Electronic-structure calculations at macroscopic scales

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Predicting Properties of Matter from Electronic Structure

- The quantum mechanics of electrons and ions lies at the foundation of a large part of low-energy physics, chemistry and biology
- The Born-Oppenheimer approximation: Decouples the electronic and nuclear motion, electrons respond instantaneously to any change in nuclear coordinates
- Time-independent Schrödinger equation for an isolated N-electron atomic or molecular system:

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} = \sum_{i=1}^{N}(-\frac{1}{2}\nabla_i^2) + \sum_{i=1}^{N} v(\boldsymbol{r}_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

Quantum mechanics and material properties

Quantum Mechanics of Many-Electron Systems.

By P. A. M. Dirac, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

§ 1. *Introduction.*

The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

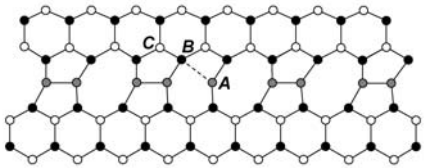
Perfect crystals – Periodic systems

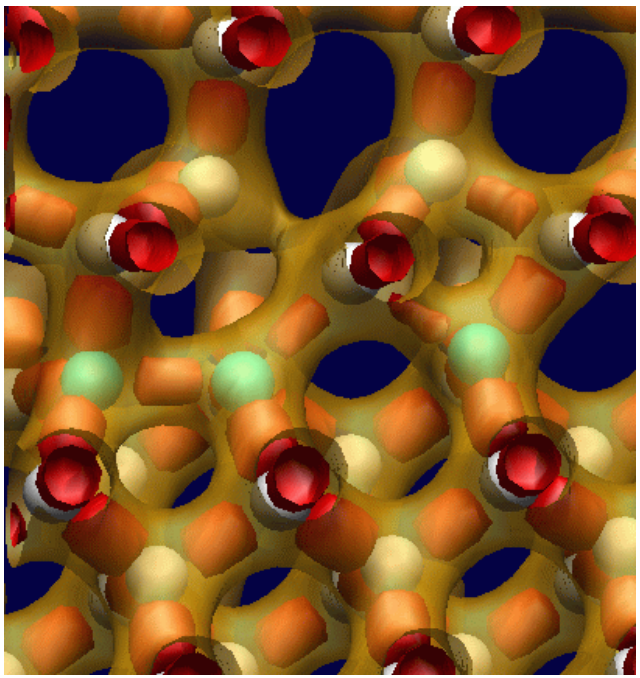
- Many fundamental properties of materials can be elucidated by considering perfect crystal order:
  - *Excitation spectra and optical properties*
  - *Equations of state, elastic moduli, phase diagrams*
  - *Piezoelectric, ferroelectric, magnetic properties*
  - *…*
- Bloch's theorem: Representation of the wave function in terms of plane waves → *Fourier transform*
- Pseudopotentials: Core electrons are replaced by an effective potential → *Pseudopotentials*

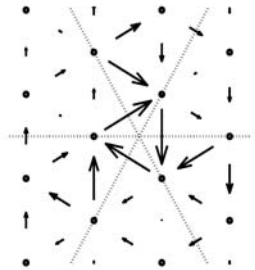
Defective crystals – Supercells

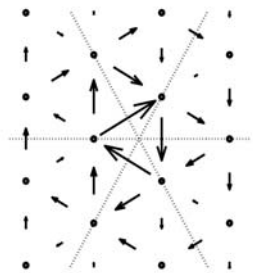
- Some macroscopic properties of materials are mediated by lattice defects:
  - *Vacancies: Creep, spall, prismatic loops, radiation ageing*
  - *Dislocations: Metal plasticity*
  - *Domain walls, grain boundaries, free surfaces, interfaces*
  - *…*
- The core structure of these defects can be elucidated at the atomic level → Electronic structure calculations?
- Lattice defects break the translational symmetry of the crystal → Nonperiodic calculations
- Recover periodic case by considering periodic distributions of defects → *Supercells*

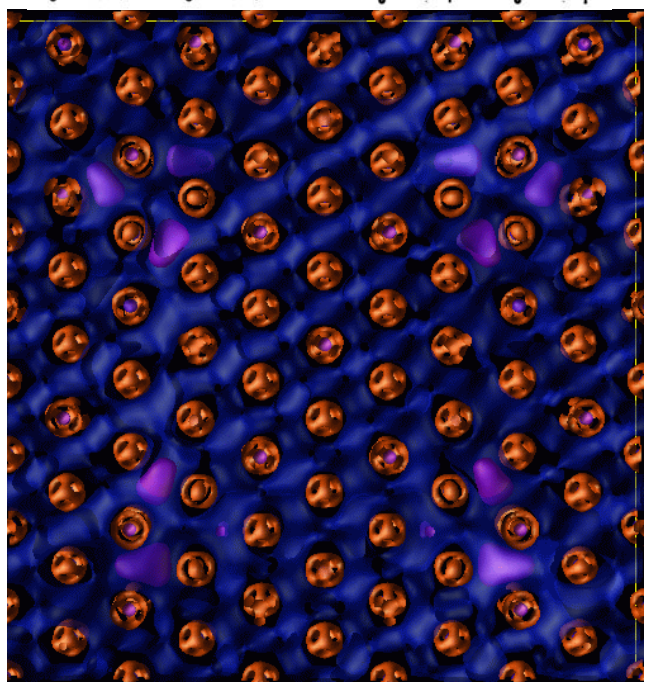
Defective crystals – Supercells











Electronic structure of the 30° partial dislocation in silicon (Csányi, Ismail-Beigi and Arias, *Phys. Rev. Let*. **80** (1998) 3984).

Ab initio study of screw dislocations in Mo and Ta (Ismail-Beigi and Arias, *Phys. Rev. Let*. **84** (2000) 1499).

Defective crystals – The chasm

- Because of computational cost, supercells limited to small sizes → Exceedingly large defect concentrations
- Often the objective is to predict *bulk properties* of defects:
  - *Vacancies: cell size* ~ 100 nm
  - *Dislocation cores: cell size* ~ 100 nm
  - *Domain walls: cell size* ~ 1 μm
  - *Grain boundaries: cell size* ~ 20 μm
- Small-cell calculations lead to discrepancies with experimental measurements!
- *How can bulk properties of defects (>> million atom computational cells) be predicted from electronic structure calculations?*

Density functional theory

- Theorem [**Hohenberg-Kohn**, 1964] *The external potential* $v(\boldsymbol{r})$ *is determined by the electron density*

$$\rho(\boldsymbol{r}) = N \int |\Psi|^2 ds_1 d\boldsymbol{x}_1 \dots \boldsymbol{x}_N$$

- Corollary: $E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho]$
- Theorem [**Hohenberg-Kohn**, 1964] $E_0 = \inf_\rho E[\rho]$
- Levy's constrained-search representation:

$$E[\rho] = \inf_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{ne} + \hat{V}_{ee} | \Psi \rangle$$

Orbital-Free Density functional theory

- Total energy functional: $E[\rho] = T_s[\rho] + E_{xc}[\rho]$

$$+\frac{1}{2}\int_\Omega\int_\Omega \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}\,d\boldsymbol{r}' + \int \rho(\boldsymbol{r})v(\boldsymbol{r})\,d\boldsymbol{r}$$

- Thomas-Fermi-Weizsacker (TF-λW) KE:

$$T_s(\rho) = \frac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3}(\boldsymbol{r})d\boldsymbol{r} + \frac{\lambda}{8}\int \frac{|\nabla\rho(\boldsymbol{r})|^2}{\rho(\boldsymbol{r})}d\boldsymbol{r}$$

- Kernel-energies: Subsequent enhancements by Wang and Teter (1992), Smargiassi and Madden (1994), Wang, Govind and Carter (1998, 1999)...

Orbital-Free Density functional theory

- Exchange-correlation energy (LDA + gradient expansion):

$$E_{xc}[\rho] \approx \int \epsilon_c(\rho)\rho(\boldsymbol{r})\, d\boldsymbol{r} - \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3}(\boldsymbol{r}) d\boldsymbol{r}$$

$$-\frac{7}{144}(81\pi^5)^{-1/3} \int \frac{|\nabla\rho(\boldsymbol{r})|^2}{\rho^{4/3}(\boldsymbol{r})}\, d\boldsymbol{r} + \ldots$$

- OFDFT is a good model for systems with electronic structure close to that of a free-electron gas
- Still: Severe cell-size limitations, $\sim$ 100-1000 atoms!

OFDFT Coarse-graining

- Defective lattices, well-separated defects:
  - *Away from defects, atoms 'see' the electron density of a uniformly distorted periodic lattice: Cauchy-Born electron density + slowly varying modulation (Blanc, Le Bris and Lions, ARMA, 2002)*
  - *Only near defect cores the electron density and the electrostatic potential deviate significantly from those of a periodic lattice*
- All-atom OFDFT calculations are inherently wasteful!
- Objective: Model reduction such that:
  - *The coarse graining is unstructured and adaptive*
  - *OFDFT is the sole input to the model (no spurious physics)*
  - *Reduced solutions → all-atom OFDFT in fully-resolved limit*
- General approach (QC-OFDFT):
  - *Derive a real space, nonperiodic, formulation of OFDFT*
  - *Effect a quasi-continuum (QC) model reduction*

OFDFT – Real space formulation

- Total energy functional:

$$E[\rho] = \int \epsilon_{loc}(\boldsymbol{r}, \rho, \nabla\rho)\, d\boldsymbol{r} + \underbrace{\frac{1}{2}\int_\Omega \int_\Omega \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d\boldsymbol{r}\, d\boldsymbol{r}'}$$

Fourier transform → periodicity
Fast-multiple → structure

← nonlocal!

- Local Lagrangian form:

$$E[\rho] = \sup_{\phi \in H^1(\mathbf{R}^3)} L[\rho, \phi]$$

$$L[\rho,\phi] = \int \epsilon_{loc}(\boldsymbol{r}, \rho, \nabla\rho)\, d\boldsymbol{r}$$

$$-\frac{1}{8\pi}\int_\Omega |\nabla\phi(\boldsymbol{r})|^2\, d\boldsymbol{r} + \int_\Omega (\rho(\boldsymbol{r}) + \underbrace{b(\boldsymbol{r})})\phi(\boldsymbol{r})\, d\boldsymbol{r}$$

pseudopotentials

OFDFT – Real space formulation

- Enforce constraint $\rho > 0$ by setting $\rho = u^2$.
- Saddle-point problem:

$$\inf_{u \in H^1(\Omega)} \sup_{\phi \in H^1(\mathbb{R}^3)} L(u, \phi)$$

$$\text{subject to: } \int_\Omega u^2(\boldsymbol{r}) d\boldsymbol{r} = N$$

Theorem [BGKO] Let $E[u]$ be the TF-λ W + LDA energy functional, $X = \{u \in H^1(\Omega), \|u\|^2_{L^2(\Omega)} = N\}$. Then $E[u]$ has a minimum in X.

OFDFT – FE approximation

- Let $X_h \times Y_h$ be a sequence of finite-element subspaces of $H_0^1(\Omega) \times H^1(\mathbb{R}^3)$.
- Discrete problem: $F[u,\phi] \equiv$

$$-\frac{1}{8\pi}\int_\Omega |\nabla\phi(\boldsymbol{r})|^2\,d\boldsymbol{r} + \int_\Omega (u^2(\boldsymbol{r}) + b(\boldsymbol{r}))\phi(\boldsymbol{r})\,d\boldsymbol{r}$$

$$F_h[u,\phi] = \begin{cases} F[u,\phi], & \text{if } \phi \in Y_h \\ -\infty, & \text{otherwise.} \end{cases}$$

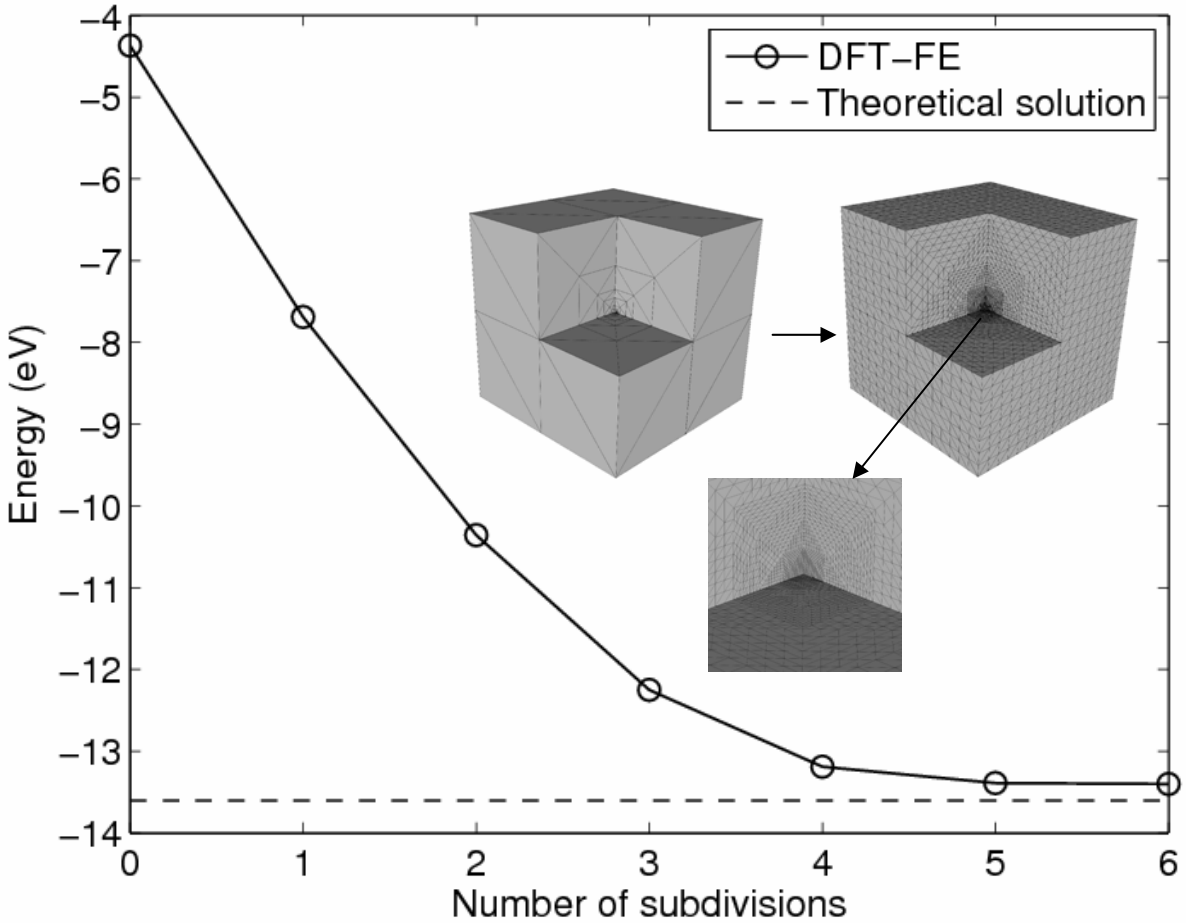
$$E_h[u] = \begin{cases} E_{loc}[u] + \sup_\phi F_h[u,\phi], & \text{if } u \in X_h \\ +\infty, & \text{otherwise.} \end{cases}$$

Theorem [BGKO] $\Gamma - \lim_{h\to 0} E_h = E$, $\inf E_h \to E_0$.

OFDFT – FE approximation

- 4-node tetrahedral finite-elements
- Second-order 4-point quadrature rule
- Optimal mesh gradation (*a priori*)
- Dirichlet boundary conditions on electrostatic potential and electron-density
- Penalty method to enforce constraint
- Nested conjugate gradients for solving the electrostatic potential, electron-density and atomic positions (configurational-force equilibrium)
- Parallel implementation with domain decomposition
- Freudenthal's algorithm for uniform subdivision of mesh

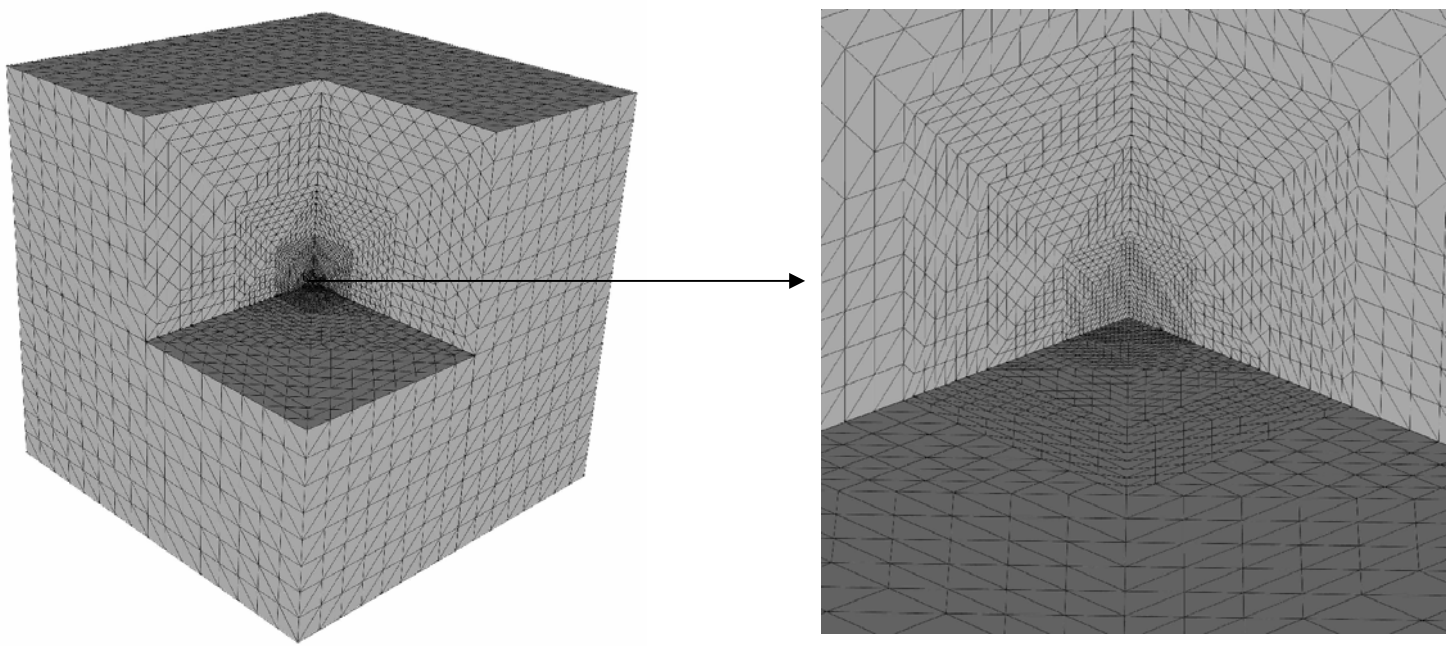
Convergence test – Hydrogen atom



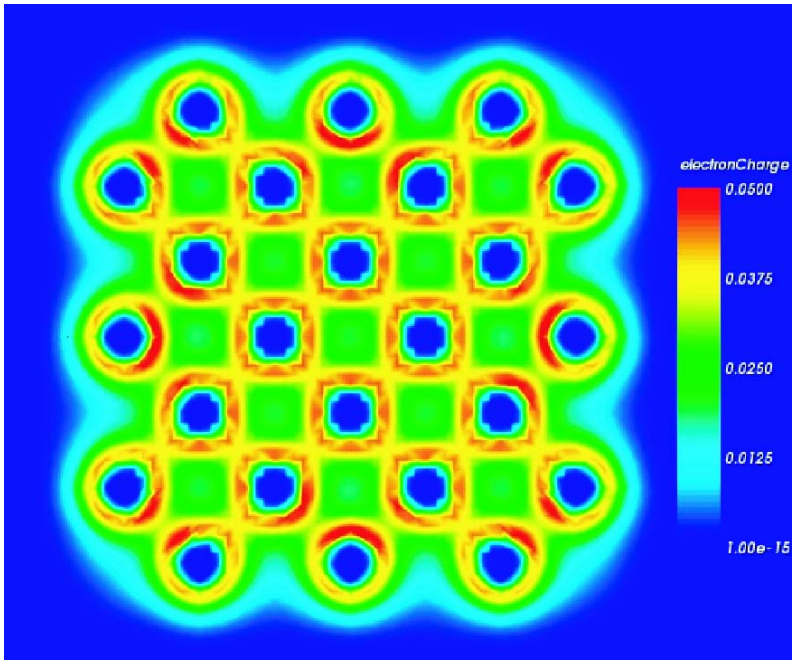
Energy of hydrogen atom as a function of number of subdivisions of initial mesh

Example – Aluminum clusters

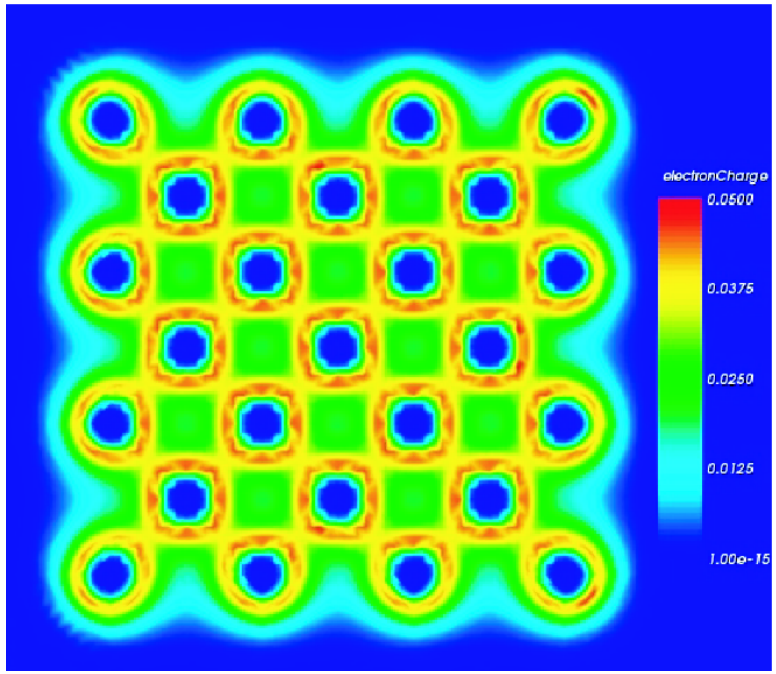
- TF-λW + LDA, λ = 1/6
- Heine-Abarenkov pseudopotential
- Simulations of 1x1x1 3x3x3 5x5x5 9x9x9 clusters
- Equilibrium configurations are determined



Example – Aluminum clusters



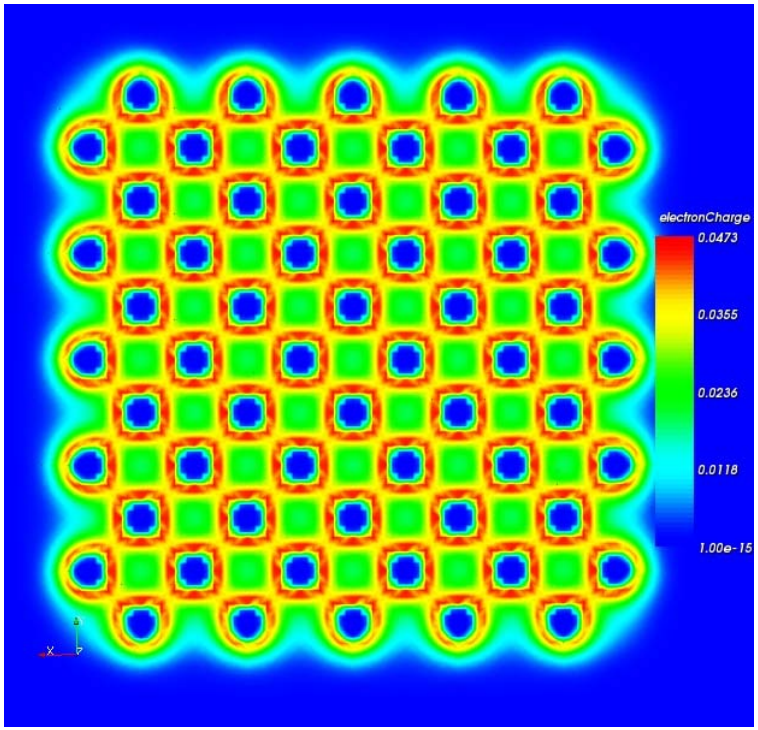
mid-plane



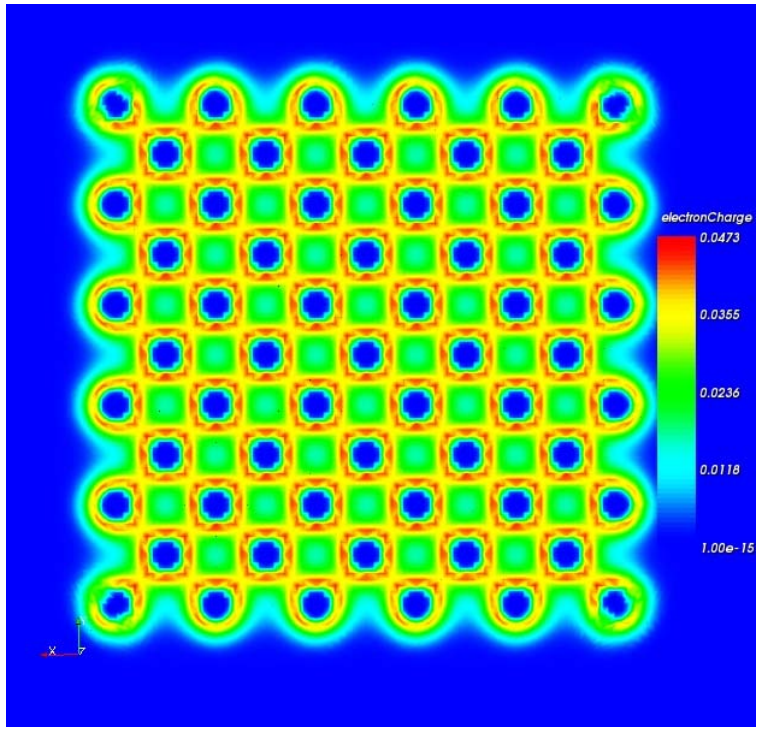
face

Contours of electron density in 3x3x3 aluminum cluster

Example – Aluminum clusters



mid-plane



face

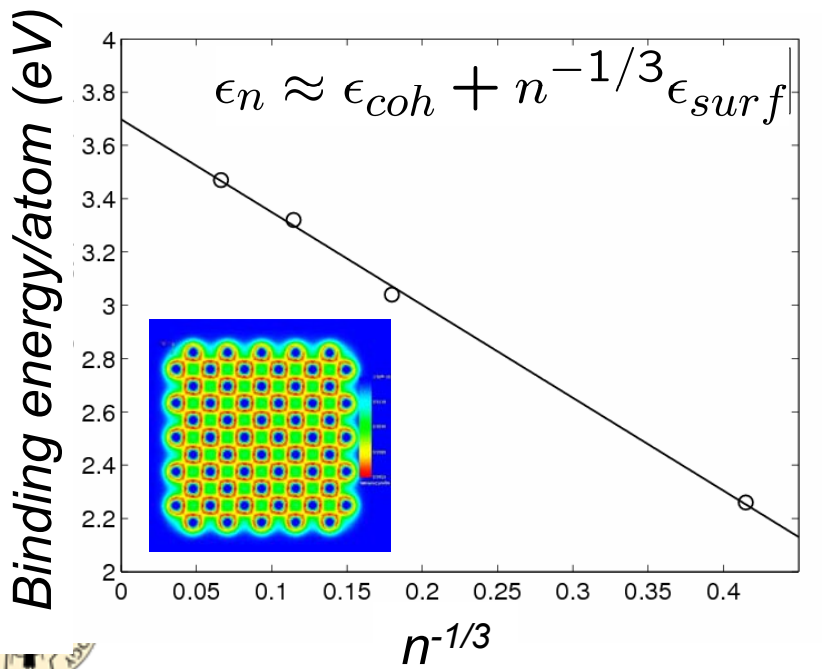
Contours of electron density in 5x5x5 aluminum cluster

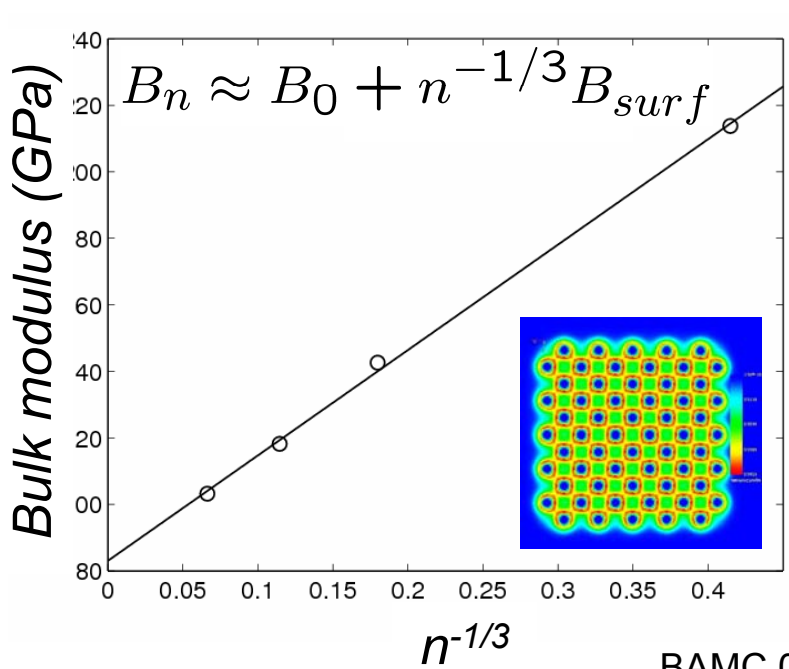
Example – Aluminum clusters

Property	DFT-FE	KS-LDA[a]	Experiments[b]
Lattice parameter (a.u.)	7.42	7.48	7.67
Cohesive energy (eV)	3.69	3.67	3.4
Bulk modulus (Gpa)	83.1	79.0	74.0

a/ Goodwin et al. (1990), Gaudion et al. (2002)

b/ Brewer (1997), Gschneider (1964)





OFDFT – Coarse-graining

- Real-space formulation and finite-element approximation → Nonperiodic, unstructured, OFDFT calculations
- However, calculations are still expensive:
  9x9x9 cluster = 3730 atoms required 10,000 CPU hours!
- Objective: Model reduction such that:
  - *The coarse graining is unstructured and adaptive*
  - *OFDFT is the sole input to the model (no spurious physics)*
  - *Reduced solutions → all-atom OFDFT in fully-resolved limit*
- General approach (QC-OFDFT):
  - *Derive a real space, nonperiodic, formulation of OFDFT* √
  - *Effect a quasi-continuum[1] (QC) model reduction*
- **Challenge**: Subatomic oscillations and lattice scale modulations of electron density and electrostatic potential

[1]Tadmor, Ortiz and Phillips, *Phil. Mag.*, **A73** (1996) 1529.

QC/OFDFT – Multigrid hierarchy

- Nuclear positions:

$$\boldsymbol{R} \in \mathbb{R}^{3M} \equiv Z$$

- Equilibrium problem:

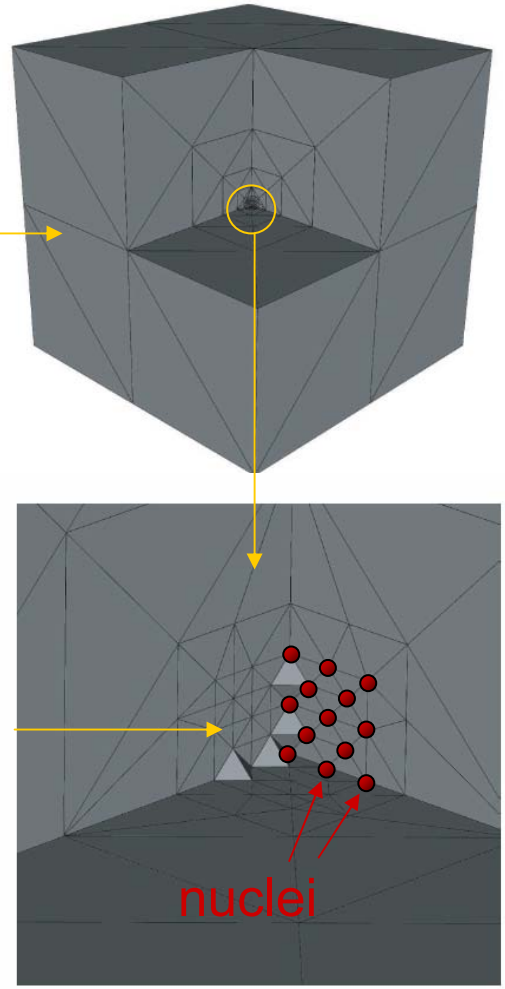
$$\inf_{\boldsymbol{R}\in Z} E_0[\boldsymbol{R}],$$

$$E_0[\boldsymbol{R}] = \inf_u \sup_\phi E[u,\phi]$$

- Reduced problem:

$$\begin{cases} \inf\limits_{\boldsymbol{R}\in Z_h} E_0[\boldsymbol{R}] \\ Z_h = \mathbb{R}^{3M_h},\ M_h \ll M \end{cases}$$

coarse resolution, nuclei in interpolated positions



atomic resolution, nuclei in arbitrary positions

Coarse grid

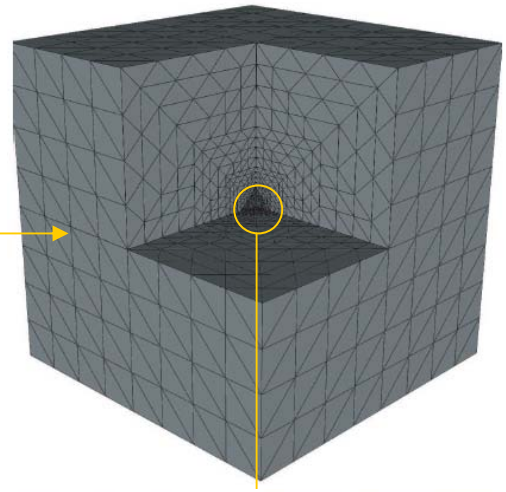
QC/OFDFT – Multigrid hierarchy

- Predictor/corrector:

$$\rho_h = \rho_h^0 + \rho_h^c$$
$$\phi_h = \phi_h^0 + \phi_h^c$$

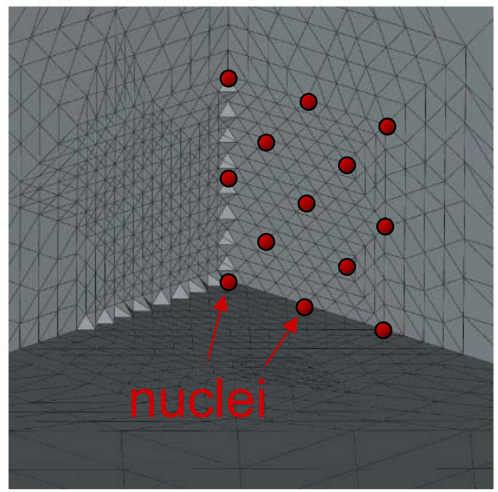
predictor corrector

coarse resolution, slowly-varying correction[1]



- Predictor: Local Cauchy-Born field (LQC/OFDFT)[2] defined everywhere
- Corrector: Interpolated on intermediate grid

subatomic resolution, rapidly-varying correction



Intermediate grid

[1]Blanc, LeBris, Lions, *ARMA*, **164** (2002) 341

[2]Fago el al., *Phys. Rev.*, **B70** (2004) 100102(R)

QC/OFDFT – Multigrid hierarchy

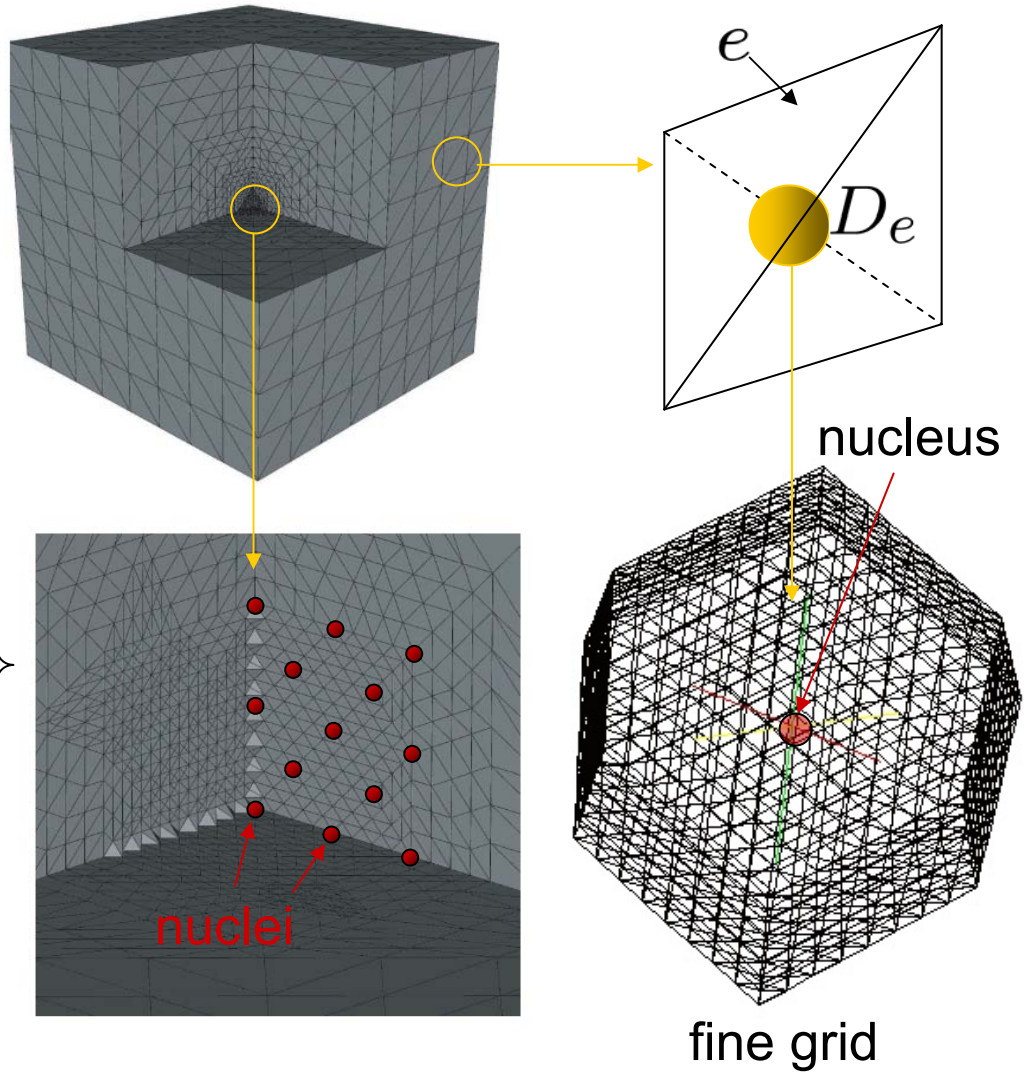
- Element quadrature:

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

- Quadrature domain:

$$D_e = \min \left\{ \begin{array}{l} \text{atomic cell} \\ \text{element } e \end{array} \right\}$$

- $\langle f \rangle_{D_e}$ evaluated using a fine grid over D_e



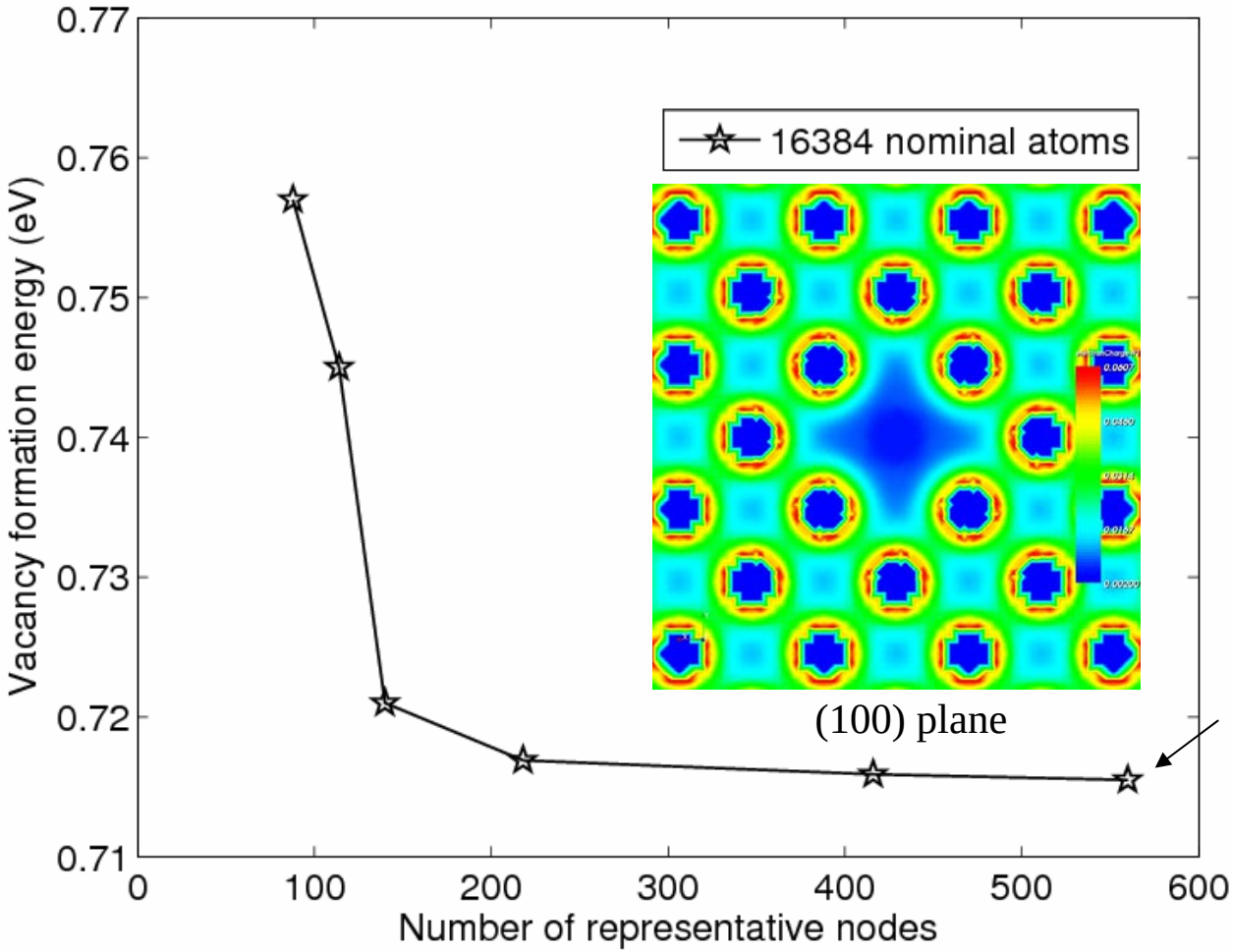
QC/OFDFT – Attributes

- The overall complexity of the method is set by the size of the intermediate mesh (interpolation of ρ_h, φ_h)
- All approximations are numerical: interpolation of fields, numerical quadrature
- No spurious physics is introduced: OFDFT is the sole input to the model
- A converged solution obtained by this scheme is a solution of OFDFT
- Coarse graining is seamless, unstructured, adaptive: no periodicity, no interfaces
- Fully-resolved OFDFT and continuum finite elasticity are obtained as extreme limits
- Million-atom OFDFT calculations possible at no significant loss of accuracy

QC/OFDFT convergence – Al vacancy

- Good test case:
  - *Both electronic core and long-range electrostatic, elastic effects are important*
  - *Vacancy formation energies are used as benchmarks for orbital free kinetic energy functionals*
- TFW + LDA, Heine-Abarenkov pseudo-potentialDirchlet boundary conditions on correction fields: all fields approach bulk values at the boundary
- Sample sizes nominally containing 4, 32, 256, 2048, 16348, and one million atoms
- Million-atom sample: ~1500 representative atoms and ~450,000 elements in the *electronic-mesh*
- Optimal mesh gradation $h(r) \sim r^{6/5}$ (*a priori*)

QC/OFDFT convergence – Al vacancy



4% of nuclei accounted for in calculation at no loss of accuracy!

Convergence of QC reduction

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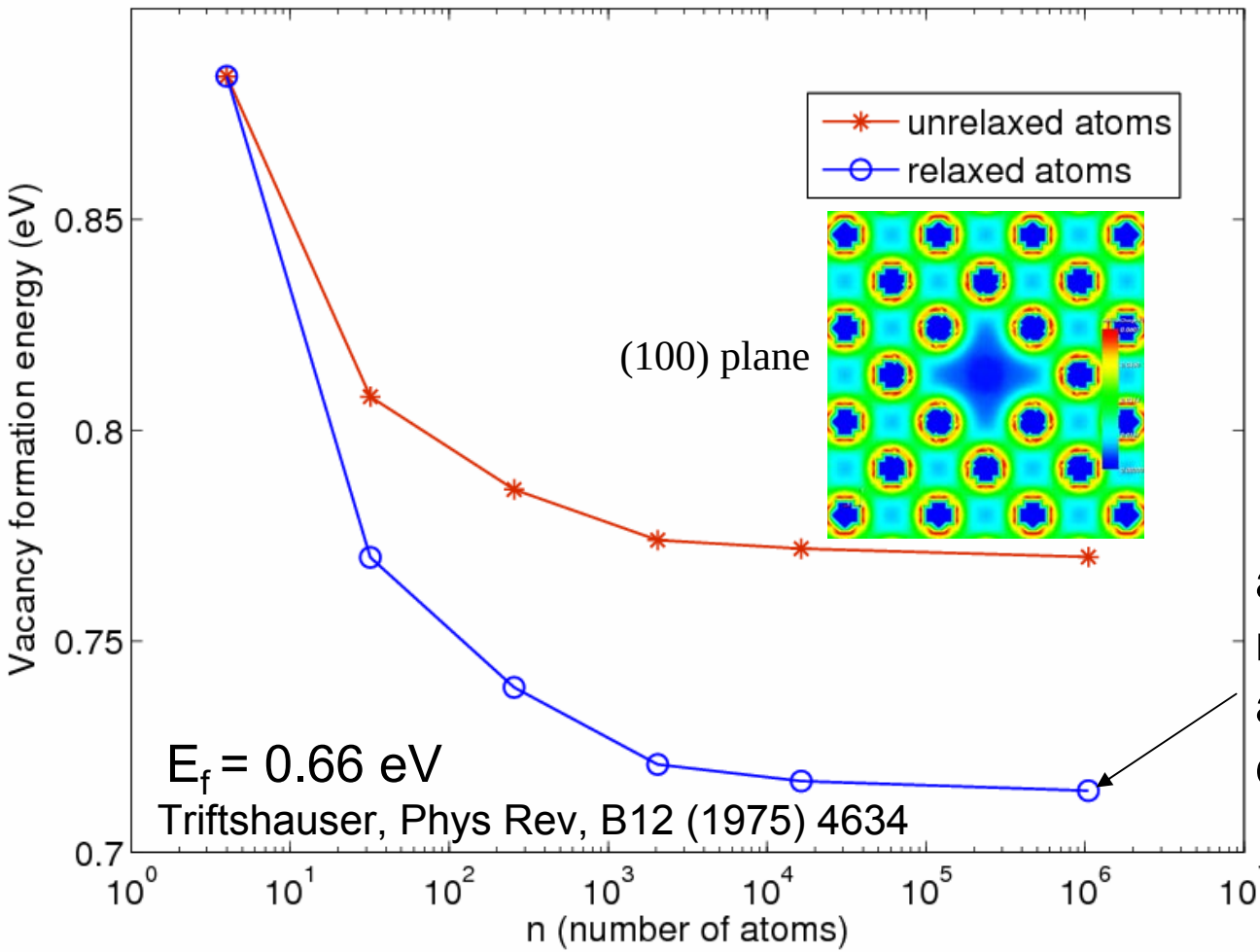
QC/OFDFT convergence – Al vacancy



1,000,000 atoms required to approach bulk conditions!

Convergence with material sample size

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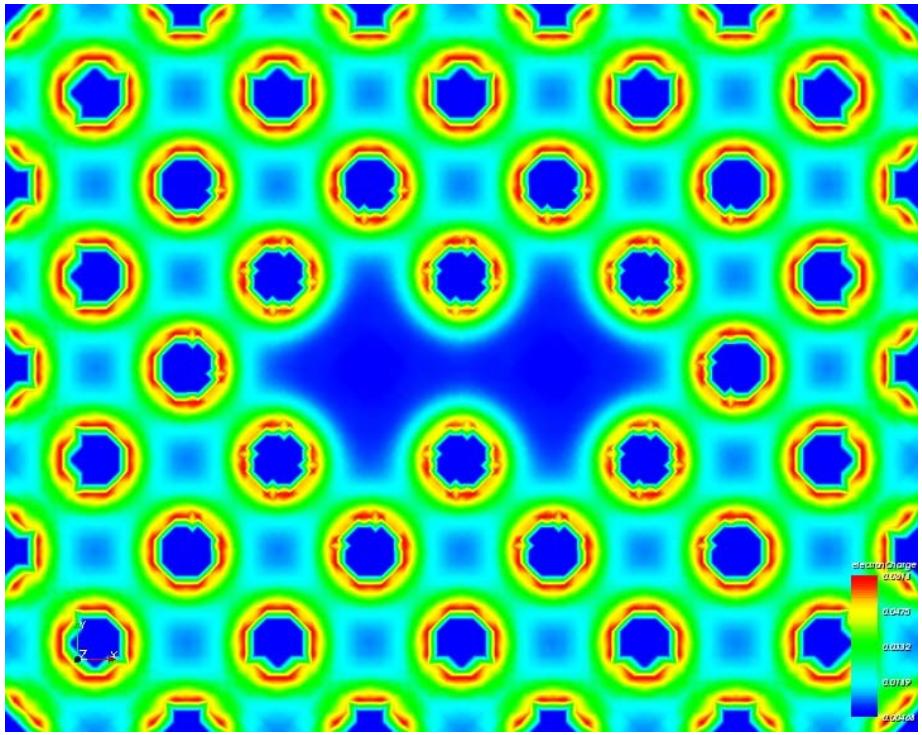
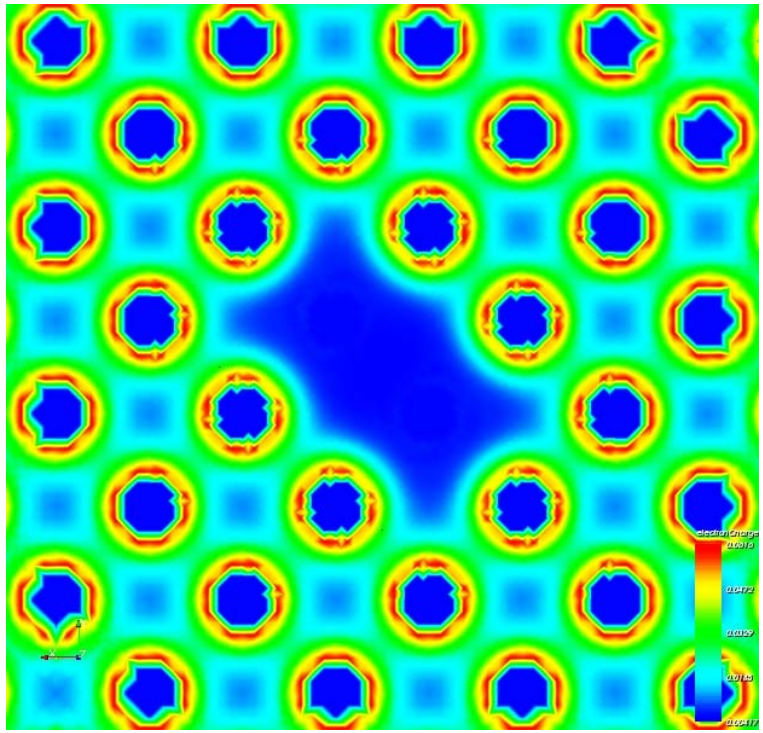
QC/OFDFT convergence – Al vacancy

- QC reduction converges rapidly:
  - *16,384-atom sample: ~200 representative atoms required for ostensibly converged vacancy formation energy.*
  - *1,000,000-atom sample: ~1,017 representative atoms and ~ 450,000 electron-density nodes give vacancy formation energy within ~0.01 eV of converged value*
- Vacancies have long-range elastic field and convergence with respect to sample size is slow: ~1,000,000 atom sample required to attain single-vacancy formation energy!
- What can we learn from large cell sizes?
  - *Case study 1: Di-vacancies in aluminum*
  - *Case studey 2: Prismatic loops in aluminum*

Case study 1 – Di-vacancies in Al



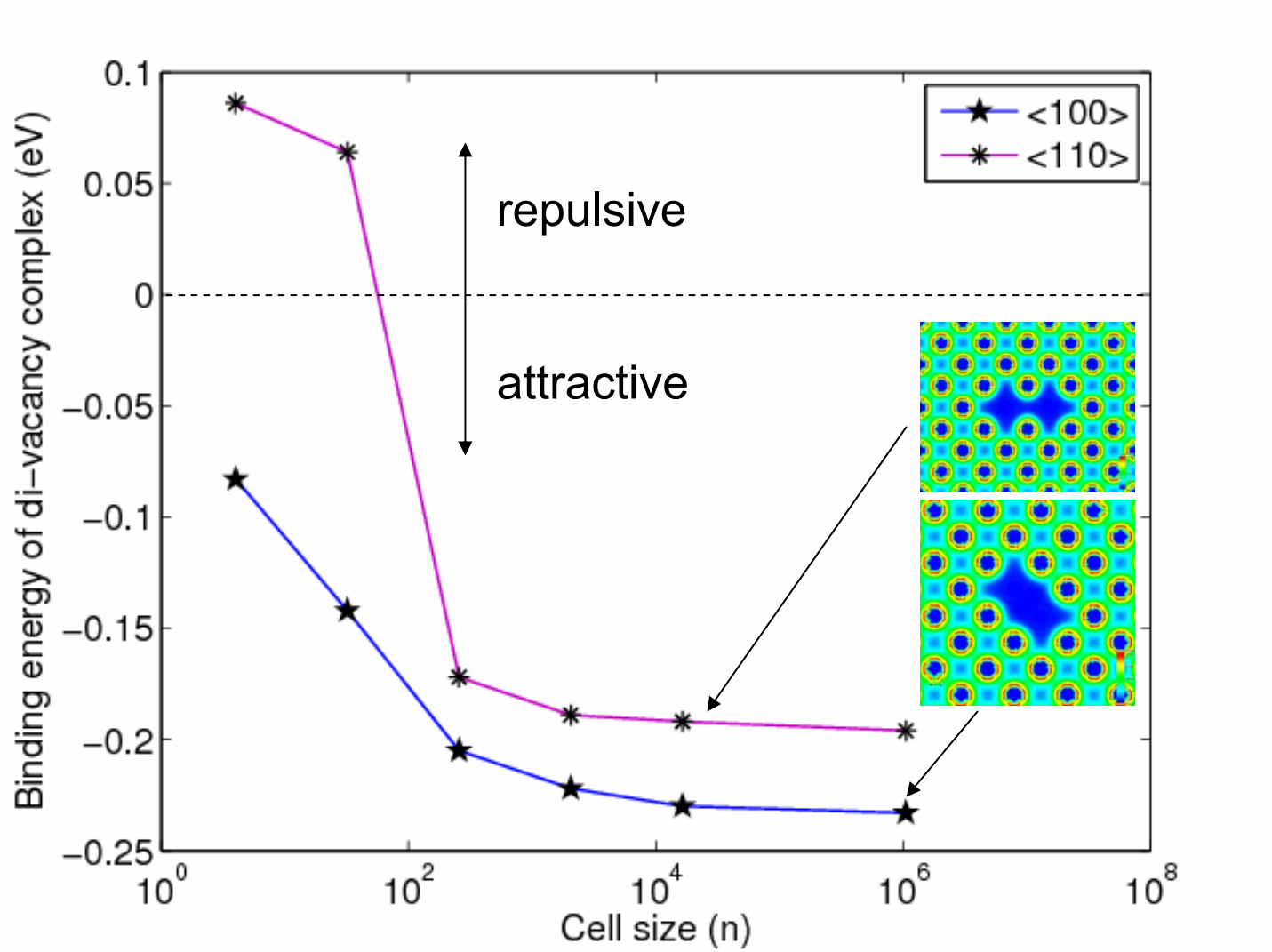
Di-vacancy along <100>



Di-vacancy along <110>

Core electronic structure

Case study 1 – Di-vacancies in Al



Binding energy *vs.* material sample size

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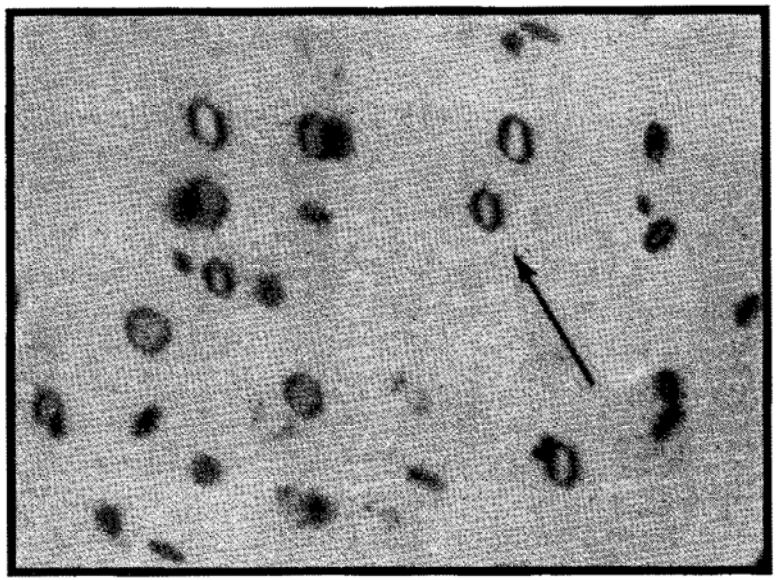
Case study 1 – Di-vacancies in Al

- Calculations evince a strong cell-size effect: binding energy changes from repulsive at large concentrations to attractive at bulk concentrations
- Sample sizes containing > 1,000,000 atoms must be used in order to approach bulk conditions
- Di-vacancy binding energies are computed to be:

  -0.19 eV for <110> di-vacancy; -0.23 eV for <100> di-vacancy
- Agreement with experimental values: -0.2 to -0.3 eV (Ehrhart et al., 1991; Hehenkamp, 1994)
- Small-cell size values consistent with previous DFT calculations (Carling et al., 2000; Uesugi et. al, 2003) :

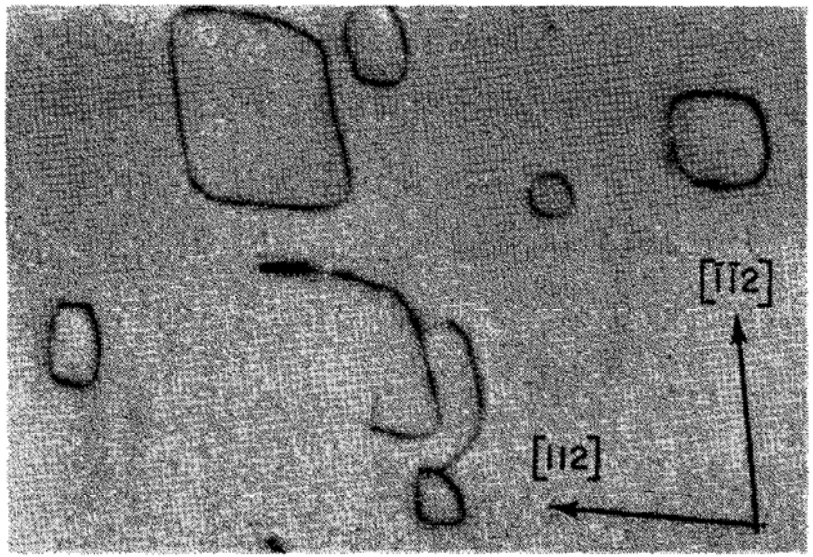
  +0.05 eV for <110> di-vacancy; -0.04 eV for <100> di-vacancy
- No discrepancy between theory and experiment, only strong vacancy-concentration effect!

Case study 2 – Prismatic loops in Al



Prismatic dislocation loops formed by condensation of vacancies in quenched aluminum

Kulhmann-Wilsdorff and Kuhlmann,
J. Appl. Phys., **31** (1960) 516.

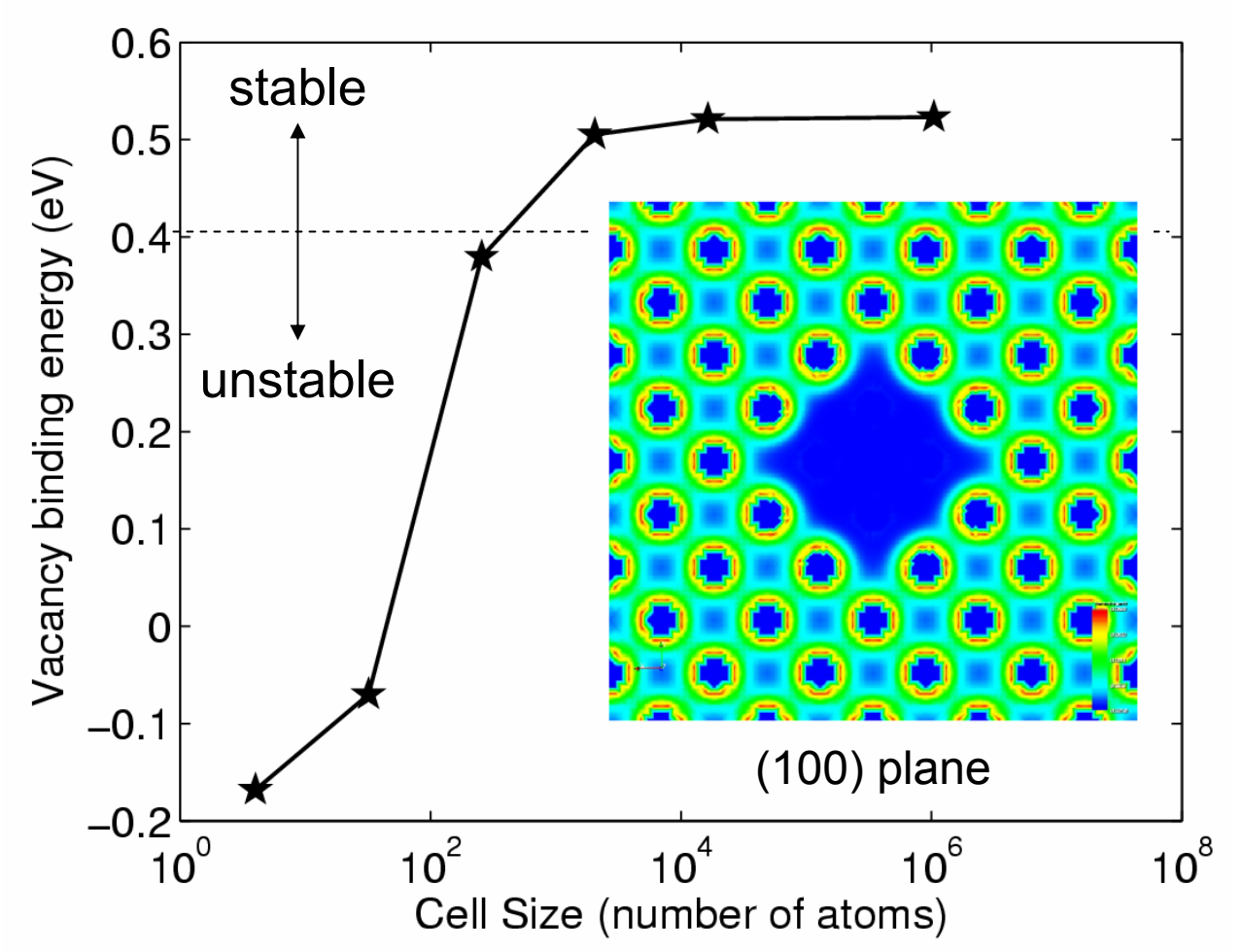


Prismatic dislocation loops formed by condensation of vacancies in quenched Al-05%Mg

Takamura and Greensfield,
J. Appl. Phys., **33** (1961) 247.

- Prismatic dislocation loops also in irradiated materials
- Loops smaller than 50 nm undetectable: Nucleation mechanism? Vacancy condensation?

Case study 2 – Prismatic loops in Al

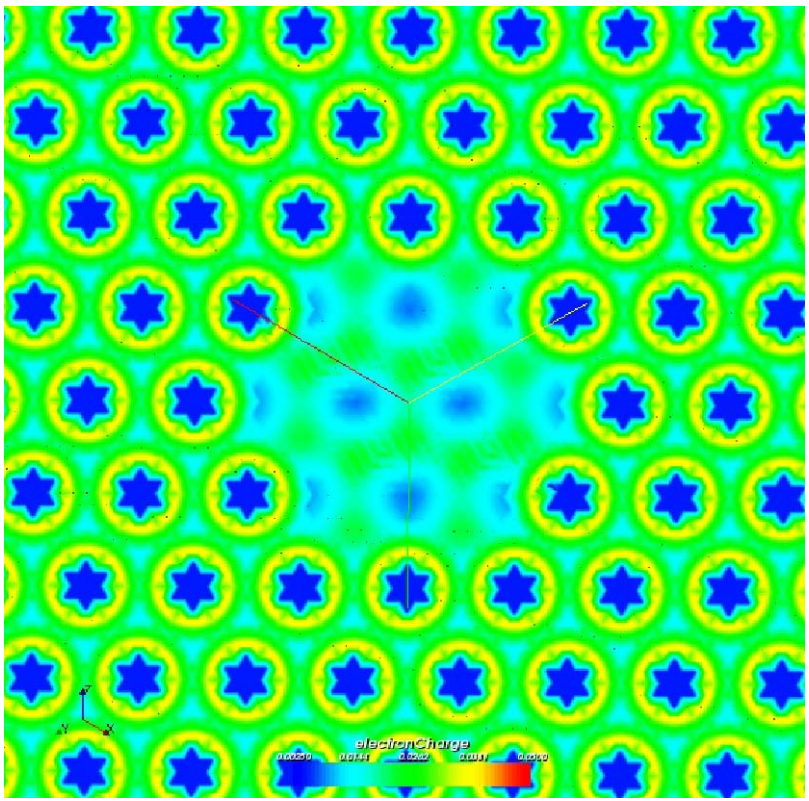


Quad-vacancy binding energy *vs.* material sample size

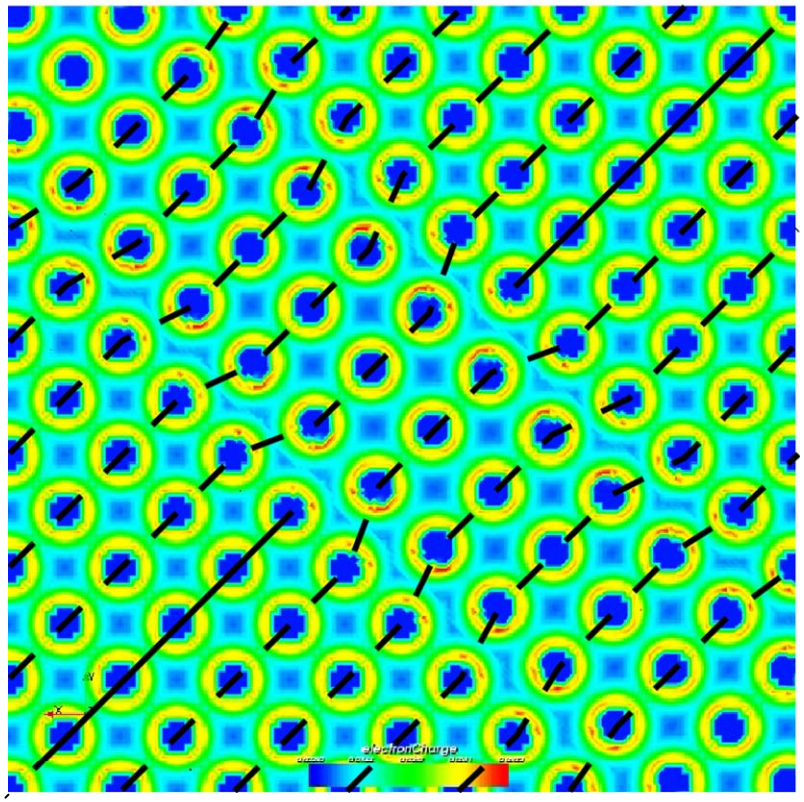
Michael Ortiz
BAMC 04/07

Case study 2 – Prismatic loops in Al

(111)



(001)



(111)

Non-collapsed configuration

Binding energy = -0.88 eV

1/2<110> prismatic loop

Binding energy = -1.57 eV

Stability of hepta-vacancy

Case study 2 – Prismatic loops in Al

- Growth of planar vacancy clusters is predicted to be energetically favorable for sufficiently small concentrations
- Elucidation of relevant conditions requires large cell-size calculations
- Vacancy clustering and subsequent collapse is a possible mechanism for formation of prismatic dislocation loops
- Prismatic loops as small as those formed from hepta-vacancies are stable!

Concluding remarks

- Models must be predictive of material behavior, especially under extreme difficult-to-test conditions
- This requires:
  - *physics-based models (Kohn-Sham DFT!)*
  - *Approximations that do not compromise the physics and that introduce controllable errors and the possibility of convergence*
- QC/OFDFT:
  - *Real-space formulation of OFDFT*
  - *Unstructured, adaptive, multi-grid finite-element discretization*
  - *Numerical quadrature*
- Behavior of material samples may change radically with size (concentration): **Need electronic structure calculations at macroscopic scales!**