Introducing PROFESS: A new program for orbital-free density functional theory calculations

Gregory S. Ho\textsuperscript{a}, Vincent L. Lignères\textsuperscript{a}, Emily A. Carter\textsuperscript{b,c,∗}

\textsuperscript{a} Department of Chemistry, Princeton University, Princeton, NJ 08544, USA
\textsuperscript{b} Program in Applied and Computational Mathematics, Princeton University, Princeton, NJ 08544, USA
\textsuperscript{c} Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544-5263, USA

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\textbf{A B S T R A C T}

We present PROFESS (PRinceton Orbital-Free Electronic Structure Software), a new software package that performs orbital-free density functional theory (OF-DFT) calculations. OF-DFT is a first principles quantum mechanics method primarily for condensed matter that can be made to scale linearly with system size. We describe the implementation of energy, force, and stress functionals and the methods used to optimize the electron density under periodic boundary conditions. All electronic energy and potential terms scale linearly while terms involving the ions exhibit quadratic scaling in our code. Despite the latter scaling, the program can treat tens of thousands of atoms with quantum mechanics on a single processor, as we demonstrate here. Limitations of the method are also outlined, the most serious of which is the accuracy of state-of-the-art kinetic energy functionals, which limits the applicability of the method to main group elements at present.

\textbf{Program summary}

Program title: PROFESS
Catalogue identifier: AEBN_v1_0
Program summary URL: http://cpc.cs.qub.ac.uk/summaries/AEBN_v1_0.html
Program obtainable from: CPC Program Library, Queen’s University, Belfast, N. Ireland
No. of lines in distributed program, including test data, etc.: 35933
No. of bytes in distributed program, including test data, etc.: 329924
Distribution format: tar.gz
Programming language: Fortran 90
Computer: Intel with ifort; AMD Opteron with pathf90
Operating system: Linux
RAM: Problem dependent, but 2 GB is sufficient for up to 10,000 ions
Classification: 7.3
External routines: FFTW (http://www.fftw.org), MINPACK-2
Nature of problem: Given a set of coordinates describing the initial ion positions under periodic boundary conditions, recovers the ground state energy, electron density, ion positions, and cell lattice vectors predicted by orbital-free density functional theory. Except for computation of the ion–ion and ion–electron terms, all other terms are effectively linear scaling. Up to ∼10,000 ions may be included in the calculation on just a single processor.
Solution method: Computes energies as described in text; minimizes this energy with respect to the electron density, ion positions, and cell lattice vectors.
Restrictions: PROFESS cannot use nonlocal (such as ultrasoft) pseudopotentials. Local pseudopotential files for aluminum, magnesium, silver, and silicon are available upon request. Also, due to the current state of the kinetic energy functionals, PROFESS is only reliable for main group metals and some properties of semiconductors.
Running time: Problem dependent: the test example provided with the code takes less than a second to run. Timing results for large scale problems are given in the paper.

\textbf{References:}
1. Introduction

In general, in order to solve for the electronic structure and properties of matter, one must solve the time-independent Schrödinger equation

\[ \hat{H}\Psi = E \Psi, \]  

(1)

where \( \hat{H} \) is the Hamiltonian operator, \( E \) is the total energy, and \( \Psi \) is the many-body electronic wavefunction under the Born–Oppenheimer approximation. The \( \Psi \) that corresponds to the lowest \( E \) then contains all information about the ground state of the system. However, \( \Psi \) contains \( 3N \) degrees of freedom (\( N \) is the number of electrons), and is expensive both to compute and to store. For example, accurate \textit{ab initio} electron correlation methods that directly use this approach (e.g., configuration interaction and coupled cluster theories) generally tend to be too expensive for studying more than tens of atoms, even with linear scaling versions, which have been used to handle up to \( \sim 130 \) atoms [1,2].

An alternative scheme to solve for ground state properties is put forth in the Hohenberg–Kohn theorems [3]. The first theorem states that the ground state electron density \( \rho \) contains everything necessary to recover all information about the electronic ground state, including, e.g., the electronic wavefunction, the total energy, the associated forces on the nuclei and the stress in the unit cell. In theory, using the density entirely obviates the need to compute or store a full \( N \)-body electronic wavefunction. Since the electron density only has three coordinates associated with it, this theorem formally reduces the number of degrees of freedom from \( 3N \) to 3, an enormous simplification. The second theorem is a variational principle that provides a way to find this ground state electron density by minimizing the electronic total energy with respect to variations in the electron density.

The most widely used DFT implementation, first introduced by Kohn and Sham [4], reintroduces wavefunctions in order to evaluate a kinetic energy that is exact in the limit of noninteracting electrons. Instead of a fully interacting \( N \)-electron wavefunction, however, Kohn and Sham introduced \( N \) one-electron orbitals \( \psi_i(\mathbf{r}) \), each providing the spatial distribution of a single noninteracting electron. For noninteracting electrons that obey the Pauli Principle, the total \( N \)-electron wavefunction is exactly given by a Slater determinant

\[ \Psi = \hat{a}\left( \prod_i \psi_i \right), \]  

(2)

where \( \hat{a} \) is the antisymmetrizer operator. Substitution of Eq. (2) into the time-independent Schrödinger equation yields \( N \) one-electron equations (the Kohn–Sham equations)

\[ \left( -\frac{1}{2} \nabla^2 + v_{KS}(\mathbf{r}) \right) \psi_i = E_i \psi_i, \]  

(3)

where the Hamiltonian operator contains an effective potential corresponding to the mean-field effect of the other \( N - 1 \) electrons on the electron described by \( \psi_i \).

In order to remain consistent with the total electron density, these orbitals are constructed such that the true density,

\[ \rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2, \]  

(4)

i.e., the density associated with these orbitals, is formally equivalent to the density associated with the fully interacting system. In fact, this only holds if \( v_{KS} \) contains the exact exchange–correlation functional, incorporating not only exact exchange and correlation potentials but also the difference between the exact kinetic energy and the noninteracting kinetic energy. Unfortunately, the exact functional form of this term is not known.

The electron density and these one-electron wavefunctions are self-consistently updated until the energy converges to a minimum. The total electronic energy in Kohn–Sham density functional theory (KS-DFT) is evaluated as

\[ E[\rho] = -\frac{1}{2} \sum_{i=1}^{N} \langle \psi_i | \nabla^2 | \psi_i \rangle - \sum_{i,j=1}^{\#\text{atoms}} \int \frac{Z_i \rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_j|} d\mathbf{r} + \frac{1}{2} \int \int \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}}[\rho], \]  

(5)

where \( \psi_i \) are the eigenfunctions of the KS equations and the KS orbitals are used to evaluate the exact noninteracting kinetic energy, \( Z_i \) and \( R_j \) are the ionic charges and positions used to evaluate the ion–electron attraction energy. Here the ion charge as written is the full nuclear charge; often \( Z_i^+ / |\mathbf{r} - \mathbf{R}_i| \) is replaced with a pseudopotential describing the valence electrons’ interaction with “ions” that are screened nuclei, i.e., each comprised of a nucleus plus its core electrons. The third term is the Hartree electron–electron repulsion energy, and \( E_{\text{xc}} \) is the exchange–correlation energy.

Although KS-DFT exhibits much better scaling than traditional correlated \textit{ab initio} quantum chemistry methods while retaining reasonable accuracy, typical implementations still scale roughly as \( O(N^3) \) where \( N \) is a measure of system size, due to necessary manipulations related to the reintroduced wavefunction (e.g., orbital orthonormalization). The scaling can vary from quadratic to quartic, depending on the implementation, and of course each algorithm and numerical implementation is subject to a different prefactor. Regardless of these details, in practice typical sample sizes studied with standard KS-DFT are of the order of tens of atoms on a desktop computer to hundreds of atoms on a supercomputer. Recent years have brought the development of a significant number of very impressive linear-scaling KS-DFT techniques [5–11]. However the “crossover point” at which the linear scaling KS-DFT algorithms become faster than \( O(N^3) \) KS-DFT can still be on the order of hundreds of atoms, especially for systems in which electrons are delocalized (i.e., metals) [10]. Furthermore, while advancing rapidly, these linear scaling methods still are best suited for materials possessing a finite band gap, and struggle to accurately describe metallic systems [12,13].

In many cases of interest, such as dislocations within a metal or moderately-sized nanostructures, far more than hundreds of atoms must be included explicitly in the modeling. As a result, it is common to resort to classical atomistic models that utilize empirical interatomic potentials (such as the embedded atom method) [14]. Although these potentials describe well atomic configurations similar to the reference environment to which the potential was fit...
(e.g., bulk crystal structures), they are less reliable for describing environments to which the potentials were not calibrated [15,16]. Thus, it is desirable to instead endow the model with the predictive (and transferable) capability of quantum mechanics. However, the size of such material features of interest (e.g., screw dislocations containing thousands of atoms experiencing nonnegligible shear forces around their cores) requires a DFT method that scales much more favorably than \( O(N^3) \). A linear scaling method is required, and since we are interested in defects in metals, the family of linear scaling KS-DFT methods cannot be employed. Instead, we adopt the only linear scaling DFT method that works well for metals, namely OF-DFT.

OF-DFT is a first principles quantum mechanics method that can be formulated to scale linearly with system size, without a crossover point characteristic of other linearly scaling DFT algorithms. By contrast, KS-DFT generally scales cubically with size initially and then can be made to scale linearly asymptotically. Currently, OF-DFT can be used to study samples consisting of tens of thousands of atoms on a single processor and hundreds of thousands of atoms on tens of processors in a parallel implementation of the algorithm [17].

OF-DFT eliminates the KS orbitals and instead relies on approximations to the kinetic energy that depend explicitly on the electron density. The viability of OF-DFT thus depends heavily on the accuracy of the kinetic energy functional chosen, another example of the age-old tradeoff between speed and accuracy. Due to limitations in the accuracy of state-of-the-art kinetic energy density functionals (KEDFs), at present OF-DFT is only as accurate as KS-DFT for main group metals, as well as for some properties of semiconductors.

Obtaining accurate KEDFs for use in OF-DFT is a decades-old formidable challenge and research is still ongoing. Currently, the best approximations available are those that explicitly account for the exact linear response of a uniform electron gas density subject to small perturbations in the potential. Consequently, these linear-response-based KEDFs work best for main group, nearly-free-electron-like metals. This class of KEDF was pioneered by Wang and Teter (WT) [18], modified by Perrot [19], and Madden and coworkers [20–22], and generalized by Wang, Govind, and Carter (WGC) [23]. WGC then introduced a significant advance by accounting for nonlocal density dependence in the linear response kernel, instead of relying upon a linear response kernel derived from a single fixed reference density [24]. The 1999 WGC KEDF shows great improvement over the WT KEDF in many cases, particularly in describing vacancies, surfaces, and equations of state. OF-DFT with the WGC KEDF has been shown to be very accurate (\(<10 \text{meV/atom differences with respect to KS-DFT}\)) for main group metals. More recently, a slight reparameterization of the original WGC functional was shown to improve the description of silicon, as a representative covalent semiconductor, although not all properties of Si were well-described [25]. Thus, sufficiently accurate functionals have yet to be developed for describing localized electron densities present in, e.g., transition metals [26], semiconductors [25,27], and insulators.

The only other potential source of error in OF-DFT compared to KS-DFT is in the evaluation of the ion–electron interaction, since KS-DFT is in the evaluation of the ion–electron interaction, since OF-DFT can be used to study samples consisting of tens of thousands of atoms experiencing nonnegligible shear forces around their cores) requires a DFT method that scales much more favorably than \( O(N^3) \). A linear scaling method is required, and since we are interested in defects in metals, the family of linear scaling KS-DFT methods cannot be employed. Instead, we adopt the only linear scaling DFT method that works well for metals, namely OF-DFT.

Here we introduce PROFESS, our new software to perform OF-DFT calculations. We focus here on the portion of the program that operates under periodic boundary conditions (PBCs), which can treat arbitrary crystal structures (arbitrarily shaped cells with nonorthogonal lattice vectors). In particular, the form of the energy, force, and stress functionals under periodic boundary conditions will be described, and various methods to optimize the electron density corresponding to an energy minimum will be compared and discussed. PROFESS also possesses the ability to minimize the forces on the ions as well as the stresses in the unit cell.

2. Orbital-free energy functionals

We now examine each term in OF-DFT individually. The OF-DFT total energy can be partitioned as

\[ E_{\text{tot}}(\rho) = E_{\text{kin}}(\rho) + E_{\text{ext}}(\rho) + E_{\text{start}}(\rho) + E_{\text{xc}}(\rho) + E_{\text{f}}(\rho) \]  

where \( T_{\text{kin}}(\rho) \) is the electronic kinetic energy, \( E_{\text{ext}}(\rho) \) is the electron–ion potential energy, \( E_{\text{start}}(\rho) \) is the Coulomb repulsion energy between electrons, \( E_{\text{xc}}(\rho) \) is the exchange–correlation energy, and \( E_{\text{f}}(\rho) \) is the ion–ion repulsion energy.

In the following, we give expressions for each term of the energy, the associated potential \( V(\rho) = \delta E(\rho)/\delta \rho \) (the functional derivative of the energy with respect to the electron density), and, where relevant, the force on each ion \( F_i = -\partial E(\rho)/\partial R_i \) (where \( R_i \) is the position for the \( i \)th ion) subject to PBCs. We also give the expressions for each OF-DFT term of the stress tensor \( \sigma_{\alpha \beta} = \frac{1}{V} \sum_{\nu} \frac{\partial^2 E(\rho)}{\partial \rho_\alpha \partial \rho_\beta} \), where \( \alpha, \beta, \) and \( \nu \) index coordinates, \( h \) is a matrix whose columns are the lattice vectors of the periodic cell, and \( \Omega \) is the volume of the cell.

2.1. Potential energy functionals

2.1.1. Ion–ion energy

The interaction energy between ions (nuclei fully screened by their associated core electrons) is given in atomic units by

\[ E_{\text{ii}} = \sum_{i=1}^{M} \sum_{j=1}^{M} \frac{q_i q_j}{R_{ij}} \]  

where \( M \) is the number of ions, \( q_i \) is the net charge on ion \( i \), and \( R_{ij} = |R_i - R_j| \).

Under PBCs, this becomes a conditionally (and notoriously slowly) convergent sum for a neutral system and diverges for a charged system. However, by introducing an artificial distribution of counter charges to screen the charges in real space, which then can be subtracted out in reciprocal space, it is possible to transform the summation into a sum of two rapidly converging series plus a constant. Ewald first originated this technique in 1921 [29], and the method has since been extended by many others [30–34]. An excellent review detailing the Ewald summation from a physical perspective can be found in [35].
The Ewald energy is given by

$$ E_{ii} = E_{\text{real}} + E_{\text{recip}} + E_{\text{self}} + E_{\text{background}} \tag{8} $$

where $E_{\text{real}}$ and $E_{\text{recip}}$ are quickly converging summations in real and reciprocal space, $E_{\text{self}}$ is a correction term to eliminate interactions between each artificial counter charge with itself, and $E_{\text{background}}$ is a uniform compensating background charge that adds a correction to the energy for a system that is not charge neutral (since only the metallic cations without their valence electrons are treated using the Ewald summation in PROFESS, this term is necessary even for a system that is charge neutral overall).

The individual terms are

$$ E_{\text{real}} = \frac{1}{2} \sum_{i=1}^{M} \sum_{j=1}^{n} q_i q_j \frac{ \text{erfc}(\eta R_{ij,n})}{R_{ij,n}} $$

$$ E_{\text{recip}} = \frac{2\pi}{\Omega} \sum_{g \neq 0} \left[ \sum_{i=1}^{M} q_i \cos(\vec{g} \cdot \vec{R}_i) \right]^2 + \left[ \sum_{i=1}^{M} q_i \sin(\vec{g} \cdot \vec{R}_i) \right] \left| \vec{g} \right|^2 e^{-\left(\frac{\eta^2}{2}\right)} \tag{9} $$

$$ E_{\text{self}} = -\frac{\pi}{2\eta^2 \Omega} \sum_{i=1}^{M} q_i \sum_{j=1}^{n} q_j (\vec{R}_i - \vec{R}_j + \vec{n}) \tag{10} $$

$$ E_{\text{background}} = -\frac{\pi}{2\eta^2 \Omega} \sum_{i=1}^{M} q_i \sum_{j=1}^{n} q_j \tag{11} $$

where $q_i$ is the charge on ion $i$, $\text{erfc}$ is the complementary error function, $n$ is a cell coordinate vector pointing from the origin of the real space cell to the origins of adjacent periodic cells, $M$ is the number of ions in the real space cell, $R_{ij,n} = |\vec{R}_i - \vec{R}_j + \vec{n}|$ is the distance between ion $i$ in the original real space cell and ion $j$ in the cell pointed to by vector $n$, $\Omega$ is the volume of the cell, $\vec{g}$ is a reciprocal space lattice vector, and $\eta$ is a parameter that can be optimized to tune the convergence rates of the sums in real and reciprocal space. The sum over $n$ in $E_{\text{real}}$ is over the infinite three-dimensional grid formed by all possible values of $n$, and the prime over the sum indicates that $i = j$ terms are omitted when $n = 0$. We use the criteria given by Karasawa and Goddard [32] to determine the optimal value of $\eta$. Note that the $\vec{g} = 0$ term in the reciprocal space summation, infinite for a charged system, is omitted. Since the systems we consider are charge neutral overall, the $\vec{g} = 0$ terms of the ion-ion, ion-electron, and electron-electron interactions will cancel exactly. Thus, we simply omit the $\vec{g} = 0$ terms for all three electrostatic terms [36].

The force on atom $i$ is given by direct differentiation of the Ewald energy with respect to the positions of the ions [32]

$$ F_i = \dot{F}_{i,\text{real}} + \dot{F}_{i,\text{recip}} \tag{13} $$

$$ \dot{F}_{i,\text{real}} = \frac{q_i}{\eta} \sum_{j=1}^{M} \sum_{j \neq i} q_j (\vec{R}_i - \vec{R}_j + \vec{n}) \left[ \text{erfc}(\eta R_{ij,n}) + 2 e^{-\left(\frac{\eta R_{ij,n}}{\sqrt{\pi}}\right)} \right] \tag{14} $$

$$ \dot{F}_{i,\text{recip}} = \frac{4\pi}{\Omega} \sum_{g \neq 0} \left[ \left( \sum_{j} q_j \sin(\vec{g} \cdot \vec{R}_j) \right) \sum_{j} q_j \cos(\vec{g} \cdot \vec{R}_j) \right] - \cos(\vec{g} \cdot \vec{R}_i) \left( \sum_{j} q_j \sin(\vec{g} \cdot \vec{R}_j) \right) \tag{15} $$

and the stress tensor components are [32]

$$ \sigma_{\alpha\beta} = \sigma_{\alpha\beta,\text{real}} + \sigma_{\alpha\beta,\text{recip}} + \sigma_{\alpha\beta,\text{background}} $$

$$ \sigma_{\alpha\beta,\text{real}} = -\frac{1}{2\Omega} \sum_{i=1}^{M} \sum_{j=1}^{n} q_i q_j \left( \frac{2\eta}{\sqrt{\pi}} e^{-\left(\frac{\eta R_{ij,n}}{\sqrt{\pi}}\right)} + \frac{\text{erfc}(\eta R_{ij,n})}{R_{ij,n}} \right) $$

$$ \sigma_{\alpha\beta,\text{recip}} = \frac{2\pi}{\Omega} \sum_{g \neq 0} \left[ \sum_{i=1}^{M} q_i \cos(\vec{g} \cdot \vec{R}_i) \right]^2 $$

$$ + \left( \sum_{i=1}^{M} q_i \sin(\vec{g} \cdot \vec{R}_i) \right)^2 \left| \vec{g} \right|^2 e^{-\left(\frac{\eta^2}{2}\right)} $$

$$ \times \left( \frac{2}{\left| \vec{g} \right|^2} \left[ 1 + \frac{\left| \vec{g} \right|^2}{2\eta^2} \right] R_{\alpha\beta} - \delta_{\alpha\beta} \right) $$

$$ \sigma_{\alpha\beta,\text{background}} = \frac{\pi}{2\eta^2 \Omega} \sum_{i=1}^{M} q_i \sum_{j=1}^{n} q_j \delta_{\alpha\beta} \tag{16} $$

Although the standard Ewald summation scales as $O(M^2)$, its use is acceptable for most OF-DFT calculations because of its very small prefactor, which makes the computation time of the Ewald summation negligible for moderate $M$. For example, the Ewald summation took less than 10 minutes on a single AMD Opteron 2.5 GHz processor for a system of 10,000 atoms. In addition, the ion–ion energy is independent of the electronic structure, and so the Ewald summation is done very infrequently, only at the beginning of a complete electronic structure optimization and whenever the ion positions or cell lattice parameters are changed.

Nevertheless, it is desirable to implement an electrostatic summation method that scales linearly with the number of atoms for large systems. The best alternative is likely the Particle-Mesh Ewald method [33,34], which scales as $O(M \ln M)$. For extremely large systems (perhaps millions of atoms), fast multipole-based methods that are theoretically $O(M)$ scaling may prove to be faster [37,38]. Both methods have been parallelized over many processors to achieve speedup [39–45].

### 2.1.2. Ion–electron energy

The interaction of the ions with the electrons in principle is a simple electrostatic interaction between the positively charged nucleus and the electrons. Although it is possible to describe the interaction of the nucleus with all the electrons in a system (both valence and core electrons), this is expensive and generally not necessary. Often, the properties of interest involve only the valence electrons, in which case the core electrons can be lumped together with the positively charged nucleus, and their combined effect on the valence electrons approximated by an effective potential, a so-called pseudopotential.

The most accurate and transferable pseudopotentials used in KS-DFT are nonlocal, meaning that the pseudopotential is separated into distinct potentials that depend on electron angular momentum. Nonlocal pseudopotentials generally are expressed as sums of orbital-based projection operators that act on the KS-DFT pseudowavefunctions that represent the valence electrons. Each projection operator contains one of the angular-momentum-dependent potentials mentioned above and therefore electrons of different angular momenta experience different pseudopotentials, leading to a more accurate ion–electron description. Since such nonlocal pseudopotentials must be projected onto orbitals, they cannot be used in an OF theory. As a result, only less flexible spherically symmetric local pseudopotentials that depend only on the radial distance from the nucleus may be used. Although error in the KEDF is usually the main source of error within OF-DFT calculations, the constraint of using local pseudopotentials accounts for large systems. The best alternative is likely the Particle-Mesh Ewald method [33,34], which scales as $O(M \ln M)$. For extremely large systems (perhaps millions of atoms), fast multipole-based methods that are theoretically $O(M)$ scaling may prove to be faster [37,38]. Both methods have been parallelized over many processors to achieve speedup [39–45].
for the majority of the error in OF-DFT in cases where the KEDF is very accurate [46]. Once a pseudopotential is constructed, the ion–electron terms are simple to compute.

Under PBCs, the pseudopotential is often expressed in reciprocal space. Then the ion–electron energy is computed as [36]

$$E_{\text{IE}}(\rho) = \Omega \sum_{\mathbf{g} \neq 0} \rho(\mathbf{g}) V_{\text{IE}}(-\mathbf{g}) + N_c V_{\text{IE}}^\text{NC}(\mathbf{g} = 0)$$  \hspace{1cm} (20)

where $\Omega$ is the volume of the computational cell, $\rho(\mathbf{g})$ are the Fourier components of the electron density, $N_c$ (i.e., $\rho(\mathbf{g} = 0)$) is the number of electrons, and $V_{\text{IE}}(-\mathbf{g})$ is the total ion–electron potential in reciprocal space. The pure Coulomb contribution to the pseudopotential gives rise to a singularity at $|\mathbf{g}| = 0$. As discussed below, this contribution is subtracted out, leaving only the average non-Coulombic contribution in the pseudopotential at $\mathbf{g} = 0$, $V_{\text{IE}}^\text{NC}(\mathbf{g} = 0)$.

The total ion–electron potential in reciprocal space is given by

$$V_{\text{IE}}(\mathbf{g}) = \sum_\alpha S_\alpha(\mathbf{g}) \nu_{\text{IE},\alpha}(|\mathbf{g}|)$$  \hspace{1cm} (21)

where $S_\alpha(\mathbf{g}) = \sum_i e^{-i\mathbf{g} \cdot \mathbf{r}_i}$ is the structure factor, $\nu_{\text{IE},\alpha}(|\mathbf{g}|)$ is the 1D Fourier component of the local pseudopotential for species $\alpha$, and $\mathbf{r}_i, \mathbf{r}_j$ are the coordinates for ion $i$ of species $\alpha$.

The force on each ion $I$ due to the ion–electron interaction is

$$\mathbf{F}_{\text{IE},\alpha} = 2\pi \sum_{\mathbf{g} \neq 0} \mathbf{g} \nu_{\text{IE},\alpha}(|\mathbf{g}|) \sum_\alpha \frac{\partial \nu_{\text{IE},\alpha}(|\mathbf{g}|)}{\partial \mathbf{G}} e^{i\mathbf{g} \cdot \mathbf{R}}$$  \hspace{1cm} (22)

and the ion–electron contribution to the Cauchy stress tensor components are [16,47]

$$\sigma_{\alpha\beta} = -\Omega \nu_{\text{IE}}^\text{NC} \sum_{\mathbf{g} \neq 0} \frac{\rho(\mathbf{g}) e^{i\mathbf{g} \cdot \mathbf{R}}}{|\mathbf{g}|} \sum_\alpha \frac{\partial \nu_{\text{IE},\alpha}(|\mathbf{g}|)}{\partial |\mathbf{g}|} e^{i\mathbf{g} \cdot \mathbf{R}}$$

$$+ \delta_{\alpha\beta} \nu_{\text{IE}}^\text{NC}$$.  \hspace{1cm} (23)

where we substitute $\sigma_{\alpha\beta}^{\text{IE}}$ for the usual notation for the stress tensor, $\sigma_{\alpha\beta}$, to avoid variable overlap. (Note that there is a typo in this expression in [16]. The braces surrounding the expression are missing, resulting in an overall positive sign on the second term, $\delta_{\alpha\beta} \nu_{\text{IE}}^\text{NC}$. With the braces, the negative sign disappears on the second term, causing its sign to be negative overall, which is correct.) The derivative of the pseudopotential is obtained by taking the derivative of the cubic spline fit to the pseudopotential at the beginning of the calculation.

Pseudopotentials in 1D can be transformed back and forth from real to reciprocal space via reverse Fourier–Bessel transforms (also known as Hankel transforms, or radial Fourier transforms, i.e., a 3D Fourier transform of a spherically symmetric function in spherical polar coordinates). The forward Fourier–Bessel transform is given by

$$\nu_{\text{IE},\alpha}(|\mathbf{g}|) = 4\pi \int_0^\infty \nu_{\text{IE},\alpha}(|\mathbf{f}|) |\mathbf{f}|^2 \sin(|\mathbf{g}| |\mathbf{f}|) \frac{\sin(|\mathbf{g}| |\mathbf{f}|)}{|\mathbf{g}| |\mathbf{f}|} d|\mathbf{f}|.$$  \hspace{1cm} (24)

The reverse Fourier–Bessel transform is similar

$$\nu_{\text{IE},\alpha}(|\mathbf{f}|) = \frac{1}{4\pi^2} \int_0^\infty \nu_{\text{IE},\alpha}(|\mathbf{g}|) |\mathbf{g}|^2 \sin(|\mathbf{f}| |\mathbf{g}|) \frac{\sin(|\mathbf{f}| |\mathbf{g}|)}{|\mathbf{f}| |\mathbf{g}|} d|\mathbf{g}|.$$  \hspace{1cm} (25)

At long range in real space, pseudopotentials die off to a pure $-Z/|\mathbf{f}|$ Coulomb potential, where $Z$ is the net charge of the screened ionic species. This corresponds to a $-4\pi Z^2/|\mathbf{g}|^2$ contribution in reciprocal space at small $|\mathbf{g}|$. (Note that these two formulas can be used to solve for the charge on the ion, $Z$, using either the last $|\mathbf{f}|$ value in real space or the first $|\mathbf{g}|$ value in reciprocal space of the pseudopotential, making it unnecessary to explicitly include the charge within the pseudopotential file.) The $1/|\mathbf{g}|^2$-dependence is problematic for reciprocal space calculations, since the pseudopotential will diverge to negative infinity at $|\mathbf{g}| = 0$, causing the ion–electron energy to diverge. Fortunately, for a charge neutral system subject to periodic boundary conditions, this singularity at $|\mathbf{g}| = 0$ is canceled exactly by similar divergences in the electron–electron and ion–ion interactions, and therefore can be neglected. However, since pseudopotentials are quite different from a pure Coulomb $-Z/|\mathbf{f}|$ potential near the core, a correction must be added to the value of the pseudopotential at small $|\mathbf{g}|$ [36]. This core correction is computed via a forward Fourier–Bessel transform of the difference between the pseudopotential and the pure Coulomb potential at $|\mathbf{g}| = 0$

$$\nu_{\text{IE},\alpha}(\mathbf{g}) = 4\pi \int_0^\infty \left( \nu_{\text{IE},\alpha}(|\mathbf{f}|) - \frac{Z}{|\mathbf{f}|} \right) |\mathbf{f}|^2 \sin(|\mathbf{g}| |\mathbf{f}|) \frac{\sin(|\mathbf{g}| |\mathbf{f}|)}{|\mathbf{g}| |\mathbf{f}|} d|\mathbf{f}|$$

$$= 4\pi \int_0^\infty \left( |\mathbf{f}|^2 \nu_{\text{IE},\alpha}(|\mathbf{f}|) + Z^2/|\mathbf{f}|^2 \right) d|\mathbf{f}|,$$  \hspace{1cm} (26)

which is assigned as the $|\mathbf{g}| = 0$ term of the reciprocal space pseudopotential.

Pseudopotentials can either be ab initio, derived from an all-electron quantum calculation, or empirical, based on fits to experiment. In the applications presented here, we use the empirical model pseudopotential for aluminum developed by Goodwin, Needs, and Heine [48], expressed in reciprocal space in Hartree atomic units as

$$\nu_{\text{IE},\text{Goodwin}}(|\mathbf{g}|) = -4\pi \frac{A}{|\mathbf{g}|^2} \left( (Z - AR) \cos(|\mathbf{g}| |\mathbf{R}|) + \frac{A}{|\mathbf{g}|} \sin(|\mathbf{g}| |\mathbf{R}|) \right)$$

$$\times e^{-|\mathbf{g}|^2/|\mathbf{g}|^2},$$  \hspace{1cm} (27)

where the values of the parameters for aluminum are $Z = 3$, $A = 0.1107$, $R = 1.150$, and $g_\nu = 1.39$. The pseudopotential core correction for the $|\mathbf{g}| = 0$ term in the Goodwin pseudopotential (Eq. (26) above) is 24,2336 Hartrees. At 9 bohrs, the Goodwin pseudopotential is essentially Coulombic, differing from the pure Coulomb interaction by less than $1 \times 10^{-6}$ Hartrees.

The cost of computing the ion–electron potential is determined by the structure factor in Eq. (21), which scales as $O(NM)$, where $N$ is the number of gridpoints and $M$ is the number of ions. Since the number of gridpoints generally scale linearly with the number of ions, this is effectively $O(N^2)$ scaling, but with a very small prefactor. Fortunately, like the ion–ion term, the ion–electron potential needs to be evaluated only once at the beginning of an energy minimization and whenever the ion positions or lattice vectors change, somewhat mitigating the expense. (Of course, the ion–electron energy needs to be recomputed whenever the electron density changes. Given the ion–electron potential, the energy is easily obtained in linear time.) Even so, evaluation of the ion–electron potential is the bottleneck in the OF-DFT program for even moderately large systems.

It is therefore important to move towards methods of computing the ion–electron potential that scale more favorably. For PBCs, Choly and Kaxiras [49] generalized particle mesh Ewald methods to derive an $O(N \ln N)$ method for computing ion–electron terms containing pseudopotentials. We have recently implemented this technique in PROFESS [17].
2.1.3. Hartree electron–electron repulsion energy

The Hartree energy for the electron density at a point \( \vec{r} \) interacting with the electron density at another point \( \vec{r'} \) is expressed as

\[
E_{H}[\rho] = \frac{1}{2} \int \int \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}'.
\]  

(28)

Under PBCs, it is possible to perform this convolution in reciprocal space with \( O(N \ln N) \) scaling to obtain the Hartree energy as

\[
E_{H}[\rho] = \frac{1}{2} \sum_{\vec{g} \neq 0} \frac{4\pi}{|\vec{g}|^2} \rho(\vec{g}) \rho(-\vec{g}).
\]  

(29)

where \( \Omega \) is the volume of the periodic cell, and \( \rho(\vec{g}) \) is obtained as \( \rho(\vec{g}) = \tilde{F}(\rho(\vec{r})), \) where \( \tilde{F} \) denotes a forward fast Fourier transform (FFT), defined as

\[
\tilde{F}(f(\vec{r})) = f(\vec{g}) = \frac{1}{N} \sum_{\vec{r}} f(\vec{r}) e^{-i\vec{g} \cdot \vec{r}}.
\]  

(30)

However, instead of directly using Eq. (29), we have found that it is more numerically stable to obtain the energy as

\[
\delta E_{H} = \frac{\Omega}{2N} \sum_{\vec{r}} \delta \tilde{E}_{H}(\vec{r}) \rho(\vec{r}).
\]  

(31)

where \( N \) is the number of gridpoints. The potential in real space given in Eq. (31) is computed as

\[
\delta \tilde{E}_{H}(\vec{r}) = \tilde{F}^{-1} \left( \frac{4\pi}{|\vec{g}|^2} \rho(\vec{g}) \right)
\]  

(32)

where \( \tilde{F}^{-1} \) denotes the reverse fast Fourier transform

\[
\tilde{F}^{-1}(f(\vec{g})) = f(\vec{r}) = \sum_{\vec{g}} f(\vec{g}) e^{i\vec{g} \cdot \vec{r}}.
\]  

(33)

This method of evaluation for \( E_{H}[\rho] \) also scales as \( O(N \ln N) \).

The Hartree stress tensor components are given by [16,47]

\[
\sigma_{\alpha\beta}^{H} = \sum_{\vec{g} \neq 0} \frac{2\pi}{\Omega} \left( \frac{\rho(\vec{g}) \rho(\vec{g})}{|\vec{g}|^2} \right) \delta_{\alpha\beta} \delta_{\vec{g}} - \delta_{\alpha\beta} \frac{E_{\text{Hart}}}{\Omega},
\]  

(34)

where \( \alpha, \beta \) denote coordinate indices \( x, y, \) and \( z \).

2.1.4. Exchange–correlation energy and potential

Since OF-DFT uses the same functionals for the exchange–correlation (XC) energy as does KS-DFT, we only briefly describe those functionals implemented in PROFESS. (PROFESS currently does not possess the capability to perform spin-polarized calculations, so none of the XC functionals currently account for spin.)

The Local Density Approximation (LDA) [50,51] assumes that the XC interactions within a small volume can be approximated by the XC interactions of a uniform electron gas of the same density. Therefore, the LDA XC energy is local and short range and thus can be evaluated completely in real space. Its evaluation scales as \( O(N) \).

The LDA XC energy is written as [51]

\[
E_{\text{XC-LDA}} = \int \left[ \epsilon_X(\rho) + \epsilon_C(\rho) \right] \rho(\vec{r}) \, d\vec{r}.
\]  

(35)

\[
\epsilon_X(\rho) = -\frac{3}{4 \pi} \left( \frac{\rho(\vec{r})}{3} \right)^{1/3},
\]  

(36)

\[
\epsilon_C(\rho) = \begin{cases} \alpha \ln(r_s) + b + cr_s \ln(r_s) + dr_s, & r_s < 1, \\ \frac{1}{1 + \alpha r_s + \beta r_s^{1/2} + \gamma r_s}, & r_s > 1. \end{cases}
\]  

(37)

where \( r_s = (3/(4\pi\rho(\vec{r})))^{1/3}, \) \( a = 0.0311, \) \( b = -0.048, \) \( c = 0.002, \) \( d = -0.0116, \) \( \gamma = -0.1423, \) \( \beta_1 = 1.0529 \) and \( \beta_2 = 0.3334. \)

The LDA XC potential is then [51]

\[
\begin{align*}
\frac{\delta E_{\text{XC-LDA}}}{\delta \rho(\vec{r})} &= \mu_X(\rho) + \mu_C(\rho), \\
\mu_X(\rho) &= \left( \frac{2}{\pi} \rho(\vec{r}) \right)^{1/3}, \\
\mu_C(\rho) &= \left( \frac{\gamma + (1 + \beta r_s^{1/2}) r_s^{1/2} + (1 + \alpha r_s + \beta r_s^{1/2}) r_s}{\gamma + (1 + \beta r_s^{1/2}) r_s^{1/2} + (1 + \alpha r_s + \beta r_s^{1/2}) r_s} \right),
\end{align*}
\]  

(38)

(39)

(40)

and the stress tensor components are written as [16,47,52]

\[
\sigma_{\alpha\beta}^{\text{XC-LDA}} = \left( \frac{\delta E_{\text{XC-LDA}}}{\delta \rho(\vec{r})} \right) \delta_{\alpha\beta}.
\]  

(41)

where \( \alpha, \beta \) denote coordinate indices \( x, y, \) and \( z \).

Though beautifully simple, the LDA XC functional typically overestimates the binding energies of molecules and solids, sometimes even leading to wrong phase ordering [53,54]. The generalized gradient approximation (GGA) for XC was designed to address this problem [55–58]. The GGA functionals depend on the gradient of the density as well as the value of the density, and they generally do not overbind, tending instead to slightly underbind.

There are many flavors of GGA XC functionals; we have chosen to implement the functional developed by Perdew, Burke, and Ernzerhof (PBE) described in [55]. The PBE energy can be split into two parts

\[
E_{\text{XC-GGA}} = E_{\text{XC-GGA-X}} + E_{\text{XC-GGA-C}}
\]  

(42)

and a = 0.0310907, \( \alpha_1 = 0.21370, \) \( \beta_1 = 7.5957, \) \( \beta_2 = 3.5876, \) \( \beta_3 = 1.6382, \) and \( \beta_4 = 0.49294. \) Finally,
\[ H = \gamma \ln \left[ 1 + \frac{\beta}{\gamma} t^2 \left( 1 + \frac{1 + At^2}{1 + At^2 + A^4t^4} \right) \right]. \]  
(53)

\[ A = \frac{\beta}{\gamma} \exp(-\varepsilon^\text{unif}/\gamma) - 1, \]  
(54)

\[ t = \frac{\left\{ \gamma (1 + At^2 + A^4t^4) + \beta t^2 (At^2 + 1) + 2 \right\}}{2k_F \rho(r)} \]  
(55)

\[ k_s = \sqrt{4k_F \rho(r)} \]  
(56)

\[ \gamma = 1 - \ln 2 \]  
(57)

and

\[ \beta = 0.066725. \]  
(58)

Under PBCs, \( \nabla \rho(r) \) is evaluated using FFTs (three convolutions, one for each component of the gradient), and therefore the PBE XC energy scales overall as \( O((N/\ln N)) \).

The PBE XC potential also can be split into its exchange and correlation parts

\[ \frac{\delta E_{\text{XC-GGA}}}{\delta \rho(r)} = \frac{\delta E_{\text{XC-GGA-X}}}{\delta \rho(r)} + \frac{\delta E_{\text{XC-GGA-C}}}{\delta \rho(r)}, \]  
(59)

where

\[ \frac{\delta E_{\text{XC-GGA-X}}}{\delta \rho(r)} = \frac{4}{3} \varepsilon^\text{unif} \left[ F_X + \frac{1 - \mu s}{1 + \mu s^2/\kappa^2} \left( \frac{3}{4k_F} \frac{d|\nabla \rho|}{d\rho} - 2 \right) \right], \]  
(60)

\[ \frac{\delta E_{\text{XC-GGA-C}}}{\delta \rho(r)} = \varepsilon^\text{unif} + H + \rho \frac{\delta \varepsilon^\text{unif}}{\delta \rho} \]  
(61)

\[ - \left( \frac{1}{\gamma} \right) \frac{d|\nabla \rho|}{d\rho} + \frac{\gamma}{\gamma} \frac{d\rho}{k_s} \left[ 1 + 2 \frac{7}{3} \left( 1 + 2 \frac{2}{9} \frac{2}{3} \right) \right] \]

\[ \frac{\delta \varepsilon^\text{unif}}{\delta \rho} = -\frac{r_s}{3\rho} \left[ 2a_0 \rho \ln \left( 1 + \frac{1}{\xi} \right) \right. \]

\[ + \left. \left( 2a_0 \rho \ln \left( 1 + \frac{1}{\xi} \right) \right) \right] \]  
(62)

Finally, the PBE XC stress tensor components are

\[ \sigma^\text{XC-GGA}_{\alpha\beta} = \sigma^\text{XC-GGA-X}_{\alpha\beta} + \sigma^\text{XC-GGA-C}_{\alpha\beta}. \]  
(63)

\[ \sigma^\text{XC-GGA-X}_{\alpha\beta} = \frac{1}{\Omega} \int \left[ \left( \frac{8 \mu s^2}{3 (1 + \mu s^2/\kappa^2)^2} - F_X \right) \right] \]  
(64)

\[ \frac{d \sigma^\text{unif}_{\alpha\beta}}{d \rho} \]  
(65)

\[ \frac{d \sigma^\text{unif}_{\alpha\beta}}{d \rho} \]  
(66)

where \( \sigma^\text{XC-GGA}_{\alpha\beta} \) has been used in place of the usual \( \sigma^\text{XC-GGA}_{\alpha\beta} \) to preserve clarity of notation.

2.2. Kinetic energy density functionals

Undoubtedly the greatest challenge for OF-DFT is to obtain an accurate and general KEFD \( T_{\text{f}}(\rho) \). The orbital-based kinetic energy expression in KS-DFT is exact in the limit of noninteracting electrons. Since we use the same XC functionals as used in KS-DFT, which formally contain the difference between the interacting and noninteracting kinetic energy, \( T_{\text{f}}(\rho) - T_{\text{f}}(\rho) \), our goal has been to develop KEFDs that approximate \( T_{\text{f}}(\rho) \) as well as possible. Thus our OF-DFT will always be at best an approximation to KS-DFT. Although in principle an exact orbital-free KEFD exists, its exact form is not known except in certain limits. Consequently, considerable research effort has been expended to obtain high quality approximations.

The most accurate functional available to date for condensed matter was developed by Wang, Govind, and Carter [24], and consists of the Thomas–Fermi (TF) functional plus the von Weizsäcker (vW) functional plus a term that accounts for the linear response of a uniform electron gas. The WGC functional builds a nonlocal density dependence into the kernel of an earlier functional proposed by Wang and Teter [18], which also consists of the TF and vW KEFDs, plus a linear response term. We next describe each of these terms and their implementations. Throughout this section, we will use \( \tilde{q} \) instead of \( \tilde{g} \) as the reciprocal space vector to maintain consistency with [23] and [24].

2.2.1. Thomas–Fermi kinetic energy density functional

The TF KEFD [60] is the simplest one available, is completely local, and depends only on the density. It is the LDA for the kinetic energy, i.e., it is exact for a uniform electron gas. It has the form

\[ T_{\text{TF}}(\rho) = C_{\text{TF}} \left( \rho(r)^{3/2} \right) \]  
(67)

where \( C_{\text{TF}} = \frac{5}{3} \rho(\rho)^{3/2} \approx 2.871 \). However, this functional by itself predicts no shell structure for atoms and no molecular binding whatsoever [61,62], and therefore is clearly inadequate on its own for describing atoms, molecules, and real materials.

The TF potential is given by

\[ \frac{\delta T_{\text{TF}}}{\delta \rho(r)} = C_{\text{TF}} \rho(r)^{3/2}, \]  
(68)

and the TF stress tensor components are [16]

\[ \sigma_{\alpha\beta}^{\text{TF}} = -\frac{2T_{\text{TF}}(\rho)}{3\Omega} \frac{\delta \varepsilon_{\alpha\beta}}{\delta \rho(r)}, \]  
(69)

where \( \alpha \) and \( \beta \) are Cartesian coordinate indices and \( \Omega \) is the volume of the cell.

2.2.2. von Weizsäcker kinetic energy density functional

The vW KEFD [63] is exact for any single orbital system, i.e., for up to two singlet-coupled fermions or any number of bosons. The vW functional by itself is a lower bound to the true kinetic energy, since it neglects spin and the Pauli Exclusion Principle. Imposition of the Pauli Principle for more than two electrons introduces nodes in the many-body wavefunction, which increase the kinetic energy. Additionally, the functional \( T_{\text{f}}(\rho) = T_{\text{TF}}(\rho) + T_{\text{vW}}(\rho) \) has...
been shown to be an upper bound to the true kinetic energy for noninteracting particles in one dimension [64,65].

The vW functional has the form

$$T_{\text{vW}}[\rho] = \int_\Omega \sqrt{\rho(\mathbf{r})} \left( -\frac{1}{2} \nabla^2 \right) \sqrt{\rho(\mathbf{r})} \, d\mathbf{r}. \quad (70)$$

This integral is simply the standard Hamiltonian form of the kinetic energy when the wavefunction is precisely the square root of the electron density. This functional also can be written as [66]

$$T_{\text{vW}}[\rho] = \frac{1}{8} \int_\Omega \frac{\nabla \rho(\mathbf{r})^2}{\rho(\mathbf{r})} \, d\mathbf{r}. \quad (71)$$

A difference of \( \int_\Omega \frac{1}{8} \nabla^2 \rho(\mathbf{r}) \, d\mathbf{r} \) exists between the two representations. This is readily proved by application of the Chain Rule to Eq. (70):

$$T_{\text{vW}}[\rho] = \int_\Omega \sqrt{\rho(\mathbf{r})} \left( -\frac{1}{2} \nabla^2 \right) \sqrt{\rho(\mathbf{r})} \, d\mathbf{r}$$

$$= \int_\Omega \frac{1}{2} \sqrt{\rho(\mathbf{r})} \nabla (\rho(\mathbf{r})) \, d\mathbf{r}$$

$$= \int_\Omega \frac{1}{2} \sqrt{\rho(\mathbf{r})} \nabla (\rho(\mathbf{r})) \nabla (\rho(\mathbf{r})) \, d\mathbf{r}$$

$$= \int_\Omega \frac{-1}{4} \sqrt{\rho(\mathbf{r})} \nabla (\rho(\mathbf{r})) \nabla (\rho(\mathbf{r})) \, d\mathbf{r}$$

$$= \int_\Omega \left( \frac{-1}{4} \nabla^2 \rho(\mathbf{r}) + \frac{1}{8} \frac{\nabla \rho(\mathbf{r})^2}{\rho(\mathbf{r})} \right) \, d\mathbf{r}. \quad (72)$$

Since the value of \( \int_\Omega \left( \frac{-1}{4} \nabla^2 \rho(\mathbf{r}) \right) \, d\mathbf{r} \) is zero under PBCs, Eqs. (70) and (71) yield the same value in a periodic system. Although we are free to use (and have implemented) both expressions, we find the first form (containing the Laplacian) more convenient for reasons outlined later.

Although no unique expression exists for the vW KEDF energy, the functional derivative of the vW KEDF (and indeed all KEDFs) is unique. In other words, although Eqs. (70) and (71) differ by \( \int_\Omega \frac{-1}{4} \nabla^2 \rho(\mathbf{r}) \, d\mathbf{r} \), which is in general nonzero for arbitrary boundary conditions, the functional derivatives of both Eqs. (70) and (71) are the same under all boundary conditions. This can be seen easily by taking the functional derivative with respect to \( \rho \) of \( \int_\Omega \left( \frac{-1}{4} \nabla^2 \rho(\mathbf{r}) \right) \, d\mathbf{r} \), which is zero.

The functional derivative with respect to \( \rho \) of the vW KEDF is given by [66]

$$\frac{\delta T_{\text{vW}}}{\delta \rho(\mathbf{r})} = - \frac{1}{8} \frac{\nabla^2 \rho}{\rho} + \frac{1}{8} \nabla \rho \cdot \nabla \rho - \frac{1}{8} \left( \frac{1}{\sqrt{\rho}} \right) \frac{\sqrt{\rho}}{\rho} \quad (73)$$

and the vW stress tensor components are given by [16]

$$\sigma_{\alpha\beta}^{\text{vW}} = - \frac{1}{4} \delta \rho \frac{1}{4} \frac{\partial}{\partial r_\alpha} \frac{\partial}{\partial r_\beta} \, \delta \rho. \quad (74)$$

where \( \alpha \) and \( \beta \) are Cartesian coordinate indices and \( \Omega \) is the volume of the cell.

The functional derivative in Eq. (73) can be used as part of the total potential \( \frac{\delta E_{\text{total}}}{\delta \rho} \) to minimize the energy, e.g., in a conjugate gradient minimization using an active-set method (see below) [67] to prevent the density from becoming negative. However, we find that minimization is more easily achieved by using a transformation of variables, such as setting \( \chi = \sqrt{\rho(\mathbf{r})} \) and minimizing the total energy with respect to \( \chi \) [24,68–71]. Using this variable transformation, the first expression for the vW functional in Eq. (70) becomes

$$T_{\text{vW}}[\chi] = \int_\Omega \chi(\mathbf{r}) \left( -\frac{1}{2} \nabla^2 \right) \chi(\mathbf{r}) \, d\mathbf{r} \quad (75)$$

and the functional derivative with respect to \( \chi \) is simply:

$$\frac{\delta T_{\text{vW}}}{\delta \chi(\mathbf{r})} = - \nabla^2 \chi(\mathbf{r}) \quad (76)$$

It is also possible to work under the transformation \( \chi = \ln \rho(\mathbf{r}) \), in which case the equations become [72]

$$T_{\text{vW}}[\chi] = \int_\Omega e^{\chi^2(\mathbf{r})/2} \left( -\frac{1}{2} \nabla^2 \right) e^{\chi^2(\mathbf{r})/2} \, d\mathbf{r} \quad (77)$$

and

$$\frac{\delta T_{\text{vW}}}{\delta \chi(\mathbf{r})} = - \frac{1}{2} e^{\chi^2(\mathbf{r})/2} \left( \frac{1}{\chi^2(\mathbf{r})} \right) \, d\mathbf{r}. \quad (78)$$

However, we use the \( \chi = \sqrt{\rho(\mathbf{r})} \) transformation for most cases, since we have found that it usually converges faster.

Under PBCs, the terms above are easily evaluated exactly using two FFTs. For instance, with \( \chi = \sqrt{\rho(\mathbf{r})} \),

$$T_{\text{vW}}[\chi] = \int_\Omega \chi(\mathbf{r}) \left( -\frac{1}{2} \nabla^2 \right) \chi(\mathbf{r}) \, d\mathbf{r}$$

$$\Rightarrow - \frac{1}{2} \int_\Omega \chi(\mathbf{r}) \tilde{\nabla}^2 \chi(\mathbf{r}) \, d\mathbf{r} \quad (79)$$

and

$$\frac{\delta T_{\text{vW}}}{\delta \chi(\mathbf{r})} = - \frac{1}{2} \chi(\mathbf{r}) \tilde{\nabla}^2 \chi(\mathbf{r}) \quad (80)$$

where \( \tilde{\nabla} \) and \( \tilde{\nabla}^2 \) are forward and reverse transforms defined in Eq. (30), and \( q \) is the norm of a reciprocal space vector.

2.2.3. The Wang–Teter functional

As previously mentioned, the TF KEDF is exact in the limit of a uniform electron gas, and the vW KEDF is exact in the limit of a single orbital, respectively. It is possible to use various linear combinations of these two KEDFs (such as by setting \( T_{\chi}[\rho] = T_{\text{TF}}[\rho] + \lambda T_{\text{vW}}[\rho] \) where \( \lambda \) is a parameter) to obtain higher accuracy than provided by either KEDF alone. \( \lambda = \frac{1}{2} \) is an especially significant choice that can be derived from a gradient expansion, but other values such as \( \lambda = \frac{1}{5} \), 0.186, \( \frac{1}{6} \) and 1 and have also been justified by Yang via the construction of closed-form density matrices [66,73]. However, these KEDFs are clearly insufficient, as atomic shell structure remains absent, and densities decay algebraically instead of exponentially. Moreover, these KEDFs do not yield the correct linear response behavior of a uniform electron gas subject to small perturbations in the potential (derived analytically by Lindhard) [74], and in general the \( T_{\chi}[\rho] + \lambda T_{\text{vW}}[\rho] \) energetics still greatly differ from KS-DFT results, with errors on the order of many Hartrees [73].

One way to improve the KEDF for nearly-free-electron materials, first developed by Wang and Teter [18] and later extended by many others [19–23], is to explicitly enforce the Lindhard linear response behavior, such that

$$\tilde{\nabla}^2 T_{\chi} \bigg|_{\rho_{\text{Lin}}} = - \frac{1}{\chi_{\text{Lin}}}. \quad (81)$$
where $\rho_0$ is the average electron density and $\chi_{\text{Lind}}$ is the Lindhard susceptibility function in reciprocal space given by

$$
\chi_{\text{Lind}} = -\frac{k_F}{\pi^2} \left( \frac{1}{2} - \frac{1 - |\eta|^2}{4|\eta|} \ln \left| \frac{1 + |\eta|}{1 - |\eta|} \right| \right) (82)
$$

in reduced units, where $k_F = (3\pi^2 \rho_0)^{1/3}$ is the Fermi wavevector and $\hat{\eta} = \hat{q}/2k_F$ is a dimensionless momentum.

The full Wang–Teter (WT) KEDF enforcing linear response has the form [18]

$$
T_{s}^{\alpha,\beta} [\rho] = T_{\text{TF}} [\rho] + T_{\text{vW}} [\rho] + T_{\text{GWC}}^{\alpha,\beta} [\rho] (83)
$$

where

$$
T_{lr}^{\alpha,\beta} [\rho] = C_{\text{TF}} [\rho^{\alpha}(r')] |w_{\alpha,\beta}(r' - r)| |\rho^{\beta}(r')| (84)
$$

Here, $\alpha$ and $\beta$ are parameters. For instance, the choice $\alpha = \beta = 1$ corresponds to the Perrot functional [19], $\alpha = \beta = 1/2$ is the Smargiassi–Madden functional [21], $\alpha = 2 + \sqrt{5}/5$, $\beta = 2 - \sqrt{5}/5$ is the first WGC functional (with a density-independent kernel $w_{\alpha,\beta}(r' - r')$) [23], and $\alpha = \beta = 5/6$ corresponds to the original WT functional [18].

Eq. (84) can be solved in reciprocal space using the convolution theorem

$$
\hat{T}_{\text{WGC}} [\rho] = \hat{C}_{\text{TF}} [\rho^{\alpha}(r')] |\hat{w}_{\alpha,\beta}(\hat{q})| |\rho^{\beta}(\hat{q})| (85)
$$

requiring only knowledge of the kernel $w_{\alpha,\beta}(r' - r)$ in reciprocal space. In order to enforce the correct linear response behavior for the entire KEDF, the linear response kernel must have the form [21]

$$
\hat{F}_{\alpha,\beta}(\hat{q}) = \delta_{\alpha,\beta} - \frac{\chi_{\text{Lind}} - \chi_{\text{vW}} - \chi_{\text{TF}}}{2\alpha \beta C_{\text{TF}} p_0} \rho^{\alpha}(\hat{q}) \rho^{\beta}(\hat{q}) (86)
$$

where $\chi_{\text{TF}} = -k_F/\pi^2$ is the response of the TF KEDF and $\chi_{\text{vW}} = \chi_{\text{TF}}/(3\pi^2)$ is the response of the vW KEDF. It is more convenient to express $\tilde{w}_{\alpha,\beta}$ in terms of $|\eta|$ [24]:

$$
\tilde{w}_{\alpha,\beta}(\eta) = \frac{5}{9 \alpha \beta p_0^{\alpha+\beta-3/2}} \left( 1 + \frac{1 - |\eta|^2}{4|\eta|} \ln \left| \frac{1 + |\eta|}{1 - |\eta|} \right| \right)^{-1}
$$

$$
- 3|\eta|^2 - 1 (87)
$$

The functional derivative of the linear response term of the WT kinetic energy with respect to the electron density is given by

$$
\frac{\delta T_{\text{GWC}}^{\alpha,\beta} [\rho]}{\delta \rho} = C_{\text{TF}} \left[ \alpha \rho^{\alpha-1}(r') \int w_{\alpha,\beta}(r' - r) \rho^{\beta}(r') \, dr' + \beta \rho^{\beta-1}(r) \int w_{\alpha,\beta}(r' - r) \rho^{\alpha}(r') \, dr' \right] (88)
$$

and the stress tensor components can be expressed as [16]

$$
\sigma_{\alpha\beta}^{\alpha,\beta} = -\frac{2 T_{\text{TF}}^{\alpha,\beta}}{3 \Omega} + \frac{\pi^2}{2 \alpha \beta p_0^{\alpha+\beta-2} k_F} \sum_{\tilde{q} \neq 0} \left[ \Delta \rho^{\alpha}(\tilde{q}) \Delta \rho^{\beta}(-\tilde{q}) \right]
$$

$$
\times \left\{ \frac{q_{\alpha} q_{\beta}}{|\tilde{q}|^2} - \frac{1}{3} \delta_{\alpha\beta} \right\}
$$

$$
\times \left\{ \frac{|\tilde{q}|}{f_{\tilde{q}}(\eta)} \left( \frac{1}{2|\eta|} - \frac{1}{4} \left( 1 + \frac{1}{|\eta|^2} \right) \ln \left| \frac{1 + |\eta|}{1 - |\eta|} \right| \right) + 6|\tilde{q}|^2 \right\}. (89)
$$

where $q_\alpha$ and $q_\beta$ are the components of the $\tilde{q}$ vectors in the directions specified by the coordinate indices $\alpha$ and $\beta$.

$$
\int_{\tilde{q}} (\eta) = \frac{1}{2} \frac{1 - |\tilde{q}|^2}{4|\eta|} \ln \left| \frac{1 + |\eta|}{1 - |\eta|} \right|. (90)
$$

$$
\Delta \rho^{\alpha}(\tilde{q}) = \hat{F} \left( \rho^{\alpha}(r') - \rho_0^{\alpha}(r') \right). (91)
$$

$$
\Delta \rho^{\beta}(\tilde{q}) = \hat{F} \left( \rho^{\beta}(r') - \rho_0^{\beta}(r') \right). (92)
$$

and where we have used $\sigma_{\alpha\beta}$ instead of the usual $\sigma_{\alpha\beta}$ to avoid overlap of notation.

2.2.4. The Wang–Govind–Carter functional

One weakness of the WT KEDF is that the electron density of the entire system is expected to obey the linear response calculated for only one unique density, $\rho_0$. A way to systematically improve the WT KEDF is to introduce a density dependence into the linear response kernel. WGC devised a way to do this within PBCs, while preserving $O(N \ln N)$ scaling [24]. The KEDF takes the form

$$
T_{s}^{\alpha,\beta,\gamma} [\rho] = T_{\text{TF}} [\rho] + T_{\text{vW}} [\rho] + T_{\text{GWC}}^{\alpha,\beta,\gamma} [\rho] (93)
$$

where

$$
T_{\text{GWC}}^{\alpha,\beta,\gamma} [\rho] = C_{\text{TF}} [\rho^{\alpha}(r')] |w_{\alpha,\beta}(\xi_{\gamma}(r', r') - F - F'') | |\rho^{\beta}(r')| (94)
$$

and

$$
\xi_{\gamma}(r', r') = \left( \frac{k_F^{\alpha} + k_F^{\beta}}{2} \right)^{1/2} (95)
$$

is the nonlocal two-body Fermi wavevector from which the density dependence arises, and $k_F = (3\pi^2 \rho(r'))^{1/3}$ is the local one-body Fermi wave vector. Although universal values of $\alpha$ and $\beta$ were derived from asymptotic analysis [24], the optimal value for $\gamma$ varies depending on whether a metallic ($\gamma_{\text{opt}} = 2.7$) or a semiconducting ($\gamma_{\text{opt}} = 4.2$) material is studied [25]. (Note that although [25] refers to $\gamma_{\text{opt}} = 3.6$ as the optimal value for semiconductors, there is recent evidence that $\gamma_{\text{opt}} = 4.2$ is superior [72].) Further mathematical details of the WGC kernel are complex, and will not be discussed here. An expression for the WGC stress is presented in [75].

Since the WGC KEDF contains a density dependence in the kernel, FFTs cannot be used directly to perform the convolution. In order to preserve linear scaling, the density dependence is factored out via a Taylor expansion around a reference electron density $\rho^*$, which is usually chosen to be the average electron density of the bulk phase of the substance under study. Since this expansion can only be carried out to second order before it diverges due to the logarithmic singularity of the Lindhard function, the more the local density in a system deviates from $\rho^*$, the less numerically stable the WGC KEDF becomes [25].

Despite this, OF-DFT using the WGC KEDF gives results significantly closer to KS-DFT than does the WT KEDF. The energies of many aluminum bulk phases are reproduced to within 10 meV/atom [24]. In addition, in contrast to the WT KEDF, the WGC KEDF was shown to produce accurate properties of Mg and Al–Mg alloys [76]. Furthermore, the WGC KEDF was found to be much more accurate for describing vacancies and surfaces than the WT KEDF [24]. For this reason, we used the WGC KEDF to study vacancy aggregation in [46].

3. Optimization methods for OF-DFT

The second Hohenberg–Kohn theorem states that for a trial density $\rho^f(r')$, in which $\rho^f(r') \geq 0$ at all points and $\int_{\Omega} \rho^f(r') \, d\Omega = N_e$, with $N_e$ the number of electrons and $\Omega$ the volume, $E[\rho^f(r')] \geq E_{\text{ground}}$, where $E_{\text{ground}}$ is the exact ground state total energy [3].
Thus, given a configuration of ions that creates an external potential and a trial electron density $\rho(\vec{r})$, we can recover the ground state electron density and energy by minimizing the total energy of the system with respect to the electron density, subject to the two constraints that the number of electrons be conserved and that the density be nonnegative everywhere. More simply, we wish to solve the nonlinear, multidimensional minimization problem

$$E_{\text{OF-DFT}} = \min_{\rho} \left( E_{\text{OF-DFT}}[\rho] - \lambda \left( \int_\Omega \rho(\vec{r}) \, d\vec{r} - N_e \right) ; \rho \geq 0 \right), \quad (96)$$

where $\lambda$ is a Lagrange multiplier used to enforce the constraint that the total number of electrons $N_e$ is conserved.

Then the Euler-Lagrange equation for minimizing the OF-DFT total energy to solve for $\rho$ is

$$\frac{\delta E}{\delta \rho}[\rho] - \lambda = 0. \quad (97)$$

where $\lambda$ is calculated as the average value of $\delta E/\delta \rho$ over all gridpoints. In practice, PROFFESs indicates a successful minimization when

$$\left[ \int_\Omega \left( \frac{\delta E}{\delta \rho} - \lambda \right)^2 \, d\vec{r} \right]^{1/2} < \text{tol}, \quad (98)$$

where tol is a small tolerance.

Generally it is also desirable to find the minimum energy with respect to the ion positions, i.e., to optimize the atomic structure. In this case, one solves the equation

$$F_1(R_I) = 0. \quad (99)$$

Whenever the ion positions are moved during the course of the optimization to a new state $\{R_I\}$, the electron density must be reoptimized as per the Born–Oppenheimer approximation. One also may wish to find the equilibrium cell shape and volume by minimizing the energy with respect to the lattice vectors, via solving

$$\sigma_{\alpha \beta} = 0 \quad (100)$$

for each of the six unique components $\sigma_{\alpha \beta}$ of the stress tensor $\sigma$. In this case, the ion positions and electron density also will require simultaneous optimization.

A variety of techniques are available for minimizing Eq. (96) (or solving Eqs. (97), (99), or (100)). Ideally, an algorithm must be robust (able to reliably minimize from some reasonable initial guess), fast, and use an $O(N)$ amount of memory. We have implemented direct gradient methods [77], the nonlinear conjugate gradient method [77], the truncated Newton method [78], and the Multigrid method [29] in PROFFESS. We briefly outline these schemes below (with the exception of the Multigrid method, leaving it as the primary subject of a future publication). However, before doing so, we first discuss strategies for imposing constraints on the density, which lead to a different choice of optimization variable, which is then used to illustrate the different optimization algorithms.

Suppose that one is trying to solve Eq. (97) to yield an energy minimum and optimized density, subject to the constraint that the total number of electrons is fixed and that the density remains nonnegative at all points. Directly solving Eq. (97) as formulated can be inconvenient, as it becomes much more difficult to enforce the global constraint that at all points the density must remain positive. For instance, a multiple of $(\delta E/\delta \rho - \lambda)$ is sometimes added to the present density to obtain the new density (as in the steepest descent method, described below). Since $(\delta E/\delta \rho - \lambda)$ contains negative values, in some cases this will predict negative density values for the next iteration.

The standard way to deal with this kind of inequality constraint is to use the active set method [67]. In this method, the inequality constraint that each gridpoint must be nonnegative can be either “active” or “inactive”. If the constraint is inactive, then a new density at that gridpoint is obtained by adding a function of $(\delta E/\delta \rho - \lambda)$ at that gridpoint, as before. If it is active, then the density at that point is fixed, and $(\delta E/\delta \rho - \lambda)$ at that point is set to zero for all further iterations (i.e., the density is not further affected by $(\delta E/\delta \rho - \lambda)$). The inequality constraint at each point starts out as inactive. When the minimizer at any iteration predicts a negative density at a gridpoint, the value of the density at that gridpoint is set to zero (or a very small positive number, in order to avoid numerical instabilities in the kinetic energy functionals) and the constraint becomes active.

However, the difficulty with the active set method is the following. Suppose that the algorithm predicts at an intermediate stage a density that is zero in some region, but the final optimized density is in fact nonzero. Once the constraint at a point has been set to become active, there are no clear criteria for making it inactive again and allowing the density to emerge from zero to the true optimized density. One possibility is to free all active constraints periodically, e.g., at the end of the minimization using the current active set. However, in the course of our development of PROFFESS, we have found this method becomes too easily stuck in local minima, and in general to be unacceptably slow.

An alternative to the active set method is to simply take the absolute value of $\rho$ whenever it becomes negative and renormalize the density. While this solution generally seems to work faster and more reliably than the active set method, there are two issues that prevent it from being ideal. First, the conjugacy in the conjugate gradient method (described below) is spoiled whenever the density becomes negative and the conjugate gradient method must be restarted. Secondly, it suffers from numerical instabilities. In particular, Eq. (73) (the vW potential) diverges as $\rho \to 0$, causing the algorithm to be extremely unstable at small values of the density.

However, it is easy to reformulate Eq. (97) in terms of $\chi$

$$\frac{\delta \rho}{\delta \chi} \left( \frac{\delta E}{\delta \rho} (\chi) - \frac{\delta \rho}{\delta \chi} \lambda \right) = 0, \quad (101)$$

where possible values of $\chi$ include $\rho$ (identical to above), $\sqrt{\rho}$ [24,68–71], and $\ln \rho$ [72]. For $\chi = \sqrt{\rho}$, $\delta \rho/\delta \chi = 2\sqrt{\rho}$, and for $\chi = \ln \rho$, $\delta \rho/\delta \chi = \rho$. The value of the density is then iterated by adding a descent direction derived from $(\delta E/\delta \chi (\chi) - \delta \rho/\delta \chi \lambda)$ to $\chi$. For example, in steepest descent, the descent direction is simply a multiple of $(\delta E/\delta \chi (\chi) - \delta \rho/\delta \chi \lambda)$, in the conjugate gradient method it is a component of $(\delta E/\delta \chi (\chi) - \delta \rho/\delta \chi \lambda)$, which is conjugate to all the previous directions, etc. The advantage of solving Eq. (101) with the last two variational parameter choices ($\sqrt{\rho}$ or $\ln \rho$) is that $\rho$ will automatically be nonnegative, regardless of the value of $\chi$, since in the first case $\rho = \chi^2$, and in the second case $\rho = e^\chi$. Even more importantly (as mentioned by many previous authors regarding the formulation $\rho = \chi^2$, e.g., [71]), the vW potential does not diverge for low values of $\chi$ (Eq. (76)), avoiding many numerical instabilities.

However, the tradeoff in both cases is that the constraint that the total number of electrons must remain constant becomes more difficult to enforce. When $\rho$ itself is the variational parameter, Eq. (97) guarantees that as long as $\lambda$ is specified correctly as the average of $\delta E/\delta \rho$ over the gridpoints, the sum of any multiple of $(\delta E/\delta \rho - \lambda)$ will be zero. Therefore, adding any multiple of $(\delta E/\delta \rho - \lambda)$ to the density $\rho$ will not change $\int_\Omega \rho(\vec{r}) \, d\vec{r}$ but the total number of electrons will be preserved automatically. However, when $\chi \neq \rho$, adding any multiple of $(\delta E/\delta \chi (\chi) - \delta \rho/\delta \chi \lambda)$ to $\chi$ will change $\int_\Omega \rho(\vec{r}) \, d\vec{r}$ unless the value of $\chi$ is assigned to preserve the number of electrons for that multiple of $(\delta E/\delta \chi (\chi) - \delta \rho/\delta \chi \lambda)$ specifically [71,72]. Since the total number of electrons is generally not
conserved in this case, each step requires $\chi$ to be renormalized to the correct number of electrons. This adds complexity to the minimization, and the effect of this renormalization step on the minimization algorithms in PROFESS has not yet been well characterized mathematically.

Working with $\chi = \ln \rho$ seems at first glance to be ideal, since there is a one-to-one correspondence between $\chi$ and $\rho$ (as opposed to the case where $\chi = \sqrt{\rho}$, where both positive and negative values of $\chi$ will give the same $\rho$). We have found $\chi = \ln \rho$ to perform more efficiently than $\chi = \rho$, but at the time of this writing $\ln \rho$ still is less stable and robust in general than working with $\chi = \sqrt{\rho}$. This may be due to the fact that, when $\chi = \ln \rho$, $\rho$ is extremely sensitive to small changes in $\chi$. See [72] for more details.

After trying still other choices for $\chi$ (e.g., $\chi = \rho^{1/4}$), we find working with $\chi = \sqrt{\rho}$ gives the fastest and most reliable convergence within all minimization methods tried. Although $\rho = \chi^2$ will never be negative regardless of the value of $\chi$, in practice it is important that $\chi$ always remain nonnegative to preserve a one-to-one correspondence between $\chi$ and $\rho$. Otherwise, for a single $\chi$ containing negative values, calculating the vW energy via Eq. (75) gives a different answer than using Eq. (70) after first obtaining $\rho = \chi^2$. Therefore, $\chi$ must be set to its absolute value every time it is updated [80].

3.1. Direct gradient methods

The most direct way of reaching an energy minimum $E_{\text{min}}[\chi]$ starting with a guess $\chi_0$ is by simply traversing in the direction opposite to the first functional derivative with respect to the density, as in the pseudocode below:

$\tilde{\chi} \leftarrow \chi_0$;

while $\left[ \int_\Omega \left[ \frac{\delta E}{\delta \chi} \mid \tilde{\chi} \right]^2 d\Omega \right]^{1/2} \geq \text{tol}$,

$g \leftarrow \frac{\delta E}{\delta \chi} \mid \tilde{\chi}$;

$\tilde{\chi} \leftarrow \text{Normalize}(\tilde{\chi} - sg)$;

end (while)

Here, $g$ is the gradient projected onto the constrained space where the total number of electrons is fixed, and $s > 0$ is a step size that either can be fixed, determined adaptively, or determined via a line search. (The function $\text{NORMALIZE}$, specific to the choice of $\chi$, ensures that the constraint on the number of electrons is observed at every $\chi_\ast$.)

A line search systematically minimizes $E[\text{Normalize}(\tilde{\chi} - sg)]$ with respect to $s$. Several methods exist for performing this line search, but all proceed by guessing an initial $s$, calculating the energy and/or potential associated with it, and then continually updating $s$ based on the energies and/or potentials from previous guesses until an optimal value is found (e.g., by extrapolating a parabola from the most recent energies and using the minimum of the parabola as the next guess). In PROFESS, we use Brent’s algorithm [77,81] or the algorithm implemented in MINPACK-2 [82].

If a line search is used, the algorithm is simply the steepest descent method. However, a line search typically requires 3–10 energy evaluations. For energy landscapes that are convex and well-behaved, it is sufficient to forego the line search and keep $s$ fixed to a relatively small value (less than 1), perhaps slowly decreasing it near the minimum in order to prevent overshooting. In fact, this type of direct gradient minimization is the primary algorithm used to minimize the stress tensor. However, the main weakness of this method is that the rate of convergence is highly dependent on the value of $s$. If $s$ is too small, progress towards the minimum will be unacceptably slow, and if $s$ is too large, the algorithm will sample values that oscillate around the minimum or will diverge.

Another alternative to an expensive line search is the quickmin method [83], a technique closely related to damped molecular dynamics. This scheme is suitable for minimization of ionic forces, faster in many cases than the conjugate gradient method. In the quickmin algorithm, there are two components to the step size: a constant step size and a step size dependent on the “velocity”, defined as the difference between the current and previous ionic positions divided by the previous total step size.

The algorithm proceeds as follows for the minimization of ionic forces. At every iteration, if the forces from the current step are antiparallel to the velocities, the velocity-dependent component of the step size is set to zero. If the velocity component of the previous step size was also zero, the constant component of the step size is decreased. Otherwise, the velocity-dependent component of the step size is set to the scalar product of the forces and the velocities. Though simple, this scheme guarantees that the step size is always large enough for the minimization to make sufficient progress, but not so large that convergence will never be reached.

While sufficient for minimization of the stress tensor and the ionic forces, direct gradient methods are too slow for minimizing the energy with respect to the electron density. This is partly due to the much larger number of degrees of freedom (equal to the number of grid points) present for the electron density than for the ions or the lattice vectors, and partly due to the constraints placed upon the electron density not present for the ions and lattice vectors (conservation of number of electrons and nonnegativity), both of which make for a much more complex minimization problem. Fortunately, methods that are generally more efficient are available, as described next.

3.2. Nonlinear conjugate gradient method

The main drawback of the steepest descent method is that the successive directions are chosen simply as a multiple of the gradient after each line search. At the minimum of the line search, however, the new gradient is always perpendicular to the old direction (otherwise, there would be a component of the new gradient in the old direction, and the line search would not be complete). However, there is no reason why this should be the most direct path to the minimum.

A better descent direction can be derived by recognizing that the primary weakness of the steepest descent method is that each new direction is based only on the gradient at that point of the minimization, and does not make use of any of the directions previously traversed. However, information from previous directions can be useful if one realizes that, after each line minimization in a given direction, the gradient in that direction is zero. Ideally, one would like all subsequent directions to leave the gradient in this direction unchanged in order to avoid wasted work. Another way of saying this is that one wants all directions to be conjugate to each other. In a perfect parabolic well representing $N$ degrees of freedom, one simply needs to minimize along $N$ such vectors in order to set all components of the gradient to zero and thus be at a minimum. The steepest descent method does not enforce conjugacy, since it has no knowledge of previous directions, forcing it to minimize along the same directions over and over again and hence to zigzag to the minimum [77].

Conjugacy of directions can be enforced in several ways. Since the Euler–Lagrange OF-DFT equation is nonlinear due to the nonlinear terms in $\delta E/\delta \rho$, we must use the nonlinear conjugate gradient method. PROFESS uses the Polak–Ribière method [84], which proceeds as follows
obtain can be used to solve this equation as long as there is a way to compute. Luckily, the Hessian does not need to be computed explicitly, but only the action of the Hessian on a vector is needed.

Of course, the OF-DFT energy landscape is not a perfect parabolic well, and so convergence in $N$ iterations is not guaranteed. In addition, given that $N$ is equal the number of gridpoints (usually millions), this would not be acceptable anyway. Fortunately, convergence is usually achieved in far fewer iterations, on the order of thirty for a well-behaved system to a few hundred for extremely ill-behaved systems.

### 3.3. Truncated Newton method

The truncated Newton method [78] was first implemented in the context of OF-DFT by García-Cervera [80], and is based on the simple principle that, given a reasonable initial guess, successive Newton iterations will solve an equation (in this case, the Euler–Lagrange equation) that can be approximated as a quadratic functional.

The truncated Newton method proceeds similarly to the nonlinear conjugate gradient method outlined above, except that $h$ is not needed, and $\chi$ are determined as

$$
g \leftarrow \left( \frac{\delta E}{\delta \chi} (\chi) - \frac{\delta \rho}{\delta \chi} \right) \bigg|_{\chi = \chi_0} \lambda; \\
s \leftarrow \min_s E [\text{Normalize}(\chi_0 - sg)]; \\
\tilde{\chi} \leftarrow \text{Normalize}(\chi_0 - sg); \\
g_{\text{old}} \leftarrow g; \ h_{\text{old}} \leftarrow s; \\
\text{while} \notag \left[ \int_{V} g_{\text{old}} \cdot g_{\text{old}} \right]^{1/2} \geq \text{tol} \notag \\
g \leftarrow \left( \frac{\delta E}{\delta \chi} (\tilde{\chi}) - \frac{\delta \rho}{\delta \chi} \right) \bigg|_{\tilde{\chi}} \lambda; \\
h \leftarrow -\left( g - g_{\text{old}} \right) \cdot g_{\text{old}}; \\
s \leftarrow \min_s E [\text{Normalize}(\chi + sh)]; \\
\tilde{\chi} \leftarrow \text{Normalize}(\chi + sh); \\
g_{\text{old}} \leftarrow g; \ h_{\text{old}} \leftarrow h; \\
\text{end (while)}$$

where $\lambda$ is the Lagrange multiplier corresponding to $\frac{\delta E}{\delta \chi} (\chi)$ and $\lambda'$ is the Lagrange multiplier corresponding to $\frac{\delta \rho}{\delta \chi} (\chi + eh)$.

The truncated Newton method using $\chi = \sqrt{\rho}$ is our fastest method for energy minimization with respect to the electron density to date, converging more than twice as fast as the nonlinear conjugate gradient method using $\chi = \sqrt{\rho}$ in most cases. However, the truncated Newton method is somewhat sensitive to the initial guess, and in many instances can fail to converge from a uniform density. In such cases, the initial guess first can be refined with several steepest-descent/conjugate-gradient iterations, after which the truncated Newton method can be used for most efficient convergence.

### 4. Results and discussion

In this section, we demonstrate the scaling and timing of PROFESS on a single 2.5 GHz AMD Opteron processor using the Intel Fortran compiler with full optimizations. Throughout this section, the ion–ion energy is calculated via the Ewald summation (Eq. (8)) and ion–electron potential (Eq. (21)) is calculated using the Goodwin pseudopotential for aluminum. The LDA exchange–correlation functional (Eq. (35)) and the WGC KEDF (Eq. (93)) are employed.

![Fig. 1](image-url) (top) Total time (wall time) used to calculate each OF-DFT energy term within the course of an electron density optimization, using truncated Newton minimization on bulk fcc aluminum supercells containing 108, 500, 1372, 2916, 5324, 8788, and 13,500 atoms (corresponding to $1.2 \times 10^{5}$, $5.3 \times 10^{5}$, $1.7 \times 10^{6}$, $3.2 \times 10^{6}$, $5.8 \times 10^{6}$, $9.3 \times 10^{6}$, and $1.4 \times 10^{7}$ gridpoints, respectively). All terms are linear scaling except the ion–ion energy. (bottom) Zoom-in to resolve the linear scaling terms. Time required to calculate the WGC energy clearly dominates among the linear scaling terms.
converge the total energy to well within 1 meV.

energy cutoff of 600 eV is used for this system, which is sufficient to bulk aluminum with a lattice constant of 4.032 Å. A kinetic energy and the ion–electron potential are subtracted out of the total time required for an electron density optimization starting at a uniform electron density as the initial guess. Clearly, all terms involving only the electron density are linear scaling for these terms so that the entire algorithm becomes much more impressive (twice as fast) with respect to the linear scaling terms.

First, we examine a periodic system of face-centered cubic (fcc) bulk aluminum with a lattice constant of 4.032 Å. A kinetic energy cutoff of 600 eV is used for this system, which is sufficient to converge the total energy to well within 1 meV/atom.

Fig. 1 shows the total time (summed over all iterations) spent calculating each of the OF-DFT energy terms throughout the course of electron density optimizations on systems containing 108 to 13,500 atoms. The truncated Newton method was used starting from a uniform electron density as the initial guess. Clearly, all terms are approximately linear scaling as the number of atoms is increased (including the calculation of the WGC energy) except for the time to compute the ion–ion energy. (In all plots, the number of gridpoints scales approximately linearly with the number of atoms.) Fig. 2 shows the same plots for the time required to calculate the OF-DFT potential terms. Here, the ion–electron term scales quadratically. However, the times spent to calculate all other potential terms scale linearly.

Clearly, all terms involving only the electron density are linear scaling, while terms involving ions start to dominate as the ions start to number in the thousands. The ion–electron energy (Eq. (20)) is linear scaling in our implementation because we store the ion–electron potential after it is computed. The expense is thus in calculating the ion–electron potential. Once the ion–electron potential is available, the ion–electron energy is obtained simply by multiplying the potential by the electron density and performing the summation in reciprocal space. While both the ion–ion energy and the ion–electron potential calculations scale quadratically, the ion–electron potential calculation is much slower than the ion–ion energy calculation, since the former is \(O(N^2)\) scaling and the latter is only \(O(N)\) scaling (see Fig. 3 for total timings). This is remarkable, considering that the ion–ion energy and the ion–electron potentials are calculated only once at the beginning of the electron density optimization, while all other energy and potential terms are calculated many times as the density is optimized. Due to the quadratic scaling of the ion–ion and ion–electron terms, systems consisting of much more than 13,500 atoms quickly become prohibitively expensive. In order to address this, we recently implemented particle-mesh Ewald algorithms [33, 34, 49] for both the ion–ion and ion–electron terms [17], which exhibit linear scaling for these terms so that the entire algorithm scales linearly.

Fig. 3 shows the total times required for the electron density optimization using both the truncated Newton and the conjugate gradient methods. Both methods show overall \(O(N^2)\) scaling as \(N\) increases to several million grid points corresponding to cases with thousands of atoms. However, once the times for the ion–ion energy and ion–electron potential are subtracted out of the total time for the calculations, the scaling for all remaining operations in the electron density optimization becomes essentially linear (Fig. 4). In addition, the performance of the truncated Newton algorithm becomes much more impressive (twice as fast) with respect to the conjugate gradient algorithm as the system size increases.

Next, we examine the percentage of time spent calculating each of the OF-DFT terms (summing both energy and potential calculations for each term) during the optimization, after the times for the ion–ion energy and ion–electron potential have been...
Fig. 4. Total timings (wall time) minus the time used for the calculation of the ion–ion energy and the ion–electron potential for OF-DFT calculations on bulk fcc aluminum using 108, 500, 1372, 2916, 5324, 8788, and 13,500 atoms (corresponding to \(1.2 \times 10^5, 5.3 \times 10^5, 1.7 \times 10^6, 3.2 \times 10^6, 5.8 \times 10^6, 9.3 \times 10^6, \) and \(1.4 \times 10^7\) gridpoints, respectively). These timings demonstrate the linear scaling of all other operations in PROFESS. Here, the truncated Newton method is more than twice as fast as the conjugate gradient method for the largest systems examined.

Fig. 5. Percentage of time spent calculating each of the OF-DFT terms (energy and potential combined for each term, ion–ion energy and ion–electron potential excluded) during electronic density optimization of 13,500 bulk Al atoms. The overhead consists of time taken for all other operations, including program initialization, housekeeping, and matrix operations within the minimization subroutines. The dominant contribution comes from the WGC energy and potential terms.

Fig. 6. Times for an electron density optimization (not including time used to compute the ion–ion energy and ion–electron potential) beginning from a uniform electron density for aluminum nanowires and bulk aluminum using the truncated Newton method and (top) the WGC KEDF and (bottom) the TF + 1/9 vW KEDF. In both cases, as the number of ions in a system increases, the number of gridpoints necessary to describe the system increases in an approximately linear fashion. For a given number of gridpoints, the nanowire systems converge more slowly than bulk crystals for a given number of gridpoints.

The amount of time required to optimize the density depends not only on the number of gridpoints, but on the particular system as well. As an example, we perform electron density optimizations on square cross-section [001] nanowires of increasing size. These nanowires were constructed by repeating a 4-atom Al fcc unit cell \(M\) times in the \(x\)- and \(y\)-directions (where \(M = 2, 3, 4, \) and 5) and 50 times in the \(z\)-direction, and then adding 10 Å of vacuum to separate the wires in both the \(x\)- and \(y\)-directions. The same parameters and functionals were used as in the above bulk crystal calculations. We compare in Fig. 6(a) the total times required for both the nanowire and the bulk crystal, excluding the time used to compute the ion–ion energy and the ion–electron potential, for electron density optimizations using the truncated Newton minimization algorithm and the WGC KEDF. The nanowires take much longer to converge than bulk crystals for a given number of gridpoints.

In order to determine whether the slower convergence of the nanowire case is a result of potential numerical instabilities in the more complicated WGC KEDF, we reran the test using the local TF + 1/9 vW KEDF. However, as seen in Fig. 6(b), the nanowires again take much longer than bulk crystals to converge for a given number of gridpoints, indicating that the underlying issue lies either in the minimization scheme or in numerical instabilities due to the increased complexity of the WGC KEDF.
to the vW KEDF for small densities (the vW KEDF content contains the density in the denominator). In all electron density optimization methods tried, the residual at points of low electron density decreases much more slowly than the residual at points of higher electron density. However, in both the bulk and nanowire systems, the truncated Newton method remains faster than the conjugate gradient method by at least a factor of 2 (Fig. 7).

5. Conclusions

In this paper, we described our implementation of the energy functionals and energy minimization schemes in PROFESS, our new software that performs OF-DFT calculations under both periodic and Dirichlet boundary conditions (implementation details of the latter will be described in a separate publication). We also demonstrated that our implementation is linear scaling when the time to compute the ion–ion energy and ion–electron energy is excluded. Remarkably, the density-only terms in the energy and potential now comprise only a small fraction of the overall calculation time, because the OF-DFT algorithm is much faster than the orbital-based KS-DFT formulation. We showed that PROFESS is able to handle more than ten thousand atoms on just a single processor under PBCs.

Since the majority of computation time is now spent computing the ion–ion energy and the ion–electron potential, particle-mesh Ewald algorithms have been implemented recently that render the remaining $O(N^2)$ terms linear scaling. Coupled with efficient parallelization, PROFESS should be able to easily handle hundreds of thousands of atoms. The last remaining bottleneck is the computation of the WGC KEDF terms, which should be the next target for further optimization. Also, we showed through our tests of nanowires versus bulk crystals that the algorithms used to minimize the energy with respect to the electron density need improvement, since even 10 Å of vacuum slows down the minimization, regardless of the KEDF used.

In conclusion, PROFESS is ready to be used to make meaningful scientific inquiries on large systems with main group metals. For example, PROFESS has been used recently to study vacancy cluster formation in bulk aluminum [46], and the mechanical response of aluminum nanowires [85].

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