# Quasi-Continuum Density Functional Theory

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# Introduction (QM2CM)

- Problems arising in the study of defective crystals are inherently *multiscale*
- Need to resolve simultaneously:
  - *Electronic structure of defect cores*
  - *Long-ran* ... *efect conce*
- Typ ... nents:
  - *Va*
  - *Dislocatio* ... m
  - *Domain walls: cell size* ~ 1 μm
  - *Grain boundaries: cell size* ~ 20 μm
- Physically relevant cell sizes are far larger than can be analyzed by conventional computational chemistry
- Need to coarse-grain quantum mechanics!

*Fundamental challenge: Quantum mechanical calculations at macroscopic scales!*

# 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-$\lambda$W) KE:

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

- Exchange-correlation energy (LDA):

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

# Orbital-Free Density Functional Theory

- Total energy functional:

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

f

*'Garden-variety' functionals amenable to standard finite-element discretization!*

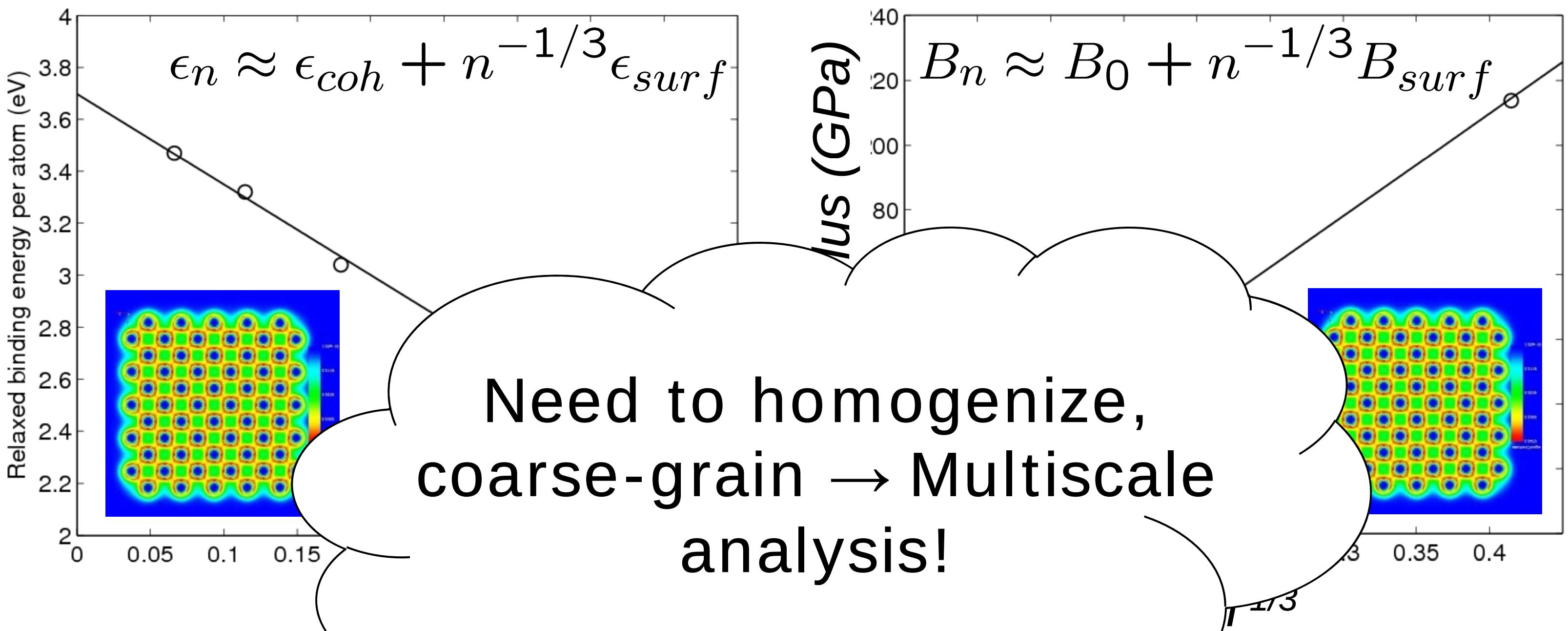
- Loca $L[\rho, \phi, \boldsymbol{R}]$

$(\mathbb{R}^3)$

$$L[\rho, \phi, \boldsymbol{R}] = \int \epsilon_{loc}($$

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

# OFDFT – Coarse-graining

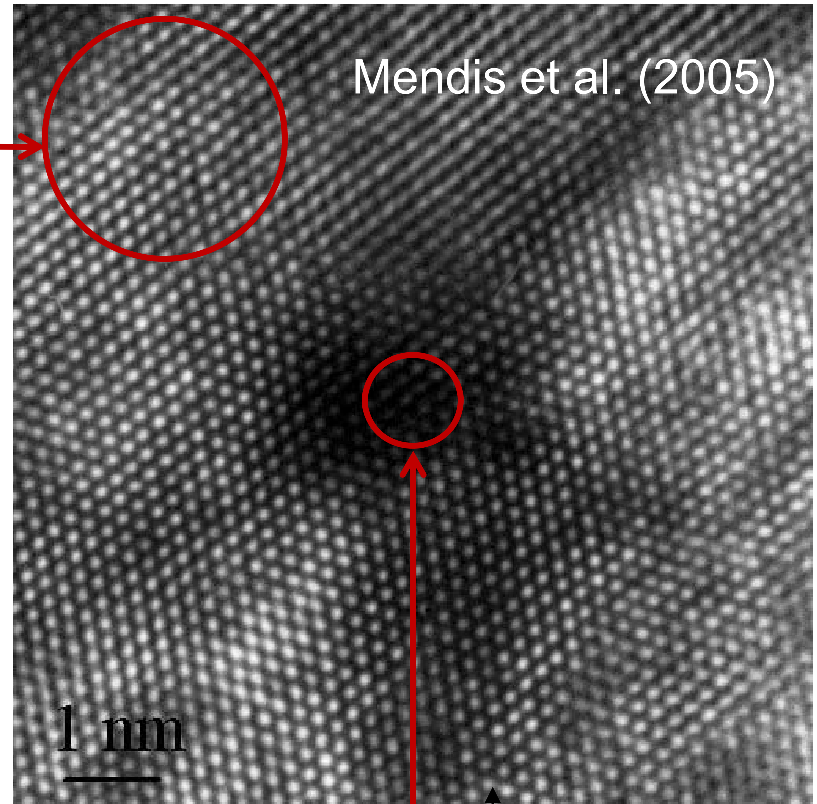



Need to homogenize, coarse-grain → Multiscale analysis!

- Real-space formulation … te-element approximation → Nonperiodic, unstructured, OFDFT calculations
- However, calculations are still expensive: 9x9x9 cluster = 3730 atoms required 10,000 CPU hours!

# Defective crystals – The bridge

- 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

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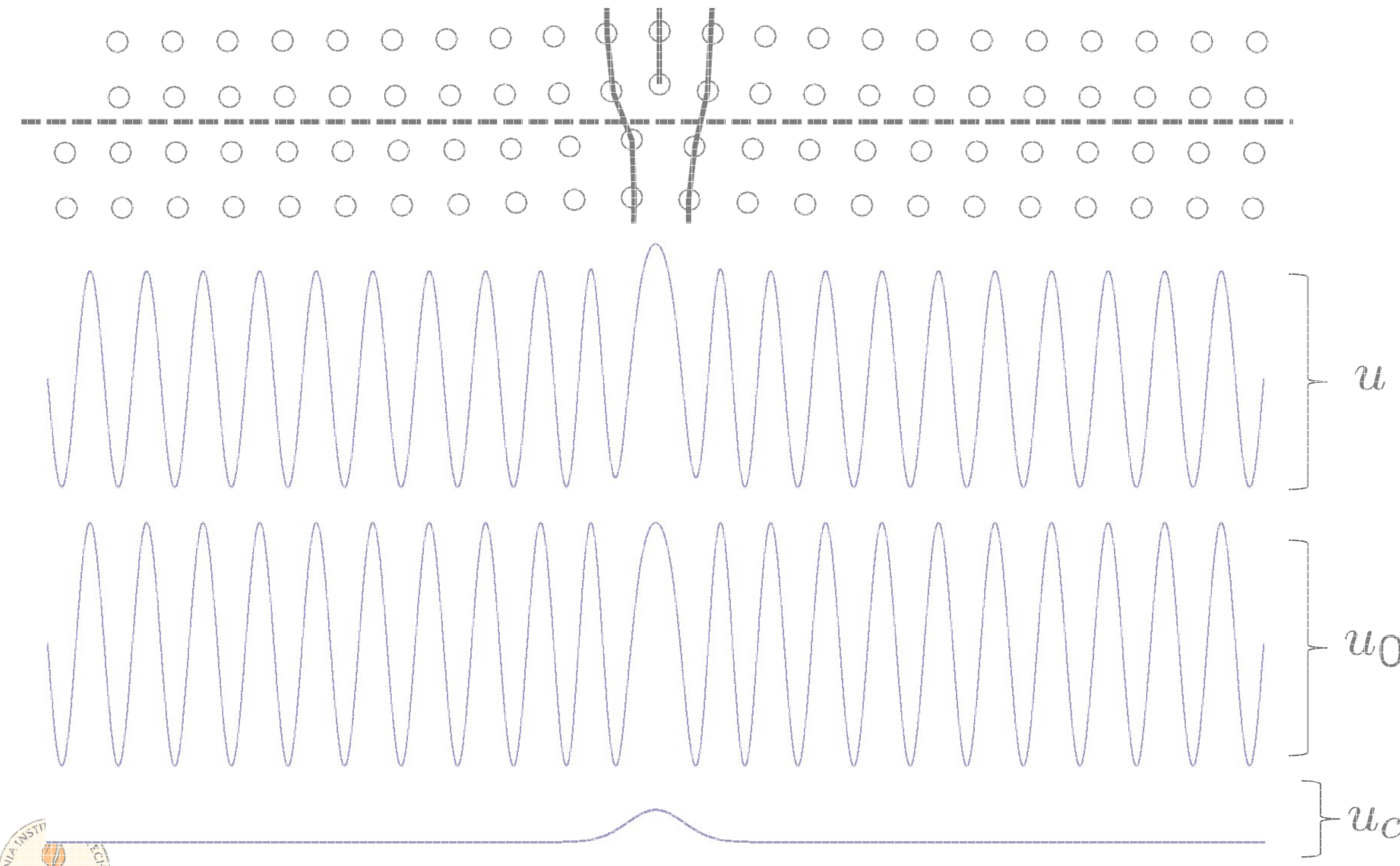
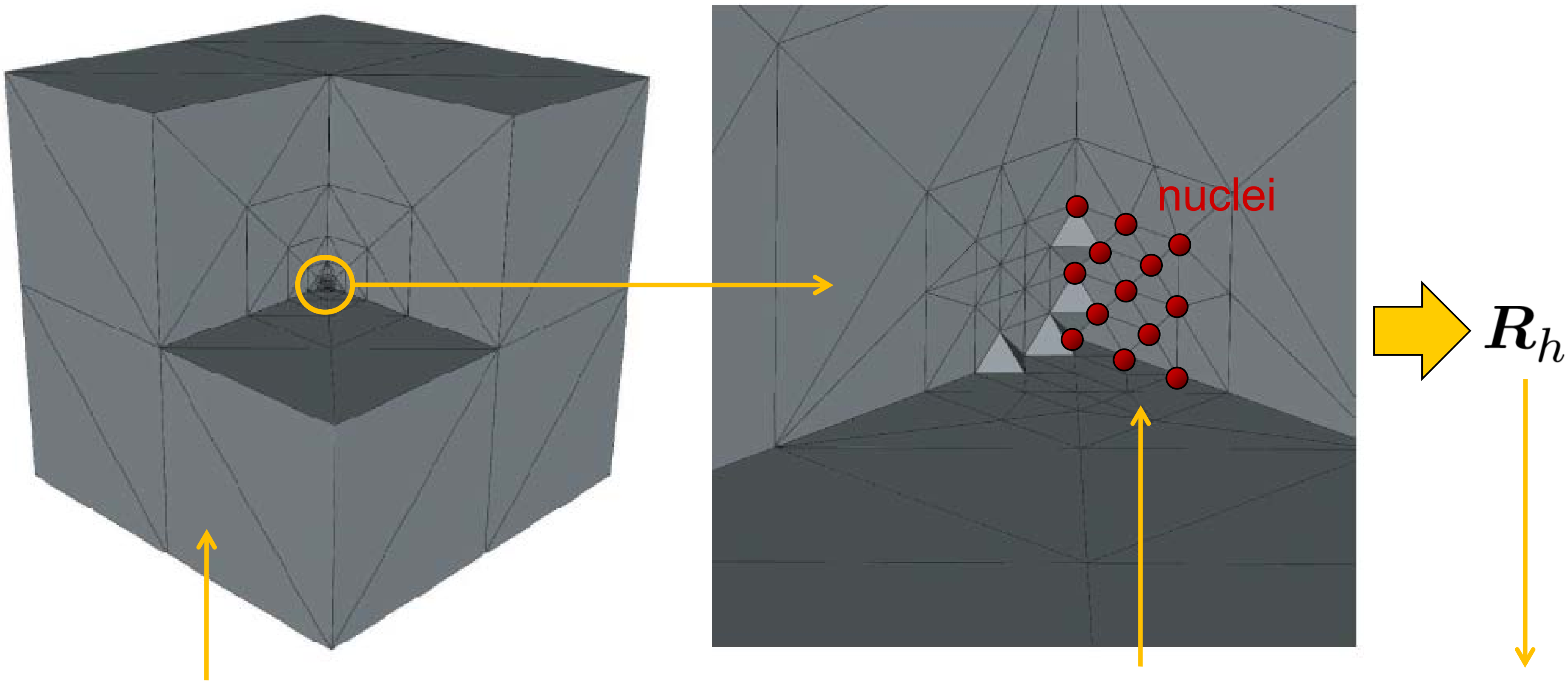
# Defective crystals – The bridge




$$u \sim u_0 + u_c$$

# QC/OFDFT – Multiscale hierarchy

- Quasi-continuum: $\boldsymbol{R} \to \boldsymbol{R}_h \in \mathbb{R}^{3N_h}, \quad N_h \ll N$



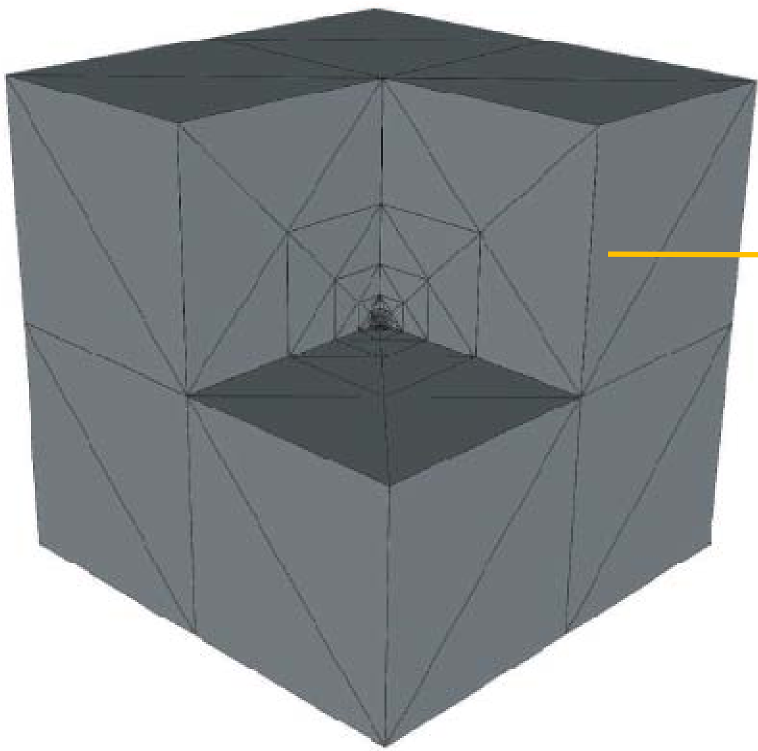

coarse resolution, nuclei in interpolated positions

atomic resolution, nuclei in arbitrary positions

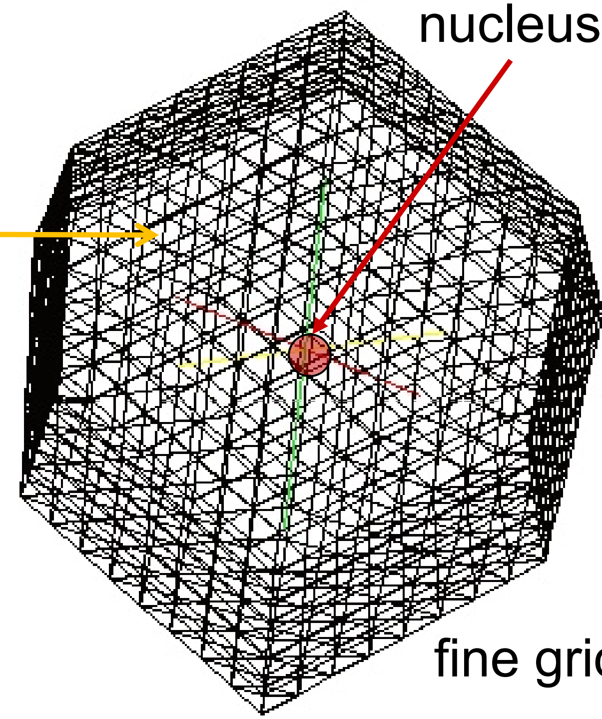
relaxed nuclei

# QC/OFDFT – Multiscale hierarchy

- Each element represents affinely deformed lattice



QC mesh, nuclei in interpolated positions




unit cell calculation, affinely deformed lattice

$$\begin{cases} \rho_h^0 \\ \phi_h^0 \end{cases}$$

Cauchy-Born predictor

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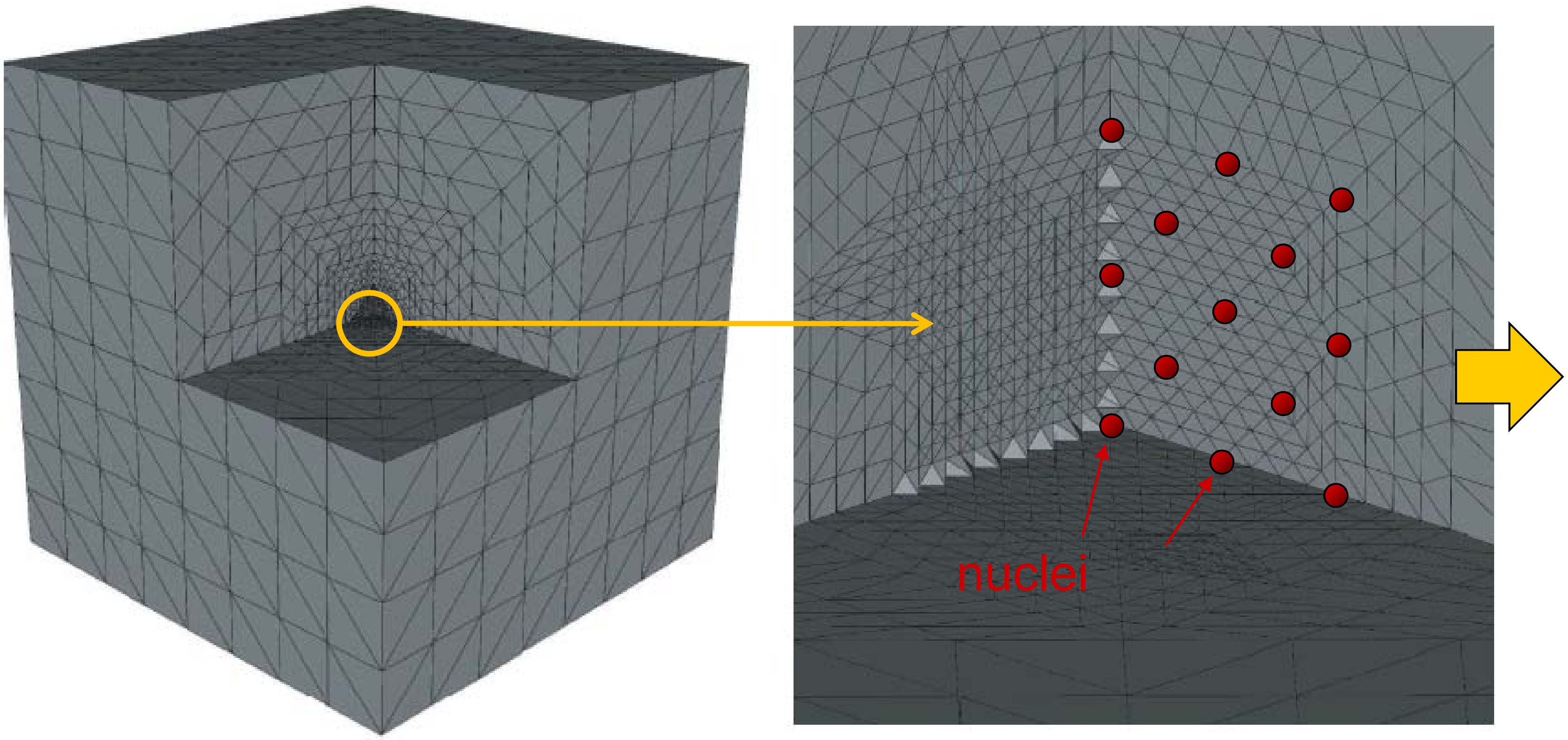
# QC/OFDFT – Multiscale hierarchy

- Localized correction to Cauchy-Born predictor:




$$\begin{cases} \rho_h^c \\ \phi_h^c \end{cases}$$

coarse mesh
macroscopic resolution

fine mesh
subatomic resolution

localized
correction

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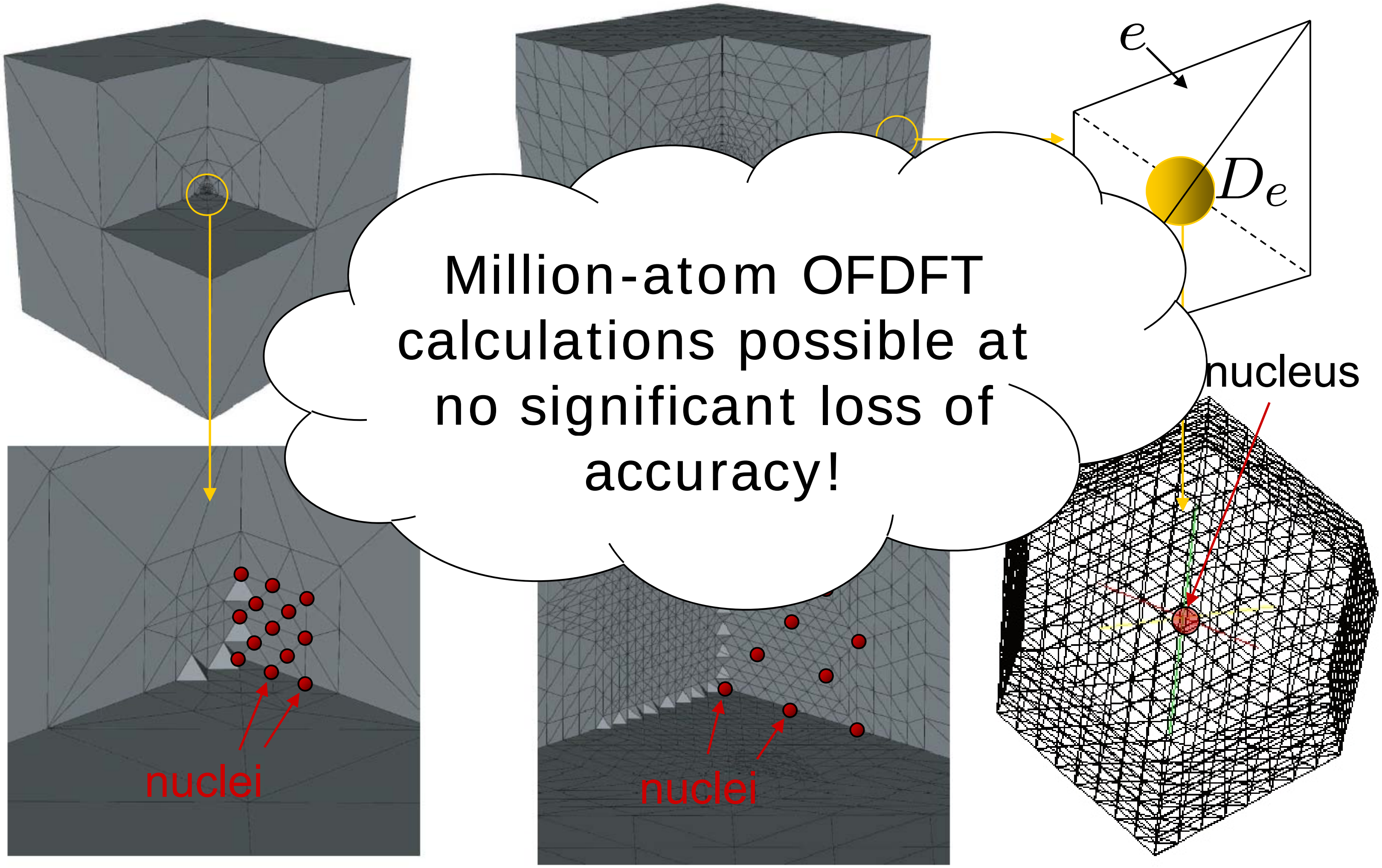
# QC/OFDFT – Multiscale hierarchy

Quasi-continuum | Corrector | Predictor/Quadrature




Million-atom OFDFT calculations possible at no significant loss of accuracy!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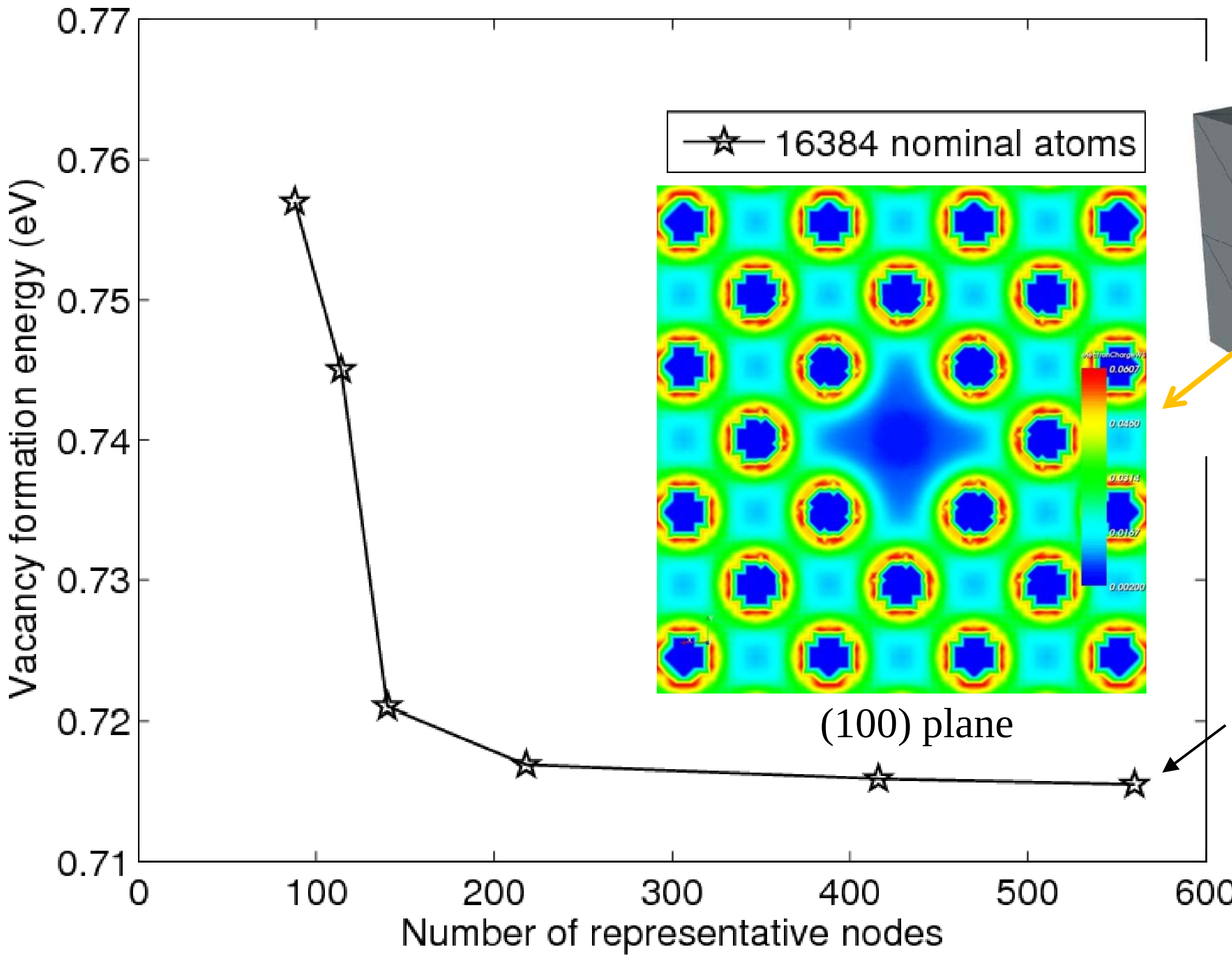
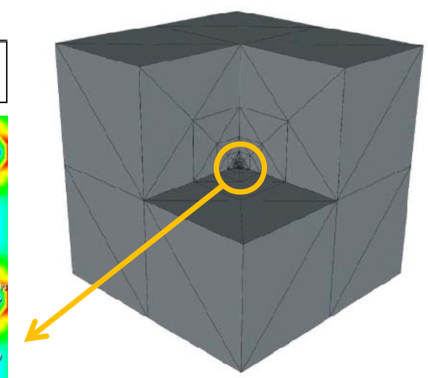
# QC/OFDFT convergence – Al vacancy

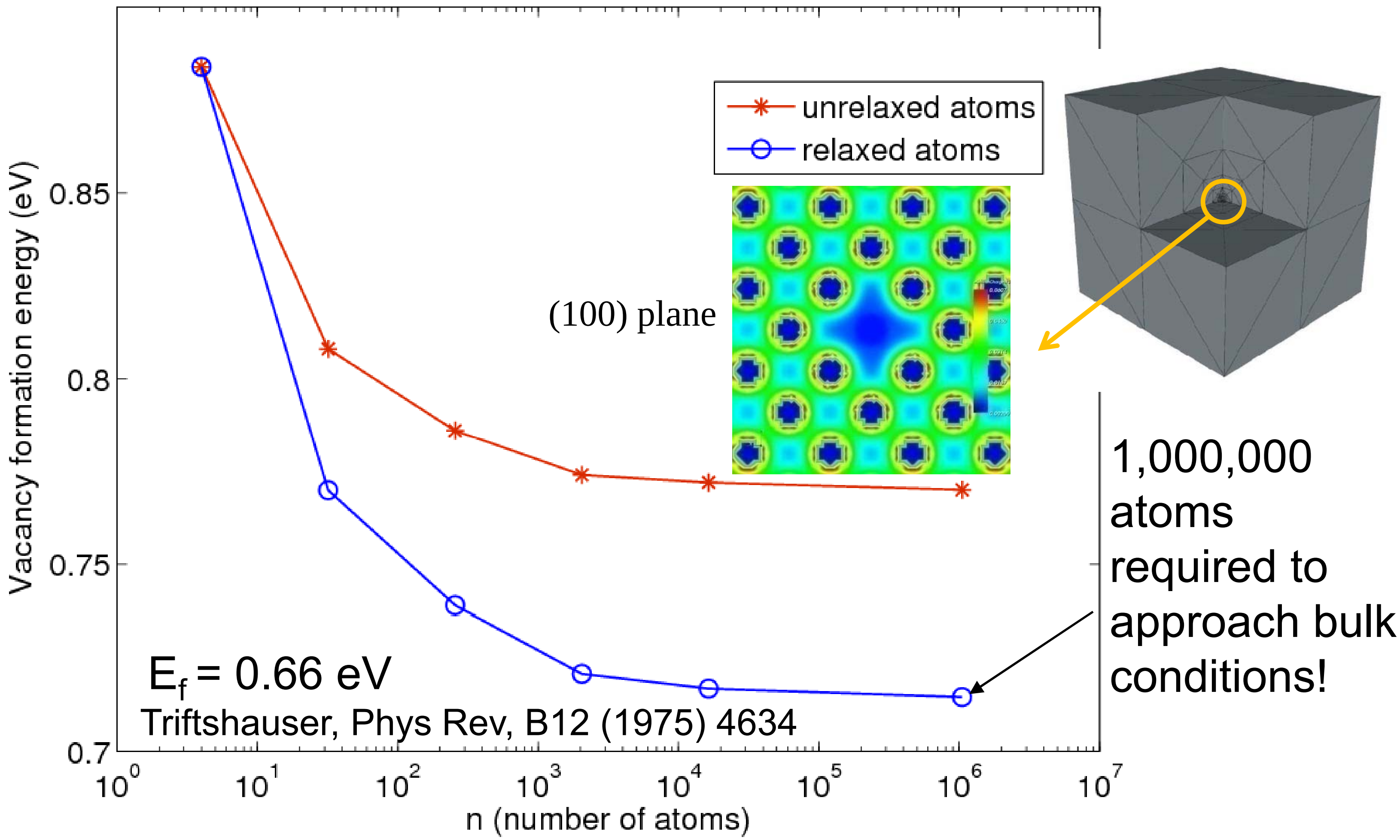


4% of nuclei accounted for in calculation at no loss of accuracy!

Convergence of multiscale scheme

# Cell-size dependence – Al vacancy




Convergence with material sample size

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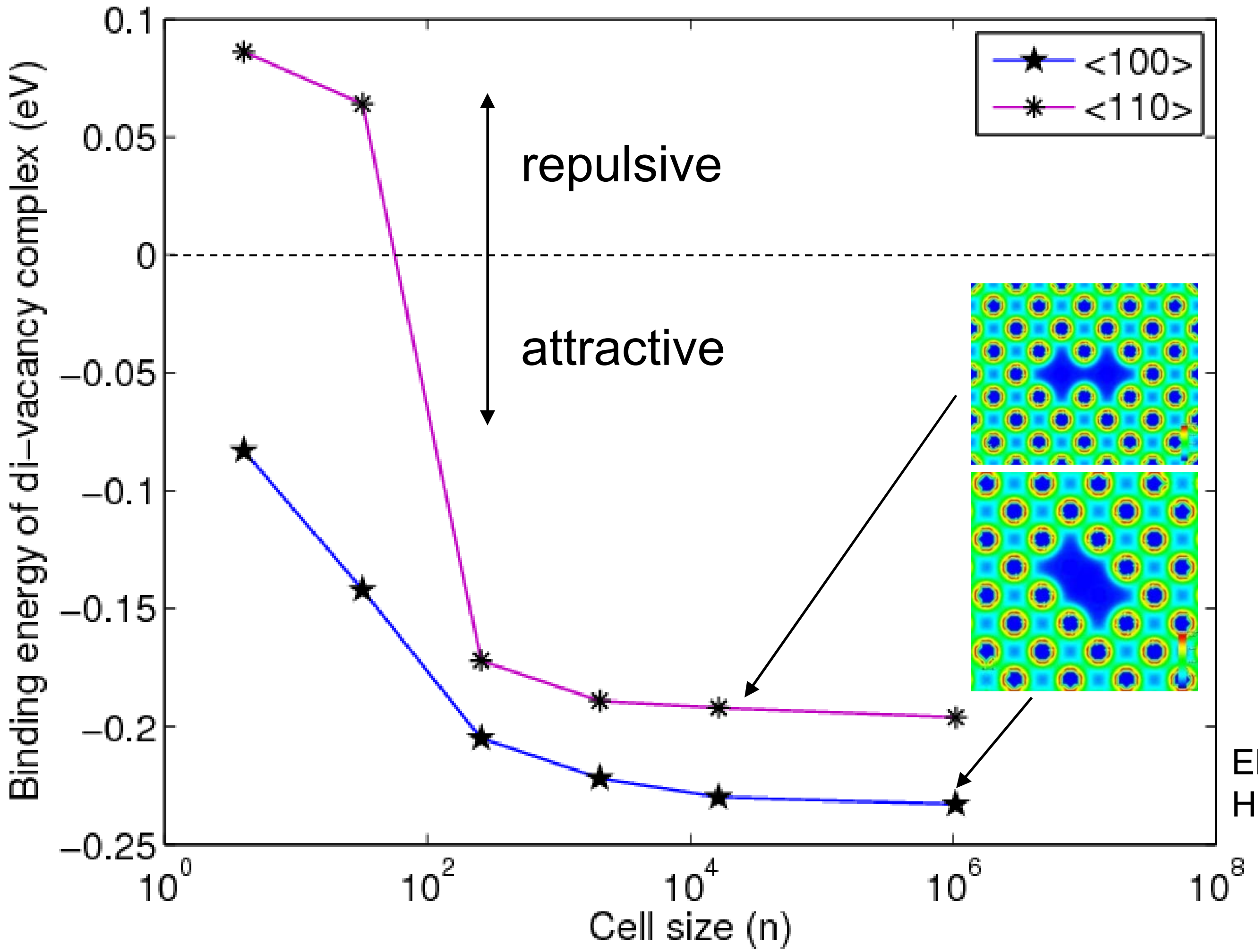
# Case study 1 – Di-vacancies in Al




$E_f$ =
-0.2 to
-0.3 eV

Ehrhart et al., 1991
Hehenkamp, 1994

Binding energy *vs.* material sample size

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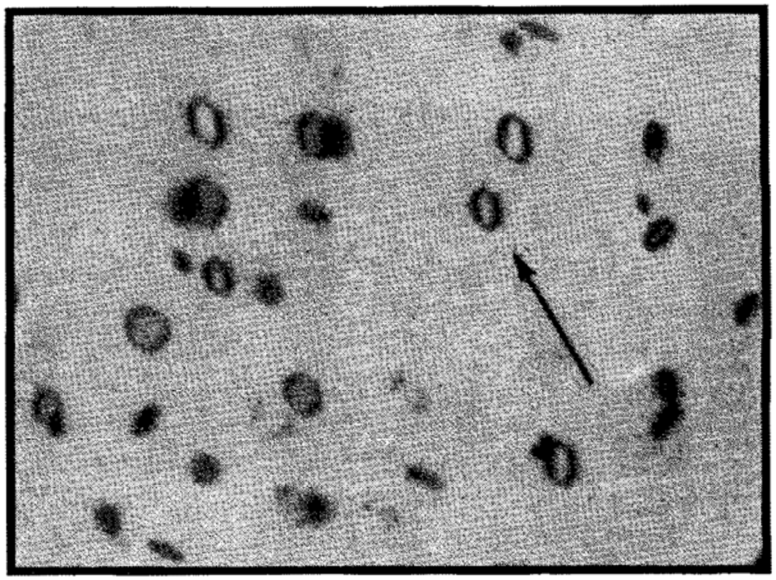
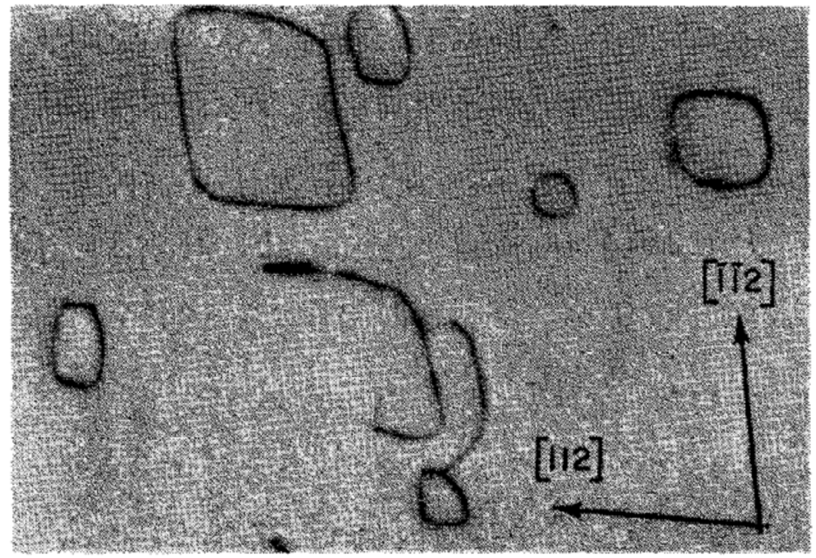
# Case study 2 – Prismatic loops in Al



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?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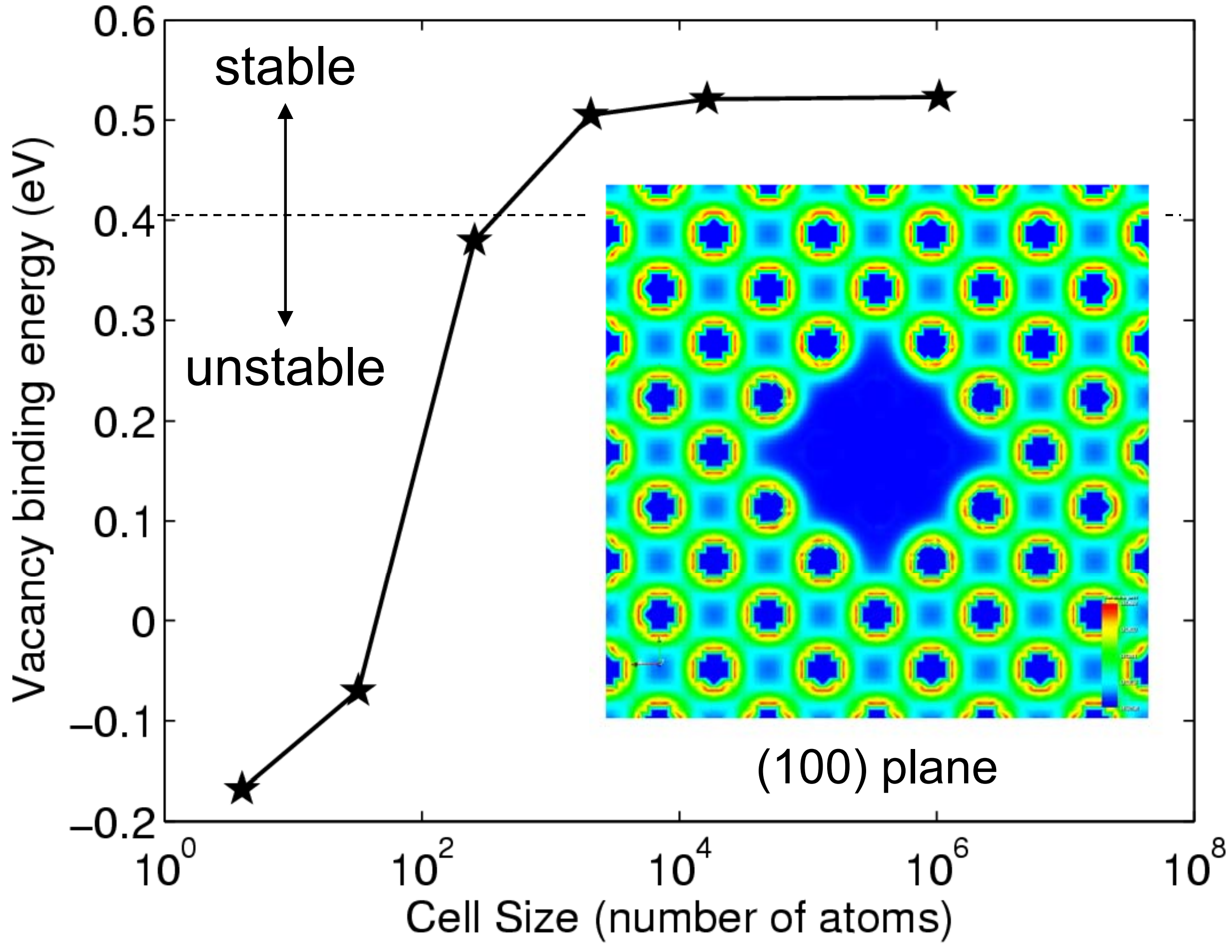
# Case study 2 – Prismatic loops in Al




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

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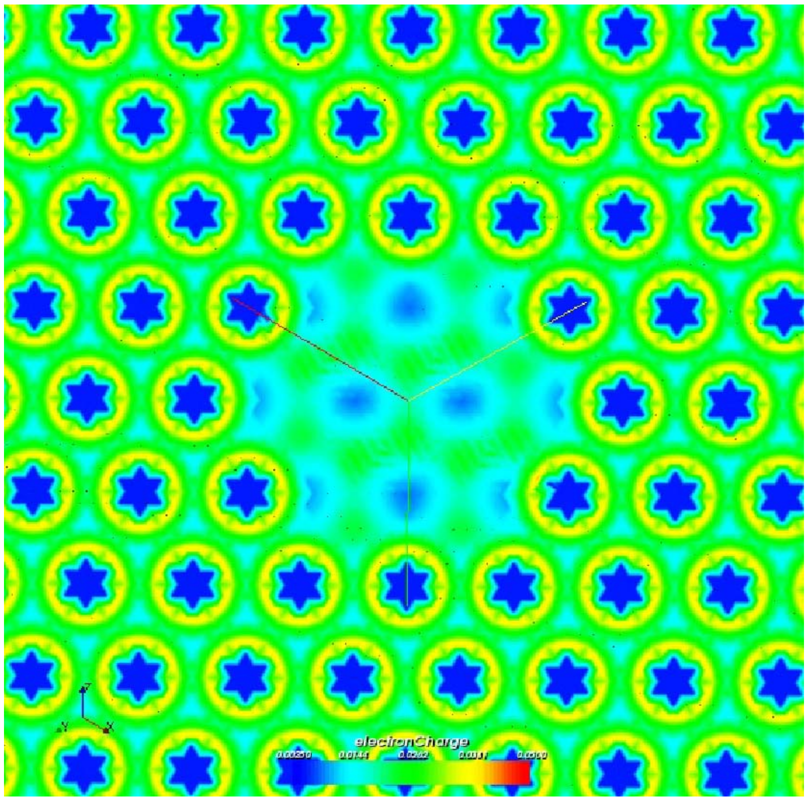
# Case study 2 – Prismatic loops in Al

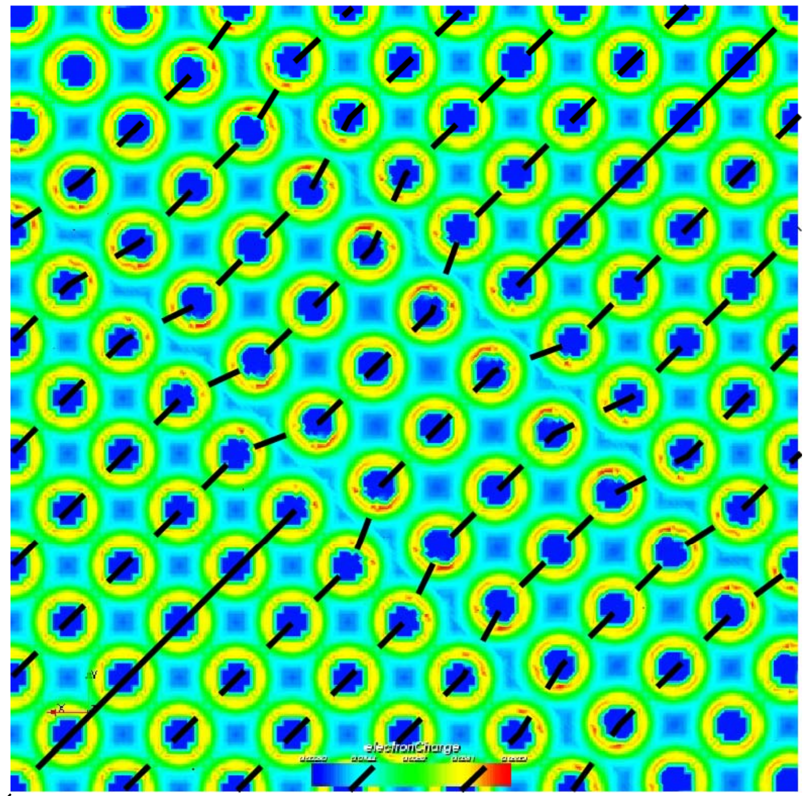
(111)



Non-collapsed configuration

Binding energy = -0.88 eV

(001)



(111)

1/2<110> prismatic loop

Binding energy = -1.57 eV

Stability of hepta-vacancy

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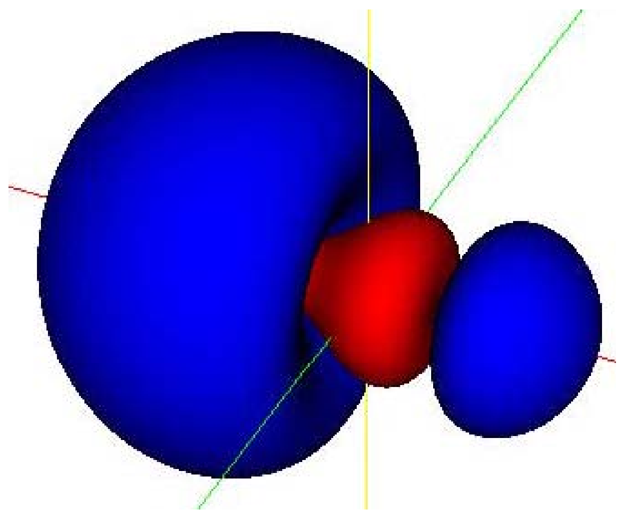
# Concluding remarks

- Behavior of material samples may change radically with size (concentration): Small samples may not be representative of bulk behavior
- Need electronic structure calculations at macroscopic scales: Quasi-continuum OFDFT (QC/OFDFT)
- Outlook: Application to general materials requires extension to Kohn-Sham DFT…



σ2px orbital in CO