xc}(x) + \phi(x) \right),
\]

where \( \eta \) is a Lagrange multiplier used to enforce the constraint \( C(u) = 0 \). Further, \( V_{LR}(x) \) is given by Eqn. 26, \( \phi(x) \) is the solution of the Poisson equation

\[
\frac{-1}{4\pi} \nabla^2 \phi(x) = u^2(x) + b(x, R)
\]

under periodic boundary conditions and

\[
V_{TF}(x) = \frac{\delta T_{TF}(u)}{\delta u^2} = \frac{5}{3} C_F u^{4/3}(x),
\]

\[
V_{xc}(x) = \frac{\delta E_{xc}(u)}{\delta u^2} = V_x(x) + V_c(x).
\]

In the above equation, \( V_{xc}(x) \) is the exchange-correlation potential with

\[
V_x(x) = - \left( \frac{3}{\pi} \right)^{1/3} u^{2/3}(x),
\]

\[
V_c(x) = \begin{cases} 
\gamma_1 + \frac{7}{3} \beta_1 \sqrt{r_s(x)} + \frac{4}{3} \alpha_3 \beta_2 r_s(x) \\
(1 + \beta_1 \sqrt{r_s(x)} + \beta_2 r_s(x))^2 
\end{cases}, \quad r_s(x) \geq 1
\]

\[
\left( A_1 + \frac{2}{3} C_1 r_s(x) \right) \log r_s(x) + \left( B_1 - \frac{1}{3} A_1 \right) + \frac{4}{3} (2D_1 - C_1) r_s(x), \quad r_s(x) < 1
\]

being the exchange and correlation potentials respectively. Even though the notation does not make it explicit, the dependence of \( \mathcal{H} \) on \( u \) makes Eqn. 35 a non-linear problem. Also, since

\[
\int_\Omega (\rho(x) + b(x, R)) \, dx = 0,
\]

the Poisson equation in Eqn. 36 with periodic boundary conditions is a well-posed problem.

The electronic ground-state can be determined by solving the non-linear eigenvalue problem in Eqn. 35 for the eigenfunction corresponding to the lowest eigenvalue. Irrespective of the technique and choice of kinetic energy functional, \( \phi(x) \) needs to be recalculated for every update in \( u(x) \). Additionally, when linear-response kinetic energy functionals are employed, \( V_{LR}(x) \) needs to be reevaluated every time \( u(x) \) is updated. Therefore, the solution of Eqn. 35 requires the repeated solution of the Poisson equation in Eqn. 36 and the complex-valued non-Hermitian Helmholtz equations in Eqns. 22 and 23. In view of this, the self-consistent field method (SCF) [46] commonly employed in DFT calculations is an attractive choice.
because of the relatively few iterations that are typically required for convergence. However, we have found such an approach to be unstable for both the TFW and WGC kinetic energy functionals, especially as the system size is increased. Since the number of Helmholtz equations that need to be solved to determine $V_{LR}(x)$ can be significantly large in practice (e.g. fifty-two in this work), they are expected to completely dominate the execution time. In order to mitigate this, we present below a fixed-point method with respect to $V_{LR}(x)$ to determine the electronic ground-state [47]. This is similar in spirit to the SCF method, and is found to converge rapidly, as demonstrated by the examples in Section 5.

In simulations which employ linear-response kinetic energy functionals, we define a fixed-point problem of the form

$$V_{LR} = \mathcal{V}[\mathcal{U}(V_{LR})],$$

where the mappings

$$\mathcal{U}(V_{LR}) = \arg \inf_{u \in \mathcal{X}} \left\{ \sup_{\phi \in \mathcal{Y}} \mathcal{F}(u, R, \phi) + \mu \int_{\Omega} V_{LR}(x) u^2(x) \, dx \right\},$$

and

$$\mathcal{V}[u] = C_F \sum_{m=0}^{L} \sum_{n=0}^{L} \sum_{p=0}^{m} \sum_{q=0}^{n} \sum_{r=0}^{n} C_{mnpq} \left[ (m - p + \alpha) u^2(m-p+\alpha-1)(x) V_{mnqbr}(x) \right. + \left. (n - q + \beta) u^2(n-q+\beta-1)(x) V_{mnpor}(x) \right].$$

In the above expression, $V_{mnqbr}(x)$ and $V_{mnpor}(x)$ are solutions to the Helmholtz equations given in Eqns. 22 and 23 respectively. We note that the Euler-Lagrange equations of the variational problem in Eqn. 43 and the OF-DFT electronic structure problem in Eqn. 34 are identical. It follows that the solution of the fixed-point problem will correspond to the ground-state kernel potential $V_{LR}^*(x)$ and ground-state square-root electron density $u^*(x)$. In order to solve this fixed-point problem, we treat it as a non-linear equation and adopt an iteration of the form [46, 48]

$$V_{LR,k+1} = V_{LR,k} - C_k \left( \mathcal{V}[\mathcal{U}(V_{LR,k})] - V_{LR,k} \right),$$

where the index $k$ represents the iteration number and $C_k$ is appropriately chosen to ensure/accelerate convergence. Once the fixed-point $V_{LR}^*(x)$ has been determined, $u^*(x)$ can be calculated by solving Eqn. 43 for $V_{LR}(x) = V_{LR}^*(x)$. In Fig. 1, we present a flowchart that outlines the aforesaid fixed-point approach. It is worth noting that for the choice of TFW kinetic energy functional ($\mu = 0$), the solution of Eqn. 43 immediately provides the electronic ground-state.

After determining the electronic ground-state square-root electron density $u^*(x)$, the corresponding energy can be evaluated using the expression

$$\mathcal{E}^*(R) = C_F \int_{\Omega} u^{10/3}(x) \, dx + \frac{\lambda}{2} \int_{\Omega} |\nabla u^*(x)|^2 \, dx + \mu \sum_{m=0}^{L} \sum_{n=0}^{L} \sum_{p=0}^{m} \sum_{q=0}^{n} \sum_{r=0}^{n} C_{mnpq} \int_{\Omega} \left[ u^2(m-p+\alpha)(x) V_{mnqbr}(x) + u^2(n-q+\beta)(x) V_{mnpor}(x) \right] \, dx$$

$$+ \int_{\Omega} \varepsilon_{xc}(u^*(x)) u^2(x) \, dx + \frac{1}{2} \int_{\Omega} \left( u^2(x) + b(x, R) \right) \phi^*(x) \, dx$$

$$- \frac{1}{2} \sum_{j} \int_{\Omega} b_j(x, R_j) V_j(x, R_j) \, dx + \mathcal{E}_c^*(R),$$

(46)
where $V_{mnpq}^*(x), V_{mnpq}^*(x)$ and $\phi^*(x)$ are solutions of Eqns. 22, 23 and 36 respectively for $u(x) = u^*(x)$.

$$
\begin{align*}
\text{Generate guess } u_0 & \quad V_{LR,0} = V[u_0] \\
\text{Constrained minimization} & \quad u_{k+1} = \arg \inf_{u \in X} \hat{E}(u, R, V_{LR,k}) \\
\text{Solve the Helmholtz equations:} & \quad V_{LR,k+1} = V[u_{k+1}] \\
\epsilon & = \frac{||V_{LR,k+1} - V_{LR,k}||}{||V_{LR,k}||} \\
\epsilon < \text{tol} ? & \quad \text{No} \quad \text{Yes} \\
\text{Calculate} & \quad \text{(i) Energy } \hat{E}^*(R) \\
& \quad \text{(ii) Forces } f_j
\end{align*}
$$

Figure 1: Fixed-point iteration for determining the electronic ground state when using linear-response kinetic energy functionals. The functional $\hat{E}(u, R, V_{LR,k}) = \{\sup_{\phi \in Y} F(u, R, \phi) + \int_{\Omega} V_{LR,k}(x)u^2(x) \, dx\}$.

3.3.2. Geometry optimization: forces on nuclei

Consider the minimization problem in Eqn. 33 for determining the equilibrium configuration of the atoms. During this geometry optimization, the forces on the nuclei can be determined using the relation

$$
f_J = -\frac{\partial \hat{E}^*(R)}{\partial R_J} = -\sum_{J'} \int_{\Omega} \frac{\partial b_{J'}(x, R_J)}{\partial R_{J'}} (\phi^*(x) - V_{J'}(x, R_J)) \, dx + f_J^c, $$

$$
= \sum_{J'} \int_{\Omega} \nabla b_{J'}(x, R_J) (\phi^*(x) - V_{J'}(x, R_J)) \, dx + f_J^c, 
$$

(47)

where $f_J$ denotes the force on the $J^{th}$ nucleus and the summation over $J'$ signifies the $J^{th}$ atom and its periodic images. Additionally, $\phi^*(x)$ is the solution of the Poisson equation in Eqn. 36 for $u(x) = u^*(x)$.
and

\[ f^c_J = -\frac{\partial E^*_c(R)}{\partial R_J} \]  (48)

corrects for the error in forces due to overlapping charge density of nuclei. The expression for this correction has been derived in Appendix B. The last equality in Eqn. 47 is obtained by using the spherical symmetry of \( b_J(x, R, R') \). Since \( \nabla b_J(x, R, R') \) has compact support in a ball of radius \( r_c \) centered at \( R_r \), only a finite number of periodic images of the \( J^{th} \) atom have an overlap with \( \Omega \). Therefore, similar to the calculation of the electronic ground state, evaluation of the forces on the nuclei is amenable to a linear-scaling real-space implementation.

4. Numerical Implementation

In this section, we describe a higher-order finite-difference implementation of the formulation presented in the previous section. We restrict our computation to a cuboidal domain \( \Omega \) of sides \( L_1, L_2 \) and \( L_3 \). We generate a uniform finite-difference grid with spacing \( h \) such that \( L_1 = n_1h \), \( L_2 = n_2h \) and \( L_3 = n_3h \), where \( n_1, n_2 \) and \( n_3 \) are natural numbers. We index the grid points by \((i,j,k)\), where \( i = 1,2,\ldots,n_1, j = 1,2,\ldots,n_2 \) and \( k = 1,2,\ldots,n_3 \). We approximate the Laplacian of any function \( f(x) \) at the grid point \((i,j,k)\) using higher-order finite-differences [49]

\[ \nabla^2 f|^{(i,j,k)} \approx \sum_{p=0}^N \overline{w}_p \left( f^{(i+p,j,k)} + f^{(i-p,j,k)} + f^{(i,j+p,k)} + f^{(i,j,k+p)} + f^{(i,j,k-p)} \right), \]  (49)

where \( f^{(i,j,k)} \) represents the value of the function \( f(x) \) at the grid point \((i,j,k)\). The weights \( \overline{w}_p \) are given by [50, 51, 28]

\[ \overline{w}_0 = -\frac{1}{h^2} \sum_{q=1}^{N} \frac{1}{q^2}, \]

\[ \overline{w}_p = \frac{2(-1)^{p+1}}{h^2p^2} \frac{(N!)^2}{(N-p)!(N+p)!}, \quad p = 1,2,\ldots,N. \]  (50)

Similarly, we approximate the gradient at the grid point \((i,j,k)\) using higher-order finite-differences

\[ \nabla f|^{(i,j,k)} \approx \sum_{p=1}^N \tilde{w}_p \left( (f^{(i+p,j,k)} - f^{(i-p,j,k)})\hat{e}_1 + (f^{(i,j+p,k)} - f^{(i,j-p,k)})\hat{e}_2 + (f^{(i,j,k+p)} - f^{(i,j,k-p)})\hat{e}_3 \right), \]  (51)

where \( \hat{e}_1, \hat{e}_2 \) and \( \hat{e}_3 \) represent unit vectors along the edges of the cuboidal domain \( \Omega \). The weights \( \tilde{w}_p \) are given by [50, 51, 28]

\[ \tilde{w}_p = \frac{(-1)^{p+1}}{hp} \frac{(N!)^2}{(N-p)!(N+p)!}, \quad p = 1,2,\ldots,N. \]  (52)

These finite-difference expressions for the Laplacian and gradient represent \( 2N \) order accurate approximations, i.e. error is \( \mathcal{O}(h^{2N}) \). While performing spatial integrations, we assume that the function \( f(x) \) is constant in a cube of side \( h \) around each grid point i.e.

\[ \int_{\Omega} f(x) \, dx \approx h^3 \sum_{i=1}^{n_1} \sum_{j=1}^{n_2} \sum_{k=1}^{n_3} f^{(i,j,k)}. \]  (53)
We enforce periodic boundary conditions on $\Omega$ by employing the following strategy. In the finite-difference representations of the Laplacian and gradient as presented in Eqns. 49 and 51 respectively, we map any index that does not correspond to a node in the finite-difference grid to its periodic image within $\Omega$.

We start with precomputed radially-symmetric and compactly-supported isolated-atom electron densities for each type of atom. We superimpose these isolated-atom electron densities for the initial configuration of the nuclei, and scale the resulting electron density such that the constraint on the total number of electrons is satisfied. We take the pointwise square-root of the electron density so obtained as the starting guess $u_0^{(i,j,k)}$. During the aforesaid calculation, we only visit atoms whose isolated-atom electron densities have non-zero overlap with $\Omega$. Similarly, for every new configuration of atoms encountered during the geometry optimization, we calculate the charge density of the nuclei using the relations

$$b^{(i,j,k)} = \sum_j b_j^{(i,j,k)}, \quad b_j^{(i,j,k)} = -\frac{1}{4\pi} \nabla^2 V_j^{(i,j,k)},$$  

where the summation reduces to all atoms whose charge density has non-zero overlap with $\Omega$. The localized nature of the above operations ensures that the evaluation of $u_0^{(i,j,k)}$ and $b^{(i,j,k)}$ scales linearly with the number of atoms.

We solve the variational problem in Eqn. 43 using a conjugate gradient method that was originally developed for DFT [52, 53] and later adopted in simplified form for OF-DFT [14, 54, 24]. Specifically, we utilize the Polak-Ribiere update [55] with Brent’s method [56] for the line-search. We refer the reader to Appendix C for further details on the algorithm implemented in this work. For every update in the square-root electron density, we solve the Poisson equation in Eqn. 36 under periodic boundary conditions using the Generalized minimal residual method (GMRES) [57] with the block-Jacobi preconditioner [58]. Since the solution so obtained is accurate to within an indeterminate constant, we enforce the condition $\int_\Omega \phi(x) \, dx = 0$ for definiteness. In every subsequent Poisson equation encountered, we use the previous solution as starting guess. For the complex-valued Helmholtz equations in Eqns. 22 and 23, we first separate out each equation into its real and imaginary parts. Then we solve the resulting coupled equations simultaneously under periodic boundary conditions using the GMRES method with block-Jacobi preconditioners. In every iteration of the fixed-point method, we use the solution of the Helmholtz equations from the previous iteration as the starting guess. We accelerate the convergence of the fixed-point iteration by utilizing Anderson mixing [59], details of which can be found in Appendix D.

Once the electronic ground-state square-root electron density has been determined, the energy and forces are evaluated using Eqns. 46 and 47 respectively. While doing so, we restrict the summation over the periodic images to atoms whose charge density has non-zero overlap with $\Omega$. We solve for the equilibrium configuration of the atoms by using the conjugate gradient method with the Polak-Ribiere update and secant line search [55]. We have developed a parallel implementation of the proposed approach using the Portable, Extensible Toolkit for scientific computations (PETSc) [60, 61] suite of data structures and routines. Within PETSc, we have utilized distributed arrays with the star-type stencil option. The communication between the processors is handled via the Message Passing Interface (MPI) [62].

5. Examples and Results

In this section, we validate the proposed formulation and higher-order finite-difference implementation of periodic OF-DFT through selected examples. We shall refer to the implementation developed in this work as RS-FD, which is an acronym for Real-Space Finite-Differences. In all the simulations, we employ the Goodwin-Needs-Heine pseudopotential [63] and wherever applicable, we compare our results with the
plane-wave code PROFESS [24, 25]. We choose $\lambda = \frac{1}{2}$ for the TFW functional, and $\lambda = 1$, $L = 2$, $R = 4$, $\alpha = \frac{5}{6} + \sqrt{\frac{5}{6}}$ and $\beta = \frac{5}{6} - \sqrt{\frac{5}{6}}$ for the WGC functional. Within PROFESS, we utilize a plane-wave energy cutoff of $E_{\text{cut}} = 1200$ eV, which results in energies and forces that are converged to within $1 \times 10^{-6}$ eV/atom and $6 \times 10^{-4}$ eV/Bohr respectively. Unless specified otherwise, we use sixth-order accurate finite-differences and a mesh size $h = 0.5$ Bohr within RS-FD, which results in energies and forces that are converged to within $0.006$ eV/atom and $0.007$ eV/Bohr respectively.

5.1. Convergence of energy with spatial discretization

We start by verifying convergence of the computed energy with respect to the finite-difference approximation. We choose a FCC unit cell of Aluminum with lattice constant $a = 8.0$ Bohr as the representative example. We evaluate the energy of this system as a function of mesh size $h$ for the TFW and WGC kinetic energy functionals while utilizing second and sixth order accurate finite-differences. Anticipating polynomial convergence with respect to $h$, we fit the data to a power law of the form

$$E = C_E h^p + E_c,$$  \hspace{1cm} (55)

where the prefactor $C_E$, convergence rate $p$, and estimate of the $h \rightarrow 0$ energy $E_c$ are the parameters to be fitted. We present the results so obtained in Table 1, and verify the quality of the fit in Fig. 2. In this plot, we have utilized $E_c$ as the reference value and $h_0 = 0.08$ Bohr to normalize the mesh size.

When the electronic kinetic energy is modeled using the TFW functional, sixth-order accurate finite-differences is able to achieve significantly higher rates of convergence compared to second-order finite-differences. In fact, the extrapolated value of $E_c = -60.2210$ eV/atom for sixth-order finite-differences is in good agreement with energy $E = -60.2207$ eV/atom obtained by PROFESS. However, the extrapolated value of $E_c = -60.2535$ for second-order finite-differences is appreciably different. This indicates that even finer meshes are required for an accurate extrapolation. Irrespective of this issue, it can be concluded from Fig. 2 that second-order finite-differences will be prohibitively expensive for obtaining the chemical accuracies desired in OF-DFT calculations. Notably, higher-order finite-differences are able to perform equally well when the WGC kinetic energy functional is employed. In particular, sixth-order finite-differences is able to achieve a convergence rate of $p = 4.96$ with respect to the mesh-size. Further, the predicted value of $E_c = -58.2671$ eV/atom is in good agreement with the energy $E = -58.2658$ eV/atom calculated by PROFESS.

Overall, we conclude that higher-order finite-differences are necessary for performing accurate and efficient electronic structure calculations based on OF-DFT. Indeed, larger convergence rates may be possible as the order of the finite-difference approximation is increased. However, this comes at the price of increased computational cost per iteration due to the reduced locality of the discretized operators and larger inter-processor communication. We have found sixth-order finite-differences to be an efficient choice, which is in agreement with our previous conclusions for the non-periodic setting [28]. In view of this, we will employ sixth-order finite-differences for the remaining simulations in this work.

5.2. Convergence of forces with spatial discretization

In this study, we verify the convergence of the forces with respect to the finite-difference discretization. Specifically, we choose an Aluminum dimer with bond length of $R = 8.0$ Bohr as the representative example. We employ the TFW kinetic energy functional, choose a domain such that the minimum distance between any atom and the boundary is 12.0 Bohr, and use sixth-order accurate finite-differences. We calculate the interatomic force $f$ for different mesh sizes $h$ and fit the data to a power law of the form

$$f = C_f h^q + f_c,$$  \hspace{1cm} (56)

12
Table 1: Parameters for the convergence in energy obtained by fitting Eqn. 55. The system under consideration is a single FCC unit cell of Aluminum with lattice constant \(a = 8.0\) Bohr.

| Kinetic energy functional | FD order | \(C_f\)     | \(q\) | \(\mathcal{E}_c\) (eV/atom) |
|--------------------------|----------|--------------|--------|-------------------------------|
| TFW                      | Second   | +0.1557      | 1.01   | \(-60.2535\)                 |
| TFW                      | Sixth    | -0.2121      | 5.46   | \(-60.2210\)                 |
| WGC                      | Sixth    | -0.1206      | 4.96   | \(-58.2671\)                 |

Table 2: Parameters for the convergence in the interatomic force obtained by fitting Eqn. 56. The system under consideration is an Aluminum dimer with bond length \(R = 8.0\) Bohr.

| Kinetic energy functional | FD order | \(C_f\) | \(q\) | \(f_c\) (eV/Bohr) |
|--------------------------|----------|---------|--------|-------------------|
| TFW                      | Sixth    | 0.0147  | 4.99   | 0.1220            |

Figure 2: Convergence in the energy as a function of mesh size for a single FCC unit cell of Aluminum with lattice constant \(a = 8.0\) Bohr.

where the prefactor \(C_f\), convergence rate \(q\), and estimate of the \(h \rightarrow 0\) force \(f_c\) are the parameters to be fitted. We present the results so obtained in Table 2, which demonstrates that the error in the force scales as \(O(h^5)\). Additionally, the value of \(f_c = 0.1220\) eV/Bohr is in good agreement with the force of \(f = 0.1224\) eV/Bohr calculated by PROFESS. Overall, we conclude that higher-order finite-differences are capable of achieving relatively large convergence rates in both the energies and the forces. This feature along with the notable simplicity in implementation makes them very attractive for performing electronic structure calculations based on OF-DFT.

5.2.1. Convergence of the fixed-point method

We now demonstrate convergence of the fixed-point method for simulations involving the WGC kinetic energy functional. We choose two examples, namely a supercell consisting of \(6 \times 6 \times 6\) FCC Aluminum unit cells with and without a vacancy. We utilize a lattice constant of \(a = 7.50\) Bohr, mesh-size of \(h = 0.5\) Bohr, and history of three iterations for Anderson mixing. In Fig. 4, we present the error in the fixed-point iteration for the two aforementioned examples. Specifically, we compare the performance of Anderson mixing with the standard fixed-point iteration, i.e. without mixing. We observe that Anderson mixing significantly accelerates the convergence of the fixed-point iteration, with the mixing parameter \(\zeta = 1\) demonstrating the
best performance. We have found these results to be representative of other simulations utilizing the WGC kinetic energy functional. In view of this, we will utilize Anderson mixing with $\zeta = 1$ for the remaining simulations in this work. It is worth noting that using a larger number of previous iterates in Anderson mixing has the potential to further reduce the number of fixed-point iterations required for convergence.

In this work, we have presented a fixed-point iteration with respect to $V_{LR}(x)$ for simulations involving linear-response kinetic energy functionals. However, it is also possible to develop an analogous fixed-point iteration with respect to $u(x)$. In Table 3, we compare the performances of the fixed-point iterations with respect to $u(x)$ and $V_{LR}(x)$ for a couple of examples employing the WGC kinetic energy functional. In both cases, we have employed Anderson mixing with a history of three iterations. We can see that the relative performance of each of the fixed-point choices is system dependent. However, we have found the fixed-point iteration with respect to $V_{LR}(x)$ to be significantly more robust than the one with respect to $u(x)$. Therefore, we have chosen the fixed-point iteration with respect to $V_{LR}(x)$ for all simulations involving the
WGC kinetic energy functional.

| System | Fixed-point iterations for $u$ | Fixed-point iterations for $V_{LR}$ |
|--------|-------------------------------|-------------------------------------|
| $3 \times 3 \times 3$ FCC unit cells perfect crystal | 15 | 22 |
| $6 \times 6 \times 6$ FCC unit cells with a vacancy | 29 | 18 |

Table 3: Comparison of the performances for different fixed-point iterations accelerated by Anderson mixing. The atoms are held fixed in their original lattice positions.

5.3. Examples

5.3.1. Aluminum clusters

First, we study Aluminum clusters consisting of $M_a = 14, 172, 666, 1688$ and $3430$ atoms that are arranged as $1 \times 1 \times 1, 3 \times 3 \times 3, 5 \times 5 \times 5, 7 \times 7 \times 7$ and $9 \times 9 \times 9$ FCC unit cells of Aluminum respectively. The atoms are held fixed, with the lattice constants chosen to minimize the energy \[ 64 \]. Further, the size of the cubical domains are such that the minimum distance of any atom to the boundary is $12$ Bohr. In order to avoid the vacuum resulting divergences encountered when using the WGC functional, we employ the TFW kinetic energy functional. In Tables 4 and 5, we compare the energies and forces as computed by RS-FD with PROFESS. It is clear that there is very good agreement in the energies and forces. In particular, the maximum difference in the energy is $0.005$ eV/atom with the difference in the forces being $0.00160$ eV/Bohr ($l_1$ norm), $0.00013$ eV/Bohr ($l_2$ norm) and $0.00683$ eV/Bohr ($sup$ norm).

| FCC Aluminum unit cells | No. of atoms ($M_a$) | $a_e$ (Bohr) | $\mathcal{E}$ (eV/atom) | $\mathcal{E}$ (eV/atom) |
|-------------------------|----------------------|-------------|-------------------------|-------------------------|
|                         |                      |             | RS-FD                   | PROFESS                 |
| $1 \times 1 \times 1$   | 14                   | 7.73        | -59.246                 | -59.241                 |
| $3 \times 3 \times 3$   | 172                  | 7.89        | -59.813                 | -59.808                 |
| $5 \times 5 \times 5$   | 666                  | 7.93        | -59.965                 | -59.960                 |
| $7 \times 7 \times 7$   | 1688                 | 7.95        | -60.035                 | -60.030                 |
| $9 \times 9 \times 9$   | 3430                 | 7.96        | -60.075                 | -60.071                 |

Table 4: Energy of $m \times m \times m$ FCC Aluminum unit cell clusters, where $m = 1, 3, 5, 7$ and 9.

| FCC Aluminum unit cells | $l_1$ norm/($3M_a$) (eV/Bohr) | $l_2$ norm/($3M_a$) (eV/Bohr) | $sup$ norm (eV/Bohr) |
|-------------------------|-------------------------------|-------------------------------|----------------------|
| $1 \times 1 \times 1$   | 0.00070                       | 0.00013                       | 0.00133               |
| $3 \times 3 \times 3$   | 0.00082                       | 0.00004                       | 0.00211               |
| $5 \times 5 \times 5$   | 0.00160                       | 0.00004                       | 0.00409               |
| $7 \times 7 \times 7$   | 0.00038                       | 0.00001                       | 0.00217               |
| $9 \times 9 \times 9$   | 0.00158                       | 0.00002                       | 0.00683               |

Table 5: Comparison of forces with PROFESS for $m \times m \times m$ FCC Aluminum unit cell clusters, where $m = 1, 3, 5, 7$ and 9.

5.3.2. Aluminum crystal

Next, we calculate the bulk properties of FCC Aluminum for the TFW and WGC kinetic energy functionals using a supercell consisting of $5 \times 5 \times 5$ FCC Aluminum unit cells ($M_a = 600$). We start by
calculating the energy $E$ using RS-FD and PROFESS for various lattice constants $a$, the results of which are presented in Fig. 5. Next, we employ a cubic fit to the data to determine the equilibrium lattice constant $a_e$ and the bulk modulus $B$.

$$B = \frac{4}{9a_e} \frac{\partial^2 E}{\partial a^2} \bigg|_{a_e} .$$

(57)

It is evident from the results in Table 6 that the predictions of RS-FD are in very good agreement with PROFESS. In fact, the equilibrium lattice constants are identical to within 0.01 Bohr for both the TFW and WGC functionals. The difference in the energy for the TFW and WGC functionals is 0.005 eV/atom and 0.003 eV/atom respectively, with the difference in the bulk modulus being 0.006 GPa and 0.859 GPa respectively. The slight difference in bulk modulus for the WGC functional can be attributed to the fact that RS-FD approximates the kernels $K_{mn}(|x - x'|)$ in Fourier space using rational functions. Indeed, we anticipate that using a larger number of rational functions to approximate $K_{mn}(|x - x'|)$ will further improve the agreement between RS-FD and PROFESS.

![Figure 5: Variation of energy with lattice constant for FCC Aluminum.](image)

**Table 6: Bulk properties of FCC Aluminum.**

| Kinetic energy functional | Method  | $\mathcal{E}$ (eV/atom) | $a_e$ (Bohr) | $B$ (GPa) |
|---------------------------|---------|-------------------------|-------------|-----------|
| TFW                       | RS-FD   | $-60.226$               | 8.00        | 57.3      |
|                           | PROFESS | $-60.221$               | 8.00        | 57.3      |
| WGC                       | RS-FD   | $-58.335$               | 7.62        | 68.1      |
|                           | PROFESS | $-58.332$               | 7.62        | 68.9      |

**5.3.3. Vacancy formation energy in Aluminum**

Finally, we calculate the vacancy formation energy in stress-free FCC Aluminum. We consider a supercell consisting $6 \times 6 \times 6$ FCC Aluminum unit cells ($M_a = 864$), and remove an atom from the center to create a vacancy. We calculate the vacancy formation energy $\mathcal{E}_{vf}$ using the relation [65, 66]

$$\mathcal{E}_{vf} = \mathcal{E} \left( M_a - 1, 1, \frac{M_a - 1}{M_a} \Omega \right) - \left( \frac{M_a - 1}{M_a} \right) \mathcal{E}(M_a, 0, \Omega) ,$$

(58)
where $E(M_a, n, \Omega)$ is used to denote the energy of a periodic cell $\Omega$ with $M_a$ occupied lattice sites and $n$ vacancies. We present the results so obtained in Table 7, and plot the electron density contours on the mid-plane for the TFW and WGC kinetic energy functionals in Figs. 6 and 7 respectively. We observe that the computed vacancy formation energies are in good agreement with PROFESS. In fact, the relaxed vacancy formation energies are identical to within 0.01 eV and 0.02 eV when using the TFW and WGC functionals respectively. As discussed in the previous section, the larger discrepancy in WGC can be attributed to the approximate kernels $K_{mn}(|x - x'|)$ employed in RS-FD. From the final relaxed configuration of the atoms, we find that the average $l_2$ norm of the difference in the positions of the nuclei obtained by RS-FD and PROFESS to be $4.6 \times 10^{-5}$ Bohr for TFW functional case and $7.0 \times 10^{-6}$ Bohr for WGC functional.

| Kinetic energy functional | Method  | $a_e$ (Bohr) | $E_{vf}$ (unrelaxed) (eV) | $E_{vf}$ (relaxed) (eV) |
|--------------------------|---------|--------------|--------------------------|--------------------------|
| TFW                      | RS-FD   | 8.00         | 0.87                     | 0.83                     |
|                          | PROFESS | 8.00         | 0.87                     | 0.83                     |
| WGC                      | RS-FD   | 7.62         | 0.60                     | 0.49                     |
|                          | PROFESS | 7.62         | 0.59                     | 0.47                     |

Table 7: Vacancy formation energy in stress-free FCC Aluminum

Figure 6: Electron density contours on the mid-plane of FCC Aluminum with a vacancy. The TFW kinetic energy functional has been employed.
Figure 7: Electron density contours on the mid-plane of FCC Aluminum with a vacancy. The WGC kinetic energy functional has been employed.

6. Concluding Remarks

We have presented a real-space formulation and higher-order finite-difference implementation of periodic Orbital-free Density Functional Theory (OF-DFT). Specifically, utilizing a local reformulation of the electrostatics and kernel energy/potential, we have developed a generalized framework for performing OF-DFT simulations that is able to accommodate the different variants of the electronic kinetic energy. In particular, for linear-response kinetic energy functionals, we have developed a fixed-point technique that is similar in spirit to the self-consistent field (SCF) method employed in DFT calculations. We have also developed a parallel finite-difference implementation of this formulation, using which we have demonstrated that higher-order finite-differences can achieve relatively large convergence rates with respect to mesh-size in both the energies and forces. Additionally, we have established that the fixed-point iteration converges rapidly, and that it can be further accelerated using extrapolation schemes like Anderson mixing. We have validated the accuracy of our results by comparing the energies and forces with plane-wave methods for selected examples.

Overall, we conclude that higher-order finite-differences are an attractive choice for performing electronic structure calculations based on OF-DFT. This is due to their simplicity, potential for scalability to massively-parallel distributed-memory computer architectures, and ability to efficiently achieve chemical accuracies desired in electronic structure calculations. One limitation of the developed implementation is the lack of an effective real-space preconditioner, which is currently being pursued by the authors. Finally, we note that extending the current work to finite-temperatures and therefore enabling molecular dynamics simulations is a worthy subject of future research.

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A. Coefficients in the Helmholtz equations for the WGC kinetic energy functional

The coefficients $P_{mnr}$ and $Q_{mnr}$ arising in the Helmholtz equations given in Eqns. 22 and 23 are determined by fitting the kernels $K_{mn}(|\mathbf{x} - \mathbf{x}'|)$ in Fourier space using rational functions [40]. In Table 8, we present the values for the WGC functional when a fourth-order expansion ($R = 4$) is employed. The coefficients satisfy the relations $P_{mnr} = P_{nmr}$ and $Q_{mnr} = Q_{nmr}$, with $P_{mn2} = P_{mn1}^*$, $Q_{mn2} = Q_{mn1}^*$, $P_{mn4} = P_{mn3}^*$ and $Q_{mn4} = Q_{mn3}^*$. Here, the superscript * denotes the complex conjugate.

| Coefficients | $r = 1$ | $r = 3$ |
|--------------|---------|---------|
| $P_{00r}$    | +0.108403 + i0.079657 | −0.908403 + i0.439708 |
| $Q_{00r}$    | −0.470923 − i0.465392 | +0.066051 − i0.259678 |
| $P_{10r}$    | −0.030515 + i0.015027 | +0.028915 − i0.008817 |
| $Q_{10r}$    | −0.597793 − i0.294130 | −0.087917 − i0.164937 |
| $P_{20r}$    | +0.008907 − i0.032841 | −0.034974 + i0.009116 |
| $Q_{20r}$    | −0.537986 − i0.233840 | −0.041565 − i0.196662 |
| $P_{11r}$    | +0.012423 − i0.034421 | −0.031907 + i0.007392 |
| $Q_{11r}$    | −0.511699 − i0.0266195 | −0.034031 − i0.188927 |

Table 8: Coefficients in the Helmholtz equations (Eqns. 22 and 23) for the WGC kinetic energy functional [40].

B. Electrostatic correction for overlapping charge density of nuclei

In the local electrostatic reformulation presented in Section 3.2, the repulsive energy can be expressed as

$$
\mathcal{E}_{zz}(\mathbf{R}) = \frac{1}{2} \int_{\Omega} \left( \sum_{I} \sum_{J} I_{J} b_I(\mathbf{x}, \mathbf{R}_I) V_J(\mathbf{x}, \mathbf{R}_J) \right) d\mathbf{x} - \frac{1}{2} \sum_{J} \int_{\Omega} b_I(\mathbf{x}, \mathbf{R}_I) V_J(\mathbf{x}, \mathbf{R}_J) d\mathbf{x},
$$

(59)

where the second term accounts for the self energy of the nuclei. Using Eqn. 28, we arrive at

$$
\mathcal{E}_{zz}(\mathbf{R}) = \frac{1}{2} \sum_{I} \sum_{J} I_{J} b_I(\mathbf{x}, \mathbf{R}_I) V_J(\mathbf{x}, \mathbf{R}_J) d\mathbf{x} - \frac{1}{2} \sum_{J} \int_{\Omega} b_I(\mathbf{x}, \mathbf{R}_I) V_J(\mathbf{x}, \mathbf{R}_J) d\mathbf{x}
$$

(60)

$$
= \frac{1}{2} \sum_{I} \sum_{J \neq I} I_{J} b_I(\mathbf{x}, \mathbf{R}_I) V_J(\mathbf{x}, \mathbf{R}_J) d\mathbf{x}.
$$

Above, the summations over $I$ and $J$ extends to all atoms in $\mathbb{R}^3$. If the charge density of the nuclei do not overlap, Eqn. 60 can be rewritten as

$$
\mathcal{E}_{zz}(\mathbf{R}) = \frac{1}{2} \sum_{I} \sum_{J \neq I} Z_J \int_{\Omega} b_I(\mathbf{x}, \mathbf{R}_I) V_J(\mathbf{x}, \mathbf{R}_J) d\mathbf{x} = \frac{1}{2} \sum_{I} \sum_{J \neq I} Z_J I_{J} V_I(\mathbf{R}_J, \mathbf{R}_I)
$$

$$
= \frac{1}{2} \sum_{I} \sum_{J \neq I} Z_I Z_J I_{J} I_{J} \frac{1}{|\mathbf{R}_I - \mathbf{R}_J|},
$$

(61)

which is exactly the expression given in Eqn. 14 for the repulsive energy prior to reformulation. However, the use of relatively ‘soft’ pseudopotentials — which are attractive because of the significant reduction in the
number of basis functions required for convergence — can frequently result in overlapping charge density of
the nuclei. In this situation, the repulsive energy and the forces on the nuclei will be inaccurately calculated.
Below, we present a technique to correct for these errors.

We start by generating a ‘reference’ charge density
\[ \tilde{b}(x, R) = \sum_J \tilde{b}_J(x, R_J), \]  
which is the superposition of spherically symmetric and compactly supported ‘reference’ charge densities \( \tilde{b}_J(x, R_J) \). These nuclei-centered charge densities satisfy the relations
\[ \int_{\mathbb{R}^3} \tilde{b}_J(x, R_J) \, dx = Z_J, \quad \int_{\Omega} \tilde{b}(x, R) \, dx = N_e. \]

Thereafter, the correction to the repulsive energy can be expressed as
\[ E^*_c(R) = \frac{1}{2} \int_{\Omega} \left( \tilde{b}(x, R) + b(x, R) \right) V_c(x, R) \, dx + \frac{1}{2} \sum_J \int_{\Omega} \tilde{b}_J(x, R_J) V_J(x, R_J) \, dx \] 
\[ - \frac{1}{2} \sum_J \int_{\Omega} \tilde{b}_J(x, R_J) \tilde{V}_J(x, R_J) \, dx, \]
where \( V_c(x, R) \) is the solution to the Poisson equation
\[ \frac{-1}{4\pi} \nabla^2 V_c(x, R) = \tilde{b}(x, R) - b(x, R) \]
with periodic boundary conditions. The potential \( V_c(x, R) \) so calculated is accurate to within a constant, which can be determined by evaluating \( \sum_J (V_J(x, R_J) - \tilde{V}_J(x, R_J)) \) at any point in space.

The correction to the forces on the nuclei
\[ f^c_J = -\frac{\partial E^*_c(R)}{\partial R_J} \]
can be represented as
\[ f^c_J = -\frac{1}{2} \sum_{J'} \int_{\Omega} \left[ \frac{\partial \tilde{b}_J(x, R_J)}{\partial R_{J'}} \left( V_c(x, R) - \tilde{V}_{J'}(x, R_{J'}) \right) + \frac{\partial b_J(x, R_J)}{\partial R_{J'}} \left( V_c(x, R) + V_{J'}(x, R_{J'}) \right) \right. \]
\[ + \frac{\partial V_c(x, R)}{\partial R_J} \left( \tilde{b}(x, R) + b(x, R_J) \right) + b_J(x, R_J) \frac{\partial V_J(x, R_J)}{\partial R_J} - \tilde{b}_J(x, R_J) \frac{\partial \tilde{V}_J(x, R_J)}{\partial R_J} \] 
\[ \left. + \nabla \tilde{b}_{J'}(x, R_{J'}) \left( V_c(x, R) - \tilde{V}_{J'}(x, R_{J'}) \right) + \nabla b_{J'}(x, R_{J'}) \left( V_c(x, R) + V_{J'}(x, R_{J'}) \right) \right] \, dx, \]
where the summation $J'$ is over $J^{th}$ atom and its periodic images. Additionally,
\[
\nabla V_{c,J'}(x, R_{J'}) = \nabla \tilde{V}_{J'}(x, R_{J'}) - \nabla V_{J'}(x, R_{J'}).
\]
(68)

It is important to note that even with these corrections to the energy and forces, the overall OF-DFT formulation maintains its linear-scaling with respect to the number of atoms.

C. Conjugate gradient method for OF-DFT

In Algorithm 1, we present the implemented conjugate gradient method to solve the variational problem in Eqn. 43. This differs from the standard non-linear conjugate gradient method in that it is able to handle the constraints $C(u) = 0$ and $u \geq 0$.

Algorithm 1: Non-linear conjugate gradient method for OF-DFT

| Input: $u_0$, $R$, $V_{LR}$ and $N_{restart}$ |
| $q = 0$ |
| repeat |
| $\eta_q = \frac{1}{N_e} \langle u_q, \mathcal{H} u_q \rangle$, where $\langle \cdot, \cdot \rangle$ denotes the inner product |
| $r_q = -2(\mathcal{H} u_q - \eta_q u_q)$ |
| $\xi = \frac{\langle r_q - r_{q-1}, r_q \rangle}{\langle r_{q-1}, r_{q-1} \rangle}$ |
| if $q = mN_{restart}$ ($m \in \mathbb{N}$) or $\xi \leq 0$ then |
| $d_q = r_q$ |
| else |
| $d_q = r_q + \xi d_{q-1}$ |
| $s = \arg\inf_{s \in \mathbb{R}} \hat{E} \left( \sqrt{N_e \frac{u_q - sr_q}{\|u_q - sr_q\|}}, R, V_{LR} \right)$ |
| $u_{q+1} = \sqrt{N_e \frac{u_q - sr_q}{\|u_q - sr_q\|}}$ |
| $q = q + 1$ |
| until $\|r\|^2 < tol$; |
| Output: $u = u_q$ |

D. Anderson Mixing

The fixed-point problem in Eqn. 42 can be rewritten as
\[
f(V_{LR}) = 0, \quad f(V_{LR}) = V[\mathcal{U}(V_{LR})] - V_{LR}.
\]
(69) This equation can be solved using an iteration of the form [46, 48]
\[
V_{LR,k+1} = V_{LR,k} - C_k f(V_{LR,k}),
\]
(70) where $C_k$ is chosen to approximate the inverse Jacobian. In multi-secant type methods, it is common to set $C_k$ to the solution of the constrained minimization problem [46, 48]
\[
\min_C \frac{1}{2}\|C - C_{k-1}\|_2^2 \quad \text{s.t.} \quad S_k = CY_k,
\]
(71) where
\[
S_k = [V_{LR,k-m+1} - V_{LR,k-m}, \ldots, V_{LR,k} - V_{LR,k-1}],
\]
\[
Y_k = [f(V_{LR,k-m+1}) - f(V_{LR,k-m}), \ldots, f(V_{LR,k}) - f(V_{LR,k-1})].
\]
In the above equations, \( m \) represents the mixing history. The solution of this variational problem is

\[
C_k = C_{k-1} + (S_k - C_{k-1}Y_k)(Y_k^T Y_k)^{-1}Y_k^T.
\]  (72)

In the specific case of Anderson mixing [59], \( C_{k-1} \) is set to \(-\zeta I\), where \( I \) is a \( m \times m \) identity matrix. This leads to the following update formula within the fixed-point iteration

\[
V_{LR,k+1} = V_{LR,k} + \zeta f(V_{LR,k}) - (S_k + \zeta Y_k)(Y_k^T Y_k)^{-1}Y_k^T f(V_{LR,k}).
\]  (73)

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