

Reduction of electronic structure problems of density functional theory

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Abstract

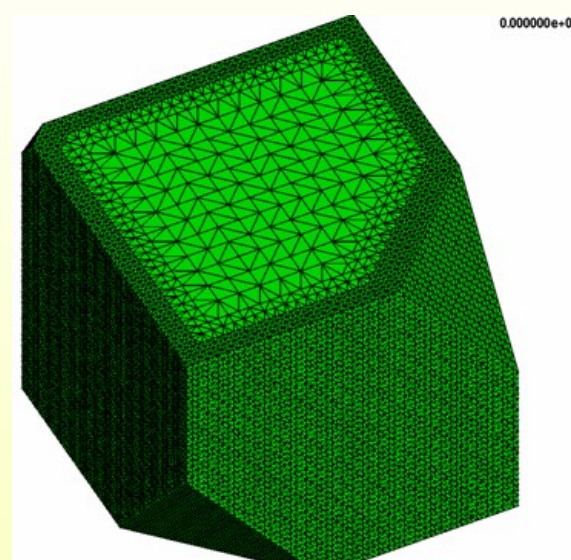
We investigate a model reduction technique for the electronic structure problem of the Density Functional Theory (DFT). This investigation is motivated by the need to extend the applicability of DFT methods to crystalline systems with numbers of atoms far beyond what can be treated using current DFT techniques. The model reduction technique presented here is based on direct minimization of the energy functional of the electronic system with respect to either the electron density in the case of Orbital-Free DFT method, or with respect to the one-electron wave functions in case of Kohn-Sham DFT approach. This solution of the minimization problem is aided by a two-level interpolation of the unknown functions using finite element (FEM) discretization of space over which the solution is sought. Two FEM grids are used. The first is a subatomic grid spanning the space over the individual unit cells, wherein the local spatial behavior of the unknown electronic functions is represented. The second is a lattice-level grid, over which the profile of the unknown functions over the unit cells interior to lattice elements is interpolated in terms of its counterparts at the unit cells located at the lattice grid points. We present the formalism of the proposed reduction technique for Orbital-Free DFT methods, and give numerical examples showing the effectiveness of the reduction technique.

Problem Statement & Solution Idea

- Current electronic structure calculation methods can only practically handle 100 to a few thousands of atoms. Yet nanostructures have sizes in the range 1-100nm and contain 10^2 - 10^8 atoms. Thus there is a need to develop computational methods for electronic structure calculations that can handle larger numbers of atoms.

- The goal of this work is to develop a computational framework to tackle the question of ionic and electronic structure in crystalline nanoscale materials systems.

- The idea is to *take advantage of regions of local periodicity* in a nanostructure to reduce the computational load using a *quasicontinuum-like method* to explicitly treat the electron density dependent quantities around *only representative atoms in the region and interpolate the rest*.



Density Functional Theory (DFT)

- DFT provides a practical framework based on electron density instead of the many-electron Schrodinger wave function.
- Theorems of Hohenberg & Kohn:
 - The electron energy $E[\rho]$ is characterized by the electron density $\rho(\mathbf{r})$.
 - A system has a ground electronic density distribution that minimizes its energy.
- Direct computation of the electron density (and ionic coordinates) is possible via a constrained minimization problem:

$$\min_{\mathbf{R}_{Ion}, \rho} E_{Total}[\mathbf{R}_{Ion}, \rho(\mathbf{r})] = \min_{\mathbf{R}_{Ion}, \rho} (E_{Ion}[\mathbf{R}_{Ion}] + E_e[\rho; \mathbf{R}_{Ion}]) \quad \text{subject to constraint} \quad \int \rho(\mathbf{r}) d\mathbf{r}$$

$$E_{Ion}[\mathbf{R}_{Ion}] = \frac{1}{2} \sum_{A=1}^M \sum_{B=1}^M \frac{z_A z_B}{|\mathbf{R}_A - \mathbf{R}_B|} \quad E_e[\rho; \mathbf{R}_{Ion}] = T[\rho] + J[\rho] + E_{Ion-e}[\rho; \mathbf{R}_{Ion}] + E_{xc}[\rho]$$

Kinetic (Thomas-Fermi)	$T[\rho] = c_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}$	Hartree Energy	$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{ \mathbf{r} - \mathbf{r}' } d\mathbf{r}d\mathbf{r}'$
Electron-ion Interaction	$E_{Ion-e}[\rho; \mathbf{R}_{Ion}] = - \sum_{A=1}^M \int \frac{z_A \rho(\mathbf{r})}{ \mathbf{R}_A - \mathbf{r} } d\mathbf{r}$	Exchange & Correlation (Dirac)	$E_{xc}[\rho] = -c_{xc} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}$

Solution Approach

- Iterative solution:
 - Ionic coordinates \rightarrow electron density \rightarrow ionic coordinates \rightarrow ... convergence.
- Ionic Problem:**
 - Solve the force equilibration problem in terms of "repnuclei", which are nodes in a Lattice Grid.
- Electronic Problem:**
 - Limit the electron density calculations to a small number of representative unit cells and use a reconstruction scheme to establish the density everywhere in the entire nanostructure.
 - Place a subatomic electronic grid inside these unit cells.
 - Re-express the density in passive cells in terms of the density corresponding the grid points in the rep-unit cells. (Quasicontinuum-like Approach)
 - Solve optimization problem: Adjust value of density at grid points of rep-unit cells to minimize the electronic energy functional.

Quasicontinuum-like Approach

Reconstruction of the electron density and functions of the electron density:

Use Finite Element shape functions ϕ and the values of the density in the "nodal unit cells" to interpolate the value at the test point.

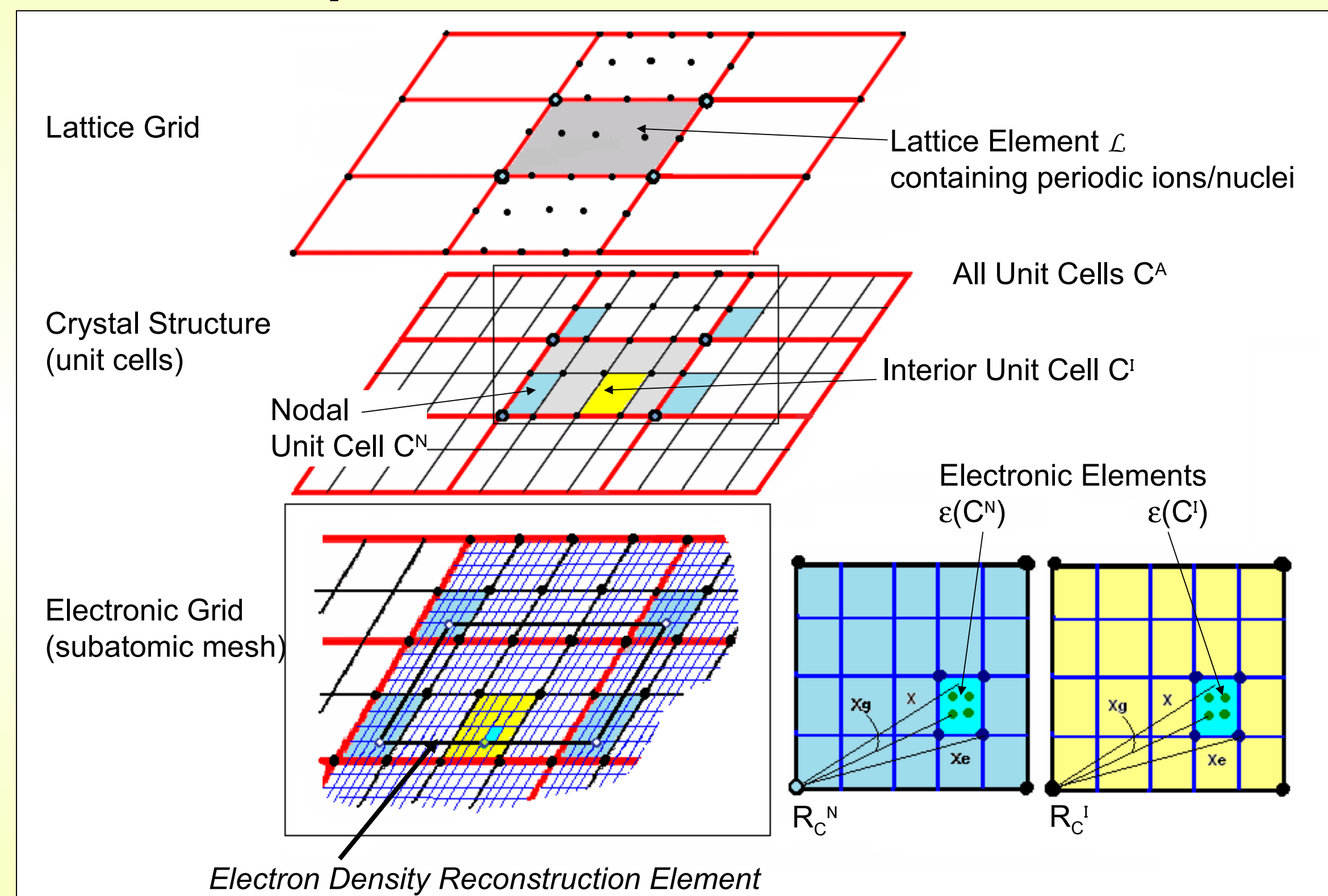
The nodal densities need to be evaluated at the positions in the nodal unit cells which correspond to the position of the test point in the test unit cell.

$$\mathbf{r}_{C^A} = \mathbf{R}_{C^A} + \mathbf{x}$$

$$\rho(\mathbf{r}_{C^I(\mathcal{L})}) = \sum_{C^N(\mathcal{L})} \rho(\mathbf{r}_{C^N}) \phi(\mathbf{R}_{C^I} | \mathbf{R}_{C^N})$$

$$F(\rho(\mathbf{r}_{C^I(\mathcal{L})})) = \sum_{C^N(\mathcal{L})} F(\rho(\mathbf{r}_{C^N})) \phi(\mathbf{R}_{C^I} | \mathbf{R}_{C^N})$$

Minimize $E[\rho]$ on a two-level FEM grid system



Evaluation of Energy Terms

The energy terms in the electronic energy functional contain integrals over the entire computational domain Ω with integrands that are functions of the electron density $F(\rho)$ and functions of the local position $G(\mathbf{r})$. Using the reconstruction scheme described, these integrals can be found as follows:

$$\int_{\Omega} F(\rho(\mathbf{r}))G(\mathbf{r})d\mathbf{r} = \sum_{\mathcal{L}} \sum_{C^A} \int_{C^A} F(\rho(\mathbf{r}))G(\mathbf{r})d\mathbf{r} = \sum_{\mathcal{L}} \sum_{C^A} \int \sum_{C^N} F(\rho(\mathbf{R}_{C^A} + \mathbf{x}))\phi_{\mathcal{L}}(\mathbf{R}_{C^A} | \mathbf{R}_{C^N})G(\mathbf{R}_{C^A} + \mathbf{x})d\mathbf{x} = \sum_{\mathcal{L}} \sum_{C^A} \sum_{C^N} \phi_{\mathcal{L}}(\mathbf{R}_{C^A} | \mathbf{R}_{C^N}) \sum_{\epsilon(C^N), \epsilon(C^I)} \int F(\rho(\mathbf{R}_{C^N} + \mathbf{x}))G(\mathbf{R}_{C^A} + \mathbf{x})d\mathbf{x}$$

$$E_{re,A}[\rho] = \int \rho(\mathbf{r}) \frac{z_A}{|\mathbf{r}_A - \mathbf{r}|} d\mathbf{r}$$

$\rho(\mathbf{r})$ $G(\mathbf{r})$

FEM interpolation of electronic elements using shape functions ψ gives:

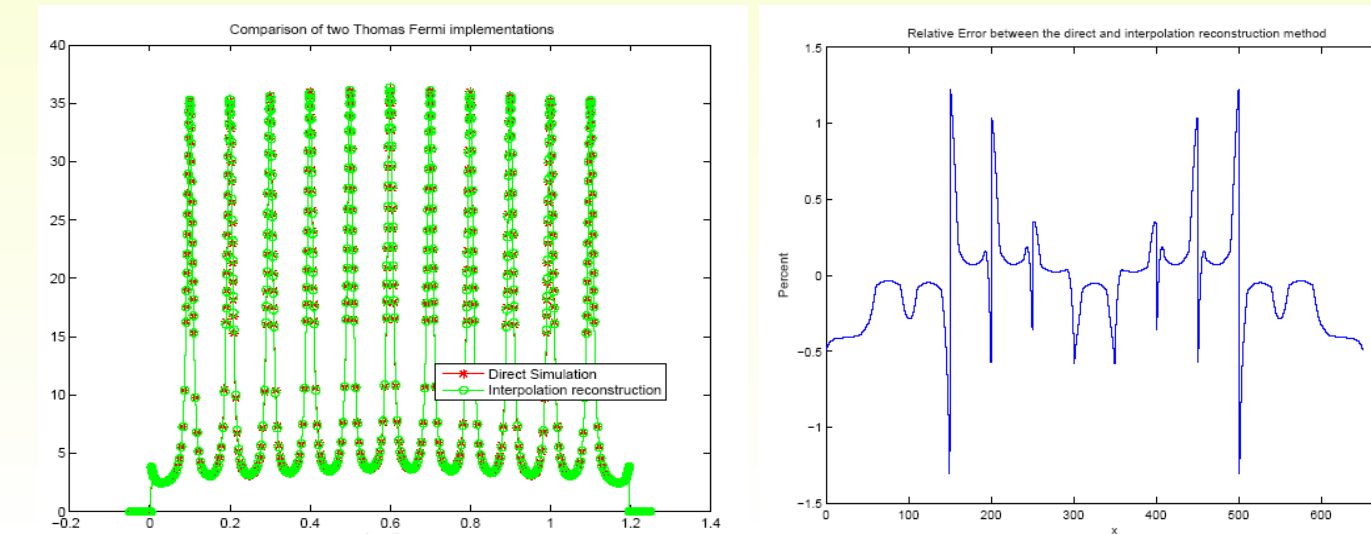
$$\int_{\epsilon(C^N)} F(\rho(\mathbf{R}_{C^N} + \mathbf{x}))G(\mathbf{R}_{C^A} + \mathbf{x})d\mathbf{x} = \sum_{\epsilon(\epsilon)} F(\rho(\mathbf{R}_{C^N} + \mathbf{x}_e))G(\mathbf{R}_{C^A} + \mathbf{x}_e) \int \psi_e(\mathbf{x} | \mathbf{x}_e)d\mathbf{x}$$

Density dependent functions only need to be evaluated at electronic FE nodes in the rep-unit cells (C^N)!

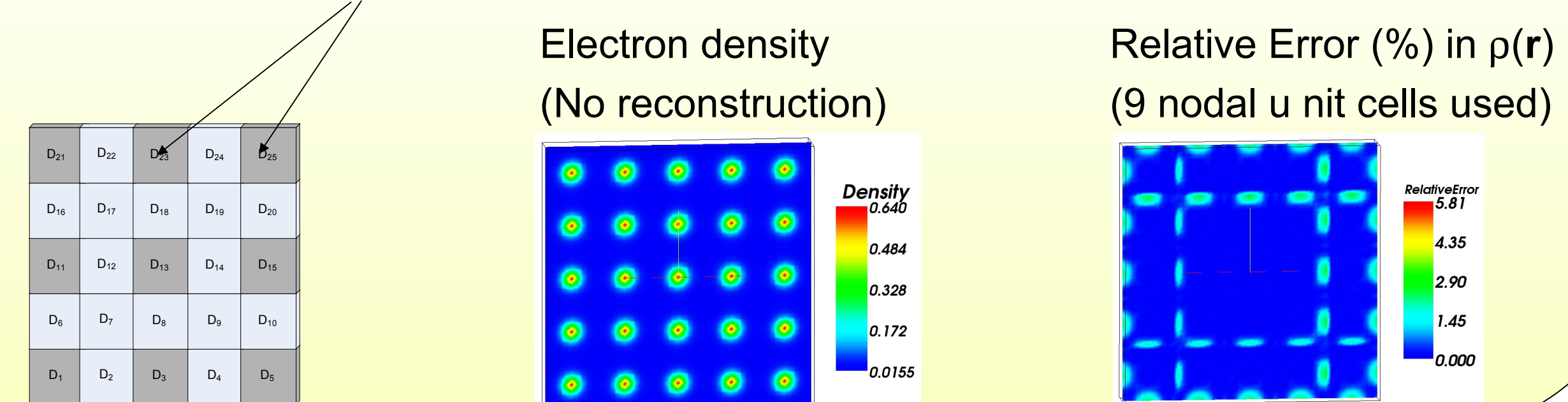
Results

Test Calculations using Thomas-Fermi Kinetic Energy and Dirac Exchange & Correlation Energy functional approximations (Ref [1]):

- Fully resolved and reconstructed electron density calculations around a row of H atoms



- Sheet of H atoms in 3D: 9 nodal unit cells, 33,275 unknowns.



Future Work

- Improve the treatment of boundaries of the electronic problem to try to decrease errors.
- Use more realistic kinetic and exchange & correlation energy functionals.
- Develop the quasi-continuum-like method with the Kohn-Sham DFT.

References

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- Quasicontinuum method for *mechanical* nanoscale systems: Tadmor & Ortiz (1996), Knap & Ortiz (2001)