Quasi-continuum orbital-free density-functional theory: A route to multi-million atom non-periodic DFT calculation

Vikram Gavini, Kaushik Bhattacharya, Michael Ortiz*

Division of Engineering and Applied Science, California Institute of Technology, CA 91125, USA

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Abstract

Density-functional theory (DFT) has provided insights into various materials properties in the recent decade. However, its computational complexity has made other aspects, especially those involving defects, beyond reach. Here, we present a method that enables the study of multi-million atom clusters using orbital-free density-functional theory (OFDFT) with no spurious physics or restrictions on geometry. The key ideas are: (i) a real-space formulation; (ii) a nested finite-element implementation of the formulation and (iii) a systematic means of adaptive coarse-graining retaining full resolution where necessary and coarsening elsewhere with no patches, assumptions or structure. We demonstrate the method, its accuracy under modest computational cost and the physical insights it offers by studying one and two vacancies in aluminum crystals consisting of millions of atoms.

Keywords: Quasi-continuum; Density-functional theory (DFT); Finite-elements; Calculus of variations; Vacancies in aluminium

1. Introduction

Ab initio calculations based on the density-functional theory (DFT) of Hohenberg, Kohn and Sham (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) have provided

*Corresponding author.
E-mail address: ortiz@caltech.edu (M. Ortiz).
extraordinary insights into the electronic structure and a wide range of materials properties in the past decade. However, it is extremely computationally demanding and many properties remain beyond its scope. The computational complexity of this approach is a result of the repeated calculation of single electron wavefunctions, which is required to estimate the kinetic energy of non-interacting electrons. There have been efforts to use an approximate *orbital-free* density-functional theory (OFDFT) where the kinetic energy is modelled and fitted to finer calculations (Parr and Yang, 1989; Smargiassi and Madden, 1994; Wang and Teter, 1992; Wang et al., 1998, 1999). Numerical investigations (Wang et al., 1998, 1999) reveal that OFDFT is a good model for systems with electronic structure close to that of free-electron gas, e.g., aluminum. Even OFDFT is sufficiently computationally expensive that many vital problems of materials science remain beyond its scope. In particular, properties of materials are influenced by defects—vacancies, dopants, dislocations, cracks, free surfaces—in small concentrations (parts per million). A complete description of such defects must include both the electronic structure of the core at the fine (sub-nanometer) scale and also the elastic, electrostatic and other interactions at the coarse (micrometer and beyond) scale. This in turn requires calculations involving millions of atoms, well beyond the current capability. In this paper, we propose and demonstrate a method for overcoming this significant hurdle.

Traditional implementations of DFT/OFDFT have for the most part been based on the use of a plane-wave basis and periodic boundary conditions (cf., e.g., Finnis, 2003). Therefore, defects have to be studied in unrealistic periodic geometries. Further, the computational limitations restrict the size of the unit cell so that the densities of defects are rarely, if ever, realized in nature. In an attempt to overcome these limitations, several schemes have been proposed for coarse-graining DFT or embedding it in computationally faster—though less accurate—models such as tight-binding (TB) or empirical potentials (Fago et al., 2004; Govind et al., 1999; Choly et al., 2005; Lu et al., 2006). Valuable as these schemes are, they suffer from a number of notable shortcomings. In some cases, uncontrolled approximations such as the assumption of linear response theory or the Cauchy–Born hypothesis are introduced. In other cases, schemes that transition from DFT to TB or empirical potentials are, *a fortiori*, not seamless and are not solely based on DFT. In particular, they introduce awkward overlaps between regions of the model governed by heterogeneous and mathematically unrelated theories. Finally, no clear notion of convergence to the full DFT solution is afforded by some of the existing methods.

We present a method for seamlessly coarse-graining OFDFT that effectively overcomes the present limitations without the introduction of spurious physics and at no significant loss of accuracy. We refer to the approximation scheme as quasi-continuum orbital-free density-functional theory (QC-OFDFT). It is similar in spirit to the quasi-continuum (QC) approach developed in the context of interatomic potentials (cf. e.g., Tadmor et al., 1996; Knap and Ortiz, 2001) as a scheme to seamlessly bridge the atomistic and continuum length scales. This bridging is achieved by adaptively selecting representative atoms and interpolating the positions of other atoms using finite-element shape-functions. The energy thus becomes a function of the representative atom-coordinates only. As a further approximation, cluster summation rules are introduced in order to avoid full lattice sums when computing the effective forces on the representative atoms. With increasing number of representative nodes and cluster sizes, the scheme converges at the expected theoretical convergence rate of finite-element approximation (Knap and Ortiz, 2001).
A local version of the QC approach based on the Cauchy–Born hypothesis has recently been developed for density-functional theory (Fago et al., 2004). The Cauchy–Born hypothesis finds formal justification in a theorem of Blanc et al. (2002) for deformation fields that slowly vary with respect to the length scale of the lattice parameter, but breaks down close to defect cores. In the context of DFT, the conventional QC reduction scheme can be applied mutatis mutandis to describe the positions of the nuclei. However, the electron-density and electrostatic potential exhibit subatomic structure as well as lattice scale modulation and therefore require an altogether different type of representation.

The QC-OFDFT method we introduce here has three important elements. First, we formulate the OFDFT including all the electrostatic interactions in real-space. Second, we implement this formulation using a finite-element method with two nested discretizations, an atomistic mesh that describes the atomic degrees of freedom and an electronic mesh that describes the electronic degrees of freedom. Importantly, information about subatomic electronic states are preserved either implicitly or explicitly at each point in the material. Third, we adaptively refine the discretization where we need more resolution while retaining a coarse description where that suffices. This refinement is completely unstructured and guided solely by the problem with no a priori restrictions like periodicity.

The proposed method has the following defining property: OFDFT is its sole input. The rest is approximation theory. There are no spurious physics, patching conditions or a priori ansatz. In fact, fully resolved OFDFT and finite lattice-elasticity are obtained as the two limiting cases. Therefore, a converged solution obtained by this method may be regarded as a solution of OFDFT. A further property of our method is that it is possible to consider any arbitrary geometry and boundary conditions in light of the real-space finite-element formulation.

We demonstrate our method by studying mono-vacancies and di-vacancies in aluminum crystals consisting of a million atoms. We restrict ourselves in this work to the Thomas–Fermi–Weizsacker kinetic energy functionals (Parr and Yang, 1989). We demonstrate elsewhere (Gavini et al., 2007) that our approach may be extended to the more recent and accurate non-local kernel functionals (Wang et al., 1998, 1999; Smargiassi and Madden, 1994; Wang and Teter, 1992).

For a mono-vacancy, we show by a convergence analysis that the electron-density field can be obtained everywhere with negligible error and through modest computational means. Our results are close to the experimentally observed values, and provide insights into the electronic structure at the core. At the same time, our results show that atomistic displacement fields decay over very large distances, underscoring the long-range nature of the underlying physics. This is significant for two reasons. First, it shows that long-range interactions beyond those considered in previous calculations (Wang et al., 1998, 1999; Gillan, 1989; Mehl and Klein, 1991; Chetty et al., 1995; Turner et al., 1997) are important. Second, it shows that errors previously attributed to the approximations of OFDFT may in fact be an artifact of small periodic computational cells.

These issues are further highlighted by the di-vacancy calculations. We find that the vacancies are attractive along both the (100) and the (110) directions. Further, the binding energy we compute is in close agreement with those inferred from experimental observations. We note that these results differ from recent calculations (Carling et al., 2000; Uesugi et al., 2003) which predict that vacancies repel along (110) direction. To understand this, we compute the di-vacancy interaction for various crystal (computational domain) sizes: we find that the interaction changes sign from attractive for physically realistic sizes to repulsive for unphysically small sizes. This demonstrates that unphysically
small computations can lead to spurious results, and thus highlights the potential of our method.

A remaining challenge is to extend the present approach to Kohn–Sham DFT, which requires the computation of the eigenvalues of large systems. This remains a challenge for the future, but we believe that the adaptive real-space character of the present approach should prove useful in that endeavor.

2. Formulation

The ground-state energy in DFT is given by (cf. e.g., Finnis, 2003; Parr and Yang, 1989)

\[ E(\rho, R) = T_s(\rho) + E_{xc}(\rho) + E_H(\rho) + E_{\text{ext}}(\rho, R) + E_{zz}(R), \]

where \( \rho \) is the electron-density; \( R = \{R_1, \ldots, R_M\} \) is the collection of nuclear positions in the system; \( T_s \) is the kinetic energy of non-interacting electrons; \( E_{xc} \) denotes the exchange correlation energy; \( E_H \) is the classical electrostatic interaction energy between electrons, also referred to as Hartree energy; \( E_{\text{ext}} \) is the interaction energy of electrons with external field induced by nuclear charges; and \( E_{zz} \) denotes the repulsive energy between nuclei. We specifically consider the Thomas–Fermi–Weizsacker family of orbital-free kinetic energy functionals, which have the form

\[ T_s(\rho) = C_F \int_{\Omega} \rho^{5/3}(r) dr + \frac{\lambda}{8} \int_{\Omega} \frac{\lvert \nabla \rho(r) \rvert^2}{\rho(r)} dr, \]

where \( C_F = \frac{3}{10}(3\pi^2)^{2/3} \), \( \lambda \) is a parameter (Parr and Yang, 1989) and \( \Omega \) contains the support of \( \rho \). We treat the exchange and correlation functionals under the local density approximation (LDA) (Ceperley and Alder, 1980; Perdew and Zunger, 1981) given by

\[ E_{xc}(\rho) = \int_{\Omega} \varepsilon_{xc}(\rho(r)) \rho(r) dr, \]

where, \( \varepsilon_{xc} = \varepsilon_x + \varepsilon_c \) is the exchange and correlation energy per electron given by

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

\[ \varepsilon_c(\rho) = \begin{cases} \frac{\gamma}{1 + \beta_1 \sqrt{r_s} + \beta_2 r_s} & r_s \geq 1, \\ A \log r_s + B + C r_s \log r_s + D r_s & r_s < 1, \end{cases} \]

where \( r_s = (3/4\pi \rho)^{1/3} \). The values of the constants are different depending on whether the medium is polarized or unpolarized. The values of the constants are \( \gamma_u = -0.1471, \beta_{1u} = 1.1581, \beta_{2u} = 0.3446, A_u = 0.0311, B_u = -0.048, C_u = 0.0014, D_u = -0.0108, \gamma_p = -0.079, \beta_{1p} = 1.2520, \beta_{2p} = 0.2567, A_p = 0.01555, B_p = -0.0269, C_p = 0.0001, D_p = -0.0046. \)

Though we restrict ourselves to the Thomas–Fermi–Weizsacker family of kinetic energy functionals, extensions to other forms of orbital-free kinetic energy functionals are possible and is demonstrated in Gavini et al. (2007). We choose the Thomas–Fermi–Weizsacker family of kinetic energy functionals and LDA treatment of exchange and correlation functionals only as a convenient case and the present formulation and all aspects to be
discussed subsequently can be extended to other forms of orbital-free kinetic energy functionals and exchange and correlation functionals.

The problem of determining the ground-state electron-density and the equilibrium positions of the nuclei can be expressed as the minimum problem

\[
\inf_{u \in X, \, R \in \mathbb{R}^M} E(u, R), \tag{6a}
\]

subject to:

\[
\int_{\Omega} u^2(r) \, dr = N, \tag{6b}
\]

where \( u = \sqrt{\rho} \) is the square-root electron-density, \( X \) is a suitable space of solutions and the energy is expressed in a local form as

\[
E(u, R) = \sup_{\phi \in H^1(\mathbb{R}^3)} L(u, R, \phi), \tag{7a}
\]

\[
L(u, R, \phi) = C_F \int_{\Omega} u^{10/3}(r) \, dr + \frac{\lambda}{2} \int_{\Omega} |\nabla u(r)|^2 \, dr + \int_{\Omega} e_{xc}(u^2(r)) u^2(r) \, dr
\]

\[
- \frac{1}{8\pi} \int_{\mathbb{R}^3} |\nabla \phi(r)|^2 \, dr + \int_{\mathbb{R}^3} (u^2(r) + b(r)) \phi(r) \, dr, \tag{7b}
\]

where \( L \) is a local Lagrangian that depends on the electrostatic field \( \phi \) and \( b(r) \) denote the regularized nuclei. A full account of the functional form of the Lagrangian \( L \), the space of solutions \( X \) and properties of the energy \( E \) may be found in Gavini et al. (2007).

3. Finite-element approximation

We recall that finite-element bases are piecewise polynomial and are constructed from a representation of the domain of analysis as a cell complex, or triangulation, \( T_h \) (cf. e.g. Ciarlet, 2002; Brenner and Scott, 2002). Often, the triangulation is chosen to be simplicial as a matter of convenience, but other types of cells, or elements, can be considered as well. Here and subsequently, \( h \) denotes the size of the triangulation, e.g., the largest circumdiameter of all of its faces. A basis-or shape-function is associated to every vertex-or node-of the triangulation. The shape functions are normalized to take the value 1 at the corresponding node and 0 at all remaining nodes. The support of each shape-function extends to the simplices incident on the corresponding node, which confers the basis a local character. In order to ensure convergence as \( h \to 0 \), finite-element shape-functions are also required to be continuous across all faces of the triangulation and to represent affine functions exactly. The interpolated fields \( U_h(r) \) spanned by a finite-element basis are of the form

\[
U_h(r) = \sum_i U_i N_i^h(r), \tag{8}
\]

where \( i \) indexes the nodes of the triangulation, \( N_i^h(r) \) denotes the shape-function corresponding to node \( i \), and \( U_i \) is the value of \( U_h(r) \) at node \( i \).

We shall denote by \( X_h \) the finite-dimensional linear subspace of \( X \) of functions of the form (8), i.e., the span of the shape-functions \( N_i^h(r) \). In problems governed by a minimum principle, the Rayleigh–Ritz or best approximation corresponding to a given discretization is obtained by effecting a constrained minimization over \( X_h \). This constrained minimization reduces the problem to the solution of a finite-dimensional system of—generally non-linear—algebraic equations and generates a sequence of approximations.
indexed by the mesh size \( h \). A central problem of approximation theory is to ascertain whether the energy of the sequence \( U^h(\mathbf{r}) \) converges the ground-state energy of the system as \( h \to 0 \) and, if the problem admits solutions, whether the sequence \( U^h(\mathbf{r}) \) itself converges to a ground-state of the system. In view of (6) and (7), in the present setting the constrained problem takes the form

\[
\inf_{u^h \in X_h} \int_\Omega (u^h(\mathbf{r}))^2 \, d\mathbf{r} = N, \quad \text{subject to: } E(u^h, \mathbf{R}) = \sup_{\phi^h \in X_h} L(u^h, \mathbf{R}, \phi^h). \tag{9c}
\]

A full account of finite-element DFT may be found in Gavini et al. (2007), where rigorous proofs of the convergence of the approximations is also presented.

4. QC reduction

We introduce three unstructured triangulations of the domain as shown in Fig. 1 to provide a complete description of the discrete fields: (i) a triangulation \( T_{h_1} \) of selected representative atoms in the usual manner of QC, which we refer to as the atomic-mesh; (ii) an everywhere subatomic triangulation \( T_{h_2} \) of the domain that captures the subatomic oscillations in the electron-density and potential, which we refer to as the fine-mesh; and (iii) a triangulation \( T_{h_3} \) subatomic close to lattice defects and increasingly coarser away from the defects, which we refer to as the electronic-mesh. We restrict the triangulations in such a way that \( T_{h_3} \) is a sub-grid of \( T_{h_1} \) and \( T_{h_2} \) a sub-grid of \( T_{h_3} \). We additionally denote by \( X_{h_1}, X_{h_2} \) and \( X_{h_3} \) the corresponding finite-element approximation spaces.

The full square-root electron-density and electrostatic potential are written as

\[
u^h = u_0^h + u_c^h, \tag{10a}
\]
\[\phi^h = \phi_0^h + \phi_c^h, \tag{10b}
\]

where \( u_0^h \in X_{h_2} \) and \( \phi_0^h \in X_{h_2} \) are the predictors for square-root electron-density and electrostatic potential obtained by performing a local periodic calculation in every element of \( T_{h_1} \). \( u_c^h \in X_{h_3} \) and \( \phi_c^h \in X_{h_3} \) are the non-local corrections to be solved for. The predictor for the electronic fields is expected to be accurate away from defect cores, in regions where the deformation field is slowly varying (Blanc et al., 2002). Hence, the non-local corrections may be accurately represented by means of a finite-element triangulation such as \( T_{h_3} \), namely, a triangulation that has subatomic resolution close to the defect and coarsens away from the defect to become superatomic.

The minimization problem given by (6) and (7) now reduces to a minimization problem for the non-local corrections and takes the form

\[
\inf_{u_c^h \in X_{h_3}} \int_\Omega (u_0^h(\mathbf{r}) + u_c^h(\mathbf{r}))^2 \, d\mathbf{r} = N, \quad \text{subject to: } E(u_0^h + u_c^h, \mathbf{R}) = \sup_{\phi_c^h \in X_{h_3}} L(u_0^h + u_c^h, \mathbf{R}, \phi_0^h + \phi_c^h). \tag{11c}
\]
In order to compute the predictor for electronic fields we begin by performing a periodic calculation in every element of $T_{h_1}$. The resulting fields are not necessarily continuous at the boundaries of the elements of $T_{h_1}$. We overcome this deficiency and obtain conforming (continuous) fields $u_0^h$ and $\phi_0^h$ over $T_{h_2}$ by performing an $L^2 \rightarrow H^1$ map. To define this mapping, denote by $s_0^k$ the $k$th node of the triangulation $T_{h_2}$. As $T_{h_2}$ is a sub-grid of $T_{h_1}$, define an index set $I_k$ which collects the element numbers of triangulation $T_{h_1}$ to which the node $s_0^k$ belongs. The map can now be defined as

$$U_0^k = \frac{1}{\#I_k} \sum_{j \in I_k} \tilde{U}_j(r_k), \quad k = 1, \ldots, n_2,$$

where, $n_2$ denotes the total number of nodes in $T_{h_2}$, $U_0^k$ is the value of the conforming field at the $k$th node, $\#I_k$ denotes the cardinality of the index set and $\tilde{U}_j(r_k)$ is the value of the field at the $k$th node computed from a periodic calculation in element $e_j \in T_{h_1}$. Note that this is simply the average value at a node of fields obtained from periodic calculations in the different elements.

Since the predictor for electronic fields is defined on the uniformly subatomic mesh $T_{h_2}$, it would appear that the computation of the system corresponding to the reduced problem (11) has complexity commensurate with the size of $T_{h_2}$, which would render the scheme infeasible. In the spirit of quadrature rules in finite-elements (e.g., Ciarlet, 2002; Brenner
and Scott, 2002), or summation rules in QC (Knap and Ortiz, 2001), we proceed to introduce integration rules that reduce all computations to the complexity of \( T_{h_3} \). The precise form of the integration rule for an element \( e \) in the triangulation \( T_{h_3} \) is
\[
\int_{e} f(\mathbf{r}) \, d\mathbf{r} \approx |e| \langle f \rangle_{D_e},
\]
where \(|e|\) is the volume of element \( e \), \( D_e \) is the unit cell of an atom if such cell is contained in \( e \) or \( e \) otherwise, and \( \langle f \rangle_{D_e} \) is the average of \( f \) over \( D_e \). Using (13), integration over the entire domain can be written as
\[
\int_{\Omega} f(\mathbf{r}) \, d\mathbf{r} = \sum_{e \in T_{h_3}} \int_{e} f(\mathbf{r}) \, d\mathbf{r} \approx \sum_{e \in T_{h_3}} |e| \langle f \rangle_{D_e},
\]
reducing all computations to have a complexity commensurate with the size of \( T_{h_3} \).

The integration rule (13) is designed to exploit the nature of the solution. As mentioned previously, the predictor for electronic fields is expected to be accurate away from defect cores where the deformation field is slowly varying. By way of construction of the meshes, this region also corresponds to large, superatomic elements of \( T_{h_3} \), where the computed non-local corrections are very small compared to the predictor. Thus, the integrand of Eq. (13) is a rapidly oscillating function with a very gradual modulation on the scale of the element. Hence, Eq. (13), for regions away from the core of a defect, denotes the zero order quadrature rule for rapidly oscillating functions. For regions close to a defect, the computed corrections to the predictor are large and thus the integration must be performed exactly. The integration rule (13) is consistent with this requirement, as the elements of \( T_{h_3} \) close to a defect are subatomic and the integration rule is exact for these elements.

Eqs. (11)–(13) describe the QC-OFDFT method.

5. Forces

We solve the variational problem (11) using conjugate gradients. This requires the calculation of generalized nodal forces, defined as the variation of the total energy with respect to \( \phi^b_k \) (correction to electrostatic potential), \( u^b_k \) (correction to electron-density) as well as the configurational forces defined as the variation of the total energy with respect to the nodal positions. The nodal forces associated with \( \phi^b_k \) and \( u^b_k \) are defined on triangulation \( T_{h_3} \) and the configurational forces of the nuclei are defined on \( T_{h_1} \).

The energy functional given in Eq. (7), can be succinctly represented as
\[
E(u^b, \mathbf{R}, \phi^b) = \int_{\Omega} f(t^b, \nabla t^b) \, d\Omega + \int_{\Omega} ((t^b)^2 + \sum_i Z_i b_i) \phi^b \, d\Omega - \frac{1}{8\pi} \int_{\Omega} |\nabla \phi^b|^2 \, d\Omega,
\]
where \( b_i \) denotes a regularized nuclear charge with charge \( Z_i \) on the \( i \)th node. The nodal forces \( f^b_k \) and \( f^u_k \) corresponding to \( \phi^b_k \) and \( u^b_k \), respectively, at the \( k \)th node of triangulation \( T_{h_3} \) are given by
\[
f^b_k(u^b, \mathbf{R}, \phi^b) = \frac{\delta E(u^b, \mathbf{R}, \phi^b) }{\delta \phi^b_k}, \quad (16a)
\]
\[
f^u_k(u^b, \mathbf{R}, \phi^b) = \frac{\delta E(u^b, \mathbf{R}, \phi^b) }{\delta u^b_k}. \quad (16b)
\]
Though these are defined on the nodes of triangulation $T_{h_3}$, they have to be evaluated using quantities defined on the finer mesh $T_{h_2}$ by taking advantage of the fact that $T_{h_2}$ is a sub-grid of $T_{h_3}$, and the finite-element shape-functions are linear. By definition

$$f_{\phi}^k(u^h, \mathbf{R}, \phi^h) = \int_{\Omega} \left( (u^h)^2 + \sum_i Z_i b_i \right) N_{kh_3}^h \, d\Omega - \frac{1}{4\pi} \int_{\Omega} \nabla \phi^h \cdot \nabla N_{kh_3}^h \, d\Omega, \quad (17)$$

where $N_{kh_3}^h$ denotes the shape-function associated with node $k$ of triangulation $T_{h_3}$. As the shape-functions are linear and $T_{h_2}$ is a sub-grid of $T_{h_3}$, $N_{kh_3}^h(\mathbf{r}) = \sum_{a \in T_{h_2}} N_{kh_2}^h(a) N_{h_2}^a(\mathbf{r})$, where $a$ denotes a node in $T_{h_2}$ and $N_{h_2}^a$ denotes the shape-function associated with node $a$ of triangulation $T_{h_2}$. Hence, the expression for the nodal force given in Eq. (17) can be rewritten as

$$f_{\phi}^k(u^h, \mathbf{R}, \phi^h) = \sum_{a \in T_{h_2}} N_{kh_3}^h(a) \left\{ \int_{\Omega} \left( (u^h)^2 + \sum_i Z_i b_i \right) N_{kh_2}^h \, d\Omega - \frac{1}{4\pi} \int_{\Omega} \nabla \phi^h \cdot \nabla N_{kh_2}^h \, d\Omega \right\}$$

$$= \sum_{a \in T_{h_2}} N_{kh_3}^h(a) f_{\phi}^{\alpha a}(u^h, \mathbf{R}, \phi^h), \quad (18)$$

where $f_{\phi}^{\alpha a}$ denotes the nodal force associated with $\phi^h$ on node $a$ of triangulation $T_{h_2}$.

We proceed similarly for $f_u^{\alpha a}$.

Taking into account the cluster rules, defined by Eq. (13), we obtain the expressions for the generalized nodal forces:

$$f_{\phi}^k(u^h, \mathbf{R}, \phi^h) = \sum_{e \in T_{h_3}} \left\{ C_e \sum_{a \in D_e} f_{\phi}^{\alpha a}(u^h, \mathbf{R}, \phi^h) N_{kh_3}^h(a) \right\}, \quad k = 1, \ldots, n_3, \quad (19a)$$

$$f_u^k(u^h, \mathbf{R}, \phi^h) = \sum_{e \in T_{h_3}} \left\{ C_e \sum_{a \in D_e} f_u^{\alpha a}(u^h, \mathbf{R}, \phi^h) N_{kh_3}^h(a) \right\}, \quad k = 1, \ldots, n_3, \quad (19b)$$

where $f_{\phi}^{\alpha a}$ and $f_u^{\alpha a}$ are the nodal forces associated with $\phi^h$ and $u^h$ on node $a$ of triangulation $T_{h_2}$; $N_{kh_3}^h(a)$ denotes the value of the shape-function associated with node $k$ of $T_{h_3}$ at the position of node $a$; $C_e$ is a constant whose value is 1 if $D_e = e$, $|e|/|D_e|$ otherwise; $n_3$ denotes the total number of nodes in $T_{h_3}$; and $'$ over summation avoids double counting. Forces $f_{\phi}^{0 a}$ and $f_u^{0 a}$ corresponding to $\phi^h$ and $u^h$, which are defined on $T_{h_2}$, are computed using standard routines for force calculations with finite-element basis.

We now turn to the configurational forces associated with the positions of the nuclei. Though these appear to be non-local at first glance, we show that they can in fact be evaluated locally. The derivation closely follows Thoutireddy (2002) and is based on ideas widely used in mechanics following Eshelby’s formulation of force on a defect (Eshelby, 1951).

For clarity of presentation, we begin with a single finite element triangulation (rather than the three considered here). In this situation, the total energy is $I_1^h + I_2^h + I_3^h$. 
where

\[ I_1^h = \int_{\Omega} f(u^h, \nabla u^h) \, d\Omega, \]
\[ I_2^h = \int_{\Omega} (u^h)^2 + \sum_i Z_i b_i \phi^h \, d\Omega, \]
\[ I_3^h = -\frac{1}{8\pi} \int_{\Omega} |\nabla \phi^h|^2 \, d\Omega \]

and \( u^h, \phi^h \in \mathcal{X}_h \). Note that

\[ I_1^h = \int_{\Omega} f(u^h, \nabla u^h) \, d\Omega = \sum_{e \in \mathcal{T}_h} \int_{\hat{\Omega}} f(u^h, \nabla u^h) \det \left( \frac{\partial X_M}{\partial \hat{X}_N} \right) \, d\hat{\Omega}, \]

where \( \hat{\Omega} \) is the reference volume in isoparametric formulation and \( \frac{\partial X_M}{\partial \hat{X}_N} \) is the Jacobian of transformation. Taking variations of \( I_1 \) with respect to \( X_h \), we have

\[
\delta I_1^h = \sum_{e \in \mathcal{T}_h} \int_{\hat{\Omega}} \left\{ -\frac{\delta f}{\delta u_J} \sum_{a=1}^n u_a \hat{N}_{a,K} \frac{\partial \hat{X}_A}{\partial X_K} \left( \sum_{b=1}^n \delta X_{b,K} \hat{N}_{b,B} \right) \frac{\partial \hat{X}_B}{\partial X_J} \right\} + f(u^h, \nabla u^h) \delta K \}
\]

\[
= \sum_{e \in \mathcal{T}_h} \int_{\hat{\Omega}} \left\{ -\frac{\delta f}{\delta u_J} \sum_{a=1}^n u_a N_{a,K} \right\} + f(u^h, \nabla u^h) \delta K \}
\]

\[
= \sum_{e \in \mathcal{T}_h} \int_{\hat{\Omega}} \left\{ -\frac{\delta f}{\delta u_J} (u^h, \nabla u^h) \delta K + f(u^h, \nabla u^h) \delta K \right\} \left( \sum_{b=1}^n \delta X_{b,K} N_{b,J} \right) \, d\Omega.
\]

Similarly, note that

\[ I_2^h = \int_{\Omega} (u^h)^2 + \sum_i Z_i b_i \phi^h \, d\Omega = \sum_{e \in \mathcal{T}_h} \int_{\hat{\Omega}} (u^h)^2 + \sum_{b=1}^n Z_i b_i \phi^h \, d\hat{\Omega} \]

Taking variations, we find

\[
\delta I_2^h = \sum_{e \in \mathcal{T}_h} \int_{\hat{\Omega}} (u^h)^2 \phi^h + \sum_{i=1}^n Z_i b_i \phi^h \left( \sum_{b=1}^n \delta X_{b,K} \hat{N}_{b,B} \right) \frac{\partial \hat{X}_B}{\partial X_K} \det \left( \frac{\partial X_M}{\partial \hat{X}_N} \right) \, d\hat{\Omega}
\]

\[
+ \sum_{e \in \mathcal{T}_h} \int_{\hat{\Omega}} \sum_{b=1}^n Z_i b_i (\delta \phi^h) \det \left( \frac{\partial X_M}{\partial \hat{X}_N} \right) \, d\hat{\Omega}
\]

\[
= \sum_{e \in \mathcal{T}_h} \int_{\hat{\Omega}} (u^h)^2 \phi^h + \sum_{i=1}^n Z_i b_i \phi^h \delta K \left( \sum_{b=1}^n \delta X_{b,K} N_{b,J} \right) \, d\Omega
\]

\[
+ \sum_{e \in \mathcal{T}_h} \int_{\hat{\Omega}} \sum_{b=1}^n Z_i b_i \left( \sum_{a=1}^n \phi_a N_{a,K} \right) \delta X_{b,K} \, d\Omega.
\]
Similarly,
\[
\delta I_3^b = -\frac{1}{8\pi} \sum_{e \in T_h} \int_{Q^e} \left( |\nabla \phi|^2 \delta_{KJ} - 2 \phi_i^h \phi_j^h \right) \left( \sum_{b=1}^{n} \delta \chi_{hK}^e \right) \ d\Omega.
\]

Collecting all terms, the configurational force on node \(b\) along the \(K\)th direction is given by
\[
f_{bK}^X = \sum_{e \in T_h} \int_{Q^e} E_{KJ} N_{hJ} \ d\Omega + \sum_{e \in T_h} \int_{Q^e} Z_{bE} \left( \sum_{a=1}^{n} \phi_a N_{aK} \right) \ d\Omega \tag{20}
\]
where
\[
E_{KJ} = \left\{ f + \left( \sum_{i} Z_{i}(h) \phi_i^h - \frac{1}{8\pi} |\nabla \phi|^2 \right) \delta_{KJ} - \frac{\delta f}{\delta u_J} (u^h, \nabla u^h) u_K^h + \frac{1}{4\pi} \phi_j^h \phi_j^h \right\}.
\]

Note that this expression is local.

We can generalize these calculations to our situation with three nested triangulations and cluster rules. We find that the configurational forces on node \(j\) of triangulation \(T_{h1}\) in the \(I\)th direction is given by
\[
f_{iI}^X(u^h, R, \phi^h) = \sum_{e_1 \in T_{h1}} \sum_{e_2 \in e_1} \sum_{e_3 \in e_2} \left\{ C_{e_2} \sum_{a \in D_{e_2}} f_{aI}^{out} (u^h, R, \phi^h) N_{jI}^{h1} (a) \right\}
\]
for \(j = 1, \ldots, n_1, \ I = 1, 2, 3, \) \tag{21}

where \(f_{aI}^{out}\) is the configurational forces on node \(a\) of triangulation \(T_{h2}\) in the \(I\)th direction given by (20), and \(N_{jI}^{h1} (a)\) denotes the value of the shape-function associated with node \(j\) of \(T_{h1}\) at the position of node \(a\). Once again, this expression is local.

6. Numerical implementation

We now turn to the numerical implementation of the QC-OFDFT scheme proposed. Triangulation \(T_{h1}\) is obtained by a Delaunay triangulation of the lattice. The representative atoms are chosen \(a\ priori\) such that the triangulation is atomistic close to the region of interest and coarsens away as shown in Fig. 2. Triangulations \(T_{h2}\) and \(T_{h3}\) are obtained from \(T_{h1}\) using Freudenthal’s subdivision algorithm (Bey, 2000). This ensures that \(T_{h2}\) and \(T_{h3}\) are sub-grids of \(T_{h1}\). The subdivisions are performed such that \(T_{h2}\) is subatomic everywhere but \(T_{h3}\) is subatomic close to the region of interest and superatomic away from the region of interest, cf. Fig. 3. All triangulations consist of 4-node tetrahedral elements and the integrals are evaluated numerically using 4-point Gaussian quadrature rules. The nodal forces and configurational forces computed in Section 5 are equilibrated in a staggered scheme using non-linear conjugate gradients with secant method for line search. Finally, we implement the computation in parallel using domain decomposition.

7. Vacancies in Aluminum

We study vacancies in aluminum as the test case for the proposed method. Vacancies are an ideal test case as they often are dilute, and both the electronic core and long-range
elastic and electrostatic interactions are important. Also, vacancy calculations are often treated as a benchmark to test various kinetic energy functionals (Wang et al., 1998, 1999). We use the QC-OFDFT approach to investigate into mono-vacancies and di-vacancies in aluminum. Thomas–Fermi–Weizsacker family of functionals with $\lambda = \frac{1}{6}$ is used for the orbital-free kinetic energy functional. All simulations are performed using a modified form of Heine-Abarenkov pseudopotential for aluminum (Goodwin et al., 1990) and LDA
treatment of exchange and correlation functionals (Ceperley and Alder, 1980; Perdew and Zunger, 1981).

7.1. Mono-vacancy

We consider a sample with a single vacancy subjected to Dirichlet boundary conditions, which implies that all fields approach the bulk values at the boundary. We repeat our calculations for samples of varying sizes, namely, samples nominally containing 4, 32, 256, 2,048, 16,384 and one million (1,048,576) atoms.

The coarse-graining inherent in our approach means that we use far fewer representative atoms in the calculations. Fig. 4 emphasizes the dramatic savings that this coarse-graining offers. It shows the vacancy formation energy of a sample containing 16,384 nominal atoms. As is evident from the figure, the calculations converge ostensibly beyond around 200 representative atoms, i.e., at an 80-fold computational savings. These savings improve with size and enables the consideration of large samples at modest computational expense.

We now describe the results of a simulation concerned with a million-atom sample performed with 1017 representative atoms and in the order of 450,000 elements in the electronic-mesh. The calculations take about 12 h on 48 700 MHz processors. By an extrapolation of the convergence analysis just described, we estimate the error in vacancy formation energy due to coarse-graining to be less than 0.01 eV. Fig. 5 shows the contours of the ground-state electron-density around the vacancy, while Fig. 6 shows the contours of the electron-density correction, i.e., the difference between the ground-state electron-density and the predictor estimate. Compared to the predictor estimate, one sees a large correction close to the defect. As expected, there is a depletion in the electron-density at the vacancy, and a small augmentation in the atoms surrounding the vacancy is also evident, cf Figs. 6(b) and (d). The vacancy formation energy is computed to be 0.72 eV, which compares well with the experimentally measured value of 0.66 eV (Triftshäuser, 1975).
Fig. 7 shows the computed variation of the vacancy formation energy with sample size. This variation is reported for two sets of calculations: one where the atomic positions are held fixed (unrelaxed) in their nominal position; and a second where the atomic positions are relaxed. The vacancy formation energy is found to follow a power law close to $n^{-0.5}$ in the unrelaxed case and $n^{-0.55}$ in the relaxed case, where $n$ is the nominal number of atoms in the sample. This power-law behavior is an indication of the long-range nature of the underlying physics. It is interesting to note that relaxation of the atomic positions reduces the vacancy formation energy by 0.06 eV.

Fig. 8 shows the radial displacement fields along $h_{100}$ and $h_{110}$ directions. The fields have a long tail, another indication of long-range nature of the field of the vacancy. The maximum displacement occurs in the $h_{110}$ direction and amounts to 0.6% of the nearest atom distance. This value is less than predicted in previous calculations using Kohn–Sham DFT with periodic boundary conditions where the maximum displacement was estimated to be 1–2% of the nearest atom distance (Mehl and Klein, 1991; Chetty et al., 1995; Turner et al., 1997). At this point there is no basis to decide whether the discrepancy is due to the orbital-free formulation or the use of periodic boundary conditions.

7.2. Di-vacancy

A di-vacancy consists of two vacancies at positions $a_1$ and $a_2$ within a crystal. We have conducted calculations with a million-atom specimen subjected to Dirichlet boundary conditions representing bulk values as before. The calculations use up to 2001 representative atoms (slightly smaller when the vacancies are close to each other), have 800,000 elements in the electronic-mesh and require 16–18 h on 64 700 MHz processors. Figs. 9 and 10 display representative results. Fig. 9 shows the contours of the ground-state electron-density around a di-vacancy complex along $(100)$ and $(110)$. Fig. 10 show the
contours of electron-density correction around a di-vacancy complex along (1 0 0) and (1 1 0). It is interesting to observe the counterparts of Friedel oscillations in these figures.

A property of primary interest is the di-vacancy binding energy. To understand this, we repeat the above calculations for various distances between the vacancies. Let $E_f^v(n)$ denote the mono-vacancy formation energy for a sample consisting of $n$ nominal atoms. Similarly, let $E_f^{2v}(n; \mathbf{a}_1, \mathbf{a}_2)$ denote the di-vacancy formation energy of a system with two vacancies of sample size $n$ positioned at $\mathbf{a}_1$ and $\mathbf{a}_2$. Then, the di-vacancy binding energy is
defined as

\[
E_{2v}^{\text{bind}}(n; \mathbf{a}_1, \mathbf{a}_2) = E_{2v}^f(n; \mathbf{a}_1, \mathbf{a}_2) - 2E_v^f(n)
\]  \hspace{1cm} (22)

Fig. 11(a) shows the unrelaxed binding energy of di-vacancies along the $\langle 1\,0\,0 \rangle$ and $\langle 1\,1\,0 \rangle$ directions in a million-atom sample over a range of distances between the two vacancies. Fig. 11(b) shows the corresponding relaxed energies. These energies are negative, signifying attractive interaction in both cases.

The binding energy for nearest-neighbor vacancies, or di-vacancy complex, is calculated to be $-0.23$ eV in the $\langle 1\,0\,0 \rangle$ direction and $-0.19$ eV in the $\langle 1\,1\,0 \rangle$ direction, i.e., attractive in both cases. This is in keeping with experimental estimates that place the binding energy of di-vacancy complexes between $-0.2$ and $-0.3$ eV (Ehrhart et al., 1991; Hehenkamp, 1994). By contrast, recently computed values (Carling et al., 2000; Uesugi et al., 2003) predict that vacancies repel in the $\langle 1\,1\,0 \rangle$ direction with a binding energy of $0.05$ eV and attract in the $\langle 1\,0\,0 \rangle$ direction with a binding energy of $-0.04$ eV.
Fig. 8. (a) Radial displacement of atoms along $<110>$ direction; (b) radial displacement of atoms along $<100>$ direction; (c) radial displacement of atoms along $<110>$ and $<100>$ directions in a million atom sample. The distance from vacancy is listed in atomic units.

Fig. 9. (a) Contours of electron-density around a di-vacancy complex along $<100>$; (b) contours of electron-density around a di-vacancy complex along $<110>$. 
To understand whether these discrepancies are, in effect, a small-size effect, we consider samples of sizes $n = 4, 32, 256, 2048, 16, 348$ and one million atoms. Fig. 12 shows the effect of cell size on the binding energies of a di-vacancy complex along $(1 \ 0 \ 0)$ and $(1 \ 1 \ 0)$. It is observed from these results that there is indeed a strong cell-size effect on the di-vacancy binding energies, especially in the $(1 \ 1 \ 0)$ direction. Strikingly, the binding energy changes sign from attractive for large cell-sizes to repulsive for small cell sizes. This suggests that the repulsive binding energies computed in Carling et al. (2000), Uesugi et al. (2003) are characteristic of small-cell sizes, and that in order to make contact with experimental measurements such as reported in Ehrhart et al. (1991), Hehenkamp (1994) much larger cell-sizes than heretofore tractable need to be analyzed.
8. Conclusions

We have presented a method, quasi-continuum orbital-free density-functional theory (QC-OFDFT), for systematically and adaptively coarse-graining OFDFT in a manner that enables consideration of multi-million atom systems at no essential loss of accuracy and without the introduction of spurious physics or assumptions, such as linear response theory or the Cauchy–Born hypothesis. The method is seamless, i.e., OFDFT provides the sole input of the method and does not resort to any form of transition to—or embeddings within—simpler theories, such as empirical potentials or tight-binding models. Because finite element bases are used to describe all fields, no restrictions on boundary conditions...
limit the applicability of the method. In particular, non-periodic boundary conditions and general geometries can be analyzed using the method. The coarse-graining is completely unstructured and can be adapted to the solution, e.g., to provide full atomic resolution in the vicinity of a defect core, and to rapidly coarse-grain elsewhere.

The method is in the spirit of previous ‘quasi-continuum’ (QC) approaches (cf. e.g., Tadmor et al., 1996; Knap and Ortiz, 2001) but differs from those earlier works in several notable respects. The conventional quasi-continuum was devised in order to coarse-grain the displacement field of an atomic lattice. By contrast, OFDFT requires the additional representation of the electron-density and electrostatic potential. Also, in the conventional QC formulations to date, the finite-element mesh is always coarser than the atomic lattice, whereas in the present setting the electron-density and electrostatic potential must be resolved on a sub-lattice lengthscale. We effect these representations by carefully nesting three distinct finite-element interpolations spanning the sub-lattice and continuum lengthscales. The coarsest of these meshes, or atomic-mesh, is equivalent to a conventional QC triangulation of representative atoms and coarse-grains the displacement field of the atomic lattice. The electronic fields which require subatomic resolution are decomposed into a predictor and a correction. The predictor for electronic fields, which requires subatomic resolution, is computed on the finest of the three meshes, or fine-mesh, using local periodic calculations in every element of the atomic-mesh. This predictor is known to be accurate in regions away from the defects, where the deformation field is slowly varying (Blanc et al., 2002). Thus, the corrections, which are non-local, are accurately represented by the electronic-mesh that has subatomic resolution close to defects and increasingly coarse-grains away from defect cores. The electronic fields are then determined by solving for the non-local corrections in a variational setting. In order to avoid computational complexities of the order of the entire model (fine-mesh), we exploit the conceptual framework of the theory of homogenization of periodic media to define quadrature rules of a complexity commensurate with that of the electronic-mesh.

The convergence of finite element approximations in OFDFT has been rigorously proven in an earlier paper (Gavini et al., 2007). In this paper, we have demonstrated the convergence of QC-OFDFT with increasing number of representative atoms by means of numerical tests. These tests show that the reduction in computational effort afforded by QC-OFDFT, at no essential loss of accuracy with respect to a full-atom calculation, is quite staggering. For instance, we have analyzed million-atom samples with modest computational resources, giving us access to cell-sizes never before analyzed using OFDFT. The examples presented in this paper showcase the importance of having access to such large cell sizes. For instance, the mono-vacancy calculations in aluminum have determined scaling relations that are indicative of slow convergence with respect to cell size. More telling still is the case of di-vacancies. Thus, whereas some di-vacancy systems are found to be repulsive for small cell sizes, in agreement with previous calculations (Carling et al., 2000; Uesugi et al., 2003), the same di-vacancy systems are found to be attractive for larger cell-sizes, in keeping with experimental observation (Ehrhart et al., 1991; Hehenkamp, 1994). Thus, in this case access to large cell sizes changes the predicted physics not only quantitatively but also qualitatively.

The present method applies quite generally regardless of the choice of OFDFT flavor, such as the particular choice of pseudopotential, kinetic energy functional, generalized approximations, and others. The particular choices made in the calculations presented here are mainly for purposes of illustration. A considerable investment has been made, which
continues at present, concerning the development of versions of OFDFT that are increasingly accurate in a given domain of application. However, it is widely regarded that in many cases Kohn–Sham DFT offers superior accuracy than OFDFT. We close by noting that, at this time, it is not clear how to extend QC-OFDFT to the Kohn–Sham setting, and that therein lies an opportunity for further research.

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References


