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Tools for fluctuation reconstruction in density functional theory, resulting optimization problems and nonlinear equations.

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1 Problem Description and Goals

The intent of this document is to provide the analytical framework for a longer term project that focuses on chemical, physical, and mechanical nanostructures investigation.

Nanostructures have dimensions in the range of 10-20 nm and typically contain tens of thousands of atoms. Applying the classical Kohn-Sham DFT method [14] for non-periodic structures of 60 atoms has led in the past to simulations that can take up to three months to complete [24]. When long term interactions are ignored and pseudo-potentials are used, *ab-initio* simulations have been carried out for non-metallic structures with up to 1500 atoms [18]. The approach used to increase the number of atoms considered belongs to the family of so called $\mathcal{O}(N)$ methods [9], which scale as N with the dimension of the problem (in this case the number of electrons).

This work will not be concerned with fundamental electronic structure computation methods. Acknowledging the small-dimension constraint placed on the problem by the existing Density Functional Theory (DFT)-based methods, the goal of the proposed work is to use techniques that by closing the spatial scale gap render electronic structure information at the nanoscale. This electronic structure information is then used to investigate the physical, chemical, and mechanical properties of the material.

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In the context of mechanical analysis of nanostructures, the methodology proposed follows in the steps of the quasi-continuum work proposed in [20, 13, 7]. This is an extension of the work in [20, 13], since rather than considering a potential-based interatomic interaction that has a limited range of validity and is difficult to generalize to inhomogeneous materials, the approach proposed uses *ab-initio* methods to provide for the particle interaction; at the same time it is a generalization of the method proposed in [7] since rather than considering each mesh discretization element to be part of a periodic and uniformly deformed infinite crystal, the proposed method treats in a generic optimization framework any structure (nonperiodic and inhomogeneous) once the electronic density distribution is available.

The benefit of this work is twofold; (a) development and software implementation of a methodology that can substantially increase the dimension attribute of the electronic structure problem, (b) support for investigation of general nanostructures (metallic and nonmetallic, non-periodic structures, inhomogeneous materials).

2 Fluctuation Reconstruction

2.1 Paradigm of the proposed approach

The fluctuation reconstruction described is done in reference to a regular lattice or domain of a regular lattice. Significant computational savings are anticipated to stem from two assumptions: (a) the lattice is only minimally deformed; (b) for a given ionic distribution, the electronic energy can be expressed like

$$E(\rho, \rho_A) = \int \theta^1(\rho, \rho_A, \mathbf{r})\mathrm{d}\mathbf{r} + \iint \theta^2(\rho, \rho_A, \mathbf{r}; \rho, \rho_A, \mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \tag{1}$$

This representation is commonly used in conjunction with the so called Orbital-Free DFT (OFDFT) method [23]. Here $\theta^{1,2}$ are the relevant energy density functions, ρ is the electronic density, ρ_A is the nuclear density (which may include delta functions). The first term typically includes the kinetic energy and the exchange-correlation term, whereas the second integral includes all pairwise interactions.

The electronic structure computation is then formulated as an optimization problem [11]: find the electronic density ρ that solves the problem

$$\min_{\rho} E(\rho, \rho_A) \tag{2a}$$

subject to the charge conservation constraint

$$\int \rho(\mathbf{r})\mathrm{d}\mathbf{r} = N_e \tag{2b}$$

where N_e represents the number of electrons present. The solution to this problem depends parametrically on the nuclear density ρ_A, $\rho = \rho(\rho_A)$, a consequence of the Born-Oppenheimer assumption. Subsequently, the computation of the ground state of the entire system as the solution of the optimization problem

$$\min_{\rho_A} E(\rho(\rho_A), \rho_A); \tag{3}$$

provides the nuclei distribution. The latter problem is the one that governs the approach to the first question.

As indicated above, one of the two *central assumptions* is that almost everywhere in the nanostructure the solution to the nuclei distribution problem results only in small deformations. To quantify the concept of small deformation the nanostructure is consider to occupy an initial reference configuration $D^0 \subset \mathbb{R}^3$. The structure undergoes a change of shape described by a deformation mapping $\mathbf{\Phi}(\mathbf{r}^0, t) \in \mathbb{R}^3$, where as indicated the mapping might depend on time t. This deformation mapping gives the location $\mathbf{r}$ in the global Cartesian reference frame of each point $\mathbf{r}^0$ represented in the undeformed material frame. Introducing the components of the deformation gradient

$$F_{iJ} = \frac{\partial \Phi_i}{\partial r_J^0} \tag{4}$$

where upper-case indices refer to the material frame, and lower-case indices to the Cartesian global frame. Thus, $\mathbf{F} = \nabla_0\ \mathbf{\Phi}$ where ∇_0 represents the material gradient operator, and therefore the deformation of an infinitesimal material neighborhood $\mathrm{d}\mathbf{r}^0$ about a point $\mathbf{r}^0$ of D^0 is expressed as

$$\mathrm{d}r_i = F_{iJ}\ \mathrm{d}r_J^0 \tag{5}$$

The concept of small distortion is equivalent to requiring that the spectral radius of $\mathbf{F}$ be sufficiently small; i.e.,

$$||\nabla_0\ \mathbf{\Phi}||_2 < \mathcal{K} \tag{6}$$

is expected to hold for almost everywhere in the domain $\mathbf{B}_0$, for a suitable chosen value of $\mathcal{K}$.

Computational savings are anticipated to result under this assumption since for all the domains that satisfy the condition of Eq.6 a two tier interpolation-based approach will reduce the dimension of the problem. First, the

electronic structure will be constructed in these domains by interpolation using adjacent regions in which a DFT-based approach has been used to accurately compute the electronic structure problem. Secondly, the position of the nuclei will be expressed in terms of the positions of a reduced set of so called representative nuclei *repnuclei*, in an approach similar to the one proposed in [20].

2.2 A simple example: a domain with a gap and Thomas-Fermi DFT

The notation introduced in section 2.1 as well as the proposed methodology is first applied when the Thomas-Fermi functional is used to describe the dependency of the energy on electronic density [21, 8]. The Thomas-Fermi functional has well known limitations and herein it is not selected for its accuracy. It is though a simple framework in which some of the key points of the methodology proposed for electronic density reconstruction are more easily introduced.

2.2.1 The Thomas-Fermi functional

The Thomas-Fermi-based energy functional assumes the form

$$E\left[\rho, \{\mathbf{R}_A\}\right] = E_{ne}\left[\rho, \{\mathbf{R}_A\}\right] + J\left[\rho\right] + K\left[\rho\right] + T\left[\rho\right] + V_{nn}\left(\{\mathbf{R}_A\}\right) \tag{7}$$

where

$$\begin{aligned}
E_{ne}\left[\rho, \{\mathbf{R}_A\}\right] &= -\sum_{A=1}^{M} \int \frac{Z_A\, \rho(\mathbf{r})}{\|\mathbf{R}_A - \mathbf{r}\|}\, d\mathbf{r} && \text{(8a)}\\
J\left[\rho\right] &= \frac{1}{2} \int\int \frac{\rho(\mathbf{r})\, \rho(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|}\, d\mathbf{r}\, d\mathbf{r}' && \text{(8b)}\\
T\left[\rho\right] &= C_F \int \rho^{\frac{5}{3}}(\mathbf{r})\, d\mathbf{r} && \text{(8c)}\\
K\left[\rho\right] &= -C_x \int \rho^{\frac{4}{3}}(\mathbf{r})\, d\mathbf{r} && \text{(8d)}\\
V_{nn}\left(\{\mathbf{R}_A\}\right) &= \sum_{A=1}^{M} \sum_{B=A+1}^{M} \frac{Z_A\, Z_B}{r_{AB}} && \text{(8e)}
\end{aligned}$$

Here $C_F = \frac{3}{10}(3\pi^2)^{2/3}$, and $C_x = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$, and the following notation is used:

- N_e - total number of electrons in the system
- E_{ne} - energy corresponding to nucleus-electron interaction
- ρ - electron density

- J - Coulomb energy
- K - Exchange energy
- T - Kinetic energy
- V_{nn} - inter-nuclear interaction energy
- T - kinetic energy
- Z_A - atomic number associated with nucleus A
- $\mathbf{r}_i$ - global position of electron i
- $\mathbf{r}_A$ - global position of nucleus of atom A
- r_{ij} - distance between electrons i and j
- r_{iA} - distance between electron i and nucleus A
- r_{AB} - distance between two nuclei A and B

The expression of the energy functional of Eq.7 justifies the notation used in Eq.1: the kinetic, exchange energy and nuclear electronic energy are represented through the θ^1 term; the electron-electron interaction is associated with the term θ^2.

In this simple example assume that there are three identical domains D_1, D_2, D_3, as in Fig.1. The electronic density in the respective domains is denoted by $\rho_1(\mathbf{r}), \rho_2(\mathbf{r}), \rho_3(\mathbf{r})$:

$$\rho(\mathbf{r}) = \begin{cases} \rho_1(\mathbf{r}) & \mathbf{r} \in D_1 \\ \rho_2(\mathbf{r}) & \mathbf{r} \in D_2 \\ \rho_3(\mathbf{r}) & \mathbf{r} \in D_3 \end{cases}$$

The definition of the density outside the domain $D_1 \cup D_2 \cup D_3$ is extended by assuming that its value is zero.

In this example the optimality conditions subject to the constraint that the total density should add up to N_e are written for the case when there is no deformation in the underlying crystal structure of the material, whose nuclei are at positions $\{\mathbf{R}_A\}$, for $A = 1 \ldots M$. The optimization problem depends parametrically on the positions of the

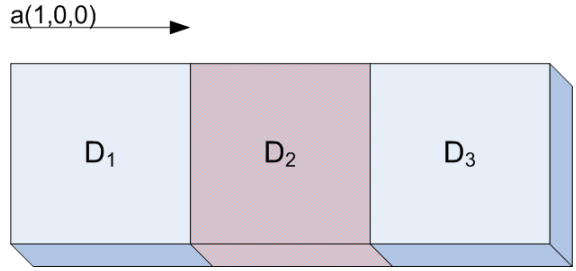

Figure 1: Fluctuation reconstruction.

nuclei:

$$\begin{aligned} &\min_\rho \quad E(\rho;\{\mathbf{R}_A\}) + \lambda\left(\int \rho dr - N\right) \\ &s.t. \quad \int \rho dr - N = 0 \end{aligned}$$

In this form, the electronic optimization problem above is a reformulation of Eq.2. In a direct approach, the dimension of the problem is prohibitive most of the time; unless simplifying assumptions are taken into account, such as periodic boundary conditions, local effects (truncation), pseudo-potentials, etc., systems that contain hundreds of atoms cannot be typically simulated. For the Thomas-Fermi functional, Appendix A shows how solving the electronic problem can be equivalently expressed as a series of optimization problems on smaller domains with suitably defined energy functionals. Thus for domain $D_i, i = 1, 2, 3$, the energy is defined as

$$\begin{aligned} E_i(\rho_i, \lambda_i; \bar{\rho}_i, \{R_A\}) &= C_F \int_{D_i} \rho_i^{\frac{5}{3}}(\mathbf{r})\, d\mathbf{r} - C_x \int_{D_i} \rho_i^{\frac{4}{3}}(\mathbf{r})\, d\mathbf{r} + \int_{D_i}\int_{D-D_i} \frac{\rho(\mathbf{r})\,\bar{\rho}(\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|}\, d\mathbf{r}\, d\mathbf{r}' \\ &+ \frac{1}{2}\int_{D_i}\int_{D_i} \frac{\rho(\mathbf{r})\,\bar{\rho}(\mathbf{r}')}{\|\mathbf{r}-\mathbf{r}'\|}\, d\mathbf{r}\, d\mathbf{r}' - \sum_{A=1}^{M}\int_{D_i} \frac{Z_A\,\rho(\mathbf{r})}{\|\mathbf{R}_A-\mathbf{r}\|}\, d\mathbf{r} + \lambda_i \int_{D_i} \rho_i\, d\mathbf{r} \end{aligned} \tag{9}$$

Appendix A shows that a domain decomposition can be carried out to solve for this example three smaller optimization problems in $D_i, i = 1, 2, 3$. The optimality conditions for these subdomain problems are

$$\nabla_{\rho_i} E_i(\rho_i, \lambda_i; \bar{\rho}_i, \{\mathbf{R}_A\}) = 0, \quad i = 1, 2, 3 \tag{10a}$$

$$\lambda_1 = \lambda_2 = \lambda_3 \tag{10b}$$

$$\int \rho \mathrm{d}\mathbf{r} - N_e = 0 \tag{10c}$$

2.2.2 Reconstruction through interpolation

Assuming that the solution is sufficiently close to, but not necessarily periodic, for $\mathbf{r} \in D_2$ the density is reconstructed by averaging, that is (see Fig.1):

$$\rho_2(\mathbf{r}) \approx \frac{1}{2}\left(\rho_1(\mathbf{r} - a(1,0,0)) + \rho_3(\mathbf{r} + a(1,0,0))\right) \tag{11}$$

This approximation can be improved by using only domains away from the endpoints of the overall slab-like domain. However, for simplicity, in this example the entire domains D_1 and D_3 are considered for reconstruction. This leads to the following coupled system of nonlinear equations

$$\nabla_{\rho_1} E_1(\rho_1, \lambda_1; \rho_3, \frac{1}{2}\left(\rho_1(r - a(1,0,0)) + \rho_3(r + a(1,0,0))\right), \{\mathbf{R}_A\}) = 0 \tag{12a}$$

$$\nabla_{\rho_3} E_3(\rho_3, \lambda_3; \rho_1, \frac{1}{2}\left(\rho_1(r - a(1,0,0)) + \rho_3(r + a(1,0,0))\right), \{\mathbf{R}_A\}) = 0 \tag{12b}$$

$$\lambda_1 = \lambda_3 \tag{12c}$$

$$\int_{D_1} \rho_1 dr + \int_{D_3} \rho_3 dr = \frac{2}{3} N_e \tag{12d}$$

which can be solved without making any reference to the second domain D_2. Note that no assumption is made in regards to charge neutrality in the domains; if an external nonsymmetric potential is present, the total charge will reflect the non-symmetry.

The condition in Eq.12a leads to the following integral equation, which must hold for any $\mathbf{r} \in D_1$:

$$\frac{5}{3} C_F \rho_1^{\frac{2}{3}}(\mathbf{r}) - \frac{4}{3} C_x \rho_1^{\frac{1}{3}}(\mathbf{r}) + \int_{D_1} \rho_1(\mathbf{r}') K_{11}(\mathbf{r}', \mathbf{r}) \mathrm{d}\mathbf{r}' + \int_{D_3} \rho_3(\mathbf{r}') K_{13}(\mathbf{r}', \mathbf{r}) \mathrm{d}\mathbf{r}' - \sum_{A=1}^{M} \frac{Z_A}{||\mathbf{r} - \mathbf{r}'||} + \lambda_1 = 0 \tag{13a}$$

where the kernels K_{11} and K_{13} are defined as

$$K_{11} = \frac{1}{||\mathbf{r} - \mathbf{r}'||} + \frac{0.5}{||\mathbf{r} - (\mathbf{r}' + \mathbf{T})||} \qquad K_{13} = \frac{1}{||\mathbf{r} - \mathbf{r}'||} + \frac{0.5}{||\mathbf{r} - (\mathbf{r}' - \mathbf{T})||} \tag{13b}$$

where $\mathbf{T} = a(1,0,0)$. Similarly, writing the optimality condition of Eq.12b leads to the following integral equation, which must hold for any $\mathbf{r} \in D_3$:

$$\frac{5}{3} C_F \rho_3^{\frac{2}{3}}(\mathbf{r}) - \frac{4}{3} C_x \rho_3^{\frac{1}{3}}(\mathbf{r}) + \int_{D_1} \rho_1(\mathbf{r}') K_{31}(\mathbf{r}', \mathbf{r}) \mathrm{d}\mathbf{r}' + \int_{D_3} \rho_3(\mathbf{r}') K_{33}(\mathbf{r}', \mathbf{r}) \mathrm{d}\mathbf{r}' - \sum_{A=1}^{M} \frac{Z_A}{||\mathbf{r} - \mathbf{r}'||} + \lambda_3 = 0 \tag{14a}$$

where the kernels K_{31} and K_{33} for this problem satisfy the condition

$$K_{31} = K_{11} \qquad\qquad K_{33} = K_{31} \tag{14b}$$

Equations 13a and 14a represent a set of non-linear integral equations that are solved through standard techniques [2]. However, these equations were derived under the assumption that there is no deformation of the domains. This assumption is eliminated if a more general interpolation algorithm is considered. Thus, Eq.11 is replaced by

$$\rho_2(\mathbf{r},t) = \rho_2(\Phi(\mathbf{r}^0,t)) \approx \frac{1}{2}\left(\rho_1(\Phi(\mathbf{r}^0,t)-\mathbf{T}) + \rho_3(\Phi(\mathbf{r}^0,t)+\mathbf{T})\right) \tag{15}$$

where the deformation Φ that depends on the position $\mathbf{r}^0$, of the point in the undeformed (material) frame, and time is as defined in section 2.1. The optimality condition $\nabla_{\rho_1} E_1 = 0$ leads to the following integral equation:

$$\frac{5}{3}C_F\rho_1^{\frac{2}{3}} - \frac{4}{3}C_x\rho_1^{\frac{1}{3}} + \int_{D_1}\frac{\rho_1(\mathbf{r}')}{||\mathbf{r}-\mathbf{r}'||}\mathrm{d}\mathbf{r}' + \int_{D_2}\frac{\rho_2(\mathbf{r}')}{||\mathbf{r}-\mathbf{r}'||}\mathrm{d}\mathbf{r}' + \int_{D_3}\frac{\rho_3(\mathbf{r}')}{||\mathbf{r}-\mathbf{r}'||}\mathrm{d}\mathbf{r}' - \sum_{A=1}^{M}\frac{Z_A}{||\mathbf{r}-\mathbf{r}'||} + \lambda_1 = 0 \tag{16}$$

A change of integration variable is performed to take the integration back to the undeformed domains:

$$\int_{D_1}\frac{\rho_1(\mathbf{r}')}{||\mathbf{r}-\mathbf{r}'||}\ \mathrm{d}\mathbf{r}' = \int_{D_1^0}\frac{\rho_1(\Phi(\mathbf{r}^{0\prime},t))}{||\Phi(\mathbf{r}^0,t)-\Phi(\mathbf{r}^{0\prime},t)||}\ |\mathbf{F}(\mathbf{r}^{0\prime})|\ \mathrm{d}\mathbf{r}^{0\prime} \tag{17a}$$

$$\int_{D_2}\frac{\rho_2(\mathbf{r}')}{||\mathbf{r}-\mathbf{r}'||}\ \mathrm{d}\mathbf{r}' = \int_{D_2^0}\frac{\rho_2(\Phi(\mathbf{r}^{0\prime},t))}{||\Phi(\mathbf{r}^0,t)-\Phi(\mathbf{r}^{0\prime},t)||}\ |\mathbf{F}(\mathbf{r}^{0\prime})|\ \mathrm{d}\mathbf{r}^{0\prime}$$

$$= \int_{D_2^0}\frac{0.5(\rho_1(\Phi(\mathbf{r}^{0\prime}-\mathbf{T},t)) + \rho_3(\Phi(\mathbf{r}^{0\prime}+\mathbf{T},t)))}{||\Phi(\mathbf{r}^0,t)-\Phi(\mathbf{r}^{0\prime},t)||}\ |\mathbf{F}(\mathbf{r}^{0\prime})|\ \mathrm{d}\mathbf{r}^{0\prime} \tag{17b}$$

$$\int_{D_3}\frac{\rho_3(\mathbf{r}')}{||\mathbf{r}-\mathbf{r}'||}\ \mathrm{d}\mathbf{r}' = \int_{D_3^0}\frac{\rho_3(\Phi(\mathbf{r}^{0\prime},t))}{||\Phi(\mathbf{r}^0,t)-\Phi(\mathbf{r}^{0\prime},t)||}\ |\mathbf{F}(\mathbf{r}^{0\prime})|\ \mathrm{d}\mathbf{r}^{0\prime} \tag{17c}$$

Therefore, the optimality condition for any point $\mathbf{r}^0$ assumes the form of an integral equation:

$$\frac{5}{3}C_F\rho_1^{\frac{2}{3}}(\Phi(\mathbf{r}^0,t)) - \frac{4}{3}C_x\rho_1^{\frac{1}{3}}(\Phi(\mathbf{r}^0,t)) + \int_{D_1^0}\rho_1(\Phi(\mathbf{r}^{0\prime},t))K_{11}(\mathbf{r}^{0\prime},\mathbf{r}^0)\mathrm{d}\mathbf{r}^{0\prime} \tag{18a}$$

$$+\int_{D_3^0}\rho_3(\Phi(\mathbf{r}^{0\prime},t))K_{13}(\mathbf{r}^{0\prime},\mathbf{r}^0)\mathrm{d}\mathbf{r}^{0\prime} - \sum_{A=1}^{M}\frac{Z_A}{||\Phi(\mathbf{r}^0,t)-\Phi(\mathbf{R}_A^0,t)||} + \lambda_1 = 0$$

where the kernels K_{11} and K_{13} are defined as

$$K_{11}(\mathbf{r}^{0\prime},\mathbf{r}^0) = \frac{|\mathbf{F}(\mathbf{r}^{0\prime})|}{||\Phi(\mathbf{r}^0,t)-\Phi(\mathbf{r}^{0\prime},t)||} + \frac{0.5\,|\mathbf{F}(\mathbf{r}^{0\prime}+\mathbf{T})|}{||\Phi(\mathbf{r}^0,t)-\Phi(\mathbf{r}^{0\prime}+\mathbf{T},t)||} \tag{18b}$$

$$K_{13}(\mathbf{r}^{0\prime},\mathbf{r}^0) = \frac{|\mathbf{F}(\mathbf{r}^{0\prime})|}{||\Phi(\mathbf{r}^0,t)-\Phi(\mathbf{r}^{0\prime},t)||} + \frac{0.5\,|\mathbf{F}(\mathbf{r}^{0\prime}-\mathbf{T})|}{||\Phi(\mathbf{r}^0,t)-\Phi(\mathbf{r}^{0\prime}-\mathbf{T},t)||} \tag{18c}$$

$$\tag{18d}$$

Similarly, writing the optimality condition of Eq.10 for domain D_3 leads to the following integral equation that must hold for any $\mathbf{r}^0$ in the undeformed domain D_3^0:

$$\frac{5}{3}C_F\rho_3^{\frac{2}{3}}(\Phi(\mathbf{r}^0,t)) - \frac{4}{3}C_x\rho_3^{\frac{1}{3}}(\Phi(\mathbf{r}^0,t)) + \int_{D_1^0}\rho_1(\Phi(\mathbf{r}^{0'},t))K_{31}(\mathbf{r}^{0'},\mathbf{r}^0)\mathrm{d}\mathbf{r}^{0'} \tag{19a}$$
$$+\int_{D_3^0}\rho_3(\Phi(\mathbf{r}^{0'},t))K_{33}(\mathbf{r}^{0'},\mathbf{r}^0)\mathrm{d}\mathbf{r}^{0'} - \sum_{A=1}^{M}\frac{Z_A}{||\Phi(\mathbf{r}^0,t)-\Phi(\mathbf{R}_A^0,t)||} + \lambda_3 = 0$$

where the kernels K_{31} and K_{33} satisfy

$$K_{31}(\mathbf{r}^{0'},\mathbf{r}^0) = K_{11}(\mathbf{r}^{0'},\mathbf{r}^0) \qquad K_{33}(\mathbf{r}^{0'},\mathbf{r}^0) = K_{31}(\mathbf{r}^{0'},\mathbf{r}^0) \tag{19b}$$

Note that Eqs.18 and 19 are similar to Eqs.13 and 14. The equations corresponding to the undeformed case are obtained by setting $|\mathbf{F}(\mathbf{r}^{0'})| = 1$, and $\Phi(\mathbf{r}^0,t) = \mathbf{r}^0$ everywhere in $D_1^0 \cup D_2^0 \cup D_3^0$. These two conditions effectively indicate that none of these domains experiences any deformation.

Finally, the expression of $\Phi(\mathbf{r}^{0'},t)$ has not been provided explicitly and most likely can not be. This deformation field actually depends parametrically on the positions $\mathbf{R}_A$ of the nuclei at time t; i.e., $\Phi = \Phi(\mathbf{r}^{0'},t;\mathbf{R_A})$, but this dependency was not made explicit to keep the notation simple. Unlike in the traditional Finite Element method, where the material obeys homogeneity and in many cases anisotropy assumptions, for the electronic problem this is not the case. Thus, it is not immediate how the mesh can be refined beyond the nuclear level, and if the integrals in Eqs.19a and 19a actually require in terms of $\Phi(\mathbf{r}^{0'},t)$ a level of accuracy beyond what a nuclear mesh can provide.

2.3 Electronic density reconstruction

The process of electronic density reconstruction is referred to as fluctuation reconstruction. The objective is to develop efficient tools that compute the solution to the electronic structure problem up to higher order terms $\mathcal{O}(\mathbf{F})^2 + \mathcal{O}(\nabla_0\,\mathbf{F})$. This is equivalent to carrying out the first step of the classical homogenization technique **(A REFERENCE HERE WOULD BE HELPFUL)**.

For simplicity, assume that two identical rectangular domains of linear size a are separated by a vector $La\,(1,0,0)$, where L is an integer. These *reference domains* $\mathcal{D}_1^r$ and $\mathcal{D}_{L+1}^r$, have electronic densities ρ_1 and ρ_{L+1}, respectively, that might have been computed using an elaborate DFT method. The goal is to reconstruct the density in the domain between the two given rectangular domains (the shaded region in Fig.1). In what follows, a vector $\mathbf{T} = a\,(1,0,0)$ is introduced to simplify the notation, and by definition $\mathbf{T}_k = k\mathbf{T}$.

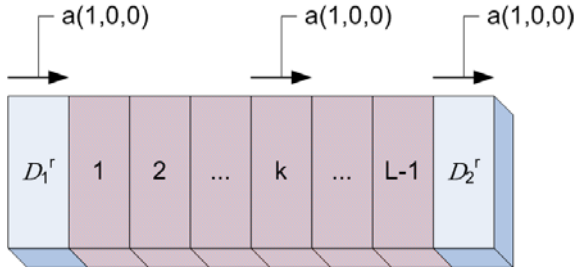

Figure 2: Fluctuation reconstruction.

The potential generatefd by the total charge in the system is

$$V(r) = \int \frac{\rho(r') + \rho_A(r')}{r - r'} dr'.$$

In our computations it is important to consider separately the potential that is generated by electronic density outside a given domain D, whose complement is $\bar{D}$, that is,

$$V^{ext}(r; D) = \int_{\bar{D}} \frac{\rho(r') + \rho_A(r')}{r - r'} dr' + \int_D \frac{\rho_A(r')}{r - r'} dr', \quad r \in D.$$

For solving the electronic problem, we may consider that the effect of the nuclei from the domain is also a part of an "external" potential, which explains the last term in the previous expression.

Clearly,

$$V(r) = V^{ext}(r; D)' + \int_D \frac{\rho(r'))}{r - r'} dr'.$$

2.3.1 The near periodicity assumption and interpolation approach

In the following, we will make the assumption that the external potential and the electronic density is nearly periodic, at least in the direction or in the subspace in which we do the reconstruction. For that assumption to be reasonable, one may imagine that the domain depicted in Figure 2 is embedded in a crystal, that is sufficiently large or that is sufficiently large in the horizontal direction and periodic across. or that the end domains D_1^r and D_{L+1}^r are sufficiently far away from the boundary of the crystal. In addition, we assume that the "periodicity defect" is slowly varying in space on the scale of the domains.

This assumption is typical in homogenization theory, and, for an observable $W(x)$, it means that it can be expressed as $W(x) = f(\frac{x}{b}, \frac{x}{a})$. Here $f(y, z)$ is a function that is periodic in z with a vector period $\hat{T} = O(1)$ and that is well-behaved in y, that is, $\frac{\partial f}{\partial y} = O(1)$. An example of such function is $ysin(z)$. Here a is the characteristic

length scale of the fluctuations (the "microscale", or a measure of the domain D_1^r in our case, such as its diameter), whereas b is the "macroscale" length scale, (in our case, the entire crystal or nanoparticle) and $a \ll b$.

As a result of our representation of $W(x)$, we have from the intermediate value theorem that, for any integer k the following holds:

$$\left|W(x+k\hat{T}a)-W(x)\right| = \left|f(\frac{x+k\hat{T}a}{b},\frac{x+k\hat{T}a}{a})-f(\frac{x}{b},\frac{x}{a})\right| = \left|f(\frac{x+k\hat{T}a}{b},\frac{x}{a})-f(\frac{x}{b},\frac{x}{a})\right| = O(\frac{ka}{b})$$

By a similar argument, the following also holds for nearly periodic $W(x)$

$$\left(1-\tfrac{k-1}{L}\right)W(x)+\tfrac{k-1}{L}W\left(x+La\hat{T}\right))-W\left(x+(k-1)a\hat{T}\right)=O((L\tfrac{a}{b})^2),\quad k=1,2,\ldots L+1$$

Therefore, the nearly periodic assumption for $V^{ext}(\mathbf{r};D)$ implies that the external potential has the following two properties

$$\left|V^{ext}(\mathbf{r}+\mathbf{T}_{k_1-1};D_{k_1})-V^{ext}(\mathbf{r}+\mathbf{T}_{k_2-1};D_{k_2})\right| \le O(\frac{(k_1-k_2)a}{b}) \le O(\frac{La}{b}),\quad \forall r\in D_1^r,\ 1\le k_1<k_2<L+1, \quad (20)$$

and

$$\left(1-\tfrac{k-1}{L}\right)V^{ext}(r;D_1)+\left(\tfrac{k-1}{L}\right)V^{ext}\left(r+\mathbf{T_L};D_{L+1}^r\right)-V^{ext}\left(r+\mathbf{T}_{k-1};D_k\right)=O(\left(\tfrac{La}{b}\right)^2)k=1,2,\ldots L+1,\ r\in D_1^r$$

In the following, we asses the error of reconstructing the electronic density in the domains D_k^r, $k=2,\ldots,L$ by interpolation between its values in domains D_1^r and D_{L+1}^r. The reconstruction rule is the following:

$$\hat{\rho}\left(\mathbf{r}+\mathbf{T}_k\right)\approx\hat{\rho}\left(\mathbf{r}+\mathbf{T}_k\right)=\left(1-\frac{k}{L}\right)\rho_1\left(\mathbf{r}\right)+\frac{k}{L}\rho_{L+1}\left(\mathbf{r}+\mathbf{T}_L\right),k=2,\ldots L,\quad r\in\mathcal{D}_1^r \quad (21)$$

where we have denoted

$$\rho_1\left(\mathbf{r}\right)=\rho(r),\quad \rho_{L+1}\left(\mathbf{r}+\mathbf{T}_L\right)=\rho\left(\mathbf{r}+\mathbf{T}_L\right)\quad r\in D_1^r$$

to emphasize the fact that the reconstructed density depends only on the density values

Theorem 1 *Assume that the external potential is nearly periodic. Then the error in the optimality conditions of the electronic structure problem is*

$$O\left(\left(\frac{La}{b}\right)^2\right)+O((\rho_1\mathbf{r}-\rho_{L+1}\left(\mathbf{r}+\mathbf{T}_L\right))^2)$$

Proof To be continued. A consequence of the potential near periodicity is a periodicity in the value of the electronic density, which translates into

$$|\rho(\mathbf{r}) - \rho(\mathbf{r} + \mathbf{T}_L)| \ll 1 \tag{22a}$$

The value of the electronic density is approximated through interpolation:

Note that this approach can accommodate high cusps in the electronic density.

MIHAI, WHY DO WE HAVE THIS DISCUSSION HERE? I WOULD EITHER MOVE IT (GIVEN THE STRUCTURE OF THE DOCUMENT, DOES IT MAKE SENSE TO PUT IT SOMEWHERE ELSE?) , OR DELETE IT FROM HERE... Assume now that we have some local optimality conditions, that I define in operator terms. That would certainly work for OFDFT and localized Kohn-Sham.

$$\Theta(\rho_1(r), V(r)) = 0,\ \Theta(\rho_2(r), V(r + La\,(1,0,0))) = 0$$

Then, we use standard interpolation theory, and the assumption that the functional that defines the optimality conditions for the energy is well behaved (without assuming that the solution itself is well behaved). An example of such functional is provided above. We obtain that

$$\Theta(\rho_1(r), V(r)) = 0,\ \Theta(\rho_2(r), V(r + La\,(1,0,0))) = 0,\ r \in \Re$$

Using standard error analysis, we obtain that

$$\begin{aligned}
&\Theta\left(\hat{\rho}\left(\tfrac{k}{L}r + \left(1 - \tfrac{k}{L}\right)(r + La\,(1,0,0))\right), V(r + ka\,(1,0,0))\right) = \\
&\Theta\left(\tfrac{k}{L}\rho_1(r) + \left(1 - \tfrac{k}{L}\right)\rho_2(r), \tfrac{k}{L}V(r) + \left(1 - \tfrac{k}{L}\right)V\left(r + La\,(1,0,0)\right)\right) + O\left(\left|V\left(r + La\,(1,0,0)\right) - V(r)\right|^2\right) = \\
&O\left(\left|V\left(r + La\,(1,0,0)\right) - V(r)\right|^2\right) + O\left(\left|\rho_1(r) - \rho_2(r)\right|^2\right),\ r \in \Re
\end{aligned}$$

... DOWN TO HERE

The proposed interpolation-based approach has certain limitations and is not expected to always work well. In this context:

1. The reconstructed density might display discontinuities at the interface between neighboring domains. This situation only arises when the periodicity assumption is violated. However, the purpose of the investigation is to consider periodic structures with small defects that are periodic almost everywhere. For the purpose of generating just the field, I can show that the above estimate is accurate.

2. **MIHAI, YOU START SAYING PERTURBATION, BUT THEN YOU SORT OF MEAN DEFORMATION. I'D SAY LET'S USE DEFORMATION THROUGHOUT THIS LIST ITEM**The density should be reconstructed in this fashion only away from major perturbations. In that case, we use a macro scale mesh to define the deformation. For reconstructing density, we map back to the undeformed mesh and we reconstruct there by interpolation. That is necessary since the density has very sharp peaks, that would not satisfy the smallness assumption above otherwise **PLEASE REFER BY EQUATION NUMBER TO WHAT SMALLNESS ASSUMPTION YOU MAKE REFERENCE**. After which we used the same deformation description to go back to the deformed domain

3.

4. **DO WE STILL NEED THIS HERE?Of course, this will result in domains that are not rectangular boxes. I hope that it is not a problem for Kohn Sham.**

2.4 Potential reconstruction

At any point we will use only the densities in a small number of domains explicitly. The density will be recomputed in the rest of the space by interpolation. In the end, the total field is obtain by superposition, where the subscripts refer to the specific regions.

$$V(r) = V_{QC}(r) + V_{KS}(r) + V_{KS,Interp}$$

Although the Kohn sham interpolated and the quasi continuum regions can be quite extended, the density in those regions is truly represented only via a set of the densities in a small set of domains, perhaps only fundamental cells that are eventually allowed to deform as the crystal relaxes.

So, we have the following

$$V_{KS,interp}(r) = \sum_j^J \int_C \rho_j^o(r')K_j(r,r')dr'$$
$$V_{QC(r)=} \sum_i^I \int_C \rho_i(r')K_i(r,r')dr'$$

where the Kernels $K_i(r,r')$, $K_j(r,r')$are obtained from the interpolation operator and the kernels of the usual electrostatic fields.

1. Computing them may be the principal task outside running DFT itself.

2. It may be useful to change variables to undeformed domain.

3. **It may be useful to compute the total field at once to get the fast decay effect Dieter Wolf was talking about, as opposed to computing separated electronic and nuclei. If not, the field of the nuclei is computed by some multipole like expansion.**

Therefore at every point there is an external interaction potential, that depends only on the computational boxes.

$$V(r) = V(r, \rho_1, \rho_2, \ldots \rho_P, \rho_A)$$

3 The Extended DFT Problem

This would be Tool 3: Emily Carter and Ortiz, combined with our density interpolation. Applies for the cases where one can use only local quasi continuum, away from major distortions. This would essentially replace the old Tool1, provide that we extended it for Kohn Sham, where the reconstruction of the density in the infinite crystal is done with our interpolation, should such a Reconstruction be needed near special boundaries where I can not apply periodic boundary conditions.

One of the ideas that seems possible to explore is to run the infinite crystal computation only a few times and then use table lookup and interpolation to compute the derivatives of the energies with respect to well selected positions of the nuclei.

3.1 The coupled non-linear problem and the optimization framework

In the following, we will use the notion of quasi continuum to describe a situation where small deformations are described with respect to a macro scale mesh. That description can be either via a finite element or by some sort of local spectral method. Of course, one would like to try finite element first.

We will use a set of models of increasing complexity.

1. Kohn Sham

2. Kohn sham in small domains with interpolation of density

3. Quasi continuum deformation with either Tool 1 or Tools 3 combined with interpolation to calculate the local change in density. Note, however, that tool 1 and tool 3 apply only when I allow the system to deform, **they are irrelevant for the electronic density problem un the undeformed domain.**

4. What density reconstruction buys you is the possibility to compute the field of the deformed quantity in the Kohn sham region without assuming periodic boundary conditions.

3.2 Cross-domain Kohn-Sham DFT

I am assuming here that Kohn Sham interacts only through the external potential.

For any of the p domains, I will have a local value of the energy, function of the external potential, that I will minimize, **Note that the external potential does depend upon the density in box p, because of the interpolation.**

Therefore, I will have to solve a system of coupled nonlinear equations.

$$\nabla_{\rho_p} E^p(\rho_{p,}\rho_{A,}V(\rho_{1,}\rho_{2,}\dots\rho_P)) = 0,\ p = 1, 2, \dots P$$

How I solve it depends on how I encapsulated the solver.

1. If all I am provided is : given external potential, compute the self-consistent ρ_P, for a given domain that solves the minimization problem then I have to solve the method using **nonlinear Gauss-Seidel. The convergence of which is tricky and needs some sort of diagonal dominance. For large domains, it seems impossible.**

2. But I can improve the rate of convergence of that doing the following. Assume that $E^p(\rho_{p,}\rho_{A,}V(\rho_{1,}\rho_{2,}\dots\rho_P)) = E^p(\rho_{p,}\rho_{A,}) + V(\rho_{1,}\rho_{2,}\dots\rho_P)),\ p = 1, 2, \dots P$, and that V is a linear functional, and I can compute its action on any vector. I can therefore create an iterative method that accommodates the entire dependence on ρ_p, by some nonlinear GMRES

3. If the method can provide the self-consistent derivatives for a given density, then I can do a nonlinear GMRES kind of approach directly.

4. Note that the same approach applies orbital free density functional theory as well.

3.2.1 The charge balancing and self-consistency problem

If there is a measure of charge equilibration $\Phi(q_1, q_2, \dots q_p)$, then I can solve the following constrained problem.

$$\min \Phi(q_1, q_2, \dots q_p)$$

$$\nabla_{\rho_p} E^p(\rho_p, \rho_A, q_p, V(\rho_1, \rho_2, \dots \rho_P)) = 0,\ p = 1, 2, \dots P$$

$$\sum_p^P w_p q_p = N$$

where w_p are the weights of each domain depending on the interpolation weights.

But a very promising idea is the use of a Lagrange multipliers. The total local energy and the respective nonlinear equations become.

$$E^p(\rho_p, \rho_A, V(\rho_1, \rho_2, \dots \rho_P), \lambda) = E^p(\rho_p, \rho_A,) + V(\rho_1, \rho_2, \dots \rho_P)) + \lambda \int_{D_p} \rho,\ p = 1, 2, \dots P$$

$$\nabla_{\rho_p} E^p(\rho_p, \rho_A, q_p, V(\rho_1, \rho_2, \dots \rho_P), \lambda) = 0,\ p = 1, 2, \dots P$$

$$\sum_p^P w_p \int_{D_p} \rho = N$$

3.3 The reduced optimization problem

It is interesting to see that we have reduced the optimization problem to a nonlinear equation, which is difficult to reconstruct back to an optimization problem. We illustrate this difficulty in the context of the quasi continuum's method applied to potential methods. The quasi continuum method appears in two flavors.

3.3.1 The local method

In the first one, a total energy is computed by using finite elements and numerical quadrature at the node points. With this formulation, the total energy is computed following a numerical quadrature based on a finite element mesh whose triangles are much larger than the distance between two consecutive atoms.

$$E \approx \sum w_k E_K(F)$$

where w_k are appropriate weight parameters, whereas$E_k(F)$ is is the energy associated with a small domain around the quadrature point P_k. Here$F$ is the deformation of the crystal under consideration, which is assumed to vary on a scale that is much larger than the distance between two consecutive atoms. The energy $E_k(F)$is computed by using the Cauchy-Born approximation of local linear deformation, followed by embedding the small domain in an infinite crystal and computing its share of energy from a periodic calculation.

Subsequently, the total energy is minimized as a function of the deformation, which is typically represented by the same element as the numerical quadrature that led to the energy approximation.

One of the advantages of the local approach is that the computation of the energy in one domain is independent of the energy in any other domain, and due to the periodicity assumption, one can consider only one fundamental cell over which the computation is done, and such the computational effort is tremendously reduced. The natural extension of this method uses density functional theory instead of potentials to predict the amount of energy, which leads to a truly *ab-initio* calculation.

In terms of disadvantages, the method deals very poorly with surfaces and special areas, such as the defect areas. Which led to the nonlocal method.

3.3.2 The nonlocal method

In this method, several representative atoms $\{R_b\}_{b\in\Im}$are chosen, and the deformation F is again represented on a mesh that lives on a much larger scale than the fundamental cell of the original crystal. After which one solves the following problem

$$P(R_b, F) = 0,\ b \in \Im$$

Where P is the force acting at the respective atom, as a function of the deformation. So, in this case, one solves a system of coupled nonlinear equations, rather than an optimization problem. We also note that, if there are long range interactions than the force at a representative atom may depend on the force at a different representative atom, but the way it is implemented in the work of Ortiz and co-authors one assumes that the potentials are truncated which results in to representative atoms interacting only through the macro scale mesh. A different variation calls for using an average of the force at atoms around the representative atom being equal to zero as opposed to the force at the representative atom being equal to zero.

3.3.3 Open issues

1. The mesh of the deformations does not have to be centered at the representative atoms, in effect, it may even be a bad idea since the nodes are the place of the largest distortion in the initial configuration of the crystal.

2. An interesting question is the situation where the number of representative atoms is over determined compared to the numbers of degrees of freedom of the mesh. First order logic would suggest that this would result in more

robust With a modest increase in the computational cost. It is clear that if too few representative atoms are chosen than the problem will suffer a degeneracy, whereby the minimal energy will correspond to a continuum of deformations that can be obtained by deformation one from the other.

3. Is it possible to obtain the appropriate optimization problem that correspond to the couple nonlinear equation, without having to explore all the atomic nodes?

4. Can one use splines to represent the deformation and such avoiding the large distortion in the crystal at the junction of two different elements?

3.4 A comparison of the coupled nonlinear equations vs. the optimization methods

In the limit there should not exist any difference between the tow methods. In an abstract formulation, we have the following problem.

$$\min_{x_1,x_2} \; f(x_1, x_2)$$

Where we assume that the variables x_1 correspond to the representative atoms whereas x_2 correspond to the rest of the atoms. The quasi continuum method is based on the observation that one expects at the solution to have $x_2 = T(x_1)$ where $T(x_1)$ is the interpolation mapping, which can in principle be replaced by any slowly varying mapping. The mapping can be a function of the representative atoms, which corresponds to an interpolation based on the mesh whose nodes are the representative atoms, but it can depend on a different mesh, with fewer nodes than the number of representative atoms.

Based on this observation, one can formulate the nonlinear equation

$$\nabla_{x_1} \; f(x_1, x_2), \; x_2 = T(x_1)$$

which will provide the same solution as the original problem. However, the problem is an equilibrium problem with equilibrium constraints rather than a minimization problem.

However, it immediately results using the chain rule that the optimization problem

$$\min_{x_1} f(x_1, T(x_1)),$$

has the same solution as the previous two, provided that the reduced Hessian is positive definite, which should be true if the original Hessian was positive definite, and the interpolation mapping is full rank. This observation presents

the advantage that one solves an optimization problem as opposed to a system of nonlinear equations, and one has a better global convergence safeguards for the situation, which should help for the case when there are many local minima to avoid the points that do not have the correct inertia of the Hessian.

The problem with this observation is that one should construct this total energy function without exploring all atoms, if at all possible, eventually by using only the interpolation mesh.

Theorem 2 *Assume that the solution $x^* = (x_1^*, x_2^*)$ of the original optimization problem satisfies $\|x_2^* - T(x_1^*)\| \ll 1$, therefore the multiscale ansatz is not perfect, it is merely very good. Then the solution $\tilde{x}_1$ of the nonlinear equation and $\hat{x}_1$ of the reduced optimization problem satisfy*

$$\|x_1^* - \tilde{x}_1\| = O(\|x_2^* - T(x_1^*)\|^2) \quad \|x_1^* - \hat{x}_1\| = O(\|x_2^* - T(x_1^*)\|^2)$$

Proof 1 *To be determined.*

Note that our main research thrust: Determining appropriate expressions of the energy function that result in an optimization problem as opposed to a coupled nonlinear equation. We are interested in the case where the interactions in the matter account for electronic effects via density functional theory, either Kohn-Sham or Orbital-Free.

The essential step is "the reconstruction of the fluctuation", that is using Tools like Tool2 to reconstruct the electronic density when necessary, especially around regions of interest, such as defects or surfaces.

Following an interpolation approach like Tool 2, that is built on top of a discretization that uses only small computational domains, this means that the total electronic density will be written as

$$\rho(r) = \sum_k^{n_D} \int_{D_k} K_{D_k}(r, r', F)\rho(r')dr'$$

The rationale behind in this ansatz is the same as the one exposed in Tool 2, and while it naturally comes by for electronic density, it may also be worth pursuing for nuclear charge density as well. The key is in the computation of $K(r, r', D)$, which includes the interpolation aspect.

If the density $\rho$is the total charge density ρ^{tot}, then we have the electrostatic interaction energy to be simply $E_{electrostatic} = \frac{1}{2}\iint \frac{\rho(r)\rho(r')}{r-r'}drdr'$, with an eventual small correction to do away with the equivalent of the self interaction energy of a nucleus, which would contain a square of a delta functional. Otherwise, one writes a different formula for ρ_A,

the nuclear (atomic) charge density.

If one has to compute the field with the total density $\rho = \rho^{tot}$, however, then the formula

$V(r) = \int \frac{\rho(r')}{|r-r'|} dr'$ is an exact formula, though it will have singularities at the atomic positions. Computing with the total energy density has the advantage of using charge neutrality or nearly charge neutrality, coupled by the near periodicity that holds for small deformations of the crystal to result in the fast decay with the distance between regions of the effects of one region on a different region.

However, the interaction terms do not contain all the energy in density functional approaches. We have that

$$E_{DFT}(\rho, \rho_A) = T[\rho] + E_{xc}[\rho] + E_{electrostatic}[\rho, \rho_A]$$

Here, T is the kinetic energy, whereas E_{xc} is the exchange energy.

The problem is that the total kinetic energy is very difficult to evaluate over a large domain. If one uses kohn sham, then the computation of the kinetic energy would be about as difficult as minimizing all the energy using kohn sham itself with the density represented everywhere as opposed to small boxes.

We therefore look for interpolation approach is again, where we can write

$$T[\rho] + E_{xc}[\rho] \approx \sum_{k}^{n_D} w_k \left(T[\rho] + E_{xc}[\rho]\right)_{r \in D_k}$$

Working with the electrostatic energy followed by the density reconstruction, we obtain, in the end the following expression for the total energy

$$E_{DFT} = \sum_{k}^{n_D} \hat{w}_k E^{id}_{D_k}(\rho, \rho_A, r \in D_k) + \sum_{k}^{n_D} \sum_{k'>k}^{n_D} \hat{w}_{k,k'} E^{dd}_{D_k, D_{k'}}(\rho, \rho_A, r \in D_k; \rho, \rho_A, r \in D_{k'})$$

All the terms in the sums are also dependent on the deformation F. Here E^{id} is an inter domain energy whereas E^{dd} is an inter-domain energy, that is computed based on the energy reconstruction outlined above.

3.5 Directions of research

3.5.1 The coupled nonlinear problem

The research topics are presented above.

3.5.2 The general optimization approach

1. Comparison between coupled nonlinear and optimization problems

2. Properties of the Hessian's and gradients of the reduced problems compared to the original problem.

3. Proof of the result of the perturbation theorem outlined above.

3.5.3 The fluctuation reconstruction and equivalent optimization problem

1. Constructing the appropriate fluctuation reconstruction operators$K(r, r', F)$. The interpolation part is somewhat clear, but it would be ideal if the approximation somehow would result in something continuous, which direct interpolation does not provide.

2. The appropriate use of the reference crystal for interpolation.

3. Efficient computation of the $E^{dd}_{D_k D_{k'}}$ This is possibly the single most important item in terms of efficient implementation. In the local quasi continuum approach with density functional theory of Ortiz and Carter, this part does not exist and is truly repackaged together with the inter-domain terms, so their computational effort in this part is the zero which is tough to beat. However I can imagine ways of changing variables in the respective intervals back to the reference crystal, where the computation is similar to the one for the periodic case except that in addition one has a small perturbations that is due to the deformation and to the interpolation. Since that effect is slow on the scale of one crystal cell, one simple idea would be to use only the rectangular elements of a reasonable aspect ratio in the interior change variable's with respect to the crystal undeformed configuration and precompute the operators $K_{D_k}(r, r', F)$, and their subsequent effect on E^{dd}

4. Determining appropriate parameterization for which we can use an interpolation like approach to reconstruct the kinetic energy outside the computational domains D_k. For orbital free DFT that is certainly possible, following an error estimation which is similar to the one presented for Tool number two.

5. How to do interpolation that results in continuous density, or even density with continuous derivatives.

4 Nanostructure shape investigation

The equilibrium configuration of a nanostructure is provided by that distribution of the nuclei that minimizes the energy

$$E_{tot} = E_e + E_{nn} \tag{23}$$

The assumption made is that the kinetic energy of the nuclei is zero, and that E_e is the electronic ground-state energy for the considered nuclear distribution. Therefore, following the Born-Oppenheimer assumption, the electronic energy depends parametrically on the position of the nuclei, through the dependence of the electronic density on the nuclei position:

$$E_e = T[\rho(\mathbf{r})] + E^{Har}[\rho(\mathbf{r})] + E^{xc}[\rho(\mathbf{r})] + \int \rho(\mathbf{r})\, V_{ext}(\mathbf{r}; \{\mathbf{R}_A\})\, \mathrm{d}\mathbf{r} \tag{24}$$

where $T[\rho(\mathbf{r})]$ is the kinetic energy functional, $E^{Har}[\rho(\mathbf{r})]$ is the electron-electron Coulomb repulsion energy, $E^{xc}[\rho(\mathbf{r})]$ is the exchange and correlation energy, and $V_{ext}(\mathbf{r}; \{\mathbf{R}_A\})$ is the ionic potential, which parametrically depends on the distribution of the nuclei $\{\mathbf{R}_A\}$. The explicit dependency of $T[\rho(\mathbf{r})]$ and $E^{xc}[\rho(\mathbf{r})]$ on the density $\rho(\mathbf{r})$ is typically not available and consequently it is approximated in some fashion, which is not an issue of concern in this document. According to the Kohn-Hochenberg theorem [11], the electronic density is such that it minimizes E_e subject to the charge conservation constraint of Eq.2b.

Theorem 3 *Consider the optimization problem*

$$\min_{\{\mathbf{R}_A\}} E_{tot} = E_e + E_{nn}$$

subject to the constraint that for a nuclear configuration $\{\mathbf{R}_A\}$ the energy E_e is the electronic ground energy, and the electronic density $\hat{\rho}$ that realizes this electronic ground energy additionally satisfies the charge constraint equation of Eq.(2b). Under these assumptions, the first order optimality conditions for the optimization problem are

$$\mathbf{F}_K = \frac{\partial E_{ext}}{\partial \mathbf{R}_K} + \frac{\partial E_{nn}}{\partial \mathbf{R}_K} = \mathbf{0} \tag{25}$$

where $\mathbf{F}_K$ is interpreted as the force acting on nucleus K, and by definition

$$E_{ext}(\mathbf{r}; \{\mathbf{R}_A\}) = -\sum_{A=1}^{M} \int \hat{\rho}(\mathbf{r})\, V_{ext}\left(\mathbf{r}; \{\mathbf{R}_A\}\right) d\mathbf{r} = -\sum_{A=1}^{M} \int \frac{Z_A \hat{\rho}(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_A|}\, d\mathbf{r} \tag{26a}$$

$$E_{nn} = \frac{1}{2} \sum_{A=1}^{M} \sum_{B=A+1}^{M} \frac{Z_A Z_B}{\mathbf{R}_{AB}} \tag{26b}$$

Proof 2 *The proof relies on the calculus of variations. Since $\hat{\rho}(\mathbf{r})$ is determined to minimize the electronic energy, there is a parametric dependency of this value on the ionic position: $\hat{\rho}(\mathbf{r}) = \rho(\mathbf{r}; \{\mathbf{R}_A\})$. Applying the chain rule, the optimality conditions for E_{tot} will read*

$$\frac{\delta E_e}{\delta \rho}\frac{\partial \rho}{\partial \mathbf{R}_k} + \frac{\partial E_e}{\partial \mathbf{R}_k} + \frac{\partial E_{nn}}{\partial \mathbf{R}_k} = 0 \tag{27}$$

where $\mathbf{R}_k$ is the position of an arbitrary nucleus k.

Based on the Hochenberg-Kohn theorem, the optimality conditions for minimizing the electronic energy as a functional of the electronic density lead to

$$\frac{\delta E_e}{\delta \rho} + \lambda \frac{\delta g}{\delta \rho} = 0 \tag{28}$$

where λ is the Lagrange multiplier associated with the constraint

$$g[\rho] = 0 \tag{29}$$

that the electronic density must satisfy. For the problem at hand the charge conservation equation results in $g[\rho] = \int \rho(\mathbf{r})\, d\mathbf{r} - N_e$. Based on Eq.(29), the variation of $\rho(\mathbf{r})$ with respect to $\mathbf{R}_k$ must satisfy

$$\frac{\delta g}{\delta \rho}\frac{\partial \rho}{\partial \mathbf{R}_K} = 0$$

Multiplying Eq.(28) from the right by $\frac{\partial \rho}{\partial \mathbf{R}_K}$ leads to $\frac{\delta E_e}{\delta \rho}\frac{\partial \rho}{\partial \mathbf{R}_K} = 0$, which substituted back into (27) yields the optimality condition stated in Eq.(25).

Therefore, for each nucleus K in the system, Eq.(25) leads to the condition

$$\int \hat{\rho}(\mathbf{r}) \frac{\mathbf{r} - \mathbf{R}_K}{||\mathbf{r} - \mathbf{R}_K||^{\frac{3}{2}}}\, \mathrm{d}\mathbf{r} + \sum_{\substack{A=1 \\ A \neq K}}^{M} Z_A \frac{\mathbf{R}_A - \mathbf{R}_K}{||\mathbf{R}_A - \mathbf{R}_K||^{\frac{3}{2}}} = \mathbf{0} \tag{30}$$

Remarks:

1. The key observation is that once the electronic density is available, the equilibrium conditions of Eq.(30) can be imposed right away. It is irrelevant if the electronic structure computation is done with KS-DFT or OF-DFT; also note that there is no need to know the explicit dependency of the energy E_e on the electronic density $\rho(\mathbf{r})$.

2. As suggested in [15], the one-atom conditions of Eq.(25) can be replaced by cluster conditions, an alternative that will be explored in the future.

3. Due to the presence of the electronic density $\rho(\mathbf{r})$ that displays very pronounced cusps in the vicinity of nuclei, the integral in Eq.(30) must be evaluated using special techniques [3, 22]. This computational aspect is central to the overall algorithm and it will be detailed in a separate document.

When a local quasicontinuum approach is used, the condition of Eq.(30) is only imposed for *repnuclei*; the position of all the atoms in the system is then expressed in terms of the position of the *repnuclei*. The *repnuclei* become the nodes of an atomic mesh, and interpolation is used to recover the position of the remaining nuclei. If the atomic mesh is denoted by $\mathbb{C}_n$, τ is an arbitrary cell in this mesh, $\mathcal{V}(\tau)$ represents the set of the nodes associated with cell τ, and φ_L is the shape function associated with node L, then the condition of Eq.(30) is approximated as

$$\int \hat{\rho}(\mathbf{r}) \frac{\mathbf{r} - \mathbf{R}_K}{||\mathbf{r} - \mathbf{R}_K||^{\frac{3}{2}}} \, \mathrm{d}\mathbf{r} + \sum_{\tau \in \mathrm{C}_n} \sum_{\alpha \in \tau} Z_\alpha \frac{\sum\limits_{L \in \mathcal{V}(\tau)} \mathbf{R}_L \varphi_L(\mathbf{R}_\alpha) - \mathbf{R}_K}{||\sum\limits_{L \in \mathcal{V}(\tau)} \mathbf{R}_L \varphi_L(\mathbf{R}_\alpha) - \mathbf{R}_K||^{\frac{3}{2}}} = \mathbf{0} \tag{31}$$

This effectively reduces the dimension of the problem from $3\,M$ (the (x, y, z) coordinates of the nuclei), to $3\,M_{rep}$, where M_{rep} is the number of nodes in the atomic mesh (the number of *repnuclei*). The sum in Eq.(31) is most likely not going to be the simulation bottleneck (solving the electronic problem for $\hat{\rho}$ is significantly more demanding), but fast-multipole methods [1, 10, 17] or Ewald summation [5, 6] can be considered to speed up the summation.

Denoting by $\mathbf{P}_i$, $i = 1, \ldots, M_{rep}$, the position of the representative nucleus n_i, the set of non-linear equations of Eq.(31) can be grouped into a non-linear system that is solved for the relaxed configuration of the structure:

$$\begin{aligned} &\mathbf{f}_1(\mathbf{P}_1, \mathbf{P}_2, \ldots \mathbf{P}_{M_{rep}}) = \mathbf{0} \\ &\mathbf{f}_2(\mathbf{P}_1, \mathbf{P}_2, \ldots \mathbf{P}_{M_{rep}}) = \mathbf{0} \\ &\ldots \\ &\mathbf{f}_{M_{rep}}(\mathbf{P}_1, \mathbf{P}_2, \ldots \mathbf{P}_{M_{rep}}) = \mathbf{0} \end{aligned} \tag{32}$$

Finding the solution of this system is done by a Newton-like method. Evaluating the Jacobian information is straightforward but not detailed here.

5 Proposed Computational Setup

The overall problem statement is as follows: a material of an arbitrary atomic structure (in the sense that it doesn't have to be mono-atomic or crystal) is provided in an initial structure (configuration). The interest is to determine

the electronic density distribution for the given nano-structure as well as its final structure (configuration). Due to the assumption that the kinetic energy of the nuclei is zero, basically the problem solved corresponds to a zero Kelvin temperature situation. Extending it to non-zero temperature it's not treated in this document, but should most likely follow an approach similar to the ones proposed by Car-Parrinello [4], or Payne, et. al [16].

At a very high level, the solution of the problem emerges as a two step approach. First compute the electronic structure, using reconstruction reconstruction techniques of sections 2 and 3. The second step is concerned with repositioning the nuclei in order to relax the overall structure to a final configuration. This is done as explained in this document, and has the following sub-steps:

1. Evaluate the integral of Eq.(31), and when necessary its partial with respect to $\mathbf{P}_i$
2. Evaluate the double sum of Eq.(31), which is based on a partitioning of the structure, and when necessary, evaluate its partial with respect to the position of the representative atoms
3. Carry out Newton step to update the positions $\mathbf{P}_i$ of the M_{rep} representative nuclei.
4. Go back to a) if not converged
5. Compare the final configuration with the one used in the electronic structure computation. If no significant change, then it means that the problem is solved, the most recent electronic structure computation and current configuration are the solutions to the problem.

Remark: The proposed approach is limited by the accuracy in the electronic density $\rho(\mathbf{r})$. The sensitivity of the solution of the non-linear system of Eq.(32) with respect to $\rho(\mathbf{r})$ needs to be further investigated. The end goal of the proposed method is to compute (A) the electronic structure and (B) the nanomaterial structure. Most likely (B) is going to be less sensitive.

5.1 Potential Computational Studies

1. Consider a slab which is periodic in two directions, and which has 15 to 20 fundamental cells in the third direction. Study either the relaxation of the surface or the situation were a molecule of a different kind is at the surface.

2. Used a cube, where the book is done with the Ortiz and Carter quasi continuum with periodic boundary conditions, but near the corners we do density reconstruction and electronic structure computation with void boundary condition.

3. The study of an inner defect with quasi continuum outside a box, and fluctuation reconstruction plus density functional computation with void boundary conditions inside.

4. Repeat the computation of Ortiz and Carter by using tabulated kohn sham plus a methodology like the one outlined above to do minimization as opposed to coupled nonlinear equations.

5.2 Conclusions

- It is not totally clear what is the effect of the inner boundary of the domain. It seems rational to assume that if the functional is a functional only of the density and not its derivatives we are in good shape. However, for forms that also included the gradients of the density something else may need to be done.

- The computation can be done for an arbitrary number of domains

- As mentioned above, one could possibly use buffers towards the end of the domain and use only the rest of the density for reconstruction in the gaps, this will reduce the effect of the boundary layers.

- Formally, the last couple system of nonlinear equation is applies for the kohn sham approach as well. It is an instance of the couple kohn sham equation above.

- The nonlinear equation approach can be considered to be an extension of the nonlocal quasi continuum approach.

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A A domain decomposition approach

B Software Implementation Details

At one of our model layers we consider OF-DFT formulations of the energy functional. Such formulations are useful for two reasons. First, they will provide reasonably accurate solutions in certain configurations, with all the need to going all the way down to a more computationally difficult Kohn-Sham description, which makes them excellent choices for guiding a systematic optimization approach toward finding the energy minimum.

A second aspect important for our research is the fact that they are an ideal test case for the various strategies of replacing the discrete atomic distribution with a continuum, as well as for characterizing the effects of the electronic structure mesh over the quality of the minimum.

Since for such explicit functional forms we can explicitly compute the energy, subject to the discretization error of the electronic density, we will carry out explicit comparisons between the function and derivative computations with this functional form as opposed to a coarse graining strategy. For the study of the discretization error, we will adapt and extend existed approaches for dealing with the singularity in the potential functions and numerical quadrature time, as well as to estimate the electronic mesh discretization error.

Among the coarse graining techniques that we will investigate are

- The resulting integral formulation based on small perturbations matching of the dispersion operator for the infinite lattice.

- By extending the quasi continuum small perturbations analysis of Kunin to finite domains. For the case over rectangular boxes, that is fairly straightforward by considering a continuum description that is the sum of a trend to match respective boundary conditions, and a periodic function. In effect, this idea goes all the way back to recent multiscale techniques of Hou and Enqvist. Subsequently, a quasi continuum is created by requesting that the continuum description match the district description at the nodal points. Than a unique extension can be imposed by similarly restricting the district we are frequencies to the appropriate domain, given by Shannon's theorem.

- Extending the similar analysis to arbitrary but smoothly bounded domains. One naturally extension here is to use the eigenvalues of the Laplace operator, that correspond to the discrete Fourier basis for that anger

domains, and carry out a similar analysis. Of course, this comes at the cost of complicating the interpolating problem, but other minimum error criteria will be pursued instead of collocation, which is what results in the interpolating conditions.

- We will use a near field far afield decomposition, based on a nuclear density representation in the far field. For interaction potential's, the local computation under the Cauchy-Born hypothesis will be very similar to the work of Ortiz, but we will study its extension to functionals like the one above as well as to other model reduction hypotheses.

- Using the quasicontinuum energy density in an interior domain coupled with explicit atomic representation in the outside. This will lead to an integral equation that is exact in the case of truncated potentials.

B.1 Numerical Approach

Two meshes are used to find the unknown spatial distribution of electronic density, and the position of the nuclei $\{\mathbf{R}_A\}$. The nodes of the first mesh are denoted by $\aleph_\rho$, and the associated tetrahedrons by $\top_\rho$. The second mesh has nodes $\aleph_N$, and tetrahedrons $\top_N$. The basis functions used for interpolation on both meshes are going to be piecewise linear, and denoted by ϕ and $\hat{\phi}$ for the electronic density and nuclei position, respectively. In general, for a tetrahedron $\tau \in \aleph_\rho$, $\mathbb{P}(\tau)$ represents the set of four vertices of the tetrahedron; likewise, for a point of location $\mathbf{r}$, $\mathbb{P}(\mathbf{r})$ provides the set of four vertices of the tetrahedron that in the undeformed initial configuration contains in its interior the point of location $\mathbf{r}$. This comes handy in identifying the set of basis functions that contribute to the value of $\rho(\mathbf{r})$:

$$\rho(\mathbf{r}) = \sum_{d \in \mathbb{P}(\mathbf{r})} \rho_d \phi(\mathbf{r}|\mathbf{r}_d) \tag{33}$$

Technically, the nodes of the electronic density mesh can be chosen arbitrarily. However, for the nuclei mesh the nodes coincide with the positions of a subset of nuclei that are in what called *representative nuclei.* Using a notation similar to the one introduced for the electronic density

$$\mathbf{R}_A = \sum_{M \in \hat{\mathbb{P}}(A)} \mathbf{R}_M \hat{\phi}(\mathbf{R}_A|\mathbf{R}_M) \tag{34}$$

The set of unknowns was reduced the electronic densities ρ_d, $d \in \aleph_\rho$, and the position of the representative atoms $\mathbf{R}_M$, $M \in \aleph_N$. It remains to express the energies of Eq. 8 in terms of these unknowns, and to search for that set

of unknowns that minimizes the expression of the total energy. To this end, the value of the total energy and its derivative with respect to the new set of unknowns are required.

The original problem

$$\min_{\rho(\mathbf{r}),\mathbf{R}_A} E \qquad \text{subject to} \int \rho(\mathbf{r})\, d\mathbf{r} = N_e \tag{35}$$

is thus reformulated as

$$\min_{(\rho_d, d\in\aleph_\rho),(\mathbf{R}_M, M\in\aleph_N)} E \qquad \text{subject to} \int \rho(\mathbf{r})\, d\mathbf{r} = N_e \tag{36}$$

Evaluation of the potential E and its derivatives is discussed in sections B.1.1 through B.1.5.

B.1.1 Function and derivative evaluation for E_{ne}

$$\begin{aligned} E_{ne}\left[\rho, \{\mathbf{R}_A\}\right] &= \sum_{A=1}^{M} \int \frac{Z_A\, \rho(\mathbf{r})}{|\mathbf{R}_A - \mathbf{r}|}\, d\mathbf{r} \\ &\approx \sum_{A=1}^{M} \sum_{\tau\in\top_\rho} \int_\tau \frac{Z_A \sum_{d\in\aleph_\rho} \rho_d \phi(\mathbf{r}|\mathbf{r}_d)}{|\mathbf{r} - \sum_{M\in\aleph_N} \mathbf{R}_M \hat{\phi}(\mathbf{R}_A|\mathbf{R}_M)|}\, d\mathbf{r} \\ &= \sum_{A=1}^{M} Z_A \left[\sum_{\tau\in\top_\rho} \sum_{d\in\mathbb{P}(\tau)} \rho_d \int_\tau \frac{\phi(\mathbf{r}|\mathbf{r}_d)}{|\mathbf{r} - \sum_{M\in\hat{\mathbb{P}}(\mathbf{R}_A)} \mathbf{R}_M \hat{\phi}(\mathbf{R}_A|\mathbf{R}_M)|}\, d\mathbf{r} \right] \end{aligned} \tag{37}$$

B.1.2 Function and derivative evaluation for the Coulomb energy J

$$\begin{aligned} J\left[\rho\right] &= \frac{1}{2} \int\int \frac{\rho(\mathbf{r})\, \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' = \frac{1}{2} \sum_{\tau\in\top_\rho} \int_\tau \rho(\mathbf{r}) \left[\sum_{\tau'\in\top_\rho} \int_{\tau'} \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}' \right] d\mathbf{r} \\ &\approx \frac{1}{2} \sum_{\tau\in\top_\rho} \left[\sum_{d\in\mathbb{P}(\tau)} \rho_d \int_{\tau\in\top_\rho} \phi(\mathbf{r}|\mathbf{r}_d) \left(\sum_{\tau'\in\top_\rho} \sum_{d'\in\mathbb{P}(\tau')} \rho_{d'} \int_{\tau'} \frac{\phi(\mathbf{r}'|\mathbf{r}'_d)}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}' \right) d\mathbf{r} \right] \end{aligned} \tag{38a}$$

For a given tetrahedron $\mathbf{r}$ defining

$$s(\mathbf{r}) = \sum_{\tau'\in\top_\rho} \sum_{d'\in\mathbb{P}(\tau')} \rho_{d'} \int_{\tau'} \frac{\phi(\mathbf{r}'|\mathbf{r}'_d)}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}' \tag{38b}$$

the approximation of $J\left[\rho\right]$ becomes

$$J\left[\rho\right] \approx \frac{1}{2} \sum_{\tau\in\top_\rho} \left[\sum_{d\in\mathbb{P}(\tau)} \rho_d \int_{\tau\in\top_\rho} \phi(\mathbf{r}|\mathbf{r}_d) s(\mathbf{r})\, d\mathbf{r} \right] \tag{38c}$$

B.1.3 Function and derivative evaluation for the Exchange energy K

$$
\begin{aligned}
K[\rho] &= -C_x \int \rho^{\frac{4}{3}}(\mathbf{r})\, d\mathbf{r} \\
&= -C_x \sum_{\tau \in \top_\rho} \int_\tau \rho^{\frac{4}{3}}(\mathbf{r})\, d\mathbf{r} \\
&\approx -C_x \sum_{\tau \in \top_\rho} \int_\tau \left[\sum_{d \in \mathbb{P}(\tau)} \rho_d \phi(\mathbf{r}|\mathbf{r}_d) \right]^{\frac{4}{3}} d\mathbf{r}
\end{aligned} \tag{39}
$$

B.1.4 Function and derivative evaluation for the kinetic component T

$$
\begin{aligned}
T[\rho] &= C_F \int \rho^{\frac{5}{3}}(\mathbf{r})\, d\mathbf{r} \\
&= C_F \sum_{\tau \in \top_\rho} \int_\tau \rho^{\frac{5}{3}}(\mathbf{r})\, d\mathbf{r} \\
&\approx C_F \sum_{\tau \in \top_\rho} \int_\tau \left[\sum_{d \in \mathbb{P}(\tau)} \rho_d \phi(\mathbf{r}|\mathbf{r}_d) \right]^{\frac{5}{3}} d\mathbf{r}
\end{aligned} \tag{40}
$$

B.1.5 Function and derivative evaluation for nucleus-nucleus interaction potential V_{nn}

$$
\begin{aligned}
V_{nn}(\{\mathbf{R}_A\}) &= \sum_{A=1}^{M} \sum_{B=A+1}^{M} \frac{Z_A\, Z_B}{r_{AB}} \\
&\approx \sum_{A=1}^{M} Z_A \left[\sum_{B=A+1}^{M} \frac{Z_B}{|\sum_{M \in \hat{\mathbb{P}}(\mathbf{R}_A)} \mathbf{R}_M \hat{\phi}(\mathbf{R}_A|\mathbf{R}_M) - \sum_{M \in \hat{\mathbb{P}}(\mathbf{R}_B)} \mathbf{R}_M \hat{\phi}(\mathbf{R}_B|\mathbf{R}_M)|} \right]
\end{aligned} \tag{41}
$$

B.2 Splitting/averaging and space reduction for efficient evaluation of energy functionals

In an explicit electron density formulation two levels of approximation will be employed to speed up energy functional evaluation. The first approximation stems from the averaging techniques used to evaluate long range interaction. The second comes from integral evaluation through quadrature rules.

In regards to the averaging aspect of the proposed approach, consider the form of the inter-nuclear interaction potential

$$V_{nn}\left(\{\mathbf{R}_A\}\right) = \sum_{A=1}^{M} \sum_{B=A+1}^{M} \frac{Z_A\, Z_B}{r_{AB}} \tag{42}$$

The three dimensional space is partitioned in volumes that span the whole set of nuclei. In what follows, a set of cubes $\mathbb{C}_A$ serves this purpose. The previous sum is equivalently formulated as

$$V_{nn}\left(\{\mathbf{R}_A\}\right) = \frac{1}{2} \sum_{\tau_A^{(1)} \in \mathbb{C}_A} \Bigg(\sum_{\substack{\tau_A^{(2)} \in \mathbb{C}_A \\ \tau_A^{(2)} \in \mathcal{N}(\tau_A^{(1)})}} + \sum_{\substack{\tau_A^{(2)} \in \mathbb{C}_A \\ \tau_A^{(2)} \notin \mathcal{N}(\tau_A^{(1)})}} \Bigg) \sum_{\alpha \in \tau_A^{(1)}} \sum_{\substack{\beta \in \tau_A^{(2)} \\ \beta \neq \alpha}} V(\tilde{\mathbf{R}}_\alpha, \tilde{\mathbf{R}}_\beta) Z_\alpha Z_\beta \tag{43}$$

Here $\tau_A^{(1)}$ and $\tau_A^{(2)}$ represent two arbitrary volumes (or cells) containing nuclei that are generically denoted by α and β. Likewise, $\mathcal{N}(\tau_A^{(1)})$ denotes the set of all volumes (cells) $\tau_A^{(2)}$ that are neighbors of the volume $\tau_A^{(1)}$. The concept of neighbor is central to the splitting of the atomic volumes. Thus, the interaction between nuclei living in neighboring cells is treated exactly. Approximations are employed to speed up the computation of the interaction between nuclei that live in non-neighbor cells. Finally, note that in general a nanostructure might be subjected to applied forces in which case it experiences displacement and or deformation. A tilde ˜ is used to mark the displaced location of the nuclei.

Based on Eq. (43) the following approximation is employed for non-neighbor interaction:

$$\begin{aligned} V_{nn}^{nonloc}\left(\{\mathbf{R}_A\}\right) &= \frac{1}{2} \sum_{\tau_A^{(1)} \in \mathbb{C}_A} \sum_{\substack{\tau_A^{(2)} \in \mathbb{C}_A \\ \tau_A^{(2)} \notin \mathcal{N}(\tau_A^{(1)})}} \sum_{\alpha \in \tau_A^{(1)}} \sum_{\substack{\beta \in \tau_A^{(2)} \\ \beta \neq \alpha}} V(\tilde{\mathbf{R}}_\alpha, \tilde{\mathbf{R}}_\beta) Z_\alpha Z_\beta \\ &\approx \frac{1}{2} \sum_{\tau_A^{(1)} \in \mathbb{C}_A} \sum_{\substack{\tau_A^{(2)} \in \mathbb{C}_A \\ \tau_A^{(2)} \notin \mathcal{N}(\tau_A^{(1)})}} V(\tilde{\mathbf{R}}_{C(\tau_A^{(1)})}, \tilde{\mathbf{R}}_{C(\tau_A^{(2)})}) Z(\tau_A^{(1)}) Z(\tau_A^{(2)}) \end{aligned} \tag{44}$$

The total cell charge $Z(\tau_A^{(1)})$ is obtained by summing up the charge of each nucleus in the volume $\tau_A^{(1)}$. For the results reported below, the position $\tilde{\mathbf{R}}_{C(\tau_A^{(1)})}$ considered was the geometric center of the volume $\tau_A^{(1)}$. Alternatively, it can be defined as the charge center of the volume by considering an averaging of the position of the nuclei weighted by their charge.

The proposed method to evaluate the nucleus-nucleus interaction replaces the individual each-to-each evaluation with many-to-many averages in the case of long range interaction. In addition to *splitting and averaging*, a second efficiency improving factor considered is the *reduction of the number of states*. Rather then considering the position of all the nuclei (M of them) only a subset of nuclei is considered. These can be physical or ghost "reference" nuclei used to represent the position of any other nucleus in an associated atomic control volume. Thus, for a cubic volume, only the eight nuclei at the vertices of the volume are added to the set of states associated with the problem. Therefore, casting the computation of $V_{nn}^{nonloc}\left(\{\mathbf{R}_A\}\right)$ in the form

$$V_{nn}^{nonloc}\left(\{\mathbf{R}_A\}\right) = V_{nn}^{nonloc}\left(\{\mathbf{R}_A\}\right) + V_{nn}^{loc}\left(\{\mathbf{R}_A\}\right) \tag{45}$$

the term V_{nn}^{nonloc} takes advantage of both the *lumping/averaging* and *state dimension reduction* factors, while the V_{nn}^{loc} only leverages the latter.

The *splitting/averaging* and *dimension reduction* are used for CPU gain for the computation of the mixed potential E_{ne} as well. Starting with the definition

$$E_{ne}\left[\rho, \{\mathbf{R}_A\}\right] = \sum_{A=1}^{M} \int \frac{Z_A\, \rho(\mathbf{r})}{|\mathbf{R}_A - \mathbf{r}|}\, d\mathbf{r} \tag{46}$$

a three dimensional electronic density mesh is used to evaluate $E_{ne}\left[\rho, \{\mathbf{R}_A\}\right]$. Mesh refinement will be employed for improved accuracy in energetically intense regions, but unlike the volumes associated with the nuclei splitting, the electronic density mesh is not deforming during simulation. A *local-nonlocal* splitting of the functional of Eq. (46) leads to:

$$E_{ne}\left[\rho, \{\mathbf{R}_A\}\right] = E_{ne}^{(nonloc)}\left[\rho, \{\mathbf{R}_A\}\right] + E_{ne}^{(loc)}\left[\rho, \{\mathbf{R}_A\}\right] \tag{47a}$$

where

$$E_{ne}^{(loc)}\left[\rho, \{\mathbf{R}_A\}\right] = \sum_{\tau \in \mathbb{C}_\tau} \sum_{d \in \mathcal{V}(\tau)} \rho_d \sum_{\substack{\tau_A \in \mathbb{C}_A \\ \tau_A \in \mathcal{N}(\tau)}} \sum_{\alpha \in \tau_A} Z_\alpha \int_\tau \frac{\Phi_d(\mathbf{r})}{|\mathbf{r} - \tilde{\mathbf{R}}_\alpha|} \tag{47b}$$

$$E_{ne}^{(nonloc)}\left[\rho,\{\mathbf{R}_A\}\right] = \sum_{\tau\in\mathbb{C}_\tau}\sum_{d\in\mathcal{V}(\tau)}\rho_d \sum_{\substack{\tau_A\in\mathbb{C}_A \\ \tau_A\notin\mathcal{N}(\tau)}} \sum_{\alpha\in\tau_A} Z_\alpha \int_\tau \frac{\Phi_d(\mathbf{r})}{|\mathbf{r}-\tilde{\mathbf{R}}_\alpha|} \tag{47c}$$

In Eqs. (47b) and (47c) the shape functions Φ_d associated with each of the vertices d of a volume τ in the electronic density mesh $\mathbb{C}_\tau$, are used to express the electronic density at any arbitrary point $\mathbf{r}$ as

$$\rho(\mathbf{r}) = \sum_{d\in\mathcal{V}(\tau)}\rho_d\Phi_d(\mathbf{r}) \tag{48}$$

where $\mathcal{V}(\tau)$ represents the set of vertices associated with the electronic density cell τ.

As mentioned at the beginning of this section, a second level of approximations comes into play when various combinations of quadrature formulas are employed to numerically evaluate the integrals in Eqs. (47b) and (47c). Although not detailed here, similar integrals associated with the expression of kinetic, exchange, and Coulomb functionals T, K, and J, respectively [12] must be evaluated by numerical quadrature. For the purpose of this discussion using the midpoint quadrature rule [19] on a uniform three dimensional cubic mesh, Eq. (47c) leads to

$$E_{ne}^{(nonloc)}\left[\rho,\{\mathbf{R}_A\}\right] = \sum_{\tau\in\mathbb{C}_\tau}\bar{s}_\rho(\tau)\ \|\tau\| \sum_{\substack{\tau_A\in\mathbb{C}_A \\ \tau_A\notin\mathcal{N}(\tau)}} \frac{Z(\tau_A)}{|\mathbf{r}_{C(\tau)}-\tilde{\mathbf{R}}_{C(\tau_A)}|} \tag{49}$$

In Eq. (49), $\bar{s}_\rho(\tau) = \sum_{d\in\mathcal{V}(\tau)}\rho_d$, $\|\tau\|$ represents the volume of the electronic cell $\tau\in\mathbb{C}_\rho$, and $\mathbf{r}_{C(\tau)}$ and $\tilde{\mathbf{R}}_{C(\tau_A)}$ represent the centers of the cells τ and τ_A, respectively.

B.3 Simulation Results

For the test case of a bcc crystal with 100,000 nuclei placed in a uniform three dimensional electronic density distribution, the partials of $E_{ne}\left[\rho,\{\mathbf{R}_A\}\right]$ with respect to the position of the nuclei present in the nanosctructure are displayed in Fig. (3). No splitting/averaging or state reduction are employed and the only errors come in this case through the quadrature-based evaluation of the integral. The figure displays the magnitude of $\frac{\partial E_{ne}}{\partial\tilde{\mathbf{R}}_A}$ at the location of each nucleus. The same quantities are displayed in Fig. (4) for the case when both splitting/averaging and state reduction are considered. Notice that the size of the partials increases, as a subset of "representative" nuclei should carry information for a whole set of nuclei that are not directly present in the problem.

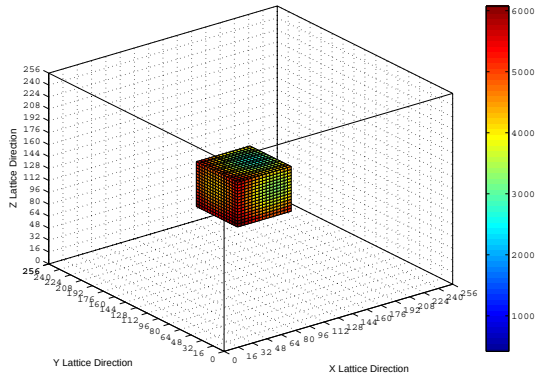

Figure 3: Magnitude of derivatives $\frac{\partial E_{pc}}{\partial \mathbf{R}_A}$. No splitting/averaging or space reduction.

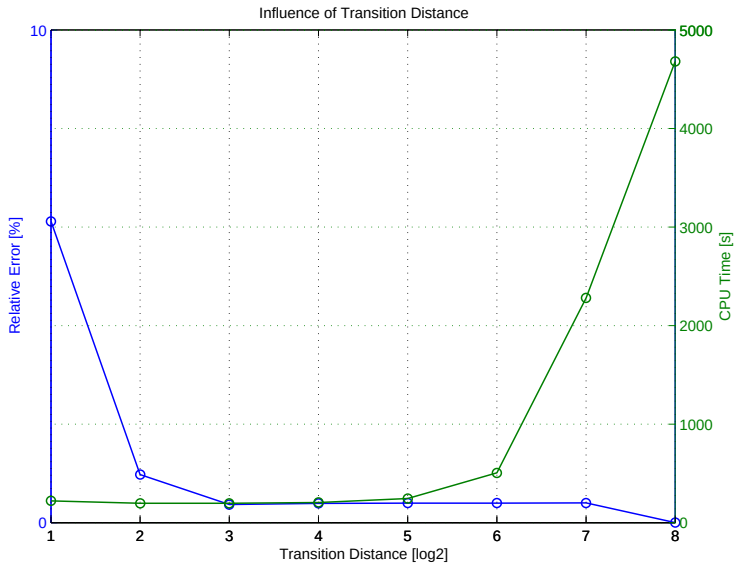

Figure 4: Magnitude of derivatives $\frac{\partial E_{pc}}{\partial \mathbf{R}_A}$. With splitting/averaging and space reduction.