DPhil Project: Electronic Density Functionals and A Field Theoretic Quasicontinuum Method

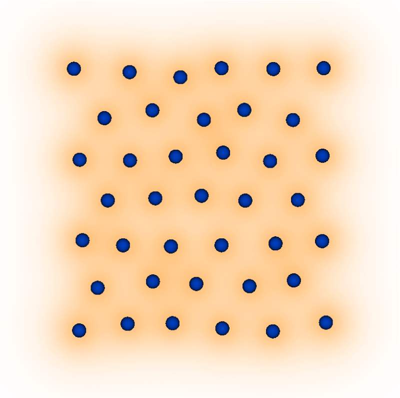
Bernhard Langwallner

Mathematical Institute, University of Oxford
OxMOS – New Frontiers in the Mathematics of Solids

OxMOS Steering Committee Meeting MT 2010
29 September 2010

The Physical Situation

$\boldsymbol{N_{at}}$ **atoms** (ideally N_{at} large), $\boldsymbol{N}$ **electrons**



Look for electronic ground state for fixed nucleus positions!

$\Rightarrow$ **Density Functional Theory**

Motivation for Density Functionals

Idea: **Look at electron density instead of wave function**

$$\boldsymbol{u}^2 : \mathbb{R}^{\mathbf{3}} \to \mathbb{R}$$

$\rho = u^2(x)\,\mathrm{d}x =$ number of electrons in $x + \mathrm{d}x$, normalization $\int u^2\,\mathrm{d}x = N$

Is knowing $\boldsymbol{u}$ sufficient?

Hohenberg–Kohn Theorem

Total energy = unique functional of the electron density

Functional unknown $\Rightarrow$ look for approximations: 2 families

Thomas–Fermi type functionals and **Kohn-Sham functionals**

A Thomas–Fermi Type Problem

Restrict functional to bounded domain Ω and apply boundary conditions

Minimize

$$E(u) = \frac{\lambda}{2} \int_\Omega |\nabla u|^2 \, \mathrm{d}x + \int_\Omega F(u) \, \mathrm{d}x + \Phi(u)$$

over $\quad X = \left\{ u \in \mathrm{H}^1(\Omega) : \; u|_{\partial\Omega} = u_{\mathrm{ex}} \;\; , \;\; c(u) = \|u\|_{\mathrm{L}^2}^2 - N = 0 \right\}$

Coulomb interaction (nonlocal): (ρ_n = nucleus charge distribution)

$$\Phi(u) = -\inf \left\{ \int_\Omega \frac{1}{8\pi} |\nabla \varphi|^2 - (u^2 - \rho_n)\varphi \, \mathrm{d}x, \;\; \varphi \in \mathrm{H}^1(\Omega), \;\; \varphi|_{\partial\Omega} = \phi_{\mathrm{ex}} \right\}$$

- Problem is nonconvex
- There exists a minimizer

First Order Optimality Conditions

Look at **optimality conditions**: ($\mu \in \mathbb{R}$ . . . Lagrange multiplier)

$$E'(u) + \mu c'(u) = 0, \qquad c(u) = 0$$

Φ, Φ' are nonlocal $\Rightarrow$ explicitly use electrostatic potential ϕ

$$\left.\begin{aligned} -\lambda \Delta u + F'(u) + 2\phi u + \mu u &= 0 \\ -\tfrac{1}{4\pi}\Delta\phi - (u^2 - \rho_n) &= 0 \\ \int_\Omega u^2 \, dx - N &= 0 \\ + \text{ boundary conditions} & \end{aligned}\right\} \qquad \mathcal{F}(u, \phi, \mu) = 0$$

System of nonlinear PDEs with constraint $\Rightarrow$ FE analysis possible

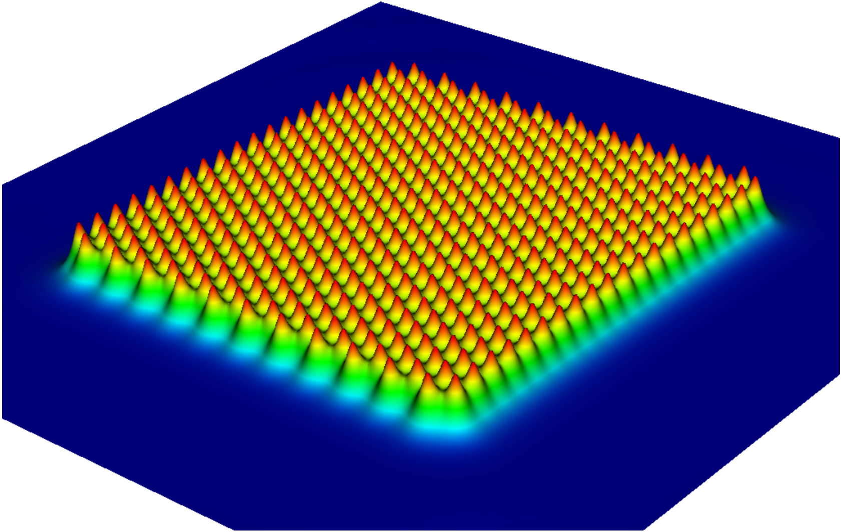
If $\bar{u}$ is minimizer of E, $\bar{\mu}$ its multiplier and $-\Delta\bar{\phi} = 4\pi(\bar{u}^2 - \rho_n)$

$$\Rightarrow \quad \mathcal{F}(\bar{u}, \bar{\phi}, \bar{\mu}) = 0$$

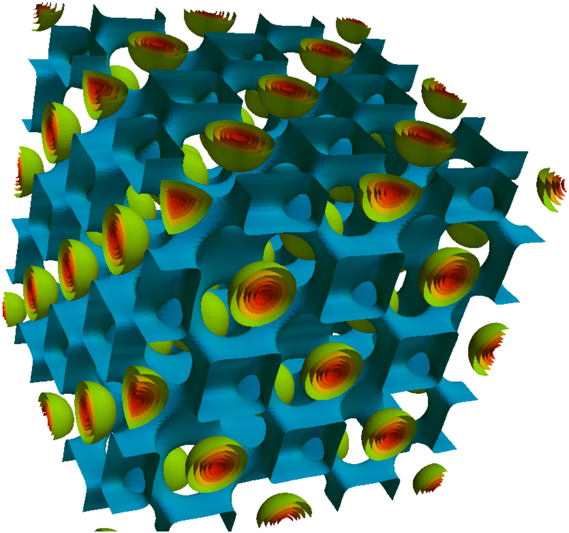
My Contributions

- **Full convergence theory** for FE and Fourier discretization
  - Stability analysis for optimality system: saddle point theory
  - Convergence theory using nonlinear analysis, duality techniques
  - Study of convergence rates: energy, Lagrange multiplier, L^2-norms
  - Article to appear in M^3AS
  - Among the first numerical studies of nonlinear eigenvalue problems
- Discretization with **Numerical Integration/Interpolation**
  - Convergence rates under minimal quadrature order

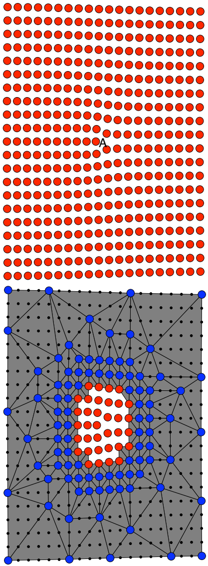
Example: 2D Crystal



Example: Electron Density in FCC Crystal



The Energy Based Quasicontinuum Method



[Tadmor, Miller, Ortiz, Shenoy, Phillips, Rodney, . . . , ≈ 2000]

1. Start with atomistic model given by energy $\mathcal{E}^a$
2. Find region $\mathcal{A}$ where atomistic detail is needed
3. Choose representative atoms → triangulation $\mathcal{T}$
4. Use continuum model in region $\mathcal{C}$

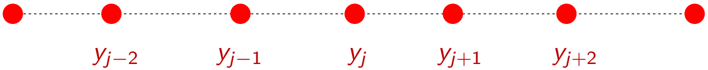
Problem: unphysical **"ghost" forces!**

reason: nonlocality, GF can be removed

New concept: interaction based on **field** ϕ

(V. Gavini)

Periodic Chain with Yukawa potential in 1D



Define atomistic potential through **introduction of field ϕ**:

$$\mathcal{E}^a(\mathbf{y}) = \inf_{\phi \in \mathrm{H}^1_\#(\Omega)} \int_\Omega \left(\tfrac{\varepsilon^2}{2}|\nabla\phi|^2 + \tfrac{1}{2}m^2\phi^2\right)\mathrm{d}x - \int_\Omega \rho_{\mathbf{y}}\phi\,\mathrm{d}x,$$

ϕ solves

$$-\varepsilon^2\Delta\phi + m^2\phi \;=\; \rho_{\mathbf{y}} \;=\; \varepsilon\sum_j \delta_\varepsilon(\cdot - y_j)$$

Forces are local !

(u = P1 interpolant of $\mathbf{u}$)

$$D_{\mathbf{y}}\mathcal{E}^a(\mathbf{y})\cdot\mathbf{u} = \mathbf{u}\cdot\int \phi(x)D_{\mathbf{y}}\rho_{\mathbf{y}}(x)\,\mathrm{d}x = \int_\Omega \sigma^a(x;\mathbf{y}) : \nabla u\,\mathrm{d}x$$

where $\boldsymbol{\sigma}^{\boldsymbol{a}}$ looks like atomistic **stress** $\rightarrow$ **coupling easier?**

Comparison

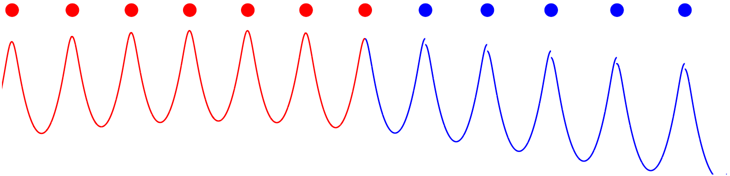
Derive continuum model $\mathcal{E}^{cb}$ using Cauchy–Born rule (cell problems) $\Rightarrow$

Atomistic vs continuum derivative

$$D\mathcal{E}^{a}(\mathbf{y}) \cdot \mathbf{u} = \int_{\Omega} \sigma^{a}(x;\mathbf{y}) \nabla u \, \mathrm{d}x \qquad D\mathcal{E}^{cb}(\mathbf{y}) \cdot \mathbf{u} = \int_{\Omega} \sigma^{cb}(x;\mathbf{y}) \nabla u(x) \, \mathrm{d}x$$

- Quasicontinuum coupling:
  - $\sigma^{a}(x;\mathbf{y})$ and $\sigma^{cb}(x;\mathbf{y})$ are very similar
  - Definition/location of atomistic/continuum interface
  - Boundary data for atomistic problem from continuum cell problems

First Idea: Boundary Condition Exchange



Brutal energy mixing "$\mathbf{y} = \mathbf{y}_a \cup \mathbf{y}_{cb}$", "$\Omega = \Omega_a \cup \Omega_{cb}$"

$$\mathcal{E}^{qc}(\mathbf{y}) = \mathcal{E}^a(\mathbf{y}_a; \text{b.c. on } \partial\Omega_a) + \mathcal{E}^{cb}(\mathbf{y}_{cb})$$

Atomistic domain: problem with Dirichlet boundary conditions $g(\mathbf{y})$

$$\mathcal{E}^a_{g(\mathbf{y})}(\mathbf{y}) = \inf_{\substack{\phi \in \mathrm{H}^1(\Omega) \\ \phi|_{\partial\Omega_a} = g(\mathbf{y})}} \int_{\Omega_a} \left(\tfrac{\varepsilon^2}{2}|\nabla\phi|^2 + \tfrac{1}{2}m^2\phi^2\right) \mathrm{d}x - \int_{\Omega_a} \rho_{\mathbf{y}}\phi \, \mathrm{d}x,$$

Boundary conditions $g(\mathbf{y})$ from cell problems $\Rightarrow$ **coupling**

Outlook

- Analysis for class of Quasicontinuum Methods (halfway done)
  - Consistency analysis
  - Stability analysis
- More difficult (realistic) models
- Higher dimensions, ...
- Density functional based Quasicontinuum Method