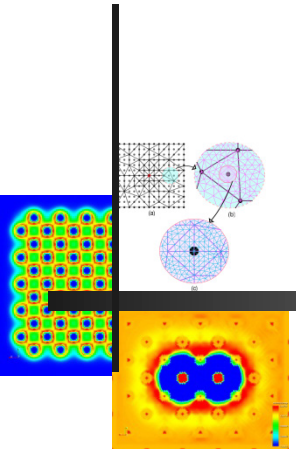

Electronic structure calculations at macroscopic scales

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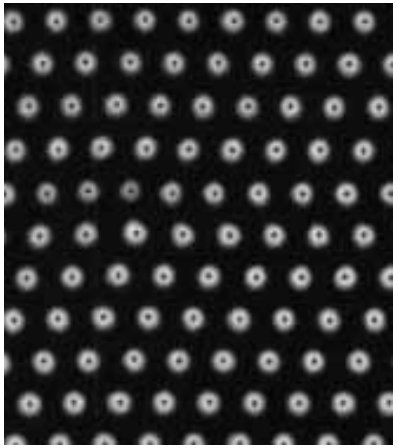
Funding: NSF, AFOSR, ARO, XSESDE

Defective Crystals

- Defects play a crucial role in influencing a variety of materials properties – mechanical, electronic, optical, chemical
- Dislocations



TEM image of dislocation partial
T.J. Balk, K.J. Hemker, Phil. Mag. A, 2001

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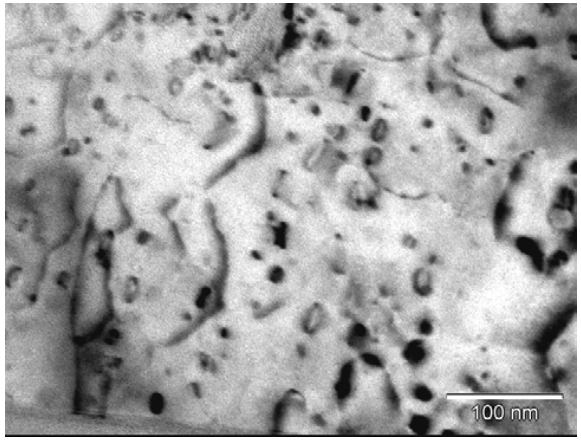
Metal Plasticity – Renders the strength of materials to 1/1000 its theoretical strength

Vacancies/Interstitials



Prismatic loops formed from vacancies,
Giess et. al, Microsc Microanal, 2005

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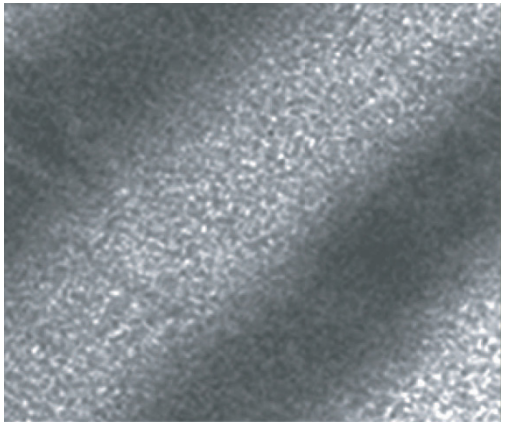
Creep, Spall, Ageing, hardening due to radiation

Interfaces/Surfaces



TEM image of Ni-Al interface,
Mann et.al, J. Appl. Phys. 1997

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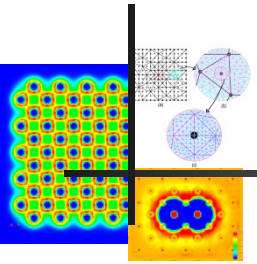
Phase stability, Energetics, Diffusion mediation, defect sources and sinks

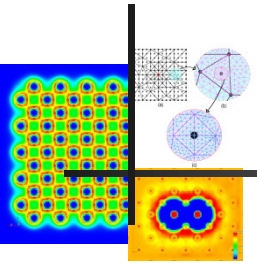


Defective crystals: The challenge

- The energetics of defects: (i) core-energy; (ii) elastic energy
- The core of a defect is governed by electronic structure – need electronic structure calculations!
- Defects result in a vast span of *interacting* length scales
  - Electronic structure of the core (10^{-12} m)
  - Complex rearrangements of atoms around the core (10^{-9} m)
  - Long ranged elastic effects (10^{-6} m)

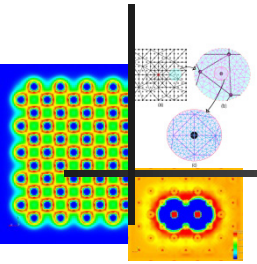
  Realistic defect concentration in materials is parts per million!

  But need single physics at all length scales! - No patching, seamless description
- Challenge : Need electronic structure calculations at macroscopic scale! (10^6 atoms and beyond)
- Idea: Systematic coarse-graining using adaptive numerical methods



Outline

- Motivation
- Background: electronic structure calculations
- *Orbital-free* density-functional theory (OFDFT)
- Quasi-continuum orbital-free density-functional theory (QC-OFDFT)
- Illustrative studies
  - Nucleation of prismatic dislocation loops
  - Nucleation of vacancies in shocks
  - Dislocation core studies
- Extensions to Kohn-Sham density functional theory (KSDFT)
- Concluding remarks



Quantum Mechanics

- Schrödinger equation - $H\psi = E\psi$

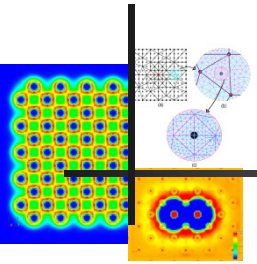
$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{A=1}^{M}\sum_{B=1,B>A}^{M}\frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}$$

$$\psi = \psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N, \mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_M)$$

- Born-Oppenheimer approximation - Classical treatment of atomic nuclei

$$\psi = \psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$$

- Computational complexity - $\psi \in \mathbf{R}^{3N}$!!



Density-functional theory – Kohn-Sham approach

- Ground-state energy is a function of electron-density !! (Kohn & Sham, 1964-65)

$$\langle\psi|H|\psi\rangle \geq E_0 \qquad \text{(Variational statement)}$$

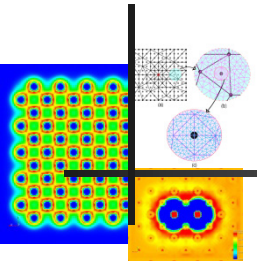
$$\begin{aligned}
E_0 &= \min_{\psi} \langle\psi|T + \frac{1}{2}\sum_i{\sum_j}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V_{ext}(\mathbf{r}_i)|\psi\rangle + E_{zz} \\
&= \min_{\psi} \langle\psi|T + \frac{1}{2}\sum_i{\sum_j}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}|\psi\rangle + \int \rho(\mathbf{r})V_{ext}(\mathbf{r})d\mathbf{r} + E_{zz} \\
&= \min_{\rho} \left\{ \underbrace{\left(\min_{\psi\to\rho} \langle\psi|T + \frac{1}{2}\sum_i{\sum_j}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}|\psi\rangle \right)}_{F(\rho)} + \int \rho(\mathbf{r})V_{ext}(\mathbf{r})d\mathbf{r} \right\} + E_{zz}
\end{aligned}$$

$$F(\rho) = T_s(\rho) + E_H(\rho) + E_{xc}(\rho) \longrightarrow$$

Exchange-correlation functional: Model using LDA, GGA

$\downarrow$

Kinetic energy of non-interacting electrons: Computed from wave-functions of the resulting E-L eqn.



Density-functional theory – *orbital-free* approach

- Model $T_s(\rho)$ ⟶ *Orbital-free* density-functional theory

- Thomas-Fermi (TF)

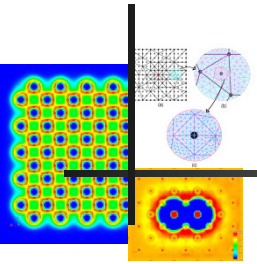
$$T_s(\rho) = \frac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3}(\mathbf{r})d\mathbf{r}$$ (Teller non-binding theorem)

- Thomas-Fermi-Weizsacker (TF-λW)

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

- Kernel-energies - subsequent improvement by Teter (1992), Smargiassi (1994), Carter (1998, 1999).

- *Orbital-free* density-functional theory is a good model for systems with electronic structure close to that of free-electron gas, e.g. aluminum, simple metals.



Orbital-free density-functional theory (OFDFT)

- The OFDFT energy functional is given by,

$$E(\rho, \mathbf{R}) = T_s(\rho) + E_{xc}(\rho) + E_H(\rho) + E_{ext}(\rho, \mathbf{R}) + E_{ZZ}(\mathbf{R})$$

$$T_s(\rho) = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} + \frac{\lambda}{8} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} + T_k[\rho, \rho'; |\mathbf{r} - \mathbf{r}'|];$$

$$E_{xc}(\rho) = \int \epsilon_{xc}(\rho(\mathbf{r}))\rho(\mathbf{r}) d\mathbf{r};$$ Local density approximation (LDA)

Non-local

$$E_H(\rho) = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}';$$

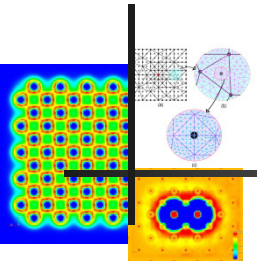
$$E_{ext}(\rho, \mathbf{R}) = \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r}$$

$$= \sum_{I=1}^{M} \int \rho(\mathbf{r}) \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} d\mathbf{r}$$

$$E_{zz}(\mathbf{R}) = \frac{1}{2} \sum_{I=1}^{M} \sum_{J=1, J \neq I}^{M} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|};$$

Classical electrostatic interaction energy :

Computed in Fourier-space (reciprocal-space) in almost all DFT implementations



OFDFT – Real-space formulation

(Gavini et al. JMPS 2007, 669-696)

Non-local

$$E_H(\rho) = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}';$$

$$E_{ext}(\rho,\mathbf{R}) = \sum_{I=1}^{M}\int \frac{\rho(\mathbf{r})Z_I}{|\mathbf{r}-\mathbf{R}_I|}d\mathbf{r};$$

$$E_{zz}(\mathbf{R}) = \frac{1}{2}\sum_{I=1}^{M}\sum_{J=1,J\neq I}^{M}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|};$$

$\frac{1}{|\mathbf{r}-\mathbf{r}'|}$ → Green's function for Poisson's equation

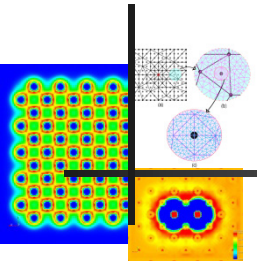
- Electrostatic interactions can be re-written locally as,

$$E_H(\rho)+E_{ext}(\rho,\mathbf{R})+E_{ZZ}(\mathbf{R}) = -\min_{\phi}\left\{\frac{1}{8\pi}\int|\nabla\phi(\mathbf{r})|^2d\mathbf{r}-\int(\rho(\mathbf{r})+b(\mathbf{r};\mathbf{R}))\phi(\mathbf{r})d\mathbf{r}\right\}$$

(Regularized nuclear charges)

- Thus, $E(\rho,\mathbf{R}) = \max_{\phi} L(\phi,\rho,\mathbf{R})$

$$L(\phi,\rho,\mathbf{R}) = C_F\int\rho^{5/3}(\mathbf{r})d\mathbf{r}+\frac{\lambda}{8}\int\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}d\mathbf{r}+\int\epsilon_{xc}(\rho(\mathbf{r}))\rho(\mathbf{r})d\mathbf{r} - \frac{1}{8\pi}\int|\nabla\phi(\mathbf{r})|^2d\mathbf{r}+\int(\rho(\mathbf{r})+b(\mathbf{r}))\phi(\mathbf{r})d\mathbf{r}$$



OFDFT – Real-space formulation

- To enforce constraint, $\rho > 0$, make substitution, $\rho = u^2$
- The problem of computing the ground state energy is given by saddle-point problem is given by,

$$\min_{\mathbf{R}} \min_{u} \max_{\phi} \; L(\phi, u, \mathbf{R}) \qquad \text{subject to:} \quad \int u^2(\mathbf{r}) d\mathbf{r} = N$$

$$\begin{aligned} L(\phi, u, \mathbf{R}) \;=\; & \frac{\lambda}{2} \int |\nabla u(\mathbf{r})|^2 d\mathbf{r} + C_F \int u^{10/3}(\mathbf{r}) d\mathbf{r} + \int \varepsilon_{xc}(u^2(\mathbf{r})) u^2(\mathbf{r}) d\mathbf{r} \\ - \; & \frac{1}{8\pi} \int |\nabla \phi(\mathbf{r})|^2 d\mathbf{r} + \int (u^2(\mathbf{r}) + b(\mathbf{r}; \mathbf{R})) \phi(\mathbf{r}) d\mathbf{r} \end{aligned}$$

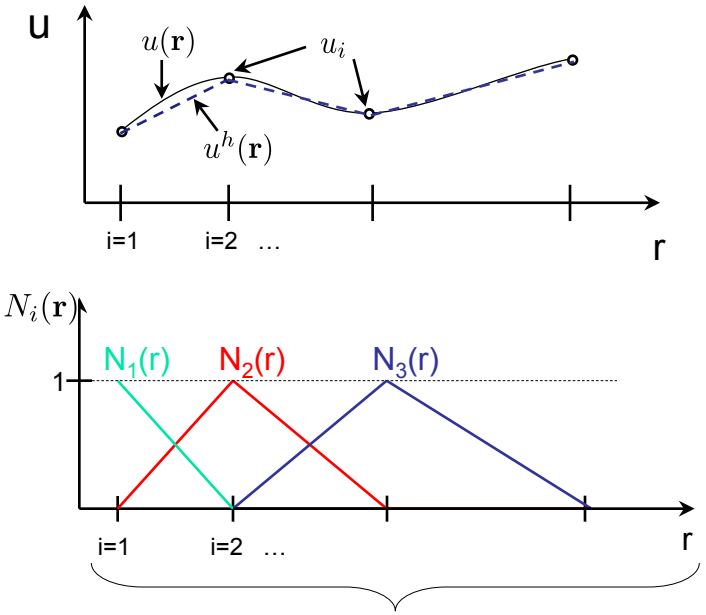
- The ground-state energy and electron-density is expressed as a variational saddle-point problem in real-space with a local functional that is amenable to computation.

OFDFT – FE discretization

- Use finite-element basis for computing –

$$u^h(\mathbf{r}) = \sum_i u_i N_i(\mathbf{r}), \quad \phi^h(\mathbf{r}) = \sum_i \phi_i N_i(\mathbf{r})$$

u_i, ϕ_i – Nodal values
$N_i(\mathbf{r})$ – Shape functions



By changing the positioning of the nodes the spatial resolution of basis can be changed/adapted

Features of finite-element basis:

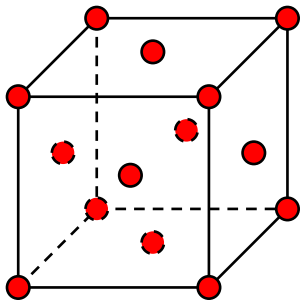
1. FE basis are local, and their spatial resolution can be changed/adapted.
2. Complex geometries can be represented, and arbitrary boundary conditions can be imposed.
3. There is a systematic way of controlling the smoothness of the basis functions, from linear functions to any higher degree polynomial.
4. The local nature of the basis enables parallel implementation of the numerical scheme with ease.

Illustrative examples – Aluminum nano-clusters

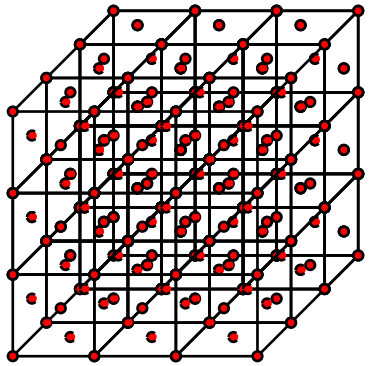
- Need a real-space formulation.
- TFW KE functionals, LDA appx. for exchange correlation functionals.
- Goodwin-Needs-Heine pseudo-potential for Aluminum

- Simulations are performed on a range of cluster sizes

1x1x1
3x3x3
5x5x5
9x9x9
} FCC unit cells

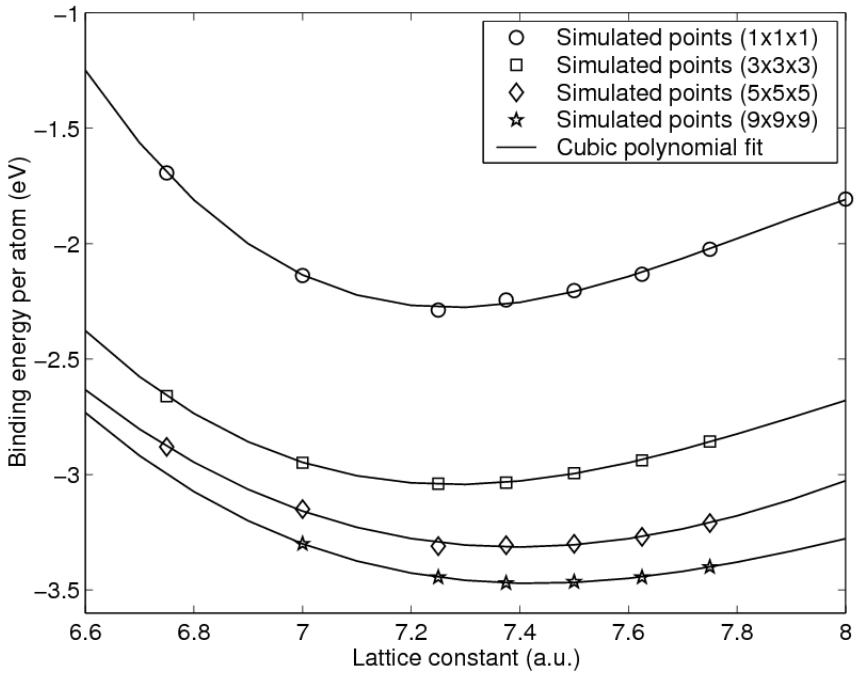


1x1x1 fcc cluster



3x3x3 fcc cluster

Results – Aluminum clusters



Binding energy per atom as a function of lattice constant

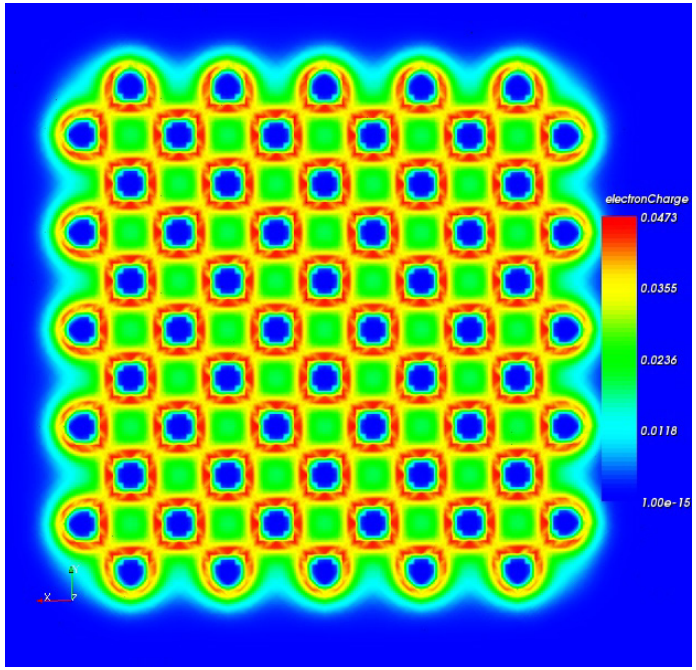
Property	OFDFT-FE	KS-LDA[a]	Experiments[b]
Lattice parameter (a.u.)	7.42	7.48	7.67
Cohesive energy (eV)	3.69	3.67	3.4
Bulk modulus (GPa)	83.1	79.0	74.0

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

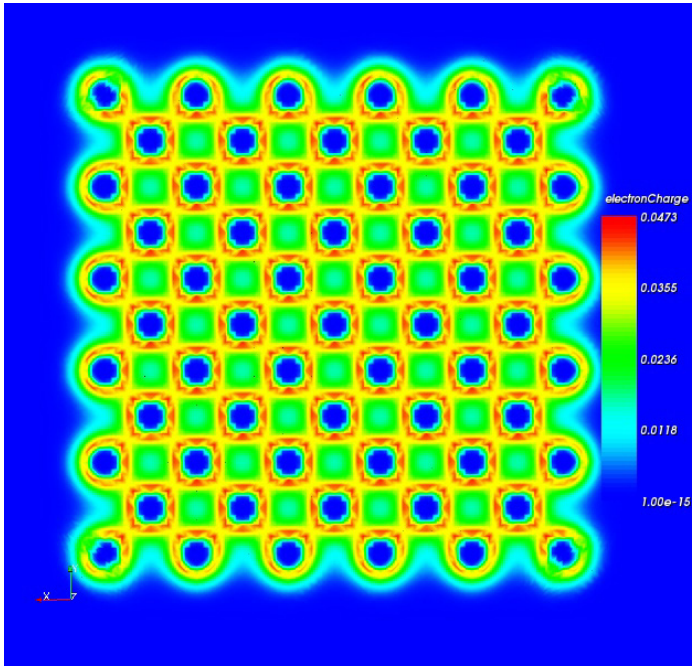
b Brewer (1997), Gschneider (1964)

Results – Aluminum clusters

Contours of electron-density in an aluminum cluster
with 5x5x5 fcc unit cells (666 atoms)



Mid-plane

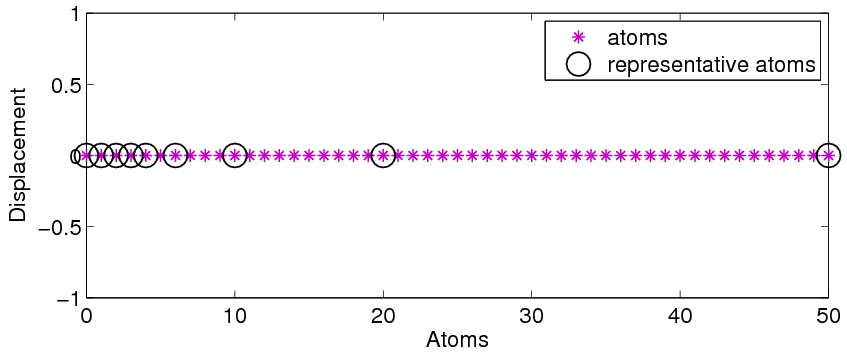


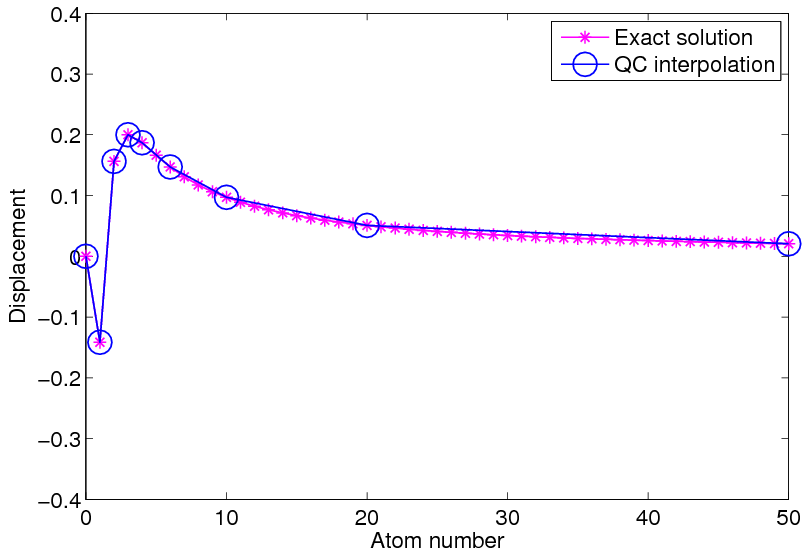
Face

3,000,000 elements; 3000 CPU hours !!

Need coarse-graining!

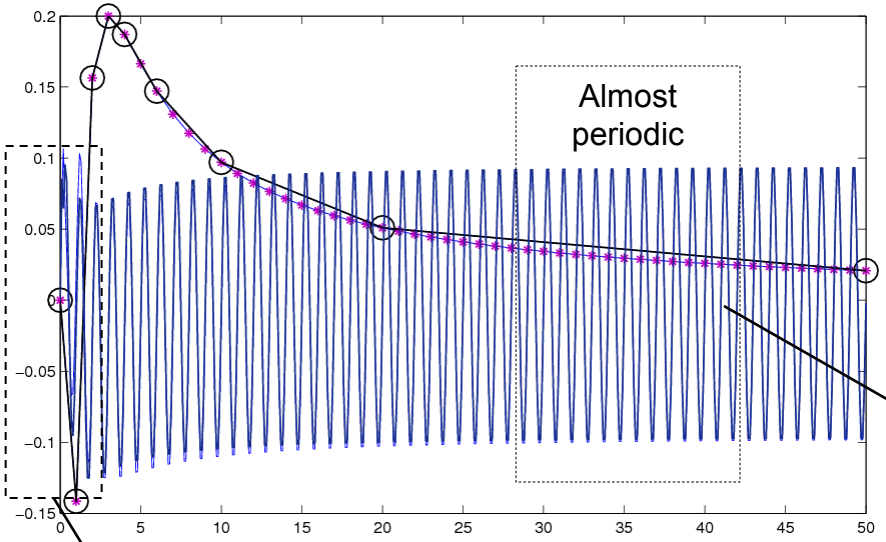
Theory of Quasi-Continuum (Tadmor et al.1995, Knap & Ortiz 2003)



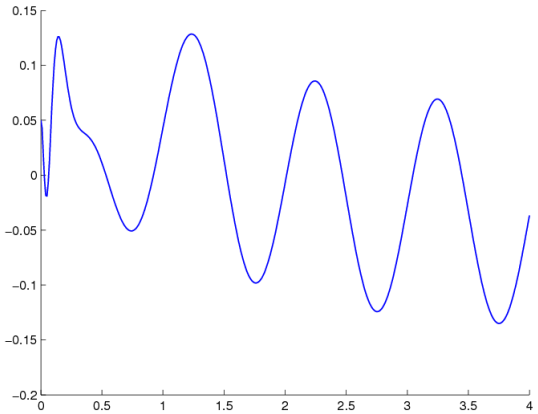


- Seamless multi-scale scheme to transition from atomistics to continuum.
- Main Features of QC:
  - Kinematically constraint atoms to finite-element mesh.
  - Adaptive mesh refinement
  - Cluster summation rules.
- Developed in the context of lattice atomistics.
- Extension to electronic structure calculations pose challenges!

Coarse-graining of OFDFT : Challenge



Far from periodic close to the defect



- Subatomic oscillations and lattice scale modulations of electron density and electrostatic potential !!

- For slowly varying deformation fields, the energy can be written as (Blanc et al. 2002),

$$\mathcal{E}(\mathbf{x}) = \int W_{Per}^{TFW}(\mathbf{F}) d\Omega$$

Periodic unit cell calculation

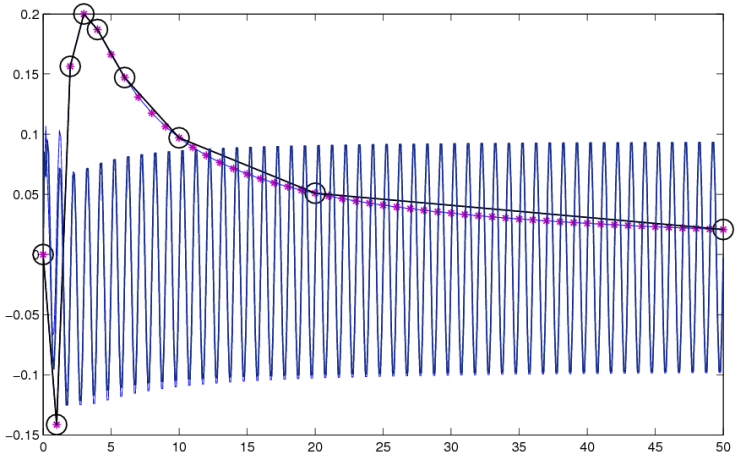
Exploit this fact in big elements while retaining full resolution in small elements.

Quasi-Continuum OFDFT (QC-OFDFT) – Key Ideas

(Gavini et al. JMPS 2007, 697-718)

- Constrain atomic positions following an adaptive supra-atomic mesh (T_{h1})
- Write electronic fields as a sum of two terms

$$\phi^h = \phi_0^h + \phi_c^h\,,$$
$$u^h = u_0^h + u_c^h$$



- Predictor $u_0^h\,,\phi_0^h$

  Computed element by element assuming periodicity on a local sub-atomic mesh

- Corrector $u_c^h\,,\phi_c^h$

  Computed on an adaptive mesh which is sub-atomic near defects and coarsens away from it (T_{h3})

$$\min_{u_c^h}\max_{\phi_c^h}\; L(\phi_0^h+\phi_c^h, u_0^h+u_c^h, \mathbf{R})$$

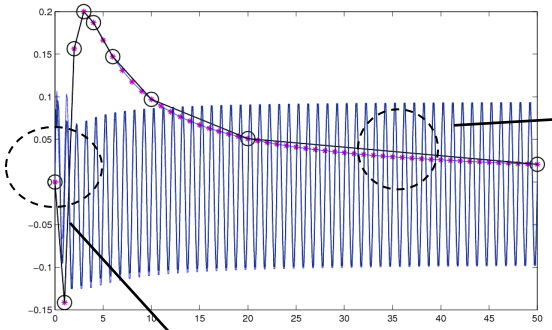
QC-OFDFT – Key Ideas

- We introduce cluster quadrature rules for an element e in T_{h3},

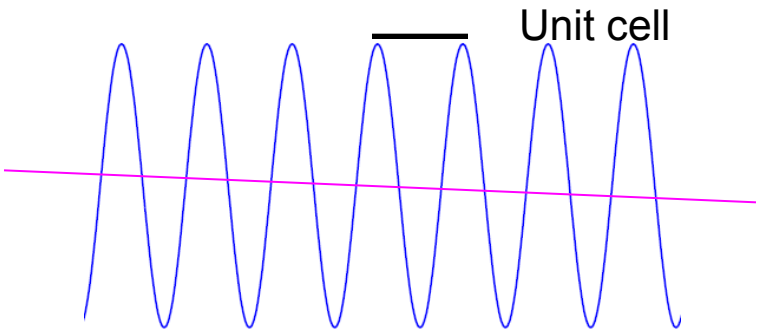
$$\int_e f(\mathbf{r})d\mathbf{r} \approx |e|\langle f\rangle_{D_e}$$

|e| is the volume of the element, D_e is the unit cell of an atom if such a cell is contained in e or e otherwise and $\langle f\rangle_{D_e}$ is the average of f over D_e.

- *Philosophy behind cluster quadrature rules:*

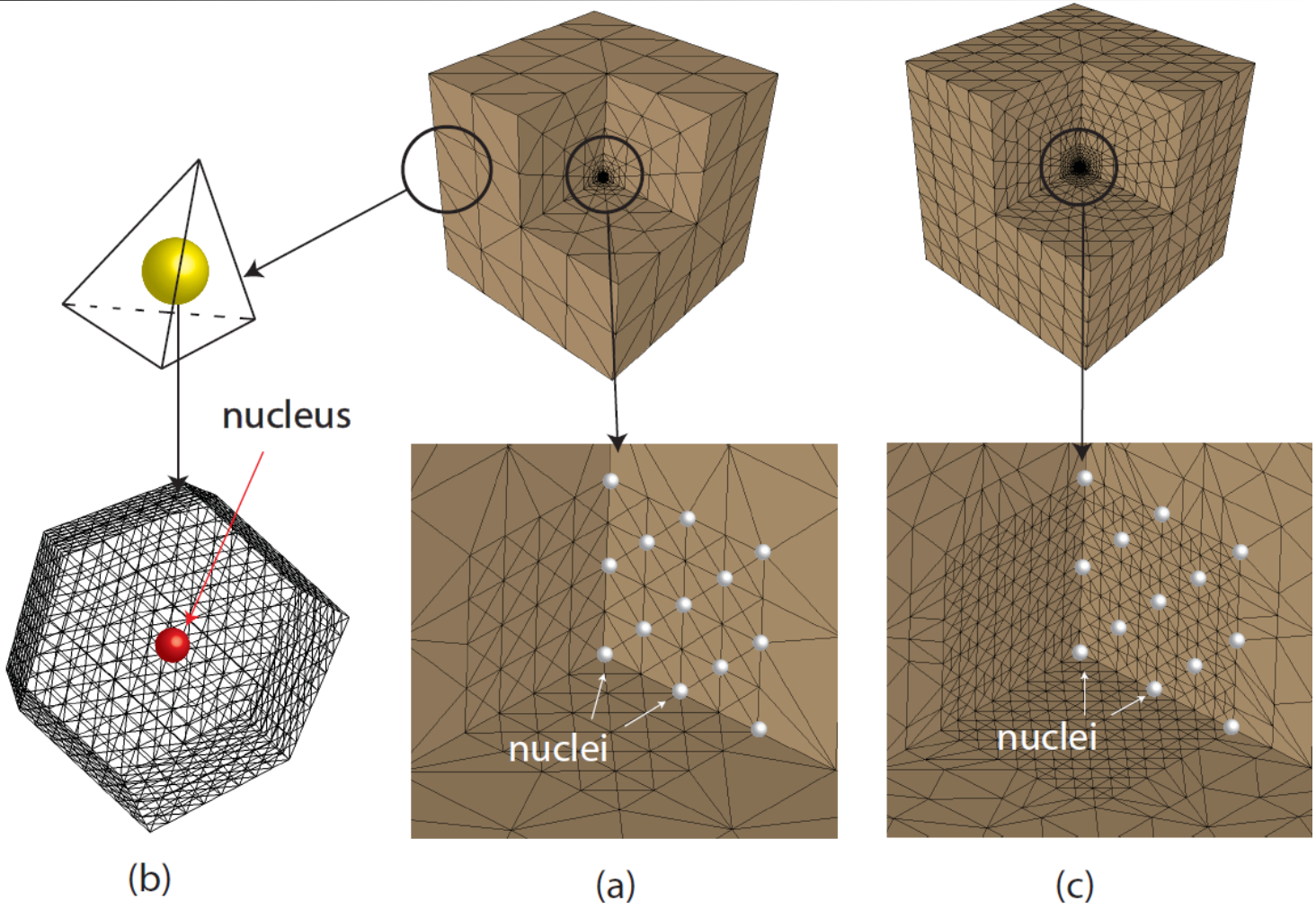


Exact integration required



Integration on unit cell –
zero order quadrature rule

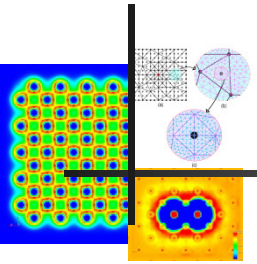
QC-OFDFT – Meshes



Mesh used to compute the predictor fields

Mesh used to compute the nuclear positions

Mesh used to compute the corrector fields

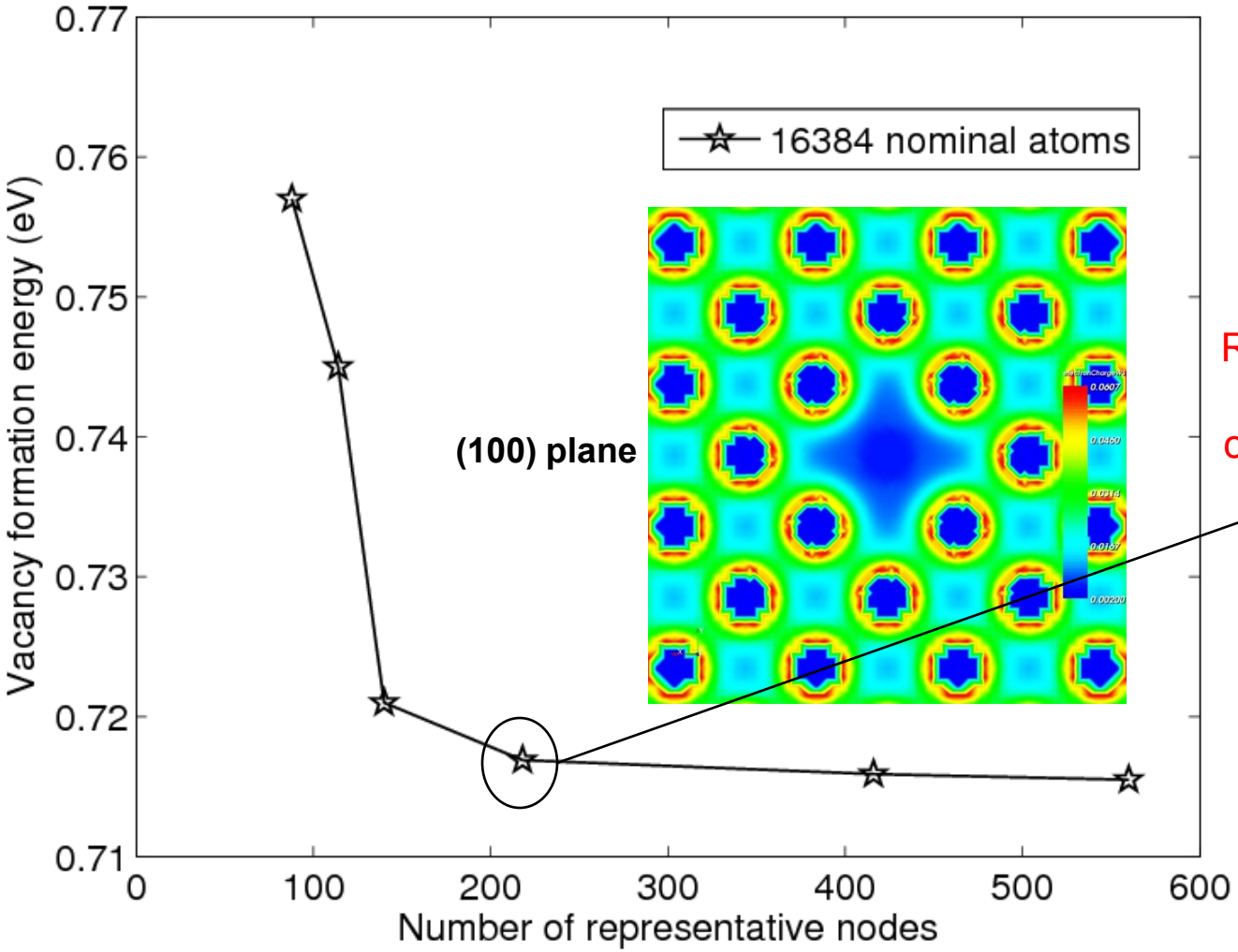


QC-OFDFT – Properties

The proposed approximation scheme (QC-OFDFT) has the following properties:

- adapts the level of spatial resolution to the local structure of the solution;
- coarse-graining is completely unstructured and seamless;
- fully-resolved OFDFT and finite lattice-elasticity are obtained as extreme limits;
- OFDFT is the sole physics input to the calculations, and no spurious physics or ansatz regarding the behavior of the system is introduced;
- a converged solution obtained by this scheme may be regarded as a solution of OFDFT;
- million atom OFDFT calculations possible at no significant loss of accuracy!!

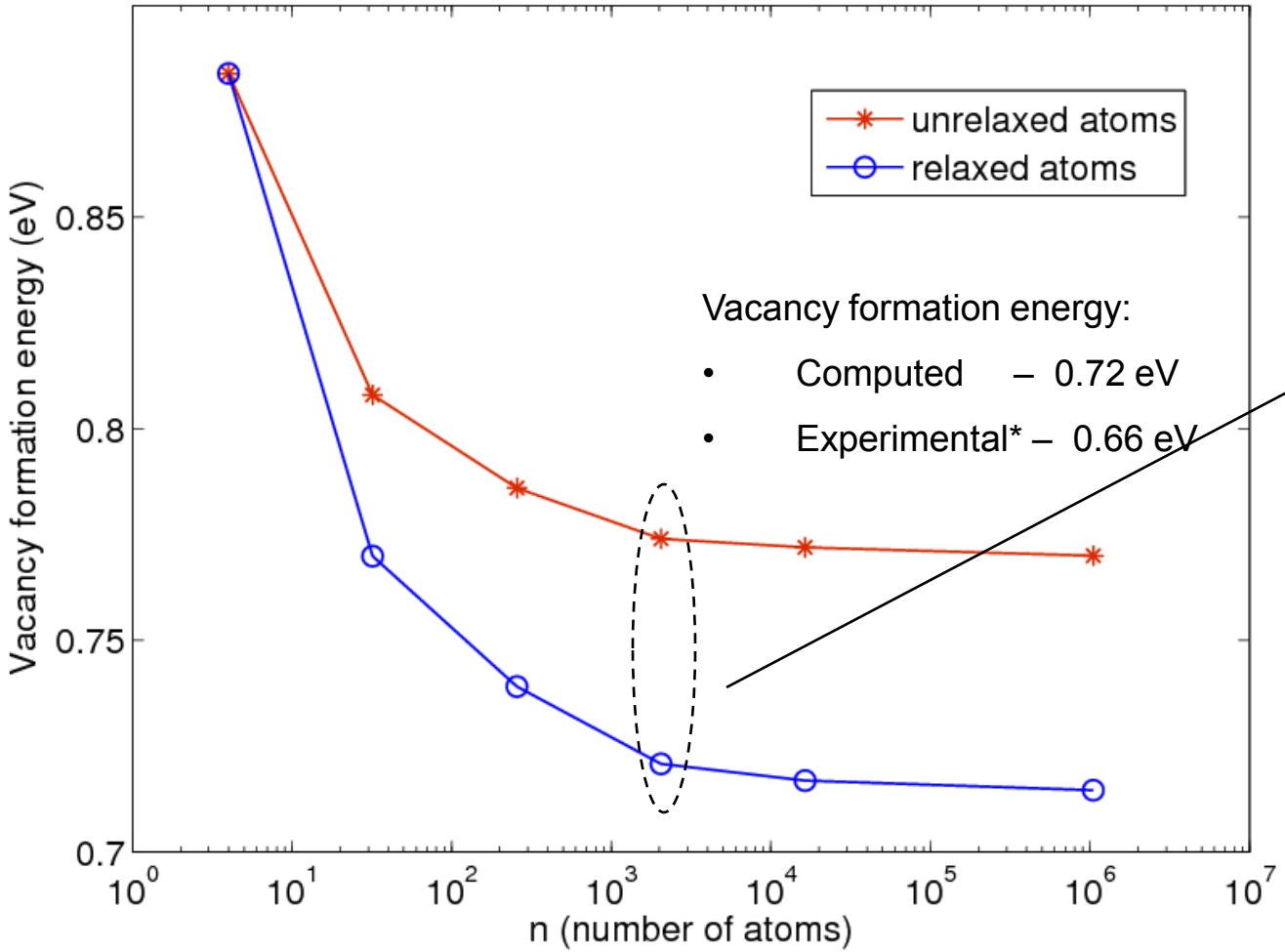
Vacancy in aluminum: Convergence of QC approximation



16,384 atoms in the computational cell

Reached convergence. Almost 80 fold computational savings!

Vacancy in Aluminum: Convergence with cell-size



Vacancy formation energy:

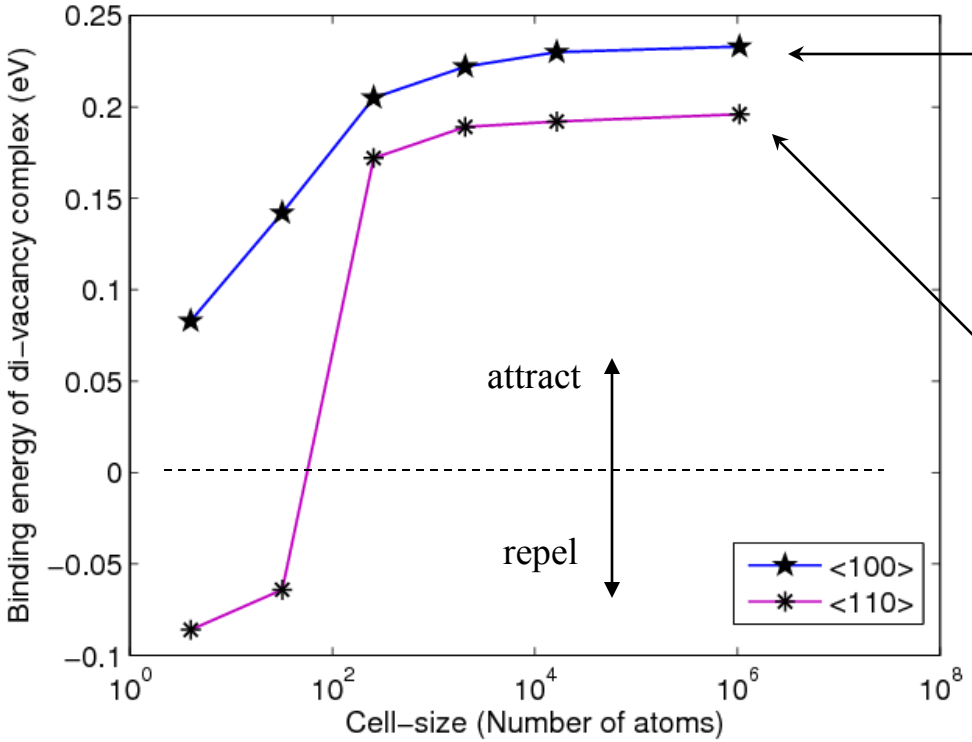
- Computed – 0.72 eV
- Experimental* – 0.66 eV

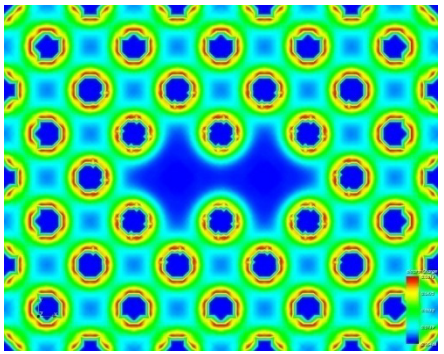
Need almost 1000 atoms for convergence w.r.t to cell-size!

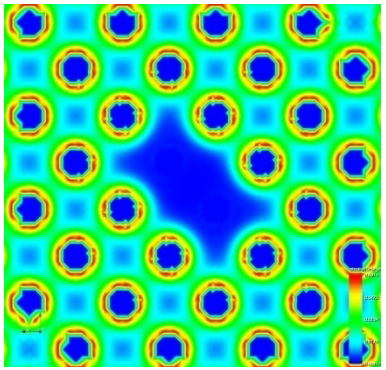
Long-ranged effects in defects

* Triftshauser 1975

Di-vacancy binding energy – cell-size effect



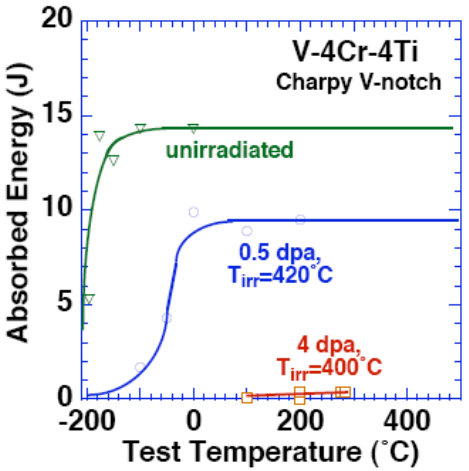




Radiation Damage

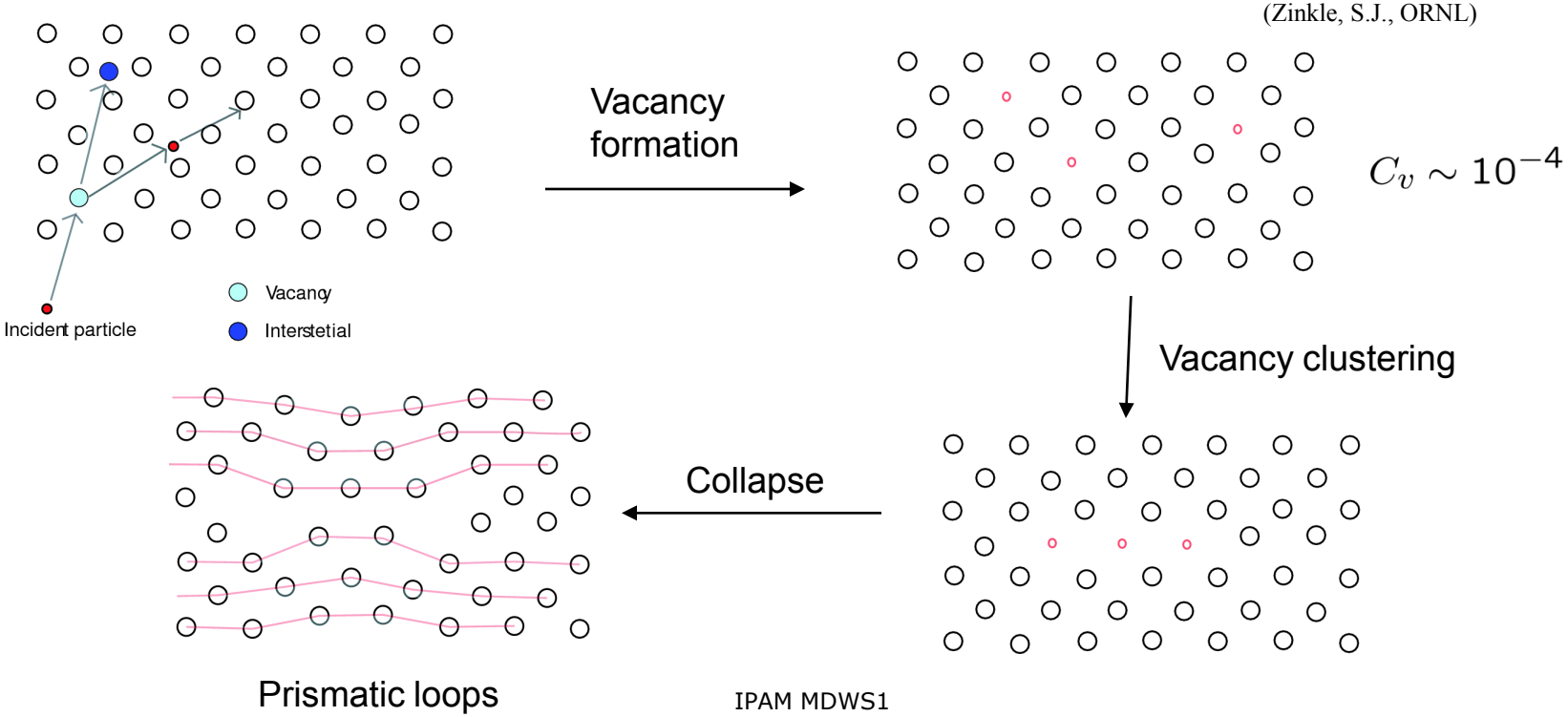
Effects of radiation on material properties :

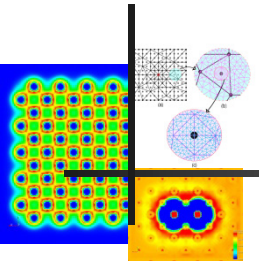
- Reduced fracture toughness; Increased hardness
- Material swelling



(Zinkle, S.J., ORNL)

Mechanism behind radiation damage (Hypothesis):





Vacancy clustering in aluminum

(Gavini et al. PRB 2007, **76** 180101(R))

- Quad-vacancies formed from two di-vacancies

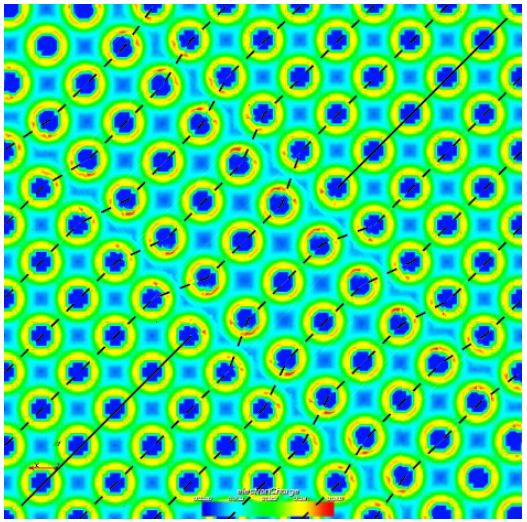
	Structure	Positions of vacancies	Vacancy binding energy (eV)
1	planar {100}	(0,0,0), (a/2,a/2,0), (a,0,0), (a/2,-a/2,0)	0.52
2	planar {100}	(0,0,0), (a/2,a/2,0), (a,0,0), (3a/2,a/2,0)	0.50
3	planar {100}	(0,0,0), (a/2,a/2,0), (a,0,0), (a,a,0)	0.48
4	planar {100}	(0,0,0), (a,0,0), (0,a,0), (a,a,0)	0.48
5	planar {110}	(0,0,0), (0,a/2,a/2), (a,0,0), (a,a/2,a/2)	0.56
6	planar {111}	(0,0,0), (0,a/2,a/2), (a/2,a/2,0), (a/2,a,a/2)	0.55
7	non-planar	(0,0,0), (0,a/2,a/2), (a/2,0,a/2), (a/2,a/2,0)	0.53
8	non-planar	(0,0,0), (a,0,0), (a/2,a/2,0), (a/2,0,a/2)	0.51
9	non-planar	(0,0,0), (a,0,0), (a/2,a/2,0), (0,a/2,a/2)	0.50

- Larger clusters
  - {110} plane
  - 6 vacancy rectangular cluster : Binding energy = 0.81eV
    9 vacancy rectangular cluster : Binding energy = 1.16eV
  - {111} plane
    7 vacancy hexagonal cluster : Binding energy = 0.88eV

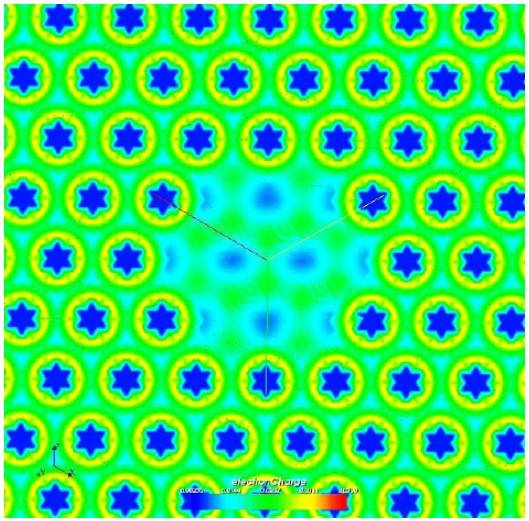
Growth of clusters appears energetically favorable!

Prismatic loop nucleation

- {111} plane - 7 vacancy hexagonal cluster
  - Binding energy = 0.88 eV (non-collapsed)
  - Binding energy = 1.55 eV (collapsed – prismatic loop)



(001)



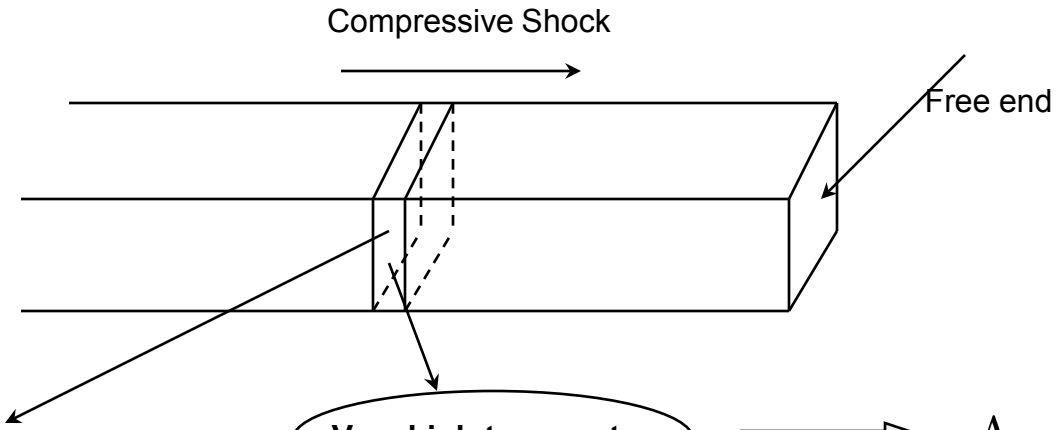
(111)

1/2<110> Vacancy prismatic loop

Cell-size	Binding energy (collapsed loop)
16,384	0.91 eV
1,048,576	1.55 eV

→ Stability observed only at multi-million atoms!

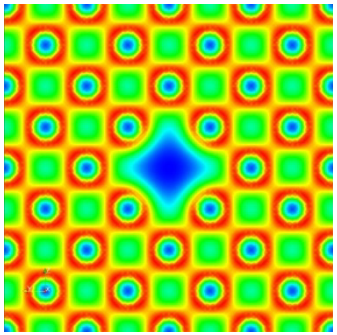
Dynamic Fracture -- Spalling



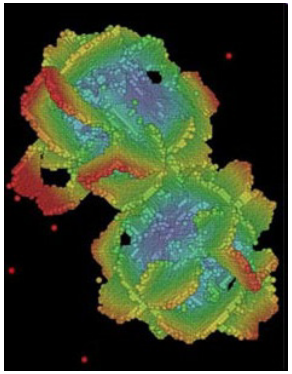
$$A = U - TS$$

Also, extreme deformations!

$U(F)$?

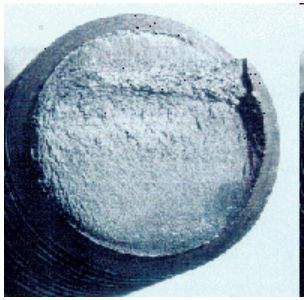


Vacancy nucleation



Void formation and coalescence

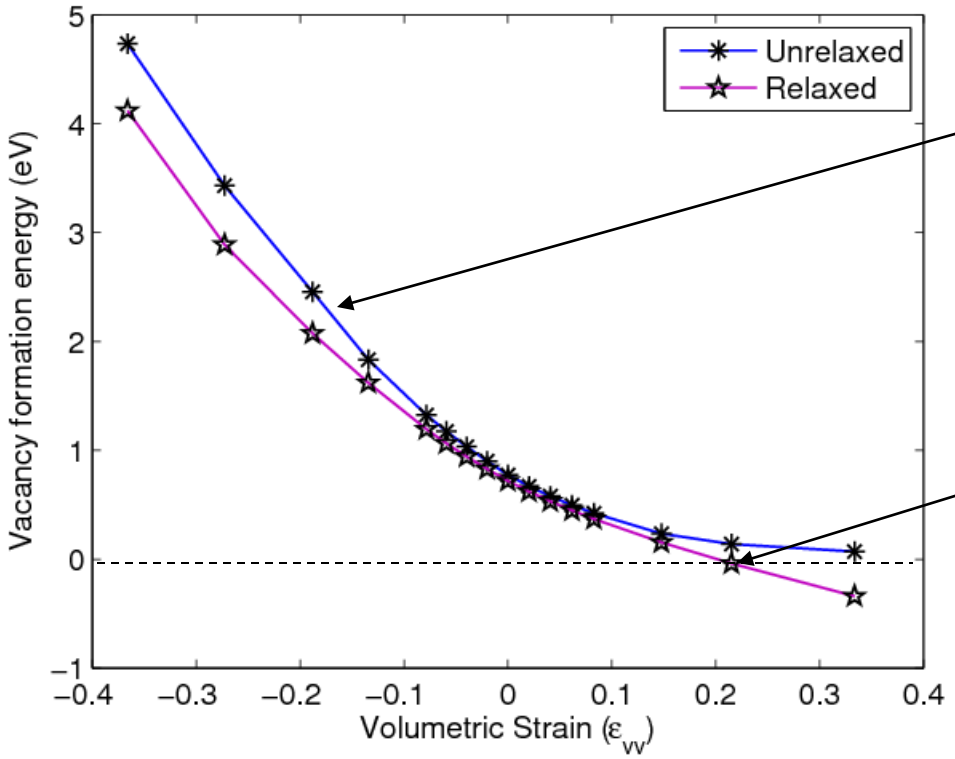
(Seppala et al, 2005)



Spall fracture

Importance of the defect-core in the energetics of defects

(Gavini, Phys. Rev. Lett 2008, **101** 205503; Gavini, Proc. Roy. Soc. **465** 3239)

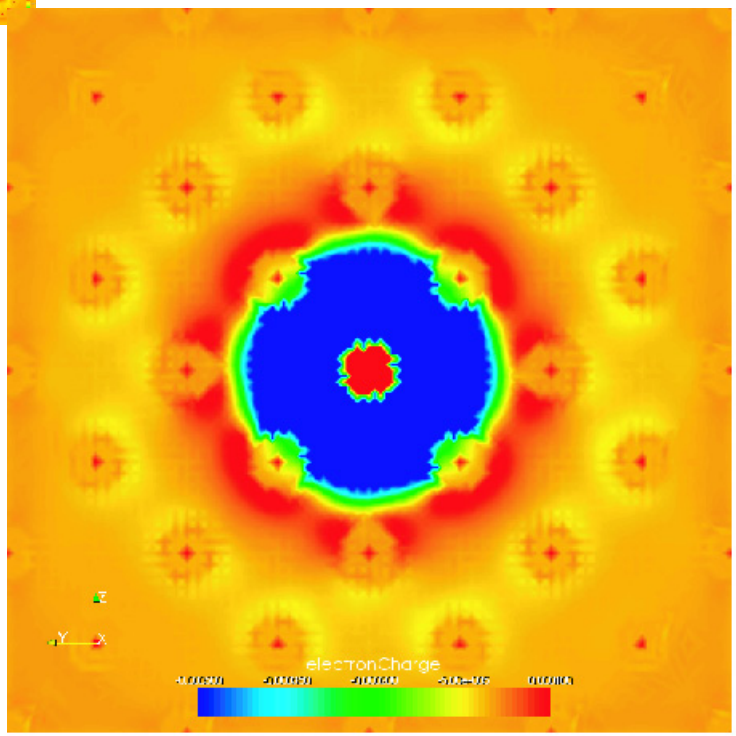


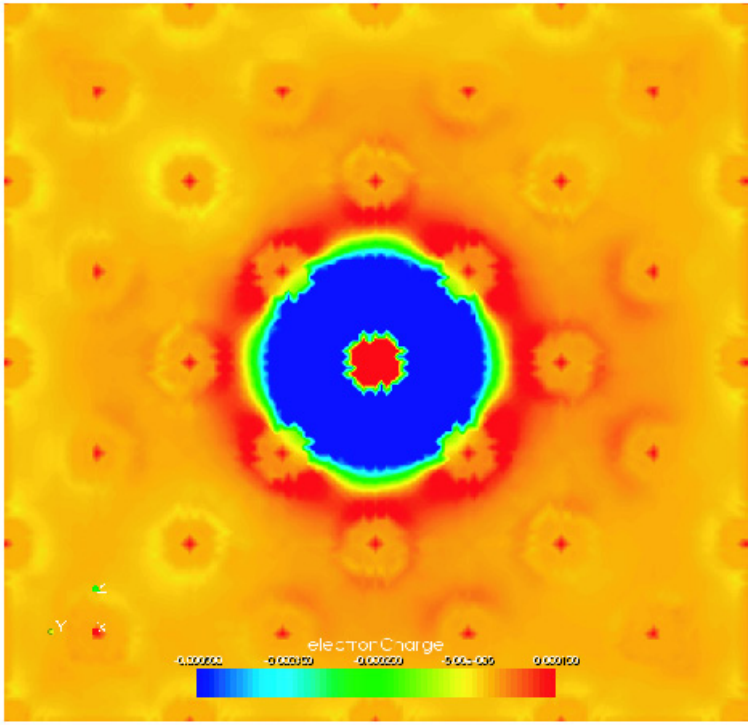
Electronic structure of the core significantly influenced by macroscopic deformations.

Core energy not an inconsequential constant!

Vacancies become thermodynamically favorable! Spontaneous nucleation of vacancies!

Changing nature of the defect core





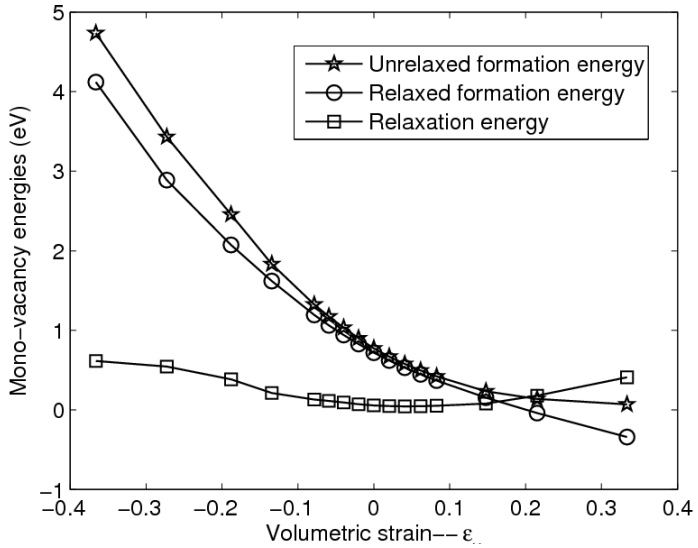
No volumetric strain

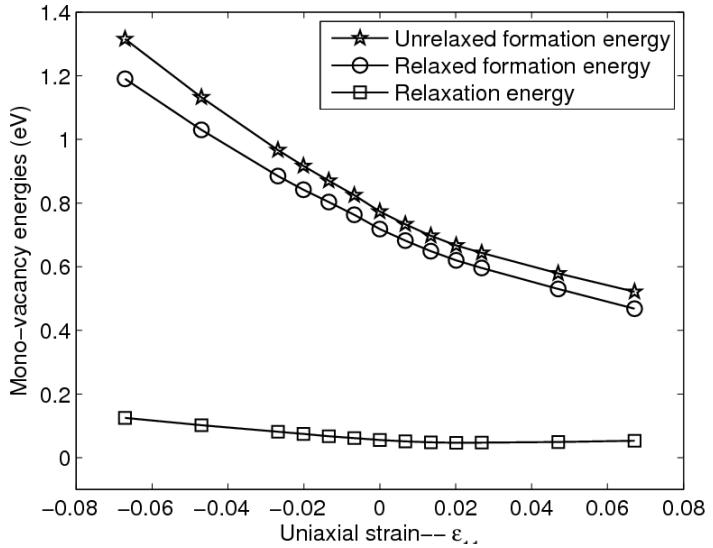
0.3 volumetric strain

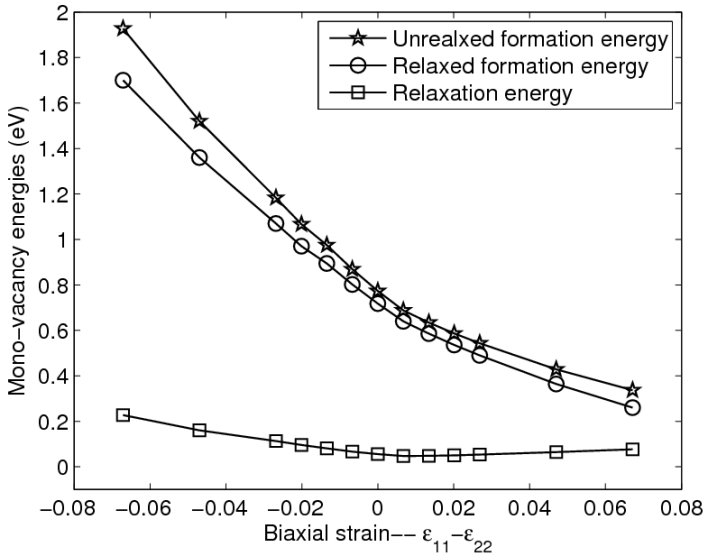
The nature of the displacement fields also change with volumetric strain:

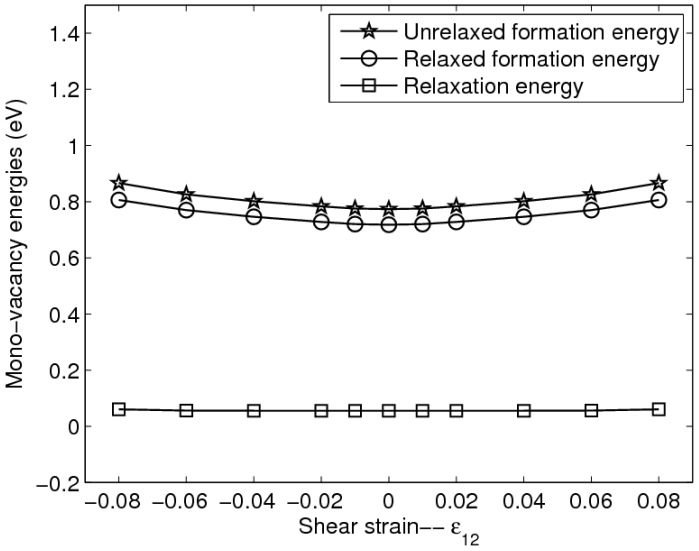
- Maximum displacement 0.17 a.u. inwards for -0.3 volumetric strain
- Maximum displacement 0.03 a.u. inwards for zero volumetric strain
- Maximum displacement 0.19 a.u. outwards for 0.3 volumetric strain

Role of macroscopic deformations on energetics of vacancies

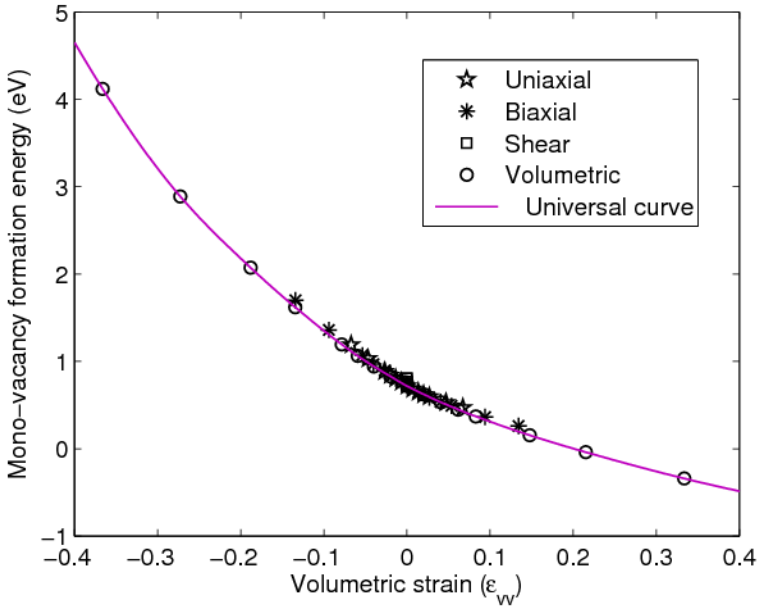


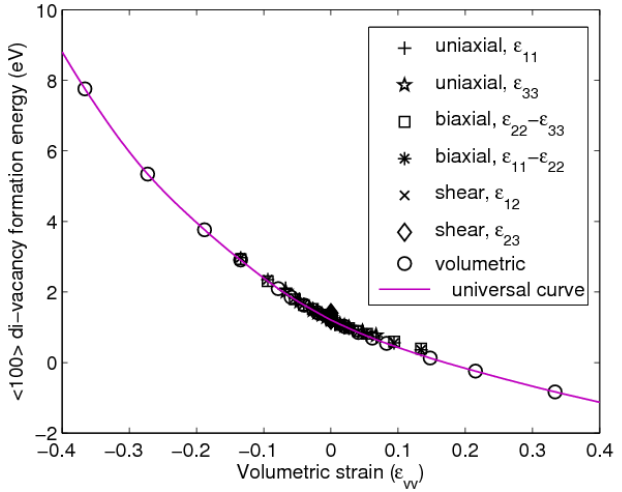


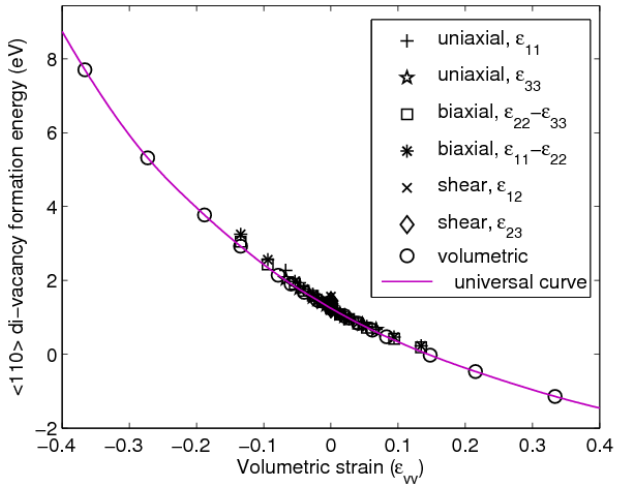




Role of macroscopic deformations on energetics of vacancies

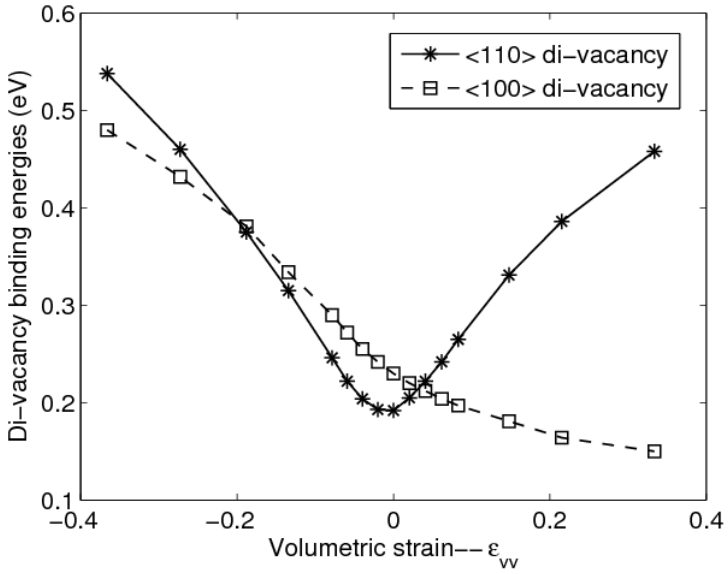


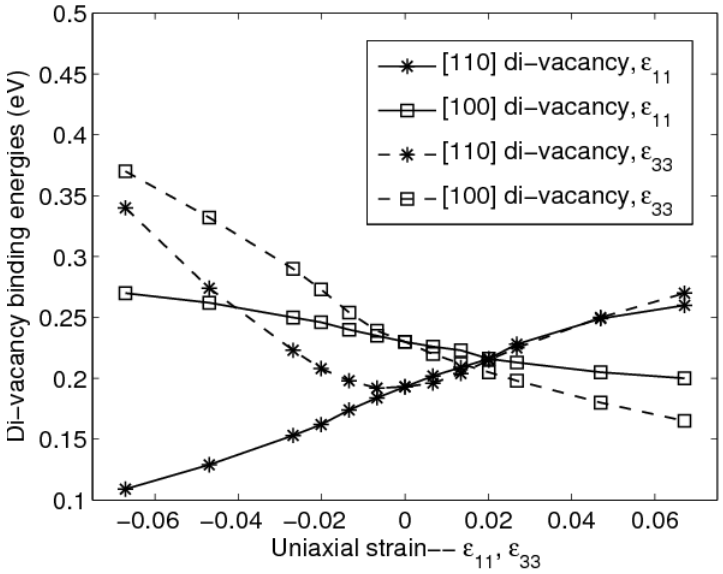


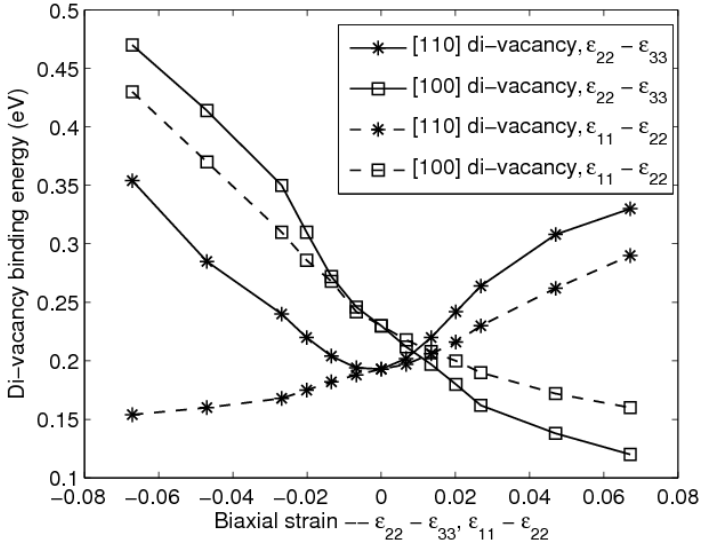


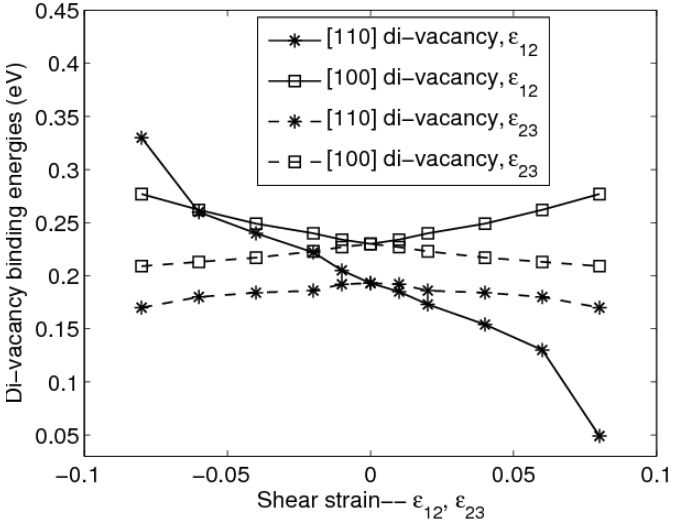
Universal dependence of formation energies on volumetric strain!

Role of macroscopic deformations on energetics of vacancies

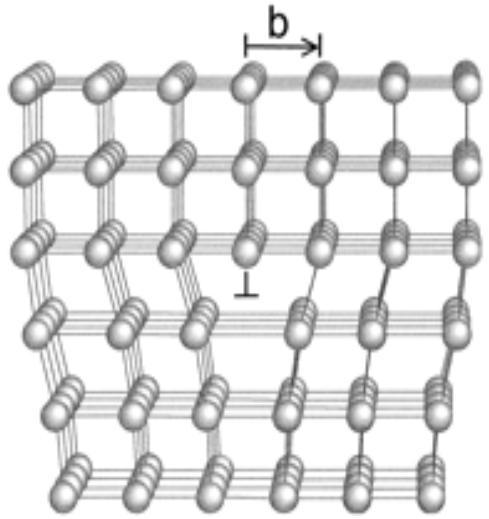


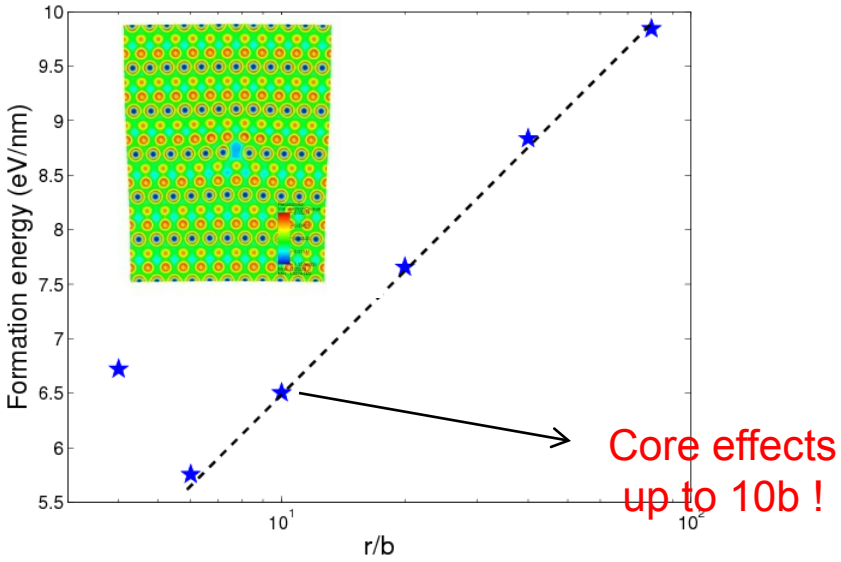




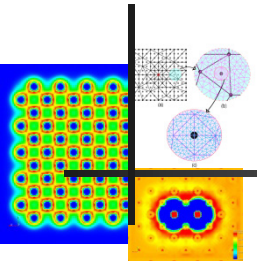


Edge dislocation (in progress)





Incremental distance from the core	Elastic energy (eV/nm)	Electronic Relaxation (eV/nm)	Electronic Relaxation/Elastic energy (Absolute value)
4*b* – 6*b*	0.66254	-1.62796	2.457145
6*b* – 10*b*	0.869453	-0.12104	0.139211
10*b* – 20*b*	1.147981	0.004236	0.00369
20*b* – 40*b*	1.17937	-0.00061	0.000513
40*b* – 80*b*	1.066039	0.000403	0.000378



Kohn-Sham approach (KSDFT)

- Ground-state energy is a function of electron-density !! (Kohn & Sham, 1964-65)

$$\langle\psi|H|\psi\rangle \geq E_0 \qquad \text{(Variational statement)}$$

$$\begin{aligned}
E_0 &= \min_{\psi} \langle\psi|T + \frac{1}{2}\sum_i{\sum_j}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V_{ext}(\mathbf{r}_i)|\psi\rangle + E_{zz} \\
&= \min_{\psi} \langle\psi|T + \frac{1}{2}\sum_i{\sum_j}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}|\psi\rangle + \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + E_{zz} \\
&= \min_{\rho} \left\{ \underbrace{\left(\min_{\psi\to\rho} \langle\psi|T + \frac{1}{2}\sum_i{\sum_j}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}|\psi\rangle \right)}_{F(\rho)} + \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} \right\} + E_{zz}
\end{aligned}$$

$$F(\rho) = T_s(\rho) + E_H(\rho) + E_{xc}(\rho) \longrightarrow$$

Exchange-correlation functional: Model using LDA, GGA

$\downarrow$

Kinetic energy of non-interacting electrons: Computed from wave-functions of the resulting E-L eqn.

Kohn-Sham approach (KSDFT)

- $$E_0 = \min_{\rho \to N} \left\{ T_s(\rho) + E_H(\rho) + E_{xc}(\rho) + E_{ext} \right\} + E_{zz}$$

- Consider the E-L equation corresponding to the variational problem:

$$\frac{\delta T_s}{\delta \rho} + \underbrace{V_H(\rho) + V_{xc}(\rho) + V_{ext}(\mathbf{R})}_{V_{eff}(\mathbf{r})} = \mu$$

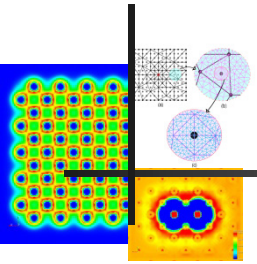
$$\left(-\frac{1}{2}\nabla^2 + V_{eff} \right) \psi_i = \epsilon_i \psi_i$$

Self consistent iteration
(Kohn-Sham map)

$$\rho = \sum_{i=1}^{N} |\psi_i|^2, \qquad V_{eff}(\mathbf{r}) = V_H(\rho(\mathbf{r})) + V_{xc}(\rho(\mathbf{r})) + V_{ext}(\rho(\mathbf{r}))$$

$$T_s(\rho) = \frac{1}{2} \sum_{i=1}^{N} \int |\nabla \psi_i|^2 \longrightarrow$$

Kinetic energy computed from the single electron wave-functions



State of the art

Solutions to Kohn-Sham Equations

Fourier Space Formulations ⟷ Real Space Formulations (LCAO, FDM, FEM)

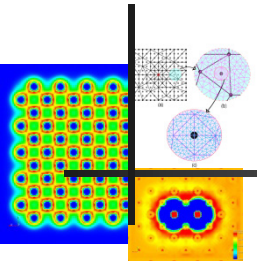
Key Features

- Captures wide range of bulk properties
- Restrictive to periodic domains
- Provide only uniform spatial resolution
- Suitable when the solution fields are smooth.

Key Features (FEM)

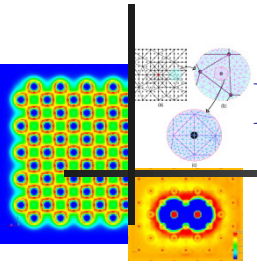
- Handle complex geometries and arbitrary boundary conditions
- Coarse Graining Capability
- Excellent Scalability of computations on massively parallel computing architectures

Though finite element basis is very versatile, number of basis functions in a linear finite element discretization required to achieve chemical accuracy is very large



Can higher-order finite-elements do any better?

- Here, we investigate the viability and computational efficiency afforded by higher-order finite-element discretization in electronic structure calculations using density functional theory to answer the following questions:
  - What is the numerical convergence rate for various orders of finite-element approximations in electronic structure calculations using DFT?
  - What is the computational advantage derived by using higher-order finite element discretization in terms of the CPU time?
- We present some of the first studies which demonstrate the computational efficiency afforded by higher-order elements for Kohn-Sham DFT calculations.



Rate of convergence of the Finite Element Approximation

- The study has been carried out by a suite of higher order elements:
  - TET 10 (TETRAHEDRAL QUADRATIC ELEMENT)
  - HEX 27 (TRI QUADRATIC HEXAHEDRAL ELEMENT)
  - HEX 64 (TRI CUBIC HEXAHEDRAL ELEMENT)
  - HEX 125 (TRI QUARTIC HEXAHEDRAL ELEMENT)
  - HEX 64 SPECTRAL, HEX 125 SPECTRAL … upto 10^{th} order

  (Lagrange Polynomials are constructed on Gauss-Lobatto Legendre Points for spectral elements)

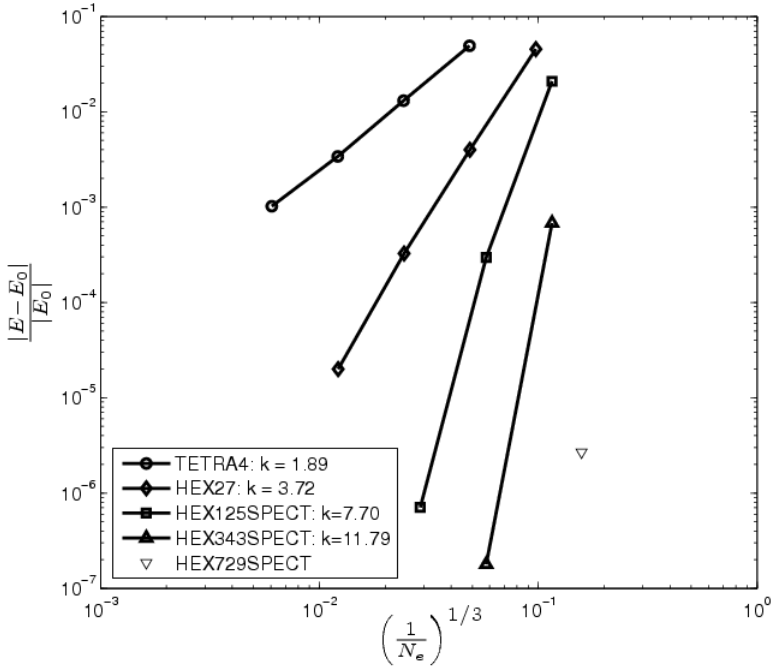
- Elements have been tested against three types of problems: (a) CH_4 (b) Barium Cluster (35 atoms)

  (a) CH_4 : An all electron calculation
  (b) Barium Cluster: Pseudopotential calculation

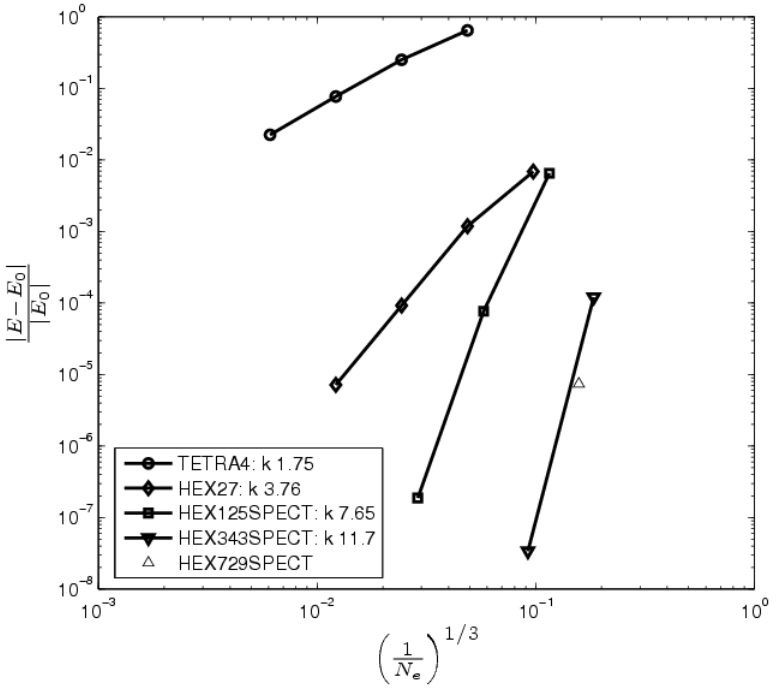
Convergence rates

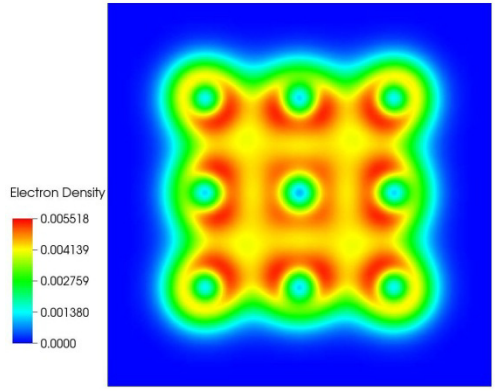
(Motamarri et al. J. Comp. Phys.)

Barium Cluster

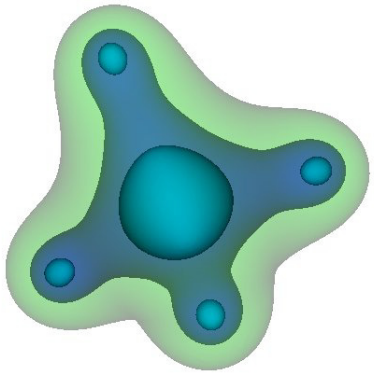


Methane Molecule

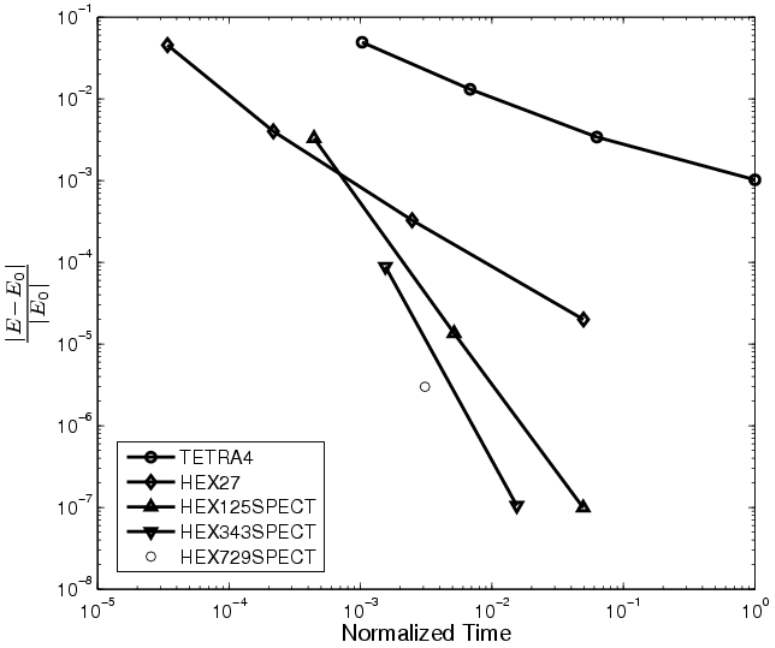




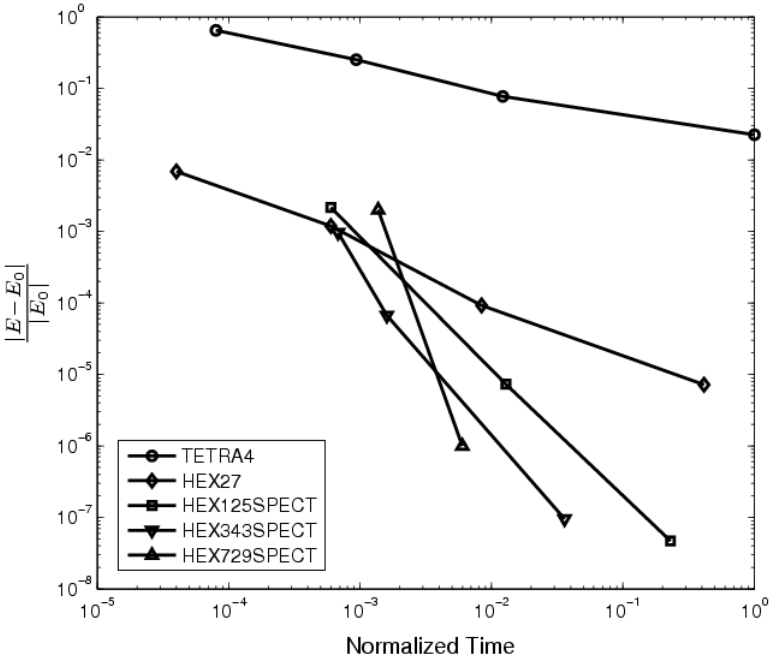
Optimal rate of convergence!



Computational efficiency

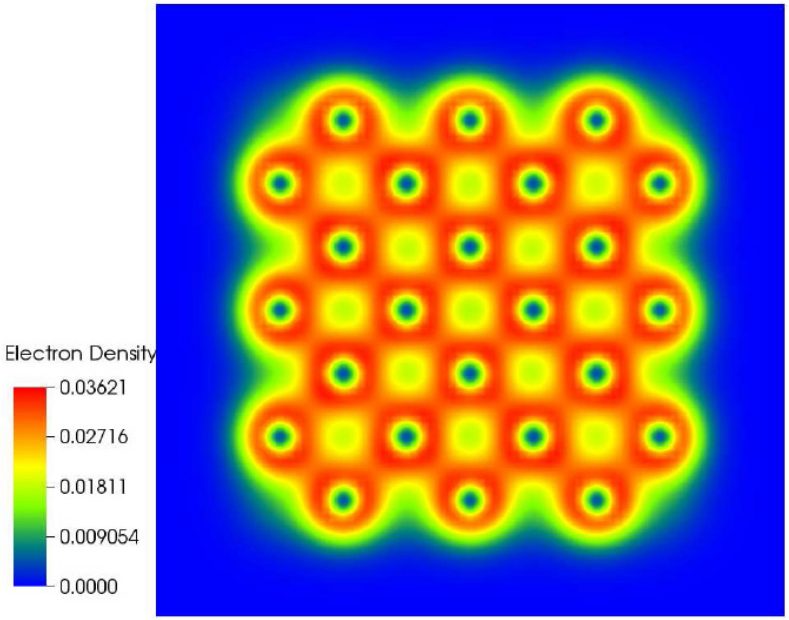


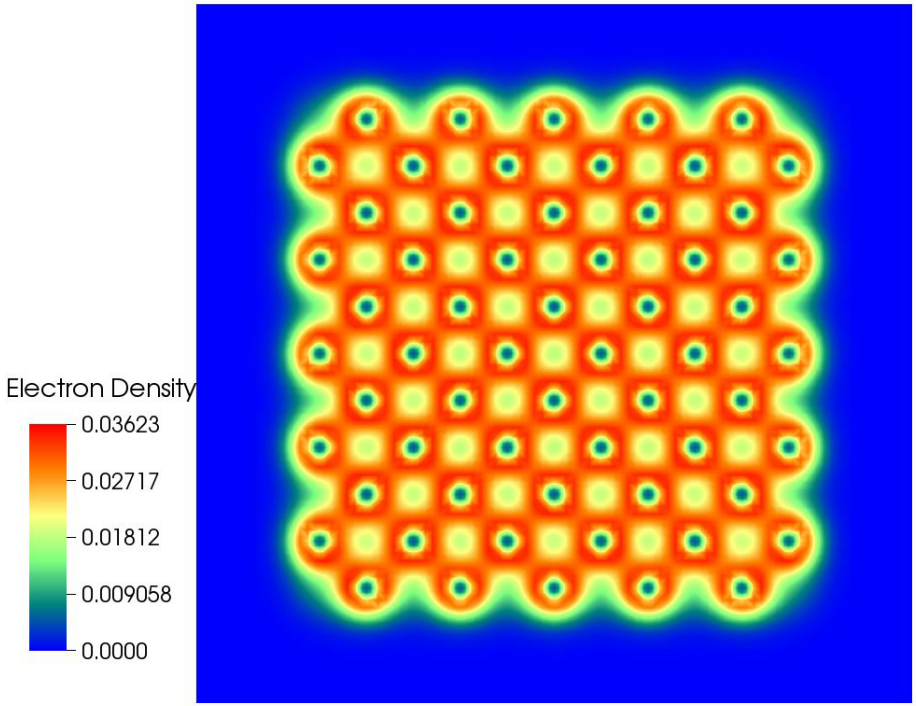
Barium Cluster



Methane Molecule

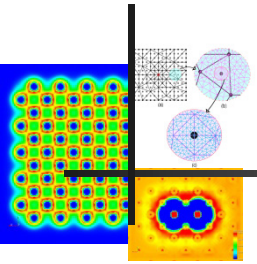
Aluminum clusters





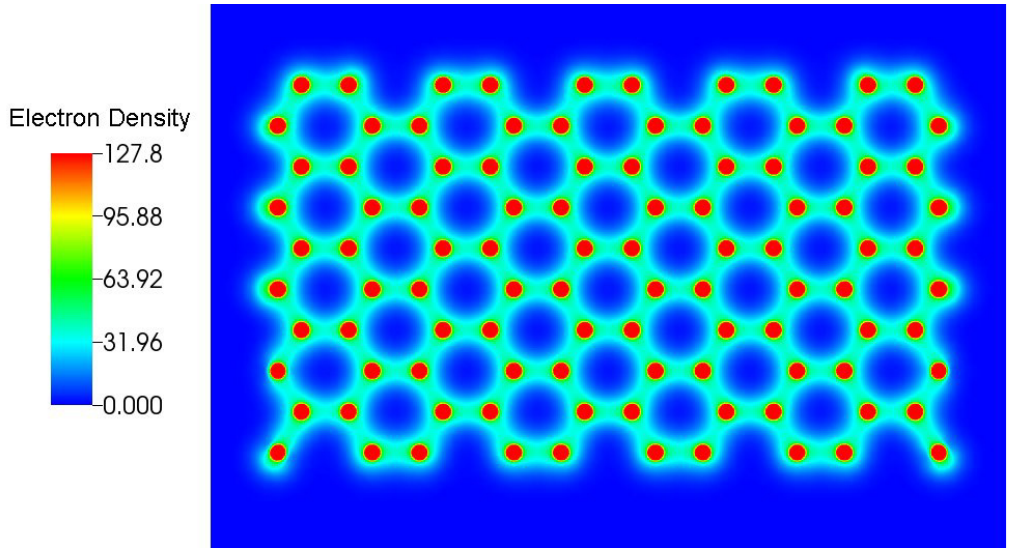
Type of basis set	Relative error	Time (CPU-hrs)
Plane-wave basis (cut-off 30 Ha, cell-size of 60 $a.u.$)	3.3×10^{-6}	646
FE basis (HEX343SPECT, $2,808,385$ nodes, domain size: 200 $a.u.$)	3.6×10^{-6}	371

Type of basis set	Relative error	Time (CPU-hrs)
Plane-wave basis (cut-off 30 Ha, cell-size of 80 a.u)	2.1×10^{-5}	7307
FE basis (HEX343SPECT, $7,875,037$ nodes, domain size: 400 $a.u.$)	7.9×10^{-6}	6619



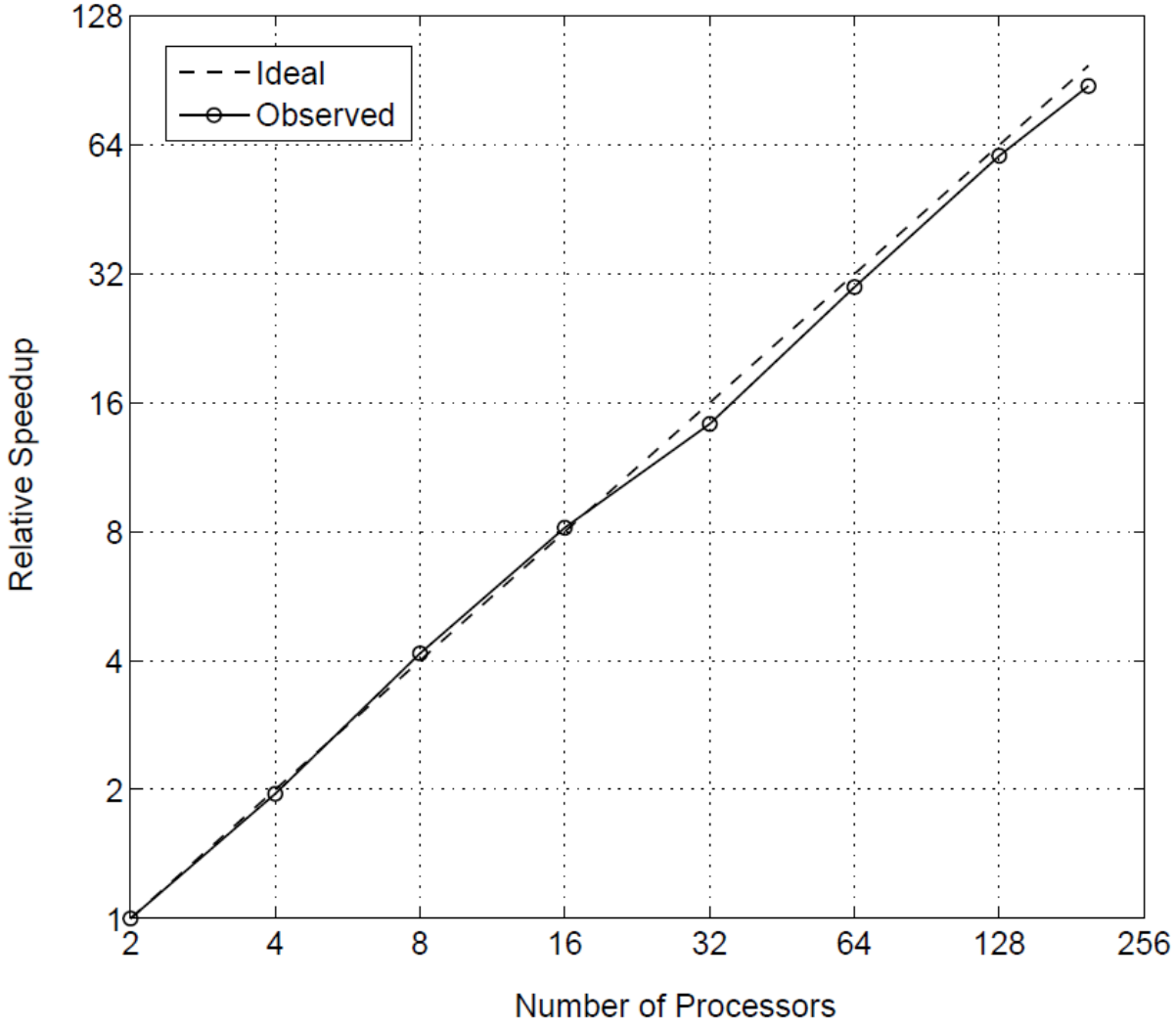
All-electron calculations

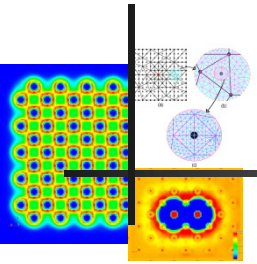
100 atom Graphene sheet



Type of basis set	Relative error	Time (CPU-hrs)
pc2 (Gaussian, 3,000 basis functions)	1.06×10^{-4}	666
FE basis (HEX125SPECT, 8,004,003 nodes)	1.2×10^{-4}	7461

Scalability





Ongoing/future work KSDFT

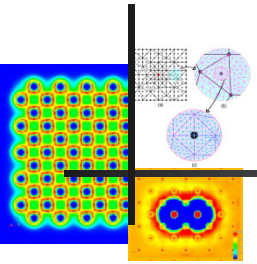
Real-space DFT-FE:

- Develop robust geometry optimization techniques
- Incorporate more advanced exchange-correlation functionals (beyond LDA, GGA)

Coarse-graining KSDFT:

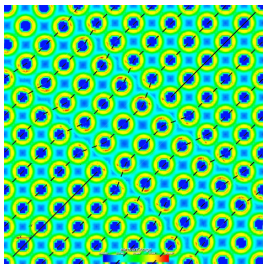
Localization of the wavefunctions is key for extending the coarse-graining ideas

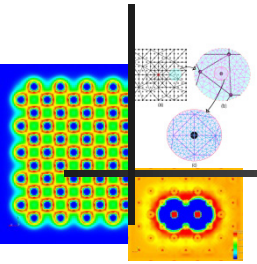
- O(N) formulations:
  - Non-orthogonal localized orbitals (based on Garcia-Cervera et al. PRB 79 115110)
- QC-KSDFT: localization -> predictor-corrector approach -> QC
- Physical applications: electronic-structure informed study of deformation and failure mechanisms for structural materials; role of defects in electronic and optical properties; electron transport in open-systems



Concluding remarks

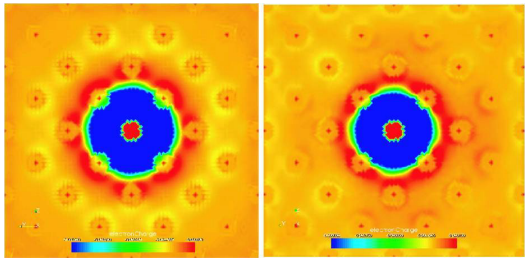
- Developed quasi-continuum orbital-free density-functional theory (QC-OFDFT)
  - Completely seamless and uses OFDFT as its sole input
  - Resolves the electronic structure of defect cores as well as macro-scale
  - Very important for accurate study of defects in materials
- The key ideas in QC-OFDFT are:
  - Real-space formulation of OFDFT
  - Finite-element discretization which is amenable unstructured coarse-graining
  - Predictor-corrector treatment of electronic fields; quadrature rules
- Study of vacancy clustering in aluminum through electronic structure calculations using QC-OFDFT
  - Vacancy clustering is energetically favorable
  - Vacancy clustering is a possible mechanism for prismatic loop formation



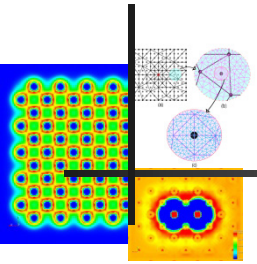


Concluding remarks

- Role of defect core in the energetics of defects
  - Influence of macroscopic deformation on the energetics of vacancies.
  - Multiple interacting length-scales
  - Volumetric strains have a dominant effect



- Real-space formulation KSDFT and finite-element discretization
  - Computational efficiency of higher-order FE
  - O(N) formulation -> QC-KSDFT



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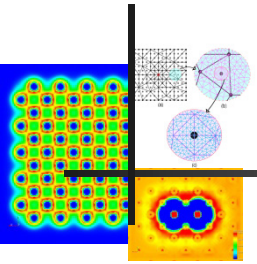
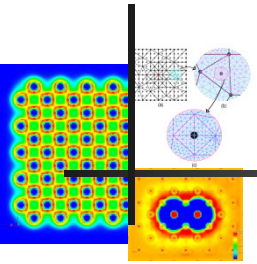


THANK YOU!



Configurational force (Eshelby tensor)

- Let $E_1(u_{eq}, \phi_{eq}, \mathbf{R}) = \min_u \max_\phi L(u, \phi, \mathbf{R})$
- Force on the I^{th} atom

$$\mathbf{f}_I = \frac{\partial E_1}{\partial \mathbf{R}_I} = \underbrace{\int_\Omega \frac{\partial b_I(\mathbf{r}-\mathbf{R}_I)}{\partial \mathbf{R}_I}\phi_{eq}}_{\text{Appears non-local}} = -\int_\Omega (\nabla b_I)\phi_{eq} = \underbrace{\int_{\Omega_c} (\nabla \phi_{eq}) b_I}_{\text{Infact, local}}$$

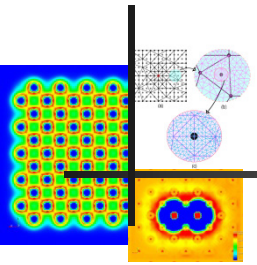
- Alternate expression:

Consider inner variations of the energy functional:

$\psi_\epsilon : \Omega \to \Omega^{'}$, $\psi_0 = id$, $\Gamma = \frac{d\psi_\epsilon}{d\epsilon}\big|_{\epsilon=0}$, such that $\Gamma = const$ in the compact support of b

$$\frac{dE_1(\psi_\epsilon)}{d\epsilon}\Big|_{\epsilon=0} = \int_\Omega \mathrm{E}_{ij}\frac{\partial \Gamma_i}{\partial y_j} d\mathbf{y}\,, \qquad \text{where}$$

$$\mathrm{E}_{ij} = L(u_{eq}, \phi_{eq}, \mathbf{R})\delta_{ij} + \frac{1}{4\pi}\frac{\partial \phi}{\partial x_i}\frac{\partial \phi}{\partial x_j} - \lambda \frac{\partial u}{\partial x_i}\frac{\partial u}{\partial x_j}$$



Orbital-free density-functional theory (OFDFT)

- The OFDFT energy functional is given by,

$$E(u,\mathbf{R}) = T_s(u) + E_{xc}(u) + E_H(u) + E_{ext}(u,\mathbf{R}) + E_{ZZ}(\mathbf{R})$$

$$T_s(u) = C_F \int u^{10/3}(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int |\nabla u(\mathbf{r})|^2 d\mathbf{r} + T_k(u);$$

→ Non-local kernel energies

$$E_{xc}(u) = \int \epsilon_{xc}(u(\mathbf{r}))u^2(\mathbf{r})d\mathbf{r};$$

Local density approximation (LDA)

Non-local

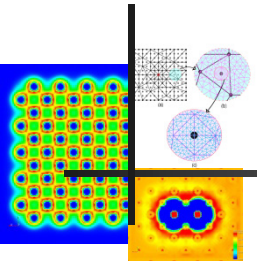
$$E_H(u) = \frac{1}{2}\int\int \frac{u^2(\mathbf{r})u^2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}';$$

$$E_{ext}(u,\mathbf{R}) = \int u^2(\mathbf{r})V_{ext}(\mathbf{r})d\mathbf{r} = \sum_{I=1}^{M}\int u^2(\mathbf{r})\frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}d\mathbf{r}$$

$$E_{zz}(\mathbf{R}) = \frac{1}{2}\sum_{I=1}^{M}\sum_{J=1,J\neq I}^{M}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|};$$

Classical electrostatic interaction energy :

Computed in Fourier-space (reciprocal-space) in almost all DFT implementations



OFDFT – Real-space formulation

- Electrostatic interactions can be re-written locally as,

$$E_H(u) + E_{ext}(u, \mathbf{R}) + E_{ZZ}(\mathbf{R}) =$$

$$- \inf_{\phi \in H^1(\mathbf{R}^3)} \left\{ \frac{1}{8\pi} \int |\nabla \phi(\mathbf{r})|^2 d\mathbf{r} - \int (u^2(\mathbf{r}) + b(\mathbf{r}; \mathbf{R}))\phi(\mathbf{r}) d\mathbf{r} \right\}$$

(Regularized nuclear charges)

- Non-local kernel energies

$$T_k(u) = \int \int u^{2\alpha}(\mathbf{r})\, K_{\alpha,\beta}(|\mathbf{r} - \mathbf{r}'|; u(\mathbf{r}), u(\mathbf{r}'))u^{2\beta}(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}'$$

- Let

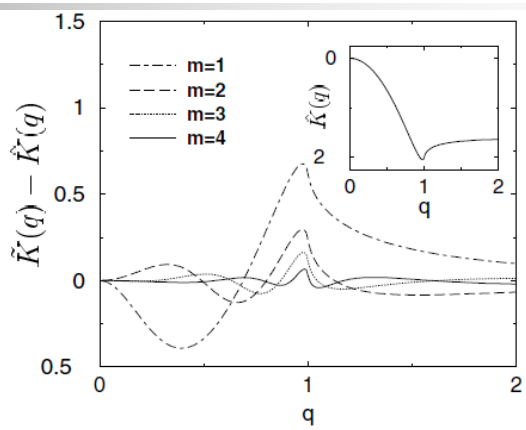
$$V_\alpha(\mathbf{r}) = \int K_{\alpha,\beta}(|\mathbf{r} - \mathbf{r}'|)u^{2\alpha}(\mathbf{r}')d\mathbf{r}', \qquad \xrightarrow{\text{FT}} \qquad \hat{V}_\alpha(\mathbf{k}) = \hat{K}_{\alpha,\beta}(\mathbf{k})\hat{u^{2\alpha}}(\mathbf{k}),$$
$$V_\beta(\mathbf{r}) = \int K_{\alpha,\beta}(|\mathbf{r} - \mathbf{r}'|)u^{2\beta}(\mathbf{r}')d\mathbf{r}'. \qquad\qquad \hat{V}_\beta(\mathbf{k}) = \hat{K}_{\alpha,\beta}(\mathbf{k})\hat{u^{2\beta}}(\mathbf{k}).$$

OFDFT – Real-space formulation (kernel energies)

(Radhakrishnan & Gavini PRB 2010)

- $$\hat{K}_{\alpha,\beta}(\mathbf{k}) \approx \sum_{j=1}^{m} \frac{A_j |\mathbf{k}|^2}{|\mathbf{k}|^2 + B_j}$$

Choly & Kaxiras (2005)



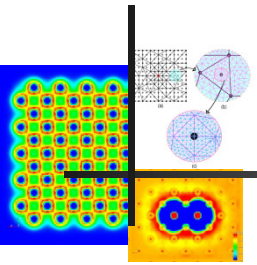
- Local reformulation of kernel energy

$$V_\alpha(\mathbf{r}) = \sum_{j=1}^{m} [\omega_{\alpha_j}(\mathbf{r}) + A_j u^{2\alpha}(\mathbf{r})], \quad V_\beta(\mathbf{r}) = \sum_{j=1}^{m} [\omega_{\beta_j}(\mathbf{r}) + A_j u^{2\beta}(\mathbf{r})]$$

$$-\nabla^2 \omega_{\alpha_j} + B_j \omega_{\alpha_j} + A_j B_j u^{2\alpha} = 0, \; -\nabla^2 \omega_{\beta_j} + B_j \omega_{\beta_j} + A_j B_j u^{2\beta} = 0 \quad j = 1 \ldots m.$$

$$T_{\mathrm{k}}(u) = \inf_{\omega_{\alpha_j} \in H^1(\mathbf{R}^3)} \sup_{\omega_{\beta_j} \in H^1(\mathbf{R}^3)} \sum_{j=1}^{m} \{ \int [\frac{1}{A_j B_j} \nabla \omega_{\alpha_j} \cdot \nabla \omega_{\beta_j} + \frac{1}{A_j} \omega_{\alpha_j} \omega_{\beta_j} + \omega_{\beta_j} u^{2\alpha} + \omega_{\alpha_j} u^{2\beta} + A_j u^{2(\alpha+\beta)}] d\mathbf{r} \}.$$

Local saddle point problem in kernel potentials



OFDFT – Real-space formulation

- The saddle-point problem is given by,

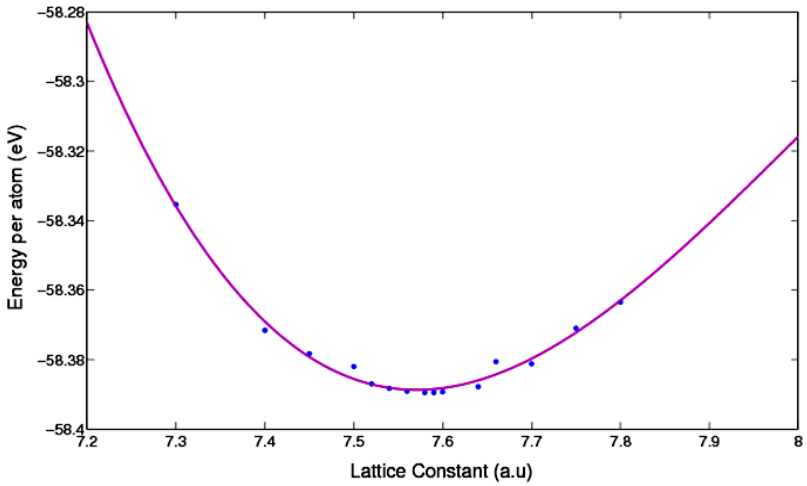
$$\inf_{\mathbf{R}\in\mathbf{R}^{3M}} \inf_{u\in H^1(\mathbf{R}^3)} \sup_{\phi\in H^1(\mathbf{R}^3)} \inf_{\omega_{\alpha_j}\in H^1(\mathbf{R}^3)} \sup_{\omega_{\beta_j}\in H^1(\mathbf{R}^3)} L(u,\mathbf{R},\phi,\omega_{\alpha_j}\omega_{\beta_j}) \quad \text{subject to:} \quad \int u^2(\mathbf{r})d\mathbf{r} = N$$

$$\begin{aligned} L(u,\mathbf{R},\phi) &= \int [\frac{1}{2}|\nabla u|^2 + C_F u^{10/3} + \varepsilon_{xc}(u^2)u^2 - \frac{1}{8\pi}|\nabla\phi|^2 + (u^2 + b(;\mathbf{R}))\phi \\ &+ \sum_{j=1}^{m}\left(\frac{1}{A_jB_j}\nabla\omega_{\alpha_j}\cdot\nabla\omega_{\beta_j} + \frac{1}{A_j}\omega_{\alpha_j}\omega_{\beta_j} + \omega_{\beta_j}u^{2\alpha} + \omega_{\alpha_j}u^{2\beta} + A_j u^{2(\alpha+\beta)}\right)]d\mathbf{r} \end{aligned}$$

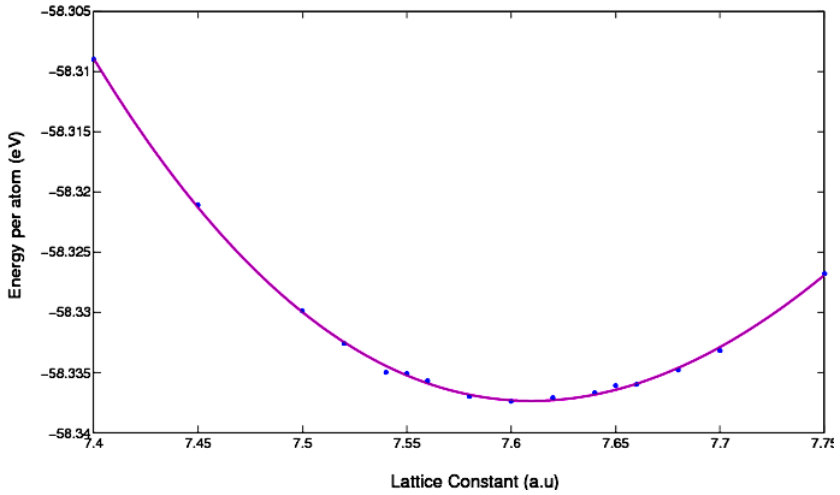
- Well-posedness is an open question! (Blanc & Cances 2005)

Bulk properties of Aluminum

Density Independent Kernels

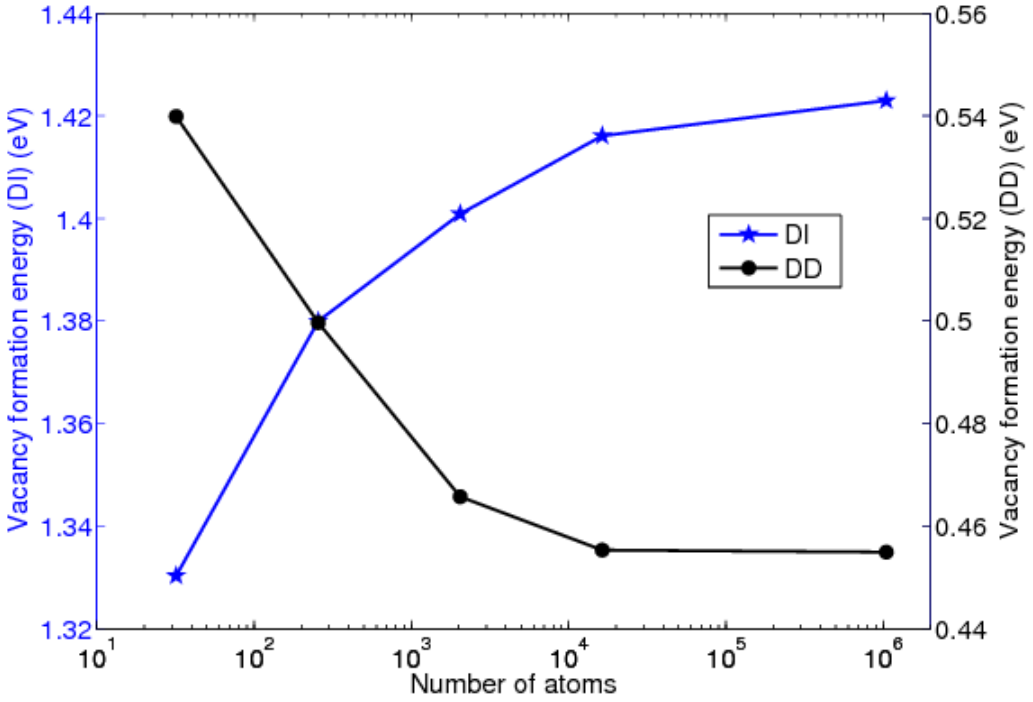


Density Dependent Kernels



	KS-DFT (Goodwin et. al.)	Gavini et al. (TF-vW)	Carter et. al. (Density Independent)	OFDFT (Density Independent)	Carter et al. (Density Dependent)	OFDFT (Density Dependent)
Bulk Modulus (GPa)	79	83.1	71.9	72	72	71.72
Energy per atom (eV)	-58.336	-58.81	-58.334	-58.3895	-58.331	-58.3374
Eq. lattice Const.	7.44	7.42	7.59	7.58	7.61	7.6

Vacancy in Aluminum: Convergence with cell-size



Domain size (No. of atoms + 1 vacancy)	Vacancy formation energy (eV)					
	OFDFT (Density Independent)	Carter et. al (Density Independent)	OFDFT (Density Dependent)	Carter et. al (Density Dependent)	Exp.	Gavini et.al (TFW-λ)
32	1.33	1.35	0.5399	0.512	0.66	0.77
256	1.38	-NA-	0.4993	0.475	0.66	0.74

Di-vacancy binding energy – cell-size effect