



Degree of freedom reduction of electronic structure problems of density functional theory

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Abstract

The model reduction technique presented here is based on direct minimization of the energy functional of a nanocrystalline electronic system with respect to the electron density. This solution of the minimization problem is aided by a two-level interpolation of the unknown functions using finite element (FEM) discretization of the physical space over which the solution is sought.

Motivation

- Nanoscale materials provide exciting opportunities for use in devices such as sensors, catalysts, and lasers because they can have surprising properties that differ greatly from bulk materials.
Density Functional Theory (DFT) methods are commonly used for electronic structure calculations, but the computational complexity of these calculations limits the number of atoms that can be included in the calculations to only a few thousands of atoms at best, far short of the number of atoms in a nanoparticle.

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[p] is characterized by the electron density rho(r).
A system has a ground electronic density distribution that minimizes its energy.

min\_{R\_{ion}, rho} E\_{Total}[R\_{ion}, rho(r)] = min\_{R\_{ion}, rho} (E\_{Ion}[R\_{ion}] + E\_e[rho; R\_{ion}]) subject to constraint integral\_{Omega} rho(r) dr

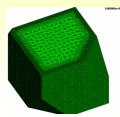
E\_{Ion}[R\_{ion}] = 1/2 \* sum\_{A=1}^M sum\_{B=1}^M (Z\_A Z\_B / |R\_A - R\_B|)
E\_e[rho; R\_{ion}] = T[rho] + J[rho] + E\_{Ion-e}[rho; R\_{ion}] + E\_{xc}[rho]

T[rho] = c\_F \* integral rho^{5/2}(r) dr
J[rho] = 1/2 \* double integral (rho(r)rho(r') / |r-r'|) dr dr' Hartree Energy

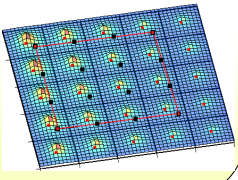
E\_{Ion-e}[rho; R\_{ion}] = -sum\_{A=1}^M integral (Z\_A rho(r) / |R\_A - r|) dr
E\_{xc}[rho] = -c\_{xc} \* integral rho^{gamma}(r) dr Exchange & Correlation (Dirac)

Energy functionals have the basic form: integral F(rho(r))G(r) dr

Interpolate Across Regions of Near-Periodicity



The idea is to take advantage of regions of local periodicity in a nanostructure by using a quasicontinuum-like method to represent the electron density dependent quantities in these regions in terms of a few representative atoms, thus reducing the degrees of freedom in the solution space of the optimization problem described above.



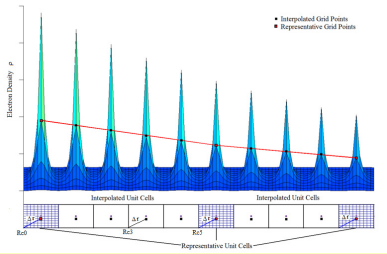
- The schematic to the right shows how the electron density might vary across an array of atoms. There is a quickly varying subatomic structure for the electron density about the nuclei, i.e. across the unit cells (larger black boxes). However, at the same local points (black points) within unit cells in this "lattice region" (red box), the electron density varies slowly.
Regions of small deformation in the ionic crystal have less unit cell to unit cell variation in the electron density, so the lattice regions across which interpolation is performed can be larger.

Quasicontinuum-like Approach

Interpolation of the electron density and functions of the electron density:

We use linear Finite Element shape functions phi and the values of the density in the "representative unit cells" to estimate the density value in "interpolated unit cells" at the same local cell positions.

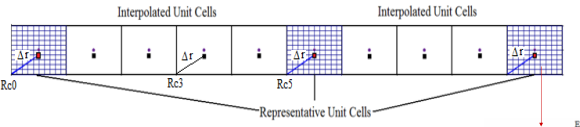
The densities need to be evaluated at corresponding local positions within the unit cells since it is assumed that the density varies nearly periodically from unit cell to unit cell, as shown in the schematic.



References

[1] Negrut D., Anitescu M., El-Azab A., and Zapol P., "Quasicontinuum-Like Reduction of Density Functional Theory Calculations of Nanostructures," Journal of Nanoscience and Nanotechnology, 8, pp. 3729-3740 (2008).
[2] Quasicontinuum method for mechanical nanoscale systems: Tadmor & Ortiz (1996), Knap & Ortiz (2001)

Quasicontinuum-like Approach



A Lattice Region is a nearly periodic region having a small deformation of the periodic structure. In other words, the non-periodic part of the electron density and functions of the electron density are assumed to be smoothly varying macroscopic fields modified by an otherwise periodic density.

A Lattice Region is composed of a set of unit cells, and can be viewed as similar to finite elements with representative cells (nodes) at the corners. The electron density rho and functions of electron density F(rho) can be interpolated as follows in terms of density in the representative cells (rho(r\_{c\_n})) and linear finite element shape functions phi\_{c\_n}(r). Note that the electron density is evaluated at the position r within the C^n unit cell domain Omega\_c. Using the notation defined in the diagram, we have

r = R\_c + Delta r
rho(r in Omega\_c) = sum\_{c\_n} rho(R\_{c\_n} + Delta r) phi\_{c\_n}(R\_c + Delta r)
F(rho(r in Omega\_c)) = sum\_{c\_n} F(rho(R\_{c\_n} + Delta r)) phi\_{c\_n}(R\_c + Delta r)

The shape functions phi\_{c\_n}(r) are evaluated at the same local position Delta r within the interpolated unit cell C and the representative unit cells C\_r. This means that as the evaluation position within unit cell C shifts, the representative cell "nodes" also shift, so the shape function value does not depend on the local position Delta r. It only depends on the representative and interpolated unit cell reference positions R\_{c\_n} and R\_c. Thus,

F(rho(r in Omega\_c)) = sum\_{c\_n} F(rho(R\_{c\_n} + Delta r)) phi\_{c\_n}(R\_c) where phi\_{c\_n}(R\_{c\_n}) = delta\_{c\_n c\_n}

For simplicity, assume the following notation, where it is assumed that functions of density will be denoted by F and functions of position will be denoted by G:

F(rho(r)) = F(rho(R\_c + Delta r)) = F\_c(R\_c)
G(r) = G(R\_c + Delta r) = G\_c(R\_c)

Therefore, the quasicontinuum-like interpolation expression for the functions of electron density becomes

F\_c(Delta r) = sum\_{c\_n} F\_{c\_n}(Delta r) phi\_{c\_n}(R\_c)

Evaluation of Energy & Energy Gradients

The ground state electron density distribution minimizes the energy. To find this g.s. density, the energy and the energy gradient must be calculated with respect to the vector of density values at the nodes of the two-level mesh. The energy terms in the electronic energy functional contain integrals over the entire computational domain Omega with integrands that are functions of the electron density F(rho) and functions of the local position G(r). Using the interpolation scheme described, these integrals can be found as follows, where Omega\_c is an electronic element domain and c-C is used to mean that the element c is contained in (and specifies) cell C:

I[F] = integral\_{Omega} F(rho(r))G(r) dr
E\_{xc,A}[rho] = integral rho(r) \* (Z\_A / |r - r\_A|) dr

= (sum\_{c\_1 in {c\_1}} integral\_{Omega\_{c\_1}} + sum\_{c\_2 in {c\_2}} integral\_{Omega\_{c\_2}}) F(rho(r))G(r) dr
= (sum\_{c\_1 in {c\_1}} integral\_{Omega\_{c\_1}} + sum\_{c\_2 in {c\_2}} integral\_{Omega\_{c\_2}}) F\_{c\_n}(Delta r)G\_{c\_n}(Delta r)dDelta r
= sum\_{c\_1 in {c\_1}} integral\_{Omega\_{c\_1}} F\_{c\_1}(Delta r)G\_{c\_1}(Delta r)dDelta r + sum\_{c\_2 in {c\_2}} integral\_{Omega\_{c\_2}} F\_{c\_2}(Delta r)G\_{c\_2}(Delta r)dDelta r

Quasicontinuum-like interpolation of F(rho(r)) using lattice level shape functions phi\_{c\_n} gives:
approx sum\_{c\_1 in {c\_1}} sum\_{c\_n in C\_{c\_1}} phi\_{c\_n}(R\_{c\_n}) integral\_{Omega\_{c\_1}} F\_{c\_n}(Delta r)G\_{c\_n}(Delta r)dDelta r + sum\_{c\_2 in {c\_2}} sum\_{c\_n in C\_{c\_2}} phi\_{c\_n}(R\_{c\_n}) integral\_{Omega\_{c\_2}} F\_{c\_n}(Delta r)G\_{c\_n}(Delta r)dDelta r
= sum\_{c in C} sum\_{c\_n in C\_c} phi\_{c\_n}(R\_c) integral\_{Omega\_c} F\_{c\_n}(Delta r)G\_c(Delta r)dDelta r where phi\_{c\_n}(R\_{c\_n}) = delta\_{c\_n c\_n}

FEM interpolation of electronic elements using shape functions phi\_{c\_n} which have compact support about the n^th electronic node, is performed as follows.

F\_{c\_n}(Delta r) = sum\_{c\_n} F\_{c\_n}(Delta r\_n) psi\_{n,c\_n}(Delta r) = sum\_{c\_n} F(p\_{c\_n}) psi\_n(r)
psi\_{n,c\_n}(Delta r) = psi\_n(R\_{c\_n} + Delta r) = psi\_n(r) = shape function for n^th FE electronic node
psi\_n(r) = 0 for r not in {Omega\_c} about n^th node (compact support)

The discretized energy and its gradient required for the optimization problem can now be written as

I[p] approx sum\_{c in C} sum\_{c\_n in C\_c} phi\_{c\_n}(R\_c) sum\_{c\_n} F\_{c\_n}(Delta r\_n) integral\_{Omega\_c} psi\_{n,c\_n}(Delta r)G\_c(Delta r)dDelta r
= sum\_{c in C} F(p\_{c\_n}) sum\_{c\_n in C\_c} phi\_{c\_n}(R\_c) integral\_{Omega\_c} psi\_n(r)G(r) dr
= F(p) \* k
nabla\_r I(p) = nabla\_p F(p) \* k

Future Work

- Implementation of energy and energy gradient calculation method described (in progress).
Integration with an optimization package to compute the representative electron density that minimizes the energy E(p).
Improve the treatment of boundaries of the electronic problem to improve the errors in previous work (see references).