

Chapter 1

Electronic Structure Calculations at Macroscopic Scales using Orbital-free DFT

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In this chapter we provide an overview of the recently developed coarse-graining technique for orbital-free density functional theory that enables electronic structure calculations on multi-million atoms. The key ideas involved are: (i) a local real-space formulation of orbital-free density functional theory; (ii) a finite element discretization of the formulation; (iii) a systematic means of adaptive coarse-graining of the finite-element basis set using quasi-continuum reduction. The accuracy and effectiveness of the computational technique is demonstrated by studying the energetics of mono- and di-vacancies in multi-million atom aluminum crystals.

1.1. Introduction

Electronic structure calculations, especially those using density-functional theory of Hohenberg, Kohn and Sham^{1,2} (KSDFT), have provided great insights into various aspects of materials properties in the last decade. Derived from quantum mechanics, electronic structure theories incorporate significant fundamental physics with little empiricism. Therefore, these theories are *transferable*, and capable of predicting a wide range of properties across various materials and external conditions. Successes of electronic structure calculations include the accurate prediction of phase transformations in a wide range of materials, and insights into the mechanical, electronic, magnetic, and optical properties of materials and compounds. More recently, for materials systems whose electronic structure is close to a free electron gas, the orbital-free approach to density-functional theory (OFDFT) has received considerable interest where the kinetic energy of non-interacting electrons is modeled.³ Recent efforts in this field have resulted in the development of accurate kinetic energy functionals for simple metals, Aluminium, as well as some covalently bonded systems like Silicon.⁴⁻⁸ The ground state energy in orbital-free approaches is explicitly determined by the ground-state electron-density without recourse to the wavefunctions, which reduces the computational complexity of determining the ground state properties to scale linearly with system size. This allows the consid-

eration of much larger systems using an orbital-free approach in comparison to the Kohn-Sham approach to density functional theory (KSDF).

Despite the many algorithmic developments in electronic structure calculations, the computational effort associated with these calculations is still enormous. Typical systems sizes accessible using the Kohn-Sham approach are of the order of a few hundred atoms, whereas orbital-free approaches can handle larger systems of about a thousand atoms. Moreover, the use of a plane-wave basis in most calculations restricts these investigations to periodic geometries. These restrictive periodic geometries in conjunction with the cell-size limitations limits the applicability of electronic structure theories to bulk properties of perfect materials. However, defects play a critical role in determining the properties of materials. These include dopants in semi-conductors to dislocations in mechanics to surfaces in nano-structures. These defects occur at very small concentrations and have long-ranged interactions. Therefore a complete and accurate description of such defects must include the electronic structure of the core of the defect at the fine (sub-nanometer) scale and the elastic, electrostatic, and other effects on the coarse (micrometer and beyond) scale. This in turn requires electronic structure calculations on systems containing millions of atoms, or in other words *electronic structure calculations at macroscopic scales*.

Various multi-scale schemes have been proposed to address this significant challenge, among which *hierarchical methods*^{9,10} and *concurrent schemes*¹¹⁻¹⁵ are the most popular. Multi-scale schemes where information is transferred from smaller to larger length scales are referred to as upscaling methods or hierarchical schemes. In such methods, electronic structure calculations are used to fit interatomic potentials/force-fields and these potentials are then used to compute materials properties on the macroscopic scale. On the other hand, the philosophy behind concurrent schemes, also referred to as embedding schemes, is to embed a refined electronic structure calculation in a coarser theory like tight-binding or atomistic calculations using empirical potentials, which in turn is embedded in a continuum theory. Valuable as these schemes are, they suffer from notable shortcomings. In some cases, uncontrolled approximations are made such as the assumption of linear response theory or the Cauchy-Born hypothesis. Others assume separation of scales, the validity of which can not be asserted. Moreover, these schemes are not seamless and are not solely based on a single electronic structure theory. In particular, they introduce undesirable overlaps between regions of the model governed by heterogeneous and mathematically unrelated theories. Finally, no clear notion of convergence to the full electronic structure solution is afforded by the existing methods. For all the above reasons, there is need for a *seamless* multi-scale scheme to perform electronic structure calculations at macroscopic scales with no *ad hoc* assumptions.

In this article we present an overview of the recently developed systematic coarse-graining of orbital-free density functional theory that effectively overcomes the present limitations and enables electronic structure calculations on multi-million

atom systems at no significant loss of accuracy.^{16,17} This multi-scale scheme is referred to as the *quasi-continuum orbital-free DFT (QC-OFDFT)* and is composed of the following building blocks: (i) a *local real-space* formulation of OFDFT; (ii) a *finite-element* discretization of the formulation; (iii) and a *quasi-continuum reduction* of the resulting equations that resolves detailed information in regions where it is necessary (such as in the immediate vicinity of the defect), but adaptively samples over details where it is not (such as in regions far away from the defect), without significant loss of accuracy.

This proposed multi-scale scheme has the following defining properties: It adapts the level of spatial resolution to the local structure of the solution, e. g., supplying higher resolution near lattice defects and rapidly coarsening the resolution away from the defects; in particular, the coarse-graining is completely *unstructured* and does not rely on periodicity. Fully-resolved electronic structure and finite lattice-elasticity are obtained as special limits. The coarse-graining is entirely *seamless* and based solely on approximation theory; in particular, a single electronic structure theory is the *sole* physics input to the calculations, and no spurious physics or *ansatz* regarding the behavior of the system is introduced as a basis for—or as a result of—the coarse-graining. The nature of the systems of interest is such that vast reductions in the size of the problem can be achieved without appreciable loss of accuracy, thus effectively permitting consideration of systems much larger than heretofore possible.

In section 1.2 we present an overview of quasi-continuum orbital-free density-functional theory and salient features of the method that enable electronic structure calculations at macroscopic scales. We refer to Gavini *et al.*^{16,17} for a more comprehensive discussion on the method. Section 1.3 provides a discussion on electronic structure studies of vacancies using QC-OFDFT. Section 1.4 provides an outlook for the proposed method and opportunities for future work.

1.2. Overview of quasi-continuum orbital-free density functional theory

1.2.1. Real-space formulation of OFDFT

The ground state energy in density functional theory is given by^{3,10}

$$E(\rho, \mathbf{R}) = T_s(\rho) + E_{xc}(\rho) + E_H(\rho) + E_{ext}(\rho, \mathbf{R}) + E_{zz}(\mathbf{R}), \quad (1.1)$$

where ρ is the ground-state electron-density; $\mathbf{R} = \{\mathbf{R}_1, \dots, \mathbf{R}_M\}$ 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_{ext} is the electrostatic interaction energy of electrons with external field induced by nuclear charges and E_{zz} denotes the repulsive energy between nuclei. The various terms and their functional forms are briefly described below.

In OFDFT the kinetic energy of non-interacting electrons, T_s , is modeled, as opposed to the more widely used KSDFT where this is evaluated exactly within the mean-field approximation by solving an effective single electron Schrödinger equation. In material systems whose electronic structure is close to a free-electron gas, e. g. simple metals, aluminum etc., very good orbital-free models for the kinetic energy term are available which have been shown to accurately predict a wide range of properties in these materials. A simple choice for this is the Thomas-Fermi-Weizsacker (TFW) family of functionals,³ which have the form

$$T_s(u) = C_F \int u^{10/3}(\mathbf{r})d\mathbf{r} + \frac{\lambda}{2} \int |\nabla u(\mathbf{r})|^2 d\mathbf{r}, \quad (1.2)$$

where $C_F = \frac{3}{10}(3\pi^2)^{2/3}$, λ is a parameter, and $u(\mathbf{r}) = \sqrt{\rho(\mathbf{r})}$ denotes the square-root electron-density. More recently, there have been efforts⁴⁻⁷ to improve these orbital-free kinetic energy functionals by introducing an additional non-local term called the kernel energy. These kinetic energy functionals have a functional form given by

$$T_s(u) = C_F \int u^{10/3}(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int |\nabla u(\mathbf{r})|^2 + \int \int f(u(\mathbf{r}))K(|\mathbf{r} - \mathbf{r}'|)g(u(\mathbf{r}'))d\mathbf{r}d\mathbf{r}', \quad (1.3)$$

where f , g and K are chosen to satisfy known limits of exact $T_s(u)$ for uniform electron gas.

The exchange correlation energy, E_{xc} , describes the quantum-mechanical interactions for which accurate models for most systems are available. The Local Density Approximation (LDA)^{18,19} given by

$$E_{xc}(u) = \int \epsilon_{xc}(u^2(\mathbf{r}))u^2(\mathbf{r})d\mathbf{r}, \quad (1.4)$$

where ϵ_{xc} has a parameterized form, has been shown to capture the exchange and correlation effects for most systems accurately.

Finally, the electrostatic interactions in equation (1.1) are given by,

$$E_H(u) = \frac{1}{2} \int \int \frac{u^2(\mathbf{r})u^2(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}', \quad (1.5)$$

$$E_{ext}(u, \mathbf{R}) = \sum_{I=1}^M \int u^2(\mathbf{r}) \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} d\mathbf{r}, \quad (1.6)$$

$$E_{zz}(\mathbf{R}) = \frac{1}{2} \sum_{I=1}^M \sum_{\substack{J=1 \\ J \neq I}}^M \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}, \quad (1.7)$$

where Z_I denotes the charge of the nucleus located at \mathbf{R}_I , $I = 1, 2, \dots, M$.

Traditionally, OFDFT (as well as KSDFT) calculations have mostly been performed in Fourier-space using plane-wave basis functions. The choice of a plane-wave basis for electronic structure calculations has been the most popular one, as it

lends itself to a computation of the electrostatic interactions naturally using Fourier transforms. However, such a Fourier-space formulation has very serious limitations in describing defects in materials. Firstly, it requires periodic boundary conditions, thus limiting an investigation to a periodic array of defects. This periodicity restriction in conjunction with the cell-size limitations (~ 200 atoms) arising from the enormous computational cost associated with electronic structure calculations, limits the scope of these studies to very high concentrations of defects that are not realized in nature. Importantly, plane-wave basis functions used in Fourier-space formulations provide a uniform spatial resolution, which is not desired in the description of defects in materials. Often, higher resolution is required in the description of the core of a defect and a coarser resolution suffices away from the defect-core. This in turn makes Fourier-space formulations *computationally inefficient* in the study of defects in materials. Further, from a numerical viewpoint, plane-wave basis functions are non-local in the real-space, thus resulting in a dense matrix which limits the effectiveness of iterative solutions. Also, a plane-wave basis requires the evaluation of Fourier transforms which affect the scalability of parallel computation.

For all the above reasons, and since it forms a key feature of the quasi-continuum reduction, a local real-space formulation of OFDFT is desired. The energy functional given by equation (1.1) is local in real-space except for the electrostatic interactions and the kernel energies which are extended in real-space. For this reason, evaluation of these energy terms is the most computationally intensive part of the calculation of the energy functional. However, noticing that $\frac{1}{|\mathbf{r}-\mathbf{r}'|}$ kernel in the electrostatic interactions is the Green's function of the Poisson's equation, the electrostatic interactions can be expressed locally as the following variational problem,

$$\begin{aligned} & \frac{1}{2} \int \int \frac{(u^2(\mathbf{r}) + b(\mathbf{r}; \mathbf{R}))(u^2(\mathbf{r}') + b(\mathbf{r}'; \mathbf{R}))}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ & = - \inf_{\phi \in H_0^1(\mathbb{R}^3)} \left\{ \frac{1}{8\pi} \int |\nabla \phi(\mathbf{r})|^2 d\mathbf{r} - \int (u^2(\mathbf{r}) + b(\mathbf{r}; \mathbf{R})) \phi(\mathbf{r}) d\mathbf{r} \right\}, \end{aligned} \quad (1.8)$$

where ϕ denotes a trial function for the electrostatic potential of the system of charges, and $b(\mathbf{r}; \mathbf{R})$ denotes the regularized nuclear charges corresponding to the pseudopotentials that provide an external potential for valence electrons. We note that equation (1.8) is a variational reformulation of solving the Poisson's equation. We remark that the left hand side of equation (1.8) differs from the sum of electrostatic terms by the self energy of the nuclei, which is an inconsequential constant and does not influence the computation of ground-state properties.

Turning to the non-local kinetic energy terms (kernel energies) given by equation (1.3), the approach suggested by Choly & Kaxiras²⁰ is used to approximate the kernel in the reciprocal space by a rational function. This results in a system of Helmholtz equations that are local in real-space. Under this approximation, whose error can be systematically controlled, the kernel energies can be expressed in a

local form given by

$$T_s(u) = C_F \int u^{10/3}(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int |\nabla u(\mathbf{r})|^2 + \sum_{j=1}^m \int w_j(\mathbf{r})g(u(\mathbf{r})) + \left(\sum_{j=1}^m P_j \right) \int f(u(\mathbf{r}))g(u(\mathbf{r}))d\mathbf{r} \quad (1.9)$$

where w_j 's denote the *kernel potentials* which are minimizers of the following sequence of variational problems

$$\inf_{w_j \in X_w} \left\{ \frac{C}{2} \int |\nabla w_j(\mathbf{r})|^2 d\mathbf{r} + \frac{Q_j}{2} \int w_j^2(\mathbf{r})d\mathbf{r} + C_j \int w_j(\mathbf{r})f(u(\mathbf{r}))d\mathbf{r} \right\} \quad (1.10)$$

$j = 1 \dots m.$

C, C_j, Q_j and $P_j, j = 1, 2, \dots, m$, are constants determined from a fitted rational function with degree $2m$, and X_w is a suitable functional space.

Finally, the problem of determining the ground-state energy, electron-density and equilibrium positions of the nuclei is determined by the following variational problem,

$$\inf_{\mathbf{R} \in \mathbb{R}^{3M}} \inf_{u \in H_0^1(\mathbb{R}^3)} E(u, \mathbf{R}) \quad (1.11a)$$

$$\text{subject to:} \quad \int u^2(\mathbf{r})d\mathbf{r} = N, \quad (1.11b)$$

where N is the total number of electrons in the system. We note that, using the reformulations in equations (1.8)-(1.10), all components of energy are local in real-space.

1.2.2. Finite-element discretization

A finite-element basis set which respects the local variational nature of the formulation and allows for arbitrary boundary conditions and complex geometries is a natural choice to discretize and compute. Importantly, a finite-element discretization is amenable to *adaptive coarse-graining*, which is a key departure from previous numerical methods relying on plane-wave basis sets that have a uniform resolution in real-space. This is the key-idea which will be exploited in the construction of the quasi-continuum reduction, presented in the following section, that will enable electronic structure calculations of multi-million atom systems. Furthermore, the compact support of a finite-element basis is a desirable property in an implementation of the formulation on parallel computing architecture, which derives considerable importance owing to the computational complexity associated with electronic structure calculations.

Finite-element bases are piecewise polynomial bases and are constructed from a discretization of the domain of analysis as a cell complex, or triangulation, T_h .^{21,22} 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. 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. The interpolated fields $u^h(\mathbf{r})$, $\phi^h(\mathbf{r})$, $w_j^h(\mathbf{r})$ spanned by a finite-element basis are of the form

$$u^h(\mathbf{r}) = \sum_i u_i N_i^h(\mathbf{r}) \quad (1.12a)$$

$$\phi^h(\mathbf{r}) = \sum_i \phi_i N_i^h(\mathbf{r}) \quad (1.12b)$$

$$w_j^h(\mathbf{r}) = \sum_i w_{j_i} N_i^h(\mathbf{r}) \quad j = 1 \dots N, \quad (1.12c)$$

where i indexes the nodes of the triangulation, $N_i^h(\mathbf{r})$ denotes the shape function corresponding to node i , and u_i, ϕ_i, w_{j_i} represent the values of $u^h(\mathbf{r})$, $\phi^h(\mathbf{r})$, $w_j^h(\mathbf{r})$ at node i respectively. Let X_h denote the subspace spanned by the finite-element basis functions that become increasingly dense in $H_0^1(\mathbb{R}^3)$. The variational problem given by equation (1.11) reduces to a constrained minimization problem given by,

$$\inf_{\mathbf{R} \in \mathbb{R}^{3M}} \inf_{u^h \in X_h} E(u^h, \mathbf{R}), \quad (1.13a)$$

$$\text{subject to:} \quad \int u^{h^2}(\mathbf{r}) d\mathbf{r} = N, \quad (1.13b)$$

where the discrete local reformulations of the extended electrostatic interactions (equation (1.8)) and kernel energies (equation (1.10)) in the finite-element basis are given by the constrained minimization problems,

$$\inf_{\phi^h \in X_h} \left\{ \frac{1}{8\pi} \int |\nabla \phi^h(\mathbf{r})|^2 d\mathbf{r} - \int (u^{h^2}(\mathbf{r}) + b(\mathbf{r}; \mathbf{R})) \phi^h(\mathbf{r}) d\mathbf{r} \right\} \quad (1.14)$$

$$\inf_{w_j^h \in X_h} \left\{ \frac{C}{2} \int |\nabla w_j^h(\mathbf{r})|^2 d\mathbf{r} + \frac{Q_j}{2} \int w_j^{h^2}(\mathbf{r}) d\mathbf{r} + C_j \int w_j^h(\mathbf{r}) f(u^h(\mathbf{r})) d\mathbf{r} \right\} \quad (1.15)$$

$$j = 1 \dots m.$$

1.2.3. Quasi-continuum reduction

The real-space formulation of density-functional theory and the finite-element discretization of the formulation described in subsections 1.2.1 and 1.2.2 is attractive, as it gives *freedom from periodicity*, which is important in modeling defects in materials. But, the computational complexity of these calculations limit investigations to systems consisting of a few thousand atoms. On the other hand, materials properties are influenced by defects—vacancies, dopants, dislocations, cracks, free surfaces—in small concentrations (parts per million). An accurate understanding

of such defects must not only include the electronic structure of the core of the defect, but also the elastic and electrostatic effects on the macro-scale. This in turn requires calculations involving millions of atoms well beyond the current capability.

The recently proposed *quasi-continuum reduction* for OFDFT¹⁷ effectively overcomes the present limitations and enables electronic structure calculations on multi-million atom systems. This is a multi-scale method which enables systematic coarse-graining of OFDFT in a *seamless* manner that resolves detailed information in regions where it is necessary (such as in the immediate vicinity of the defect) but adaptively samples over details where it is not (such as in regions far away from the defect) without significant loss of accuracy. The real-space formulation, and a finite-element discretization of the formulation which is *amenable to coarse-graining* are crucial steps in its development. The approach is similar in spirit to the quasi-continuum (QC) approach developed in the context of interatomic potentials^{23,24} 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 representative atoms are chosen such that near the defect core all atoms are represented, whereas away from the defect core the interpolation becomes coarser and a small fraction of the atoms determines the displacements of the rest.

In the context of OFDFT, the conventional QC reduction scheme can be applied *mutatis mutandis* to describe the positions of the nuclei. However, the electronic fields comprising of the electron-density, electrostatic potential and kernel potentials exhibit subatomic structure as well as lattice scale modulation, and therefore require an altogether different type of representation. To realize the coarse-graining of OFDFT, three unstructured triangulations of the domain are introduced as shown in Figure 1.1 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 in this discussion is called the *atomic-mesh*.
- (ii) A triangulation T_{h_3} subatomic close to lattice defects and increasingly coarser away from the defects, which is called the *electronic-mesh*.
- (iii) An auxiliary subatomic triangulation T_{h_2} that resolves a lattice unit-cell to capture the subatomic oscillations in the electronic fields, which is labeled as the *fine-mesh*.

The triangulations are restricted in such a way that T_{h_3} is a sub-grid of T_{h_1} for convenience. We additionally denote by X_{h_1} , X_{h_2} and X_{h_3} the corresponding finite-element approximation spaces.

The representation of the electronic fields is decomposed as predictor and corrector fields given by

$$u^h = u_0^h + u_c^h \quad (1.16a)$$

$$\phi^h = \phi_0^h + \phi_c^h \quad (1.16b)$$

$$w_j^h = w_{j0}^h + w_{jc}^h \quad j = 1 \dots m, \quad (1.16c)$$

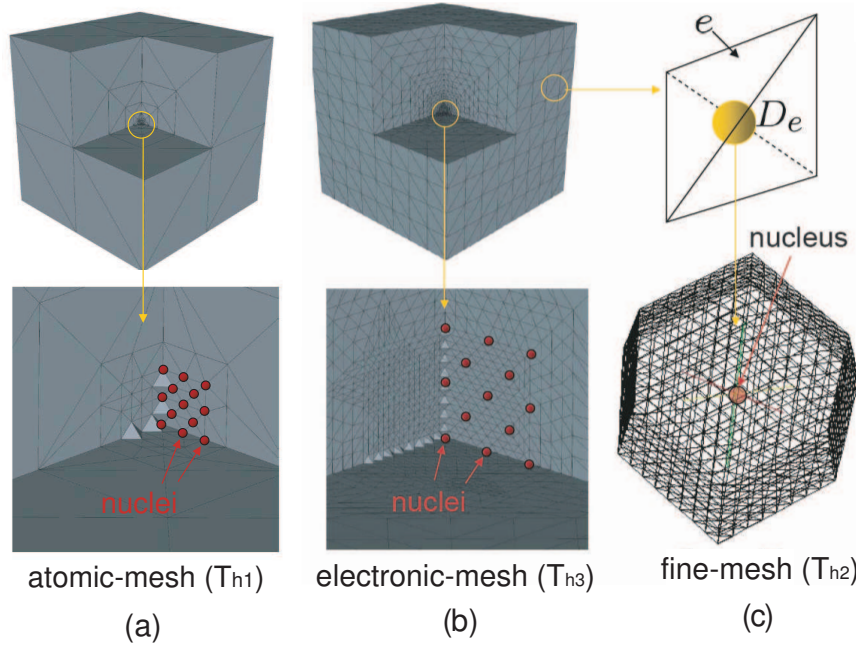


Fig. 1.1. Hierarchy of triangulations used in the QC reduction. (a) Atomic-mesh (T_{h1}) used to interpolate nuclei positions away from the fully-resolved defect-core; (b) Electronic-mesh (T_{h3}) used to represent the corrector fields. It has subatomic resolution in the defect-core, and coarsens away from the defect-core. (c) Fine auxiliary mesh (T_{h2}) is used to sample the Cauchy-Born predictor fields within an integration lattice unit cell, D_e , in each element e .

where $u_0^h, \phi_0^h, w_{j_0}^h \in X_{h2}$ denote the predictor for electronic fields and is obtained by performing a local periodic calculation in every element of T_{h1} using the Cauchy-Born hypothesis. This predictor for the electronic fields is expected to be accurate away from defect cores, in regions where the deformation field is slowly varying. There are formal mathematical results which support this hypothesis.²⁵ Hence, the corrector fields comprising of $u_c^h, \phi_c^h, w_{j_c}^h$ may be accurately represented by means of a finite-element triangulation such as T_{h3} , 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 equation (1.13) now reduces to a minimization problem for the corrector fields and takes the form

$$\inf_{\mathbf{R} \in X_{h1}} \inf_{u_c^h \in X_{h3}} E(u_0^h + u_c^h, \mathbf{R}), \quad (1.17a)$$

$$\text{subject to:} \quad \int (u_0^h(\mathbf{r}) + u_c^h(\mathbf{r}))^2 d\mathbf{r} = N, \quad (1.17b)$$

with the reformulations of electrostatic interactions and kernel energies in equations

(1.14)-(1.15) reducing to

$$\inf_{\phi_c^h \in X_{h_3}} \left\{ \frac{1}{8\pi} \int |\nabla \phi^h(\mathbf{r})|^2 d\mathbf{r} - \int (u^{h^2}(\mathbf{r}) + b(\mathbf{r}; \mathbf{R})) \phi^h d\mathbf{r} \right\} \quad (1.18)$$

$$\inf_{w_j^h \in X_{h_3}} \left\{ \frac{C}{2} \int |\nabla w_j^h(\mathbf{r})|^2 d\mathbf{r} + \frac{Q_j}{2} \int w_j^{h^2}(\mathbf{r}) d\mathbf{r} + C_j \int w_j^h(\mathbf{r}) f(u^h(\mathbf{r})) d\mathbf{r} \right\} \quad (1.19)$$

$j = 1 \dots m.$

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 (1.17) has complexity commensurate with the size of T_{h_2} , which would render the scheme infeasible. In the spirit of quadrature rules for highly oscillating functions, integration rules that reduce all computations to the complexity of T_{h_3} are introduced. The precise form of the integration rule for an element e in the triangulation T_{h_3} is

$$\int_e f(\mathbf{r}) d\mathbf{r} \approx |e| \langle f \rangle_{D_e}, \quad (1.20)$$

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 (1.20), integration over the entire domain can be written as,

$$\int_{\Omega} f(\mathbf{r}) d\mathbf{r} = \sum_{e \in T_{h_3}} \int_e f(\mathbf{r}) d\mathbf{r} \approx \sum_{e \in T_{h_3}} |e| \langle f \rangle_{D_e}, \quad (1.21)$$

reducing all computations to a complexity commensurate with the size of T_{h_3} , and thus reducing the complexity of the computations. This integration rule (1.20) is designed to be exact in regions close to the defect that correspond to sub-atomic elements of T_{h_3} , where the non-local corrections are significant. However, in regions far away from the defect, which correspond to superatomic elements of T_{h_3} , the non-local corrections are very small compared to the predictor. Thus, the integrand of equation (1.20) is a rapidly oscillating function with a very gradual modulation on the scale of the element. Hence, equation (1.20), for regions away from the core of a defect, denotes the zero order quadrature rule for rapidly oscillating functions.

Equations (1.17)-(1.20) describe the quasi-continuum reduction of OFDFT, referred to as QC-OFDFT. To end this section, we note the following defining properties of the quasi-continuum reduction:

- (1) OFDFT is the sole input physics, the rest is approximation theory. There are no spurious physics, patching conditions or *a priori* ansatz. The method is seamless and free of any structure.
- (2) 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.

- (3) Importantly, it enables electronic structure calculations of multi-million atom systems at no significant loss of accuracy as demonstrated in the next section.
- (4) A further property of the method is that it is possible to consider any arbitrary geometry and boundary conditions in light of the real-space finite-element formulation.

1.3. Vacancies in aluminum

In this section we present results that demonstrate the accuracy and effectiveness of QC-OFDFT scheme through previously conducted studies on energetics of vacancies in aluminum^{16,17,26,27} as well as some recent investigations. For the purpose of demonstration, initial studies have been conducted using the TFW family of kinetic energy functionals with $\lambda = \frac{1}{6}$, and these constitute the majority of results presented here. Later in this section, we also present some results from recent investigations that use the more accurate kernel energies. All simulations were performed using a modified form of the Heine-Abarenkov pseudopotential²⁸ for aluminum and LDA treatment of the exchange and correlation functionals.^{18,19} Numerical parameters were chosen such that errors due to mesh discretization do not exceed 0.01 eV in the computed energies.

To demonstrate the effectiveness of the coarse-graining scheme a sample containing 16,384 aluminum atoms was considered to compute the formation energy of a mono-vacancy. The kinetic energy of non-interacting electrons is modeled using the TFW family of functionals with $\lambda = \frac{1}{6}$. Dirichlet boundary conditions are applied on the corrector fields which implies all fields approach the bulk values at the boundary. Figure 1.2 shows the dramatic savings offered by coarse-graining through quasi-continuum reduction. As is evident from the figure, the formation energy attains a converged value at just 256 representative atoms which provides an 80 fold computational savings. These savings improve with the size of the sample and enable electronic structure studies on much larger samples than possible heretofore.

The energetics of vacancies are determined both by the electronic structure of the core as well as the long-ranged elastic and electrostatic interactions. Many efforts aimed towards determining the properties of vacancies using electronic structure calculations used periodic geometries with cell-sizes of at most a few hundred atoms.^{6,7,29-32} Such small cell-size may not capture the long-ranged effects in the presence of defects. To this end, QC-OFDFT scheme, which is free of cell-size limitations, was used to determine the cell-size effects of the computed energetics. Figure 1.3 shows the cell-size dependence of the vacancy formation energy in terms of the nominal number of atoms N . This study is conducted for two cases, one where the atomic relaxations are suppressed and another where the atoms are relaxed. Results indicate that large cell-sizes, consisting of more than thousand atoms, are required to obtain a converged mono-vacancy formation energy. We

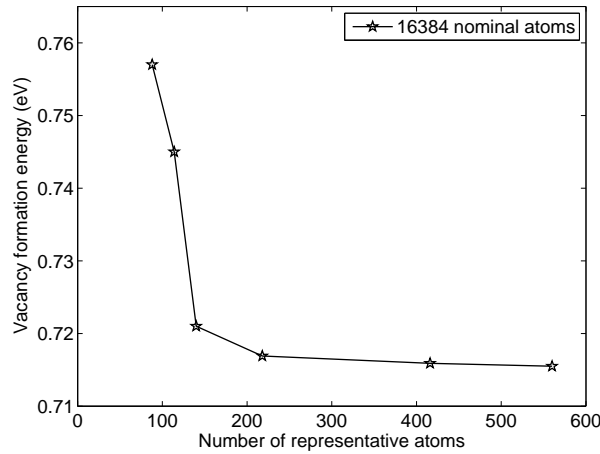


Fig. 1.2. Convergence of the QC reduction: Formation energy of a mono-vacancy as a function of number of representative atoms. Adapted from Gavini *et al.*¹⁷

note that the converged vacancy formation energy, computed to be 0.72 eV, is in good agreement with experimental estimates.³³

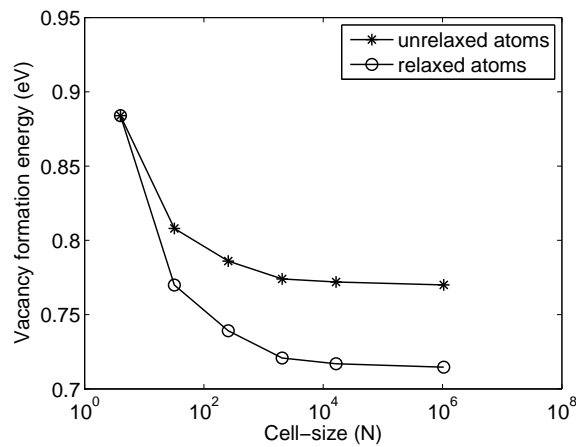


Fig. 1.3. Cell-size effects in the mono-vacancy formation energy. Adapted from Gavini *et al.*¹⁷

The cell-size dependence was more evident in a study of the energetics of di-vacancies, which are vacancy complexes formed from two adjacent vacancies. Of interest are the binding energies of the di-vacancies along $\langle 110 \rangle$ (nearest neighbor) and $\langle 100 \rangle$ (next nearest neighbor) crystallographic directions. Experimental studies

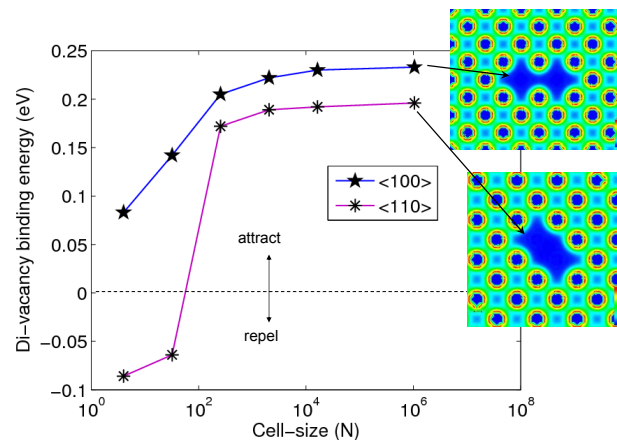


Fig. 1.4. Cell-size effects in the di-vacancy binding energy. Adapted from *Gavini et al.*¹⁷

interpret the binding energies of di-vacancies in aluminum to range between 0.2-0.3 eV,^{34,35} suggesting that vacancies attract. However, most DFT calculations performed to date on cell-sizes of the order of a hundred atoms predict either a repulsive or a negligible attractive interaction between vacancies.^{31,32} It is widely argued that this discrepancy is a result of the entropic effects as the experiments are performed at very high temperatures where as DFT can provide only ground-state properties. One other possible reason for discrepancy is that the computations are performed on very small cell-sizes representing unrealistically high concentration of vacancies. The typical concentration of vacancies is about a few parts per million.³⁶ Access to such large cell-sizes that simulate realistic vacancy concentrations is not possible using conventional methods in electronic structure calculations. However using QC-OFDFT such a study is possible, and a cell-size study of the di-vacancy binding energies was recently performed. Figure 1.4 shows that there is a very strong cell-size dependence of the binding energies of both $\langle 110 \rangle$ and $\langle 100 \rangle$ di-vacancies. More strikingly the $\langle 110 \rangle$ di-vacancy is repulsive for small cell-sizes, representative of previous computations, but becomes attractive for large cell-sizes representative of realistic vacancy concentrations with binding energies in agreement with experiments.^{34,35} These results indicate that the physics not only changes quantitatively but also qualitatively with cell-size and underscores the need to account for the long-ranged interactions, especially in the presence of defects. Similar cell-size effects have also been observed in quad-vacancy clusters where much larger cell-sizes were required to obtain a converged solution.²⁶

We note that although the computed di-vacancy binding energies are in good agreement with experiments, the calculations were performed by using the TFW family of functionals for the kinetic energy. It is well known that these functionals

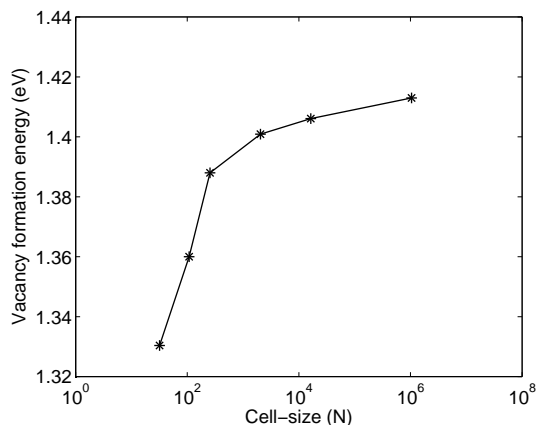


Fig. 1.5. Cell-size effects in the unrelaxed mono-vacancy formation energy using density-independent kernel energies with parameters $\{\alpha, \beta\} = \{\frac{5}{6} \pm \frac{\sqrt{5}}{6}\}$.⁷

do not satisfy the Linhards response function for small perturbations of uniform electron gas which is explicitly known. Moreover, a recent study which employed more accurate kinetic energy functionals using kernel energies showed that even up to cell-sizes of about 500 atoms the binding energy of $\langle 110 \rangle$ di-vacancy is negligible.³⁷ To this end, we reformulated the density independent kernel energies^{6,7} in a local form via equations (1.9)-(1.10) and incorporated into the QC-OFDFT scheme. We have very recently performed a cell-size study of an unrelaxed mono-vacancy using these kernel energies. As is evident from figure 1.5 there is a significant cell-size dependence. The vacancy formation energy for a 32 atom cell-size is computed to be 1.33 eV which is in excellent agreement with previous computations.⁷ However, upon increasing the cell-size to account for a million atoms, the formation energy increases by almost 0.1 eV which is significant especially in the computation of di-vacancy binding energies. The cell-size effects on the di-vacancy binding energies after incorporating the kernel energies are currently being investigated, alongside the pursuit of some algorithmic developments to improve the efficiency of computations.

1.4. Outlook

Quasi-continuum orbital-free density-functional theory is a seamless multi-scale scheme to coarse-grain OFDFT using quasi-continuum reduction. It uses a local real-space formulation of OFDFT and a systematic coarse-graining of the finite-element basis set to enable electronic structure calculations on multi-million atom systems at no significant loss of accuracy, and without the introduction of spurious physics or assumptions. An important feature of the multi-scale scheme is that OFDFT is the sole input physics and the rest is approximation theory which en-

ables a systematic convergence study of the method. As demonstrated through the studies on vacancies in aluminum, the proposed scheme can be useful in the study of defects in materials where much larger cell-sizes than those accessible through conventional techniques are required to capture the long-ranged effects present in these systems. Furthermore, as general geometries and non-periodic boundary conditions can be analyzed using this method, it enables the study of a wide range of defects, e. g. a single dislocation core-structure which is otherwise not possible in a restrictive periodic geometry.

Although the proposed quasi-continuum reduction scheme has been developed for OFDFT, the mathematical structure of the method is general and can be extended to KSDFT as well as other electronic structure theories. However to obtain similar computational savings as afforded for OFDFT, two non-trivial aspects which need to be addresses are: (i) the treatment of the delocalized nature of the wave-functions and enforcing the orthogonality constraint; (ii) development of efficient eigenvalue solvers for large systems. Herein lies the opportunity for future work, alongside the accurate electronic structure study of defects made possible by the method.

References

1. P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136**(3B), B864–B871, (1964).
2. W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* **140**(4A), A1133–A1138, (1965).
3. R. Parr and W. Yang, *Density-functional theory of atoms and molecules*. (Oxford University Press, 1989).
4. L.-W. Wang and M. P. Teter, Kinetic-energy functional of the electron density, *Phys. Rev. B.* **45**(23), 13196–13220, (1992).
5. E. Smargiassi and P. A. Madden, Orbital-free kinetic-energy functionals for first-principles molecular dynamics, *Phys. Rev. B.* **49**(8), 5220–5226, (1994).
6. Y. A. Wang, N. Govind, and E. A. Carter, Orbital-free kinetic-energy functionals for the nearly free electron gas, *Phys. Rev. B.* **58**(20), 13465–13471, (1998).
7. Y. A. Wang, N. Govind, and E. A. Carter, Orbital-free kinetic-energy density functionals with a density-dependent kernel, *Phys. Rev. B.* **60**(24), 16350–16358, (1999).
8. B. Zhou, V. L. Ligneres, and E. A. Carter, Improving the orbital-free density functional theory description of covalent materials, *J. Chem. Phys.* **122**(4):044103, (2005).
9. A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard, and W. M. Skiff, Uff, a full periodic table force field for molecular mechanics and molecular dynamics simulations, *J. Am. Chem. Soc.* **114**(25), 10024–10035, (1992).
10. M. Finnis, *Interatomic forces in condensed matter*. (Oxford University Press, 2003).
11. N. Govind, Y. A. Wang, and E. A. Carter, Electronic-structure calculations by first-principles density-based embedding of explicitly correlated systems, *J. Chem. Phys.* **110**(16), 7677–7688, (1999).
12. M. Fago, R. L. Hayes, E. A. Carter, and M. Ortiz, Density-functional-theory-based local quasicontinuum method: Prediction of dislocation nucleation, *Phys. Rev. B.* **70**(10), 100102, (2004).

13. N. Choly, G. Lu, W. E, and E. Kaxiras, Multiscale simulations in simple metals: A density-functional-based methodology, *Phys. Rev. B.* **71**(9), 094101, (2005).
14. G. Lu, E. B. Tadmor, and E. Kaxiras, From electrons to finite elements: A concurrent multiscale approach for metals, *Phys. Rev. B.* **73**(2):024108, (2006).
15. Q. Peng, X. Zhang, L. Hung, E. A. Carter, and G. Lu, Quantum simulation of materials at micron scales and beyond, *Phys. Rev. B.* **78**(5), 054118–054132, (2008).
16. V. Gavini, J. Knap, K. Bhattacharya, and M. Ortiz, Non-periodic finite-element formulation of orbital-free density functional theory, *J. Mech. Phys. Solids.* **55**(4), 669–696, (2007).
17. V. Gavini, K. Bhattacharya, and M. Ortiz, Quasi-continuum orbital-free density-functional theory: A route to multi-million atom non-periodic DFT calculation, *J. Mech. Phys. Solids.* **55**(4), 697–718, (2007).
18. D. M. Ceperley and B. J. Alder, Ground state of the electron gas by a stochastic method, *Phys. Rev. Lett.* **45**(7), 566–569, (1980).
19. J. P. Perdew and A. Zunger, Self-interaction correction to density-functional approximations for many-electron systems, *Phys. Rev. B.* **23**(10), 5048–5079, (1981).
20. N. Choly and E. Kaxiras, Kinetic energy density functionals for non-periodic systems, *Sol. State Comm.* **121**(5), 281–286, (2002).
21. P. Ciarlet, *The finite-element method for elliptic problems.* (SIAM, Philadelphia, 2002).
22. S. C. Brenner and L. R. Scott, *The mathematical theory of finite element methods.* (Springer-Verlag, New York, 2002).
23. E. B. Tadmor, M. Ortiz, and R. Phillips, Quasicontinuum analysis of defects in solids, *Philos. Mag. A.* **73**, 1529–1563, (1996).
24. J. Knap and M. Ortiz, An analysis of the quasicontinuum method, *J. Mech. Phys. Solids.* **49**(9), 1899–1923, (2001).
25. X. Blanc, C. L. Bris, and P. L. Lions, From molecular models to continuum mechanics, *Arch. Rational Mech. Anal.* **164**, 341–381, (2002).
26. V. Gavini, K. Bhattacharya, and M. Ortiz, Vacancy clustering and prismatic dislocation loop formation in aluminum, *Phys. Rev. B.* **76**(18), 180101–180105, (2007).
27. V. Gavini, Role of macroscopic deformations in energetics of vacancies in aluminum, *Phys. Rev. Lett.* **101**(20), 205503–205507, (2008).
28. L. Goodwin, R. J. Needs, and V. Heine, A pseudopotential total energy study of impurity promoted intergranular embrittlement, *J. Phys. Condens. Matter.* **2**, 351–365, (1990).
29. N. Chetty, M. Weinert, T. S. Rahman, and J. W. Davenport, Vacancies and impurities in aluminum and magnesium, *Phys. Rev. B.* **52**(9), 6313–6326, (1995).
30. D. E. Turner, Z. Z. Zhu, C. T. Chan, and K. M. Ho, Energetics of vacancy and substitutional impurities in aluminum bulk and clusters, *Phys. Rev. B.* **55**(20), 13842–13852, (1997).
31. K. Carling, G. Wahnström, T. R. Mattsson, A. E. Mattsson, N. Sandberg, and G. Grimvall, Vacancies in metals: From first-principles calculations to experimental data, *Phys. Rev. Lett.* **85**(18), 3862–3865, (2000).
32. T. Uesugi, M. Kohyama, and K. Higashi, Ab initio study on divacancy binding energies in aluminum and magnesium, *Phys. Rev. B.* **68**(18), 184103–184108, (2003).
33. W. Triftshäuser, Positron trapping in solid and liquid metals, *Phys. Rev. B.* **12**(11), 4634–4639, (1975).
34. P. Ehrhart, P. Jung, H. Schultz, and H. Ullmaier, *Atomic defects in metal.* (Landolt-Börnstein, New Series, Group 3, Vol. 25, Springer-Verlag, Berlin, 1991).
35. T. Hehenkamp, Absolute vacancy concentrations in noble metals and some of their

- alloys, *J. Phys. Chem. Solids*. **55**, 907–915, (1994).
36. M. J. Fluss, S. Berko, B. Chakraborty, K. R. Hoffmann, P. Lippel, and R. W. Siegel, Positron annihilation spectroscopy of the equilibrium vacancy ensemble in aluminium, *J. Phys. F : Met. Phys.* **14**, 2831–2854, (1984).
 37. G. Ho, M. T. Ong, K. J. Caspersen, and E. A. Carter, Energetics and kinetics of vacancy diffusion and aggregation in shocked aluminium via orbital-free density functional theory, *Phys. Chem. Chem. Phys.* **9**, 4951–4966, (2007).