Electronic structure calculations at macroscopic scales

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Defects in Materials

Crystals are like people - it's the defects in them that make them interesting

Sir F. Charles Frank

- Defects mediate many important macroscopic properties
  - Vacancies: Creep, spall, prismatic loops, radiation ageing
  - Dislocations: Metal plasticity
  - Domain walls, grain boundaries, free surfaces, interfaces

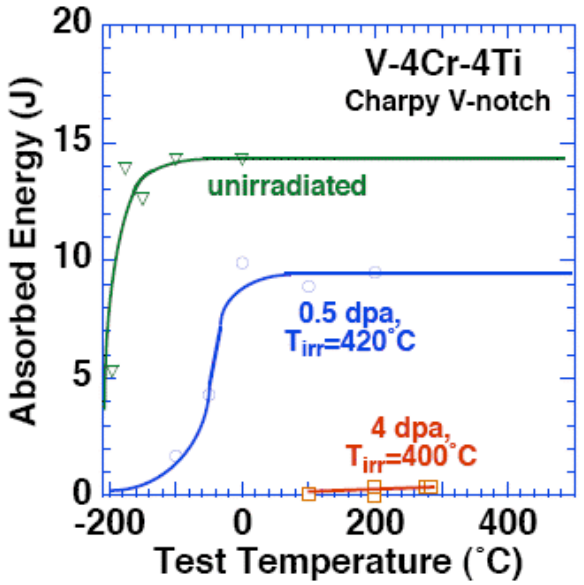
- Defects give rise to complex interactions
  - Typical concentrations are small. Eg. Vacancies: 1 part per million
  - Range of interacting scales and physics: Electronic, Atomistic, Elastic …
  - Defects break the translational symmetry (periodicity) of the lattice

- Seek a method to describe defects
  - Idea: Start with Density Functional Theory and develop a numerical method that adapts the resolution to the structure of the solution

Example: Radiation Damage and Prismatic Loops

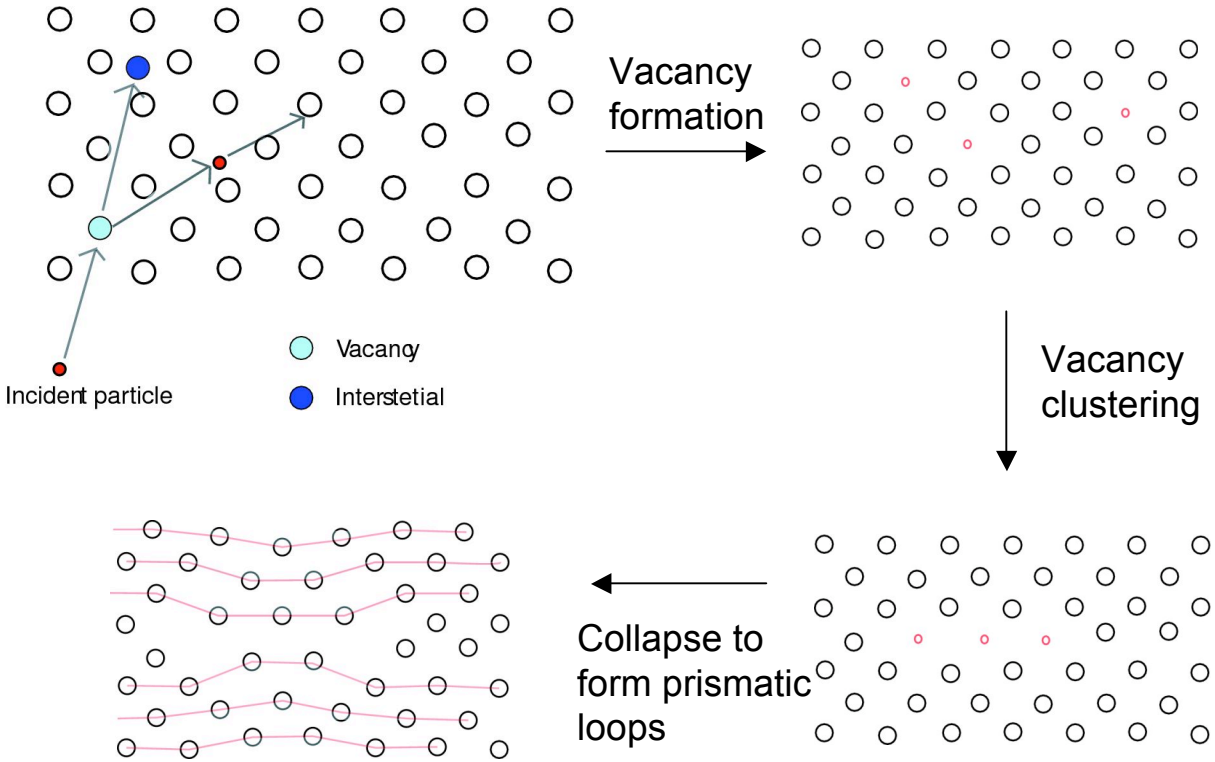
Effects of radiation on mechanical properties

- Reduced fracture toughness
- Increased hardness and reduced ductility
- Material swelling



Zinkle, S.J., ORNL

Mechanisms



Outline

- Introduction and Motivation
- (Orbital-Free) Density-Functional Theory
- Quasi-Continuum reduction
- Vacancy clustering and prismatic loop nucleation in Aluminum
- Towards Quasi-Continuum Density-Functional Theory
- Concluding Remarks

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.

Quantum mechanics of crystalline solids

- Born-Oppenheimer approximation: Treat atomic nuclei classically
- Schrödinger equation $H\psi = E\psi$

$$H = -\frac{1}{2}\sum_i \nabla^2_{\mathbf{r}_i} - \sum_{i,a} \frac{Z_a}{|\mathbf{r}_i - \mathbf{R}_a|} - \sum_{i,j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{a,b} \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|}$$

$$\psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_M)$$

- Computational difficulty: $\psi \in \mathbb{R}^{3N}$

100 points/variable, 100 electrons means $100^{300} \sim 10^{600}$ degrees of freedom!

Density Functional Theory

- Ground-state energy depends only on the electron-density

$$
\begin{aligned}
E_0 &= \min_{\psi} \langle \psi | H | \psi \rangle \\
&= \min_{\psi} \left\langle \psi \left| \frac{1}{2} \sum_i |\nabla_i \psi|^2 + \frac{1}{2} \sum_{i,j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right| \psi \right\rangle + \sum_{I,J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \\
&= \min_{\rho} \left\{ \underbrace{\min_{\psi \to \rho} \left\langle \psi \left| \frac{1}{2} \sum_i |\nabla_i \psi|^2 + \frac{1}{2} \sum_{i,j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \psi \right\rangle}_{F[\rho]} + \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + E_{ZZ} \right\}
\end{aligned}
$$

$F[\rho]$ Universal, independent of system!

$$
= \min_{\rho} \left\{ T_s[\rho] + \int \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho] + \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + E_{ZZ} \right\}
$$

Kinetic energy of a non-interacting system
Nonlinear eigenvalue problem

Unknown
Model: LDA, LSDA, GGA …

Hohenberg and Kohn, Phys. Rev (1964)
Kohn and Sham, Phys. Rev (1965)

Orbital-free Kinetic Energy Functional

- Idea: Model T_s
- Thomas-Fermi-von Weizsacker

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

- Subsequent improvements Teter, Smargiassi, Carter and others.

Orbital-free density functional theory (OFDFT)

- The ground-state energy functional:

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

$$T_s(\rho) = C_F \int_\Omega \rho^{5/3}(\mathbf{r}) d\mathbf{r} + \frac{\lambda}{8} \int_\Omega \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r};$$

$$E_{xc}(\rho) = \int_\Omega \epsilon_{xc}(\rho(\mathbf{r}))\rho(\mathbf{r}) d\mathbf{r};$$

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

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

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

Non-local:
Fourier methods, but require periodicity
Multi-pole methods, but require structure

Real-space formulation

- Observe $E_H(\rho) + E_{ext}(\rho, \mathbf{R}) + E_{ZZ}(\mathbf{R}) =$

$$-\min_{\phi} \left\{ \frac{1}{8\pi} \int_\Omega |\nabla\phi(\mathbf{r})|^2 d\mathbf{r} - \int_\Omega (\rho(\mathbf{r}) + b(\mathbf{r}))\phi(\mathbf{r}) d\mathbf{r} \right\}$$

regularization of $\sum_{I=1}^{M} Z_I \delta_{\mathbf{R}_I}$

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

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

- Finally, enforce the constraint $\rho > 0$ by setting $\rho = u^2$

Real-space formulation of OFDFT

$$\min_{u,\mathbf{R}} \max_{\phi} L(u, \mathbf{R}, \phi)$$

$$L(u, \mathbf{R}, \phi) = \frac{\lambda}{2} \int_\Omega |\nabla u(\mathbf{r})|^2 d\mathbf{r} + C_F \int_\Omega u^{10/3}(\mathbf{r}) d\mathbf{r} + \int_\Omega \varepsilon_{xc}(u^2(\mathbf{r})) u^2(\mathbf{r}) d\mathbf{r}$$

$$- \frac{1}{8\pi} \int_{\mathbb{R}^3} |\nabla \phi(\mathbf{r})|^2 d\mathbf{r} + \int_{\mathbb{R}^3} (u^2(\mathbf{r}) + b(\mathbf{r})) \phi(\mathbf{r}) d\mathbf{r}$$

- Minimizers exist
- *L* is local and can be discretized using a finite element approximation
- Finite element approximation with an approximation of degree *k* and numerical quadrature accurate to order *n* converges if

  n-2k+3>0

Force on an atom

- Let $E_1(u_{eq}, \phi_{eq}, \mathbf{R}) = \min_u \max_\phi L(u, \mathbf{R}, \phi)$

- Force on the *I*th atom

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

- In a finite-element approximation

$$f_X^{bK} = \int_\Omega \mathsf{E}_{KJ} N_{b,J} d\Omega + \int_\Omega Z_b b_b \left(\sum_{a=1}^{n} \phi_a N_{a,K} \right) d\Omega$$

Forces arising due to the configuration of nodes

Physical force on nuclei

Aluminum clusters

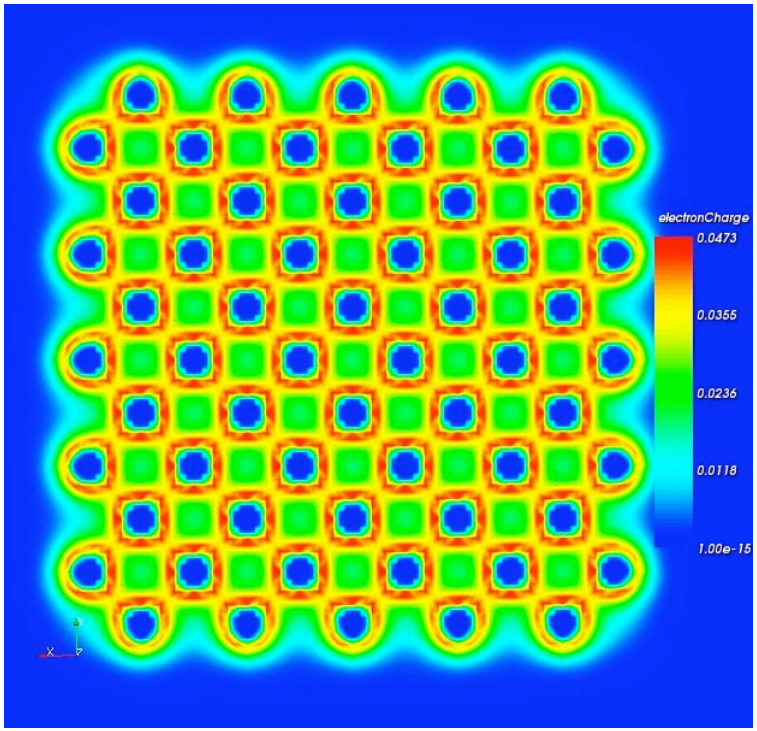
- λ = 1/6
- Heine-Abarenkov psuedopotential:

$$V_{ext} = \begin{cases} -\frac{Z_v}{r}, & \text{if } r \geq r_c; \\ -A, & \text{if } r < r_c; \end{cases}$$

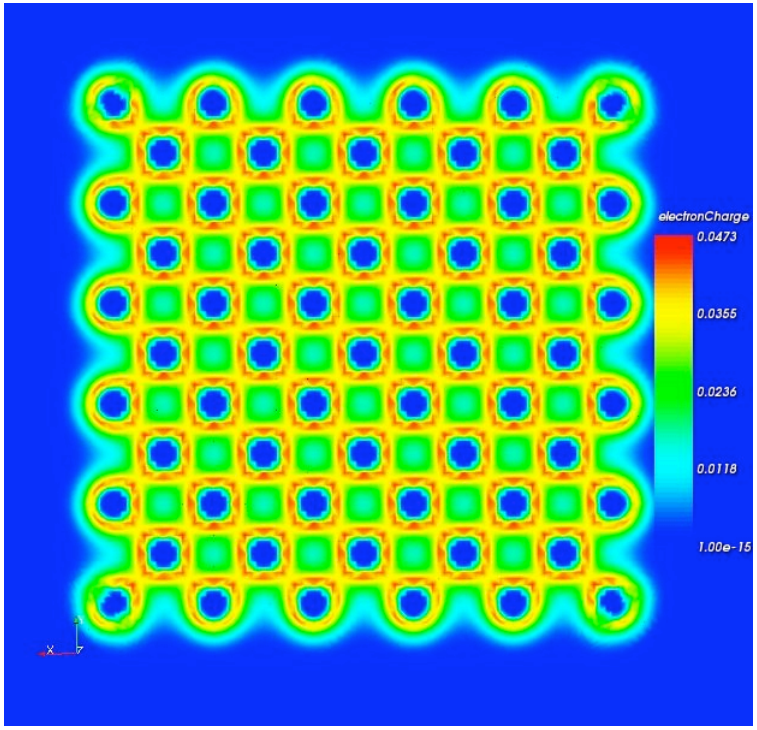
- Simulations are performed on 1x1x1 3x3x3 5x5x5 9x9x9 clusters
- Equilibrium configurations of small clusters are determined

Aluminum clusters: electron density

Contours of electron-density in an aluminum cluster of 5x5x5 fcc unit cells



mid-plane



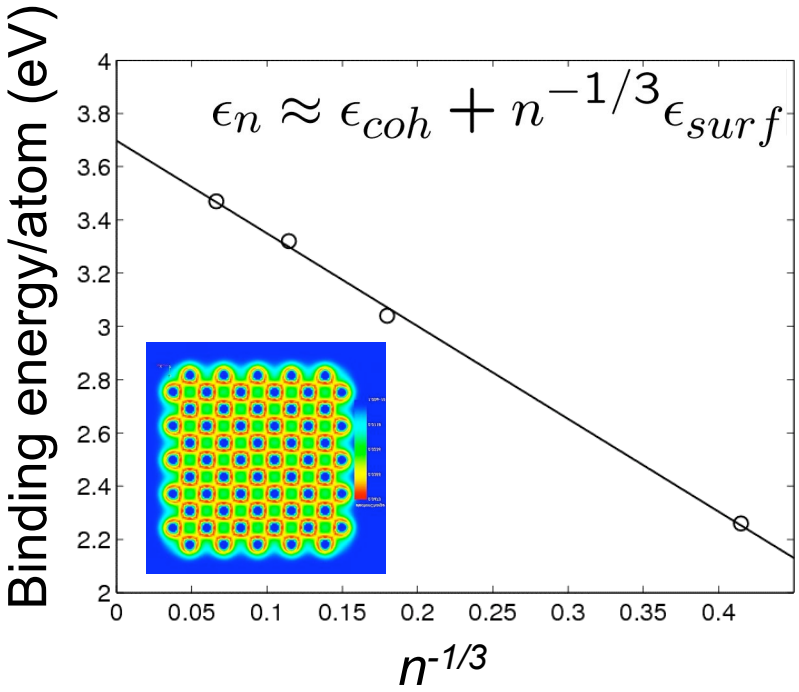
face

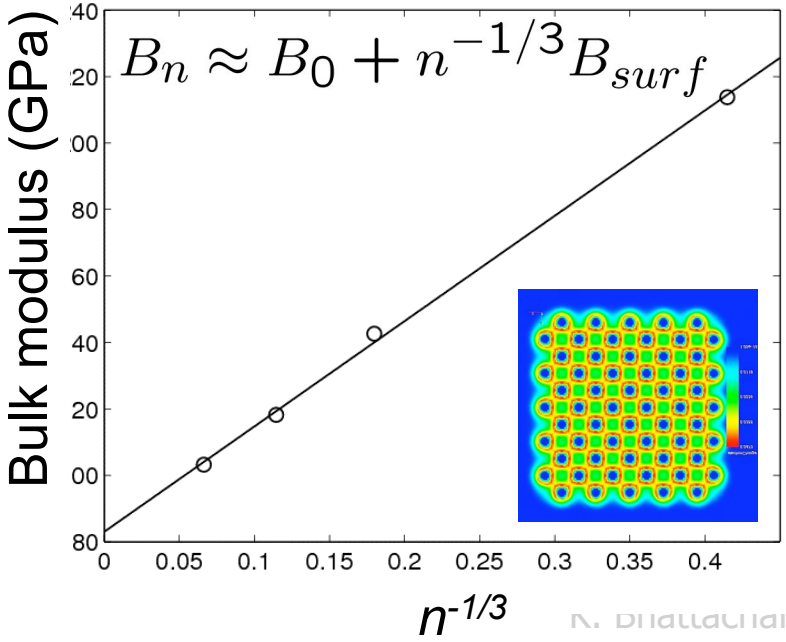
Example – Aluminum clusters

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)

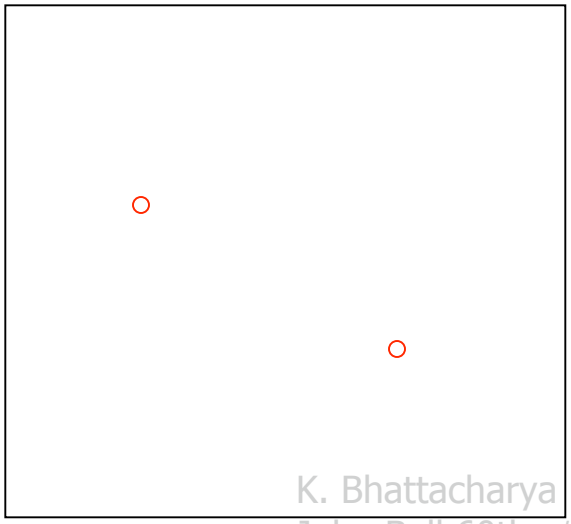
b/ Brewer (1997), Gschneider (1964)





Perspectives

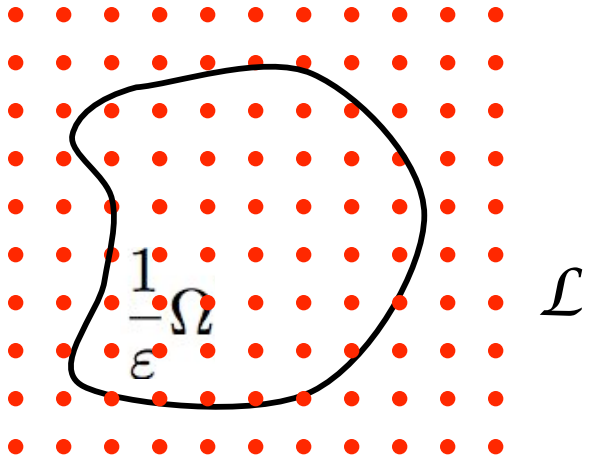
- Real-space formulation and finite-element approximation provides a viable means of computing with OFDFT
- However, it is expensive:
  9x9x9 cluster = 3730 atoms required 10,000 CPU hours!
- Have to coarse-grain away "uninteresting regions"



Some features of OFDFT

- Large body limit (Catto, Le Bris and Lions, 1998)

$$\varepsilon^3 E(\mathcal{L} \cap \frac{1}{\varepsilon}\Omega) \to E^{\#}(\mathcal{L})$$



- Slowly varying deformation
  (Blanc, Le Bris and Lions, 2002)

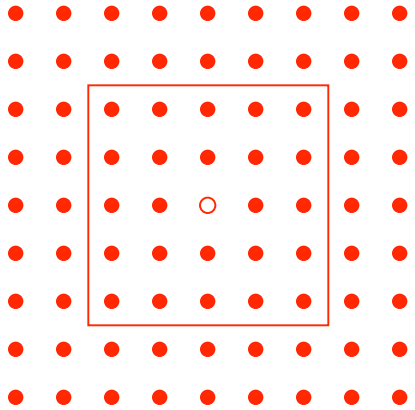
For $y \in \mathcal{C}^\infty(\Omega, \mathbb{R}^3)$,

$$\varepsilon^3 E(\frac{1}{\varepsilon} y(\varepsilon\mathcal{L} \cap \Omega)) \to \int_\Omega W(\nabla y)dx \qquad W(F) = E^{\#}(F\mathcal{L})$$

Can approximate energy of a slowly varying deformation by a local density obtained from a periodic calculation

Decay of electronic and mechanical fields

- TFW Euler-Lagrange Equation $-\Delta u + V[u, b] = \lambda u$



Consider $(-\Delta + V(x))u = \lambda u$

$$(-\Delta + V^p(x) + V^{\#}(x))u^p = \lambda u^p$$

Compact support

Then, $|u_j^p - u_j^{\#}| \leq C \exp(-\gamma_j |x|)$

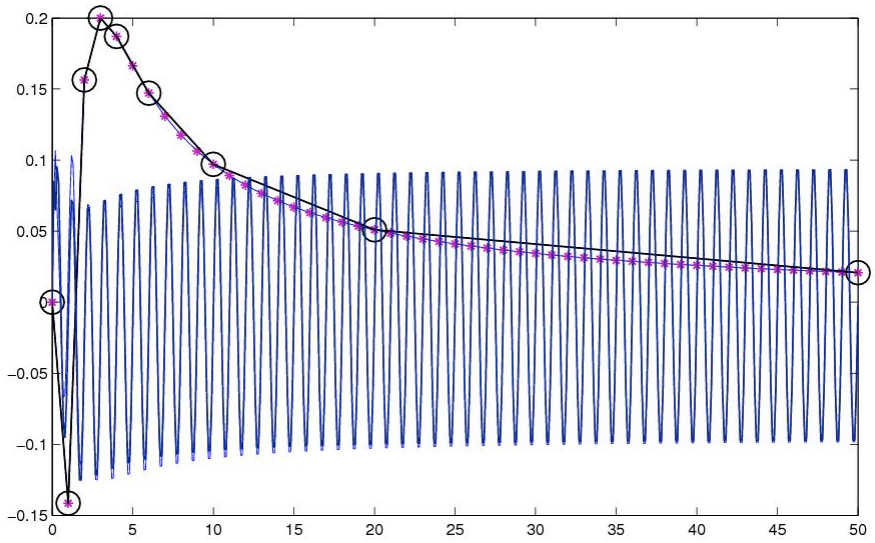
Kohn: "Near-sightedness of electronic matter"

- But, let us relax the atoms!
  Small displacement from perfect lattice
  Long-wavelength is deformation is consistent with linear elasticity

Displacements decay slowly (polynomial) away from defects

Defects and coarse-graining

- Features:
  - Details are important close to the defect
  - Displacements suffer polynomial decay consistent with elasticity
  - Electronic fields approach periodic far from the defects



- Design a numerical method that exploits this structure

Coarse-graining around defects: Key idea

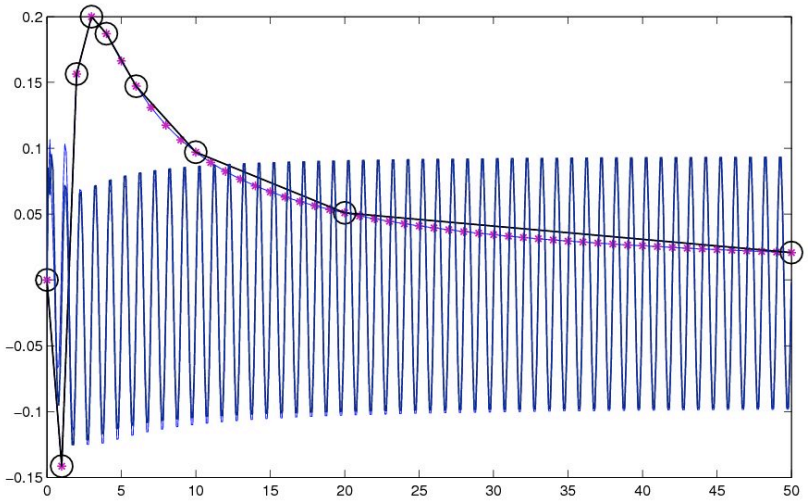
- Constrain atomic positions following an adaptive supra-atomic mesh (T_{h1})

  (Like Quasi-continuum method, Tadmor Ortiz, Phillips ….)

- Write electron density and electrostatic potential as a sum of two terms

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

  - Predictor $u_0^h\,,\phi_0^h$
    Computed element by element assuming periodicity on a local sub-atomic mesh (T_{h2}) followed by L^2 -> H^1 projection

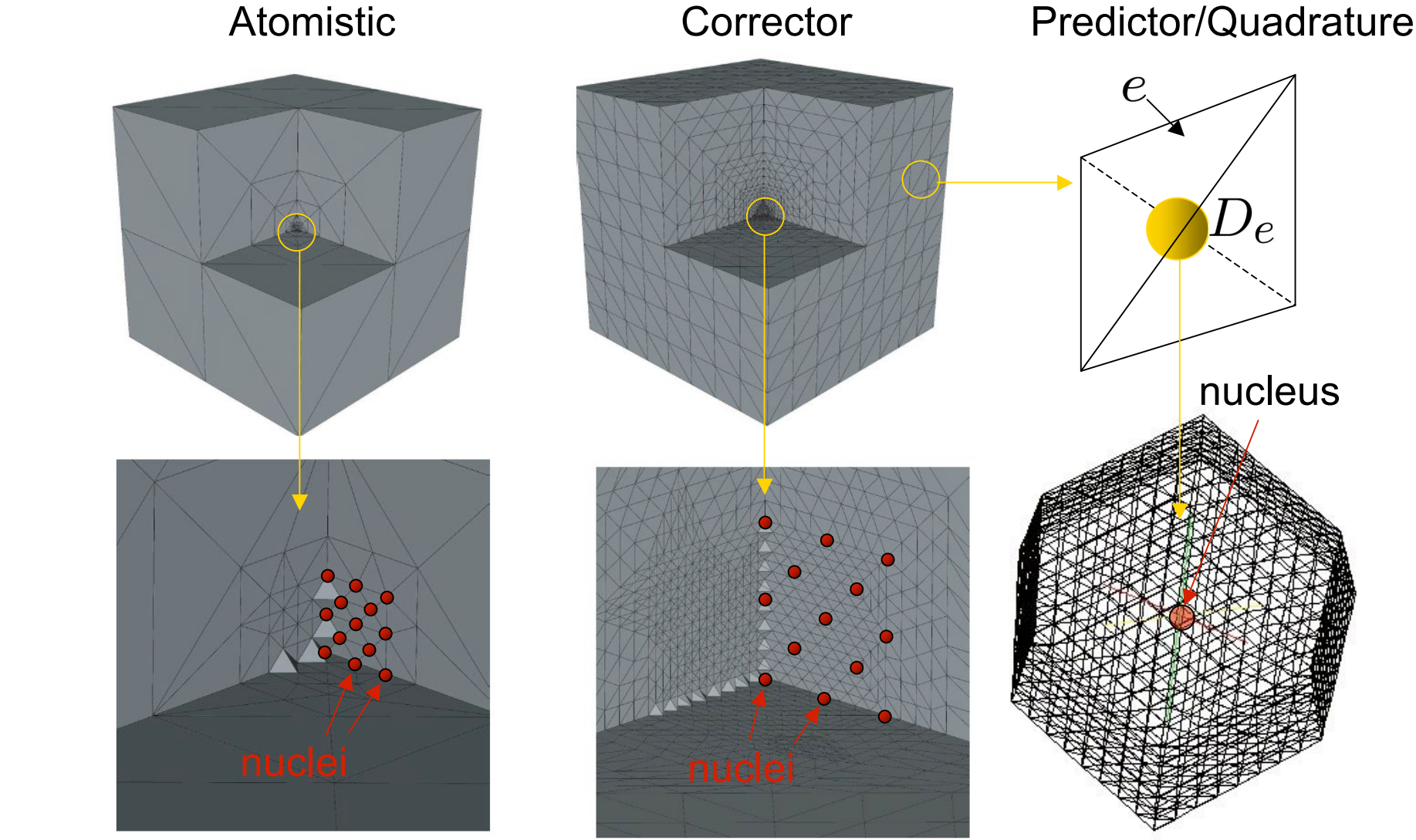


  - Corrector $u_c^h\,,\phi_c^h$
    Computed on an adaptive mesh which is sub-atomic near defects and refines away from it (T_{h3})

- Cluster quadrature rules for T_{h3}

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

QC/OFDFT – Nested meshes



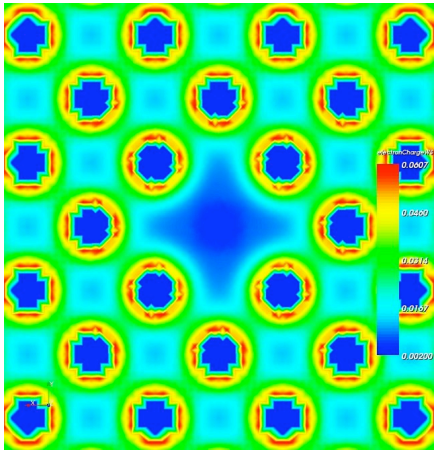
QC-OFDFT: Properties

QC-OFDFT has the following properties:

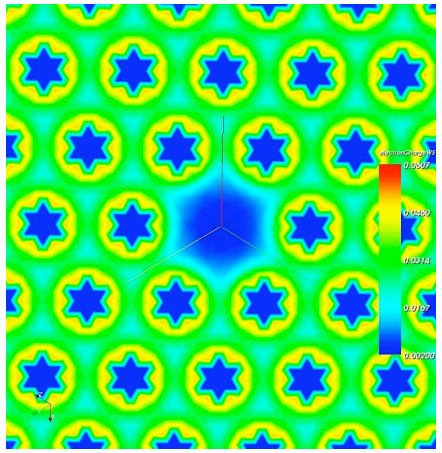
- adapts the level of spatial resolution to the local structure of the solution
- the coarse-graining is completely unstructured
- the coarse-graining is seamless
- OFDFT is the sole physics input to the calculations, and no spurious physics or a priori ansatz regarding the behavior of the system is introduced
- fully-resolved OFDFT and finite lattice-elasticity are obtained as extreme limits

Vacancy in Aluminum

- Test case
  - Simple defect with both electronic core and long-range
  - Formation energy is commonly used as benchmark
- TFW + LDA + Heine-Aberenkov pseudopotentials
  Dirichlet boundary conditions corresponding to bulk fields
- Sample size: 4, 32, 256, 2048, 16348, 1048576 atoms
- Million atom sample: 1500 atomic nodes and 450,000 electronic nodes
- Mesh gradation $h(r) \sim r^{6/5}$

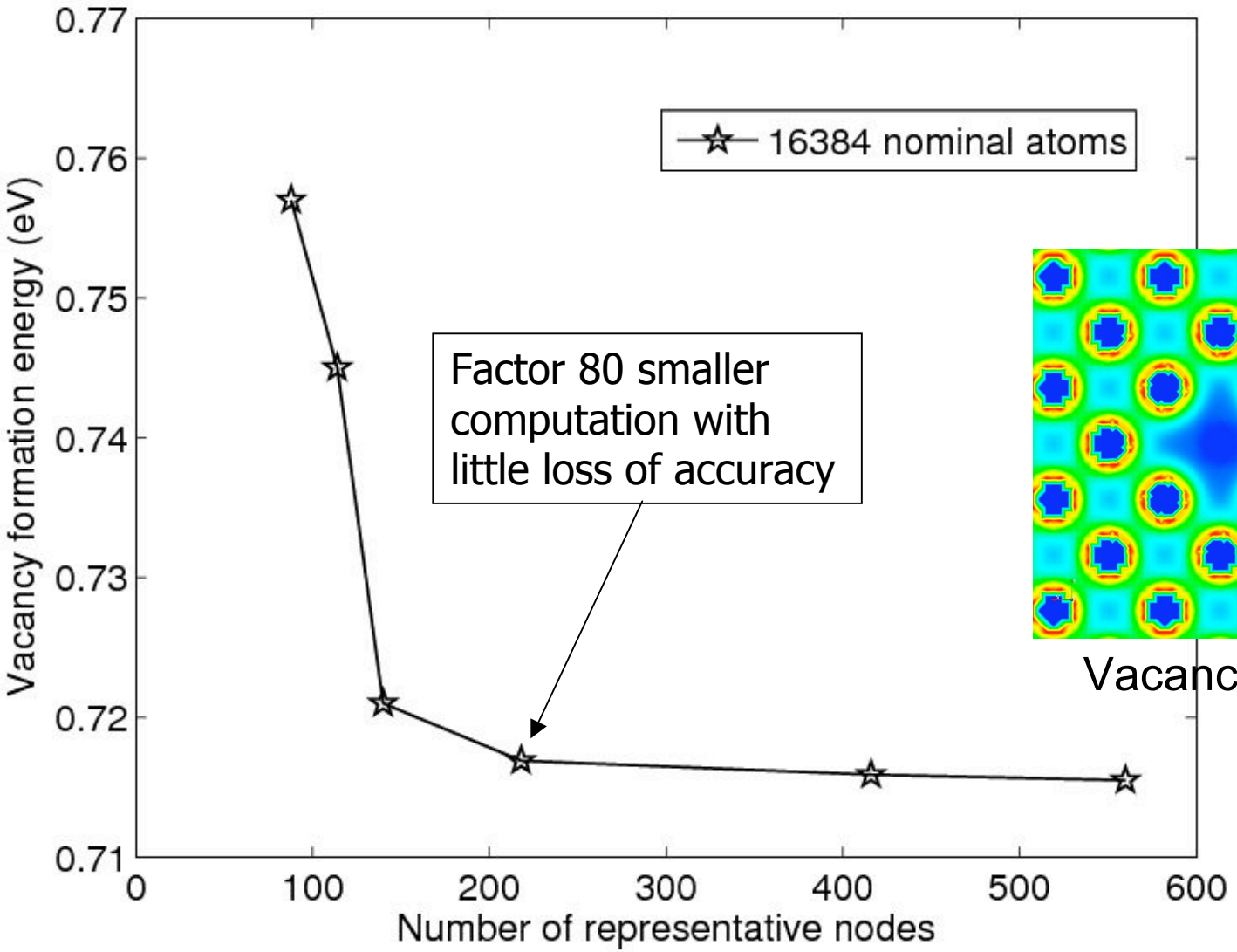


(100) plane



(111) plane

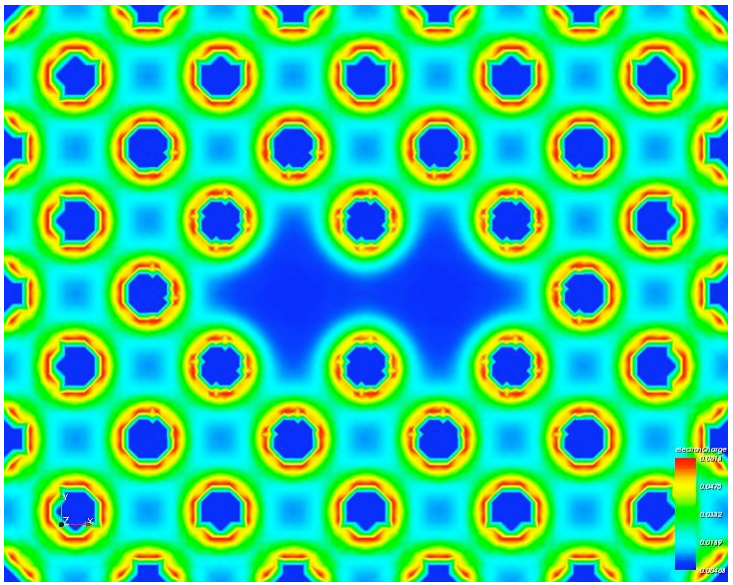
Convergence of QC approximation



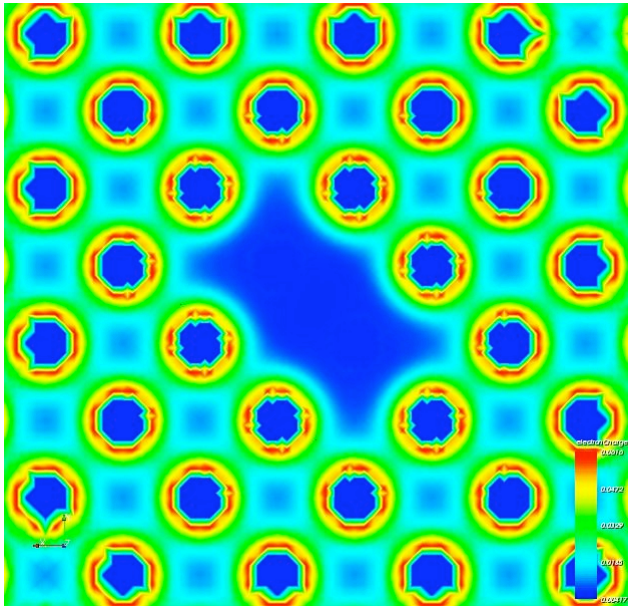
Vacancy in Al

Di-vacancies in Aluminum

Electron density along (100) plane



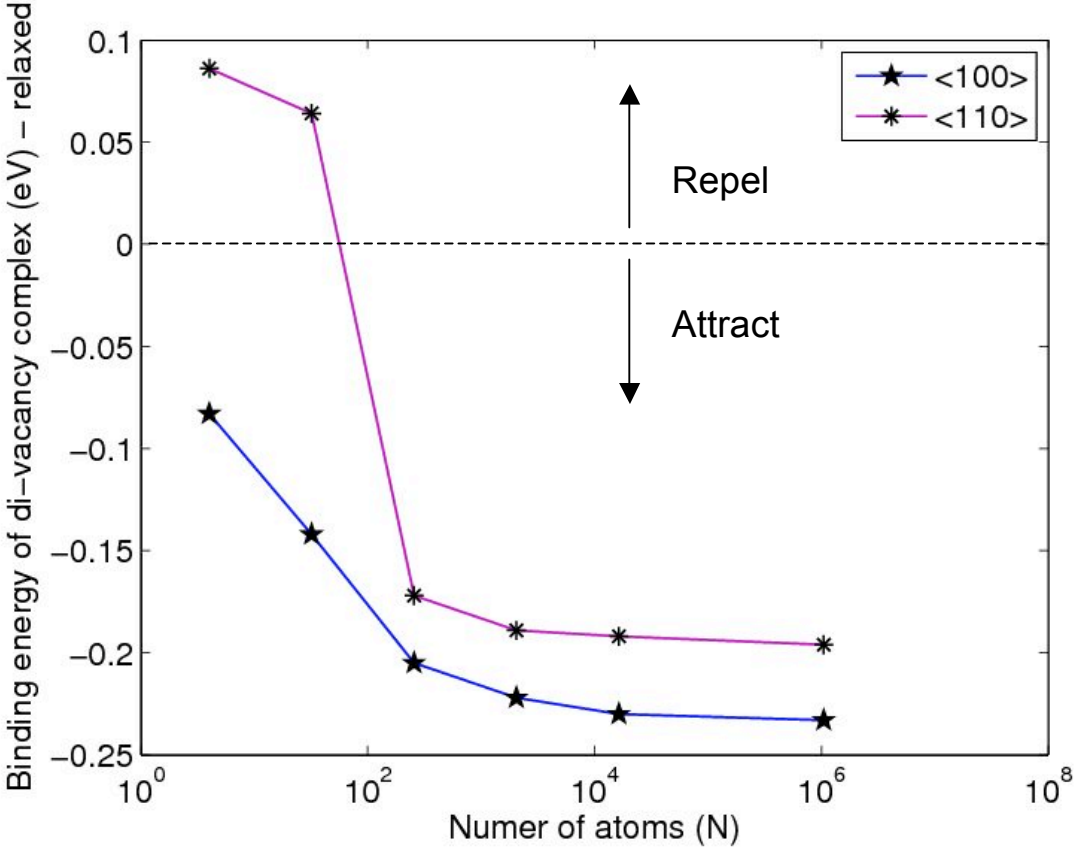
<100> di-vacancy complex



<110> di-vacancy complex

- Experimental observations (Ehrhart et al. 1991; Hehenkamp et al. 1994)
  - Vacancies attract with 0.2 to 0.3eV binding energy
- Previous DFT computations
  - Vacancies attract along <100> with 0.005-0.05 eV binding energy
  - Vacancies repel along <110> with -0.08 binding energy

Di-vacancy binding energy



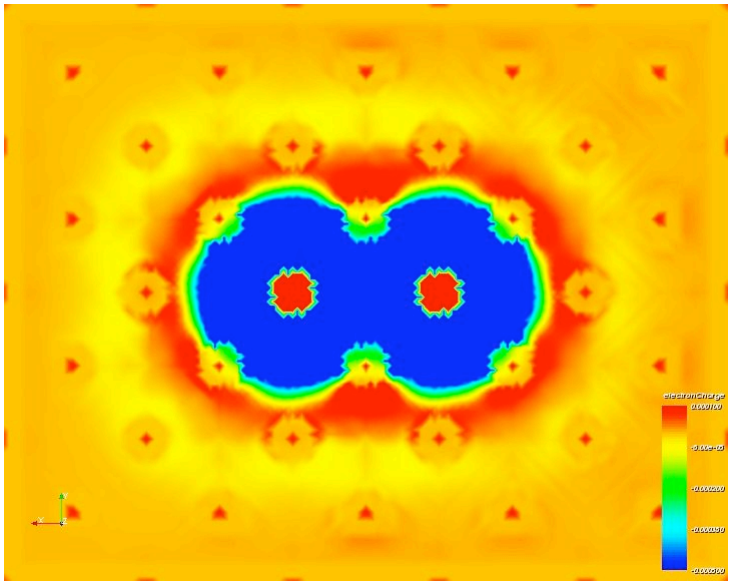
Observe the change in physics with cell-size!!

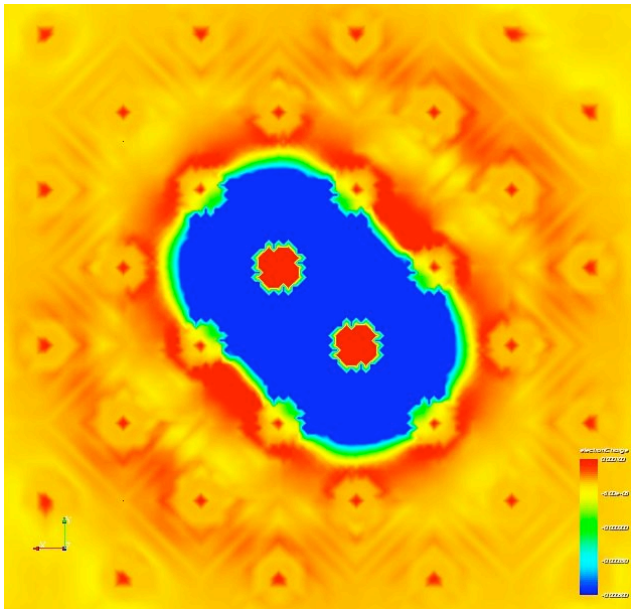
Binding energy of a di-vacancy ($E^{\text{di-vacancy}}$-$2E^{\text{vacancy}}$)

- -0.19 eV for <110> di-vacancy complex
- -0.23 eV for <100> di-vacancy complex
- Experimental estimates: -0.2 to -0.3 eV (Ehrhart et al. 1991; Hehenkamp et al. 1994)

Di-vacancies in Aluminum: Electron density

Correction to periodic electron density along (100) plane



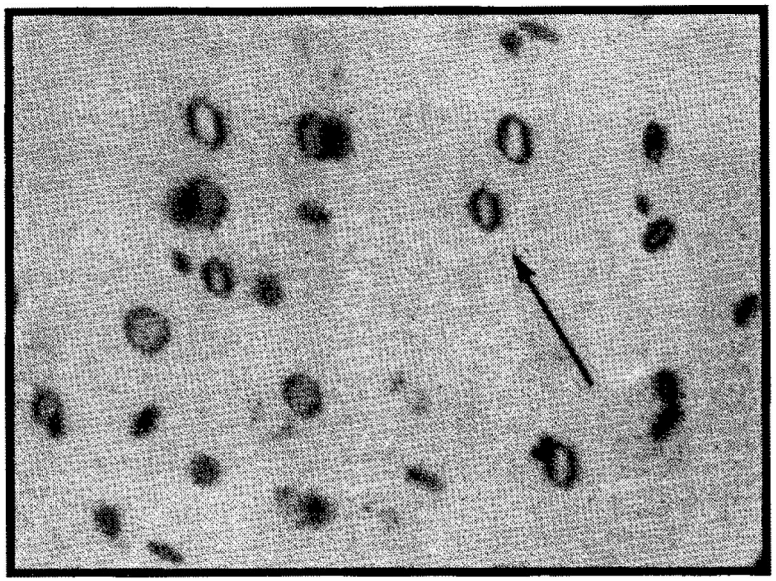


<100> di-vacancy complex

<110> di-vacancy complex

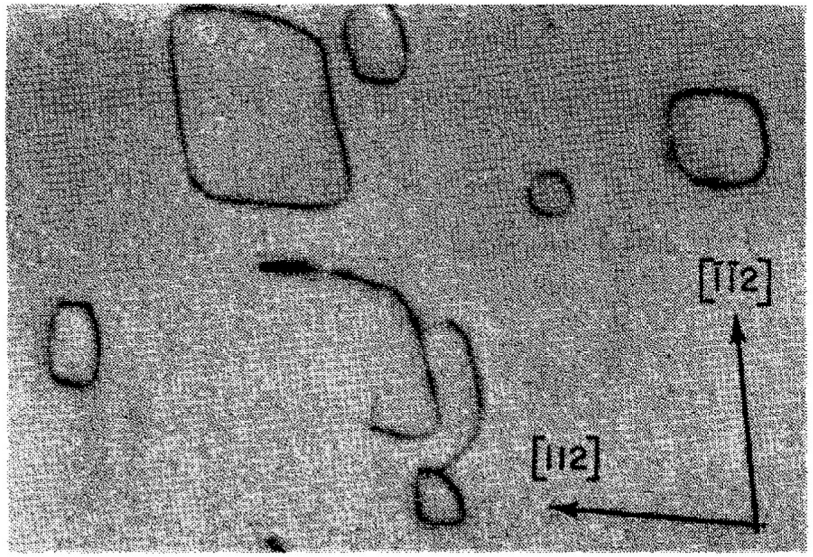
The oscillations in electron-density are counterparts of Friedel oscillations for the TFW kinetic energy functionals

Prismatic loops



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

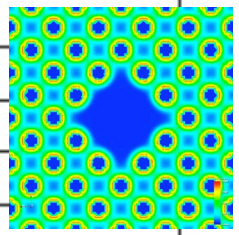
Takamura and Greensfield,
J. Appl. Phys., **33** (1961) 247.

- What is the nucleation mechanism?
  - Loops smaller than 50nm are difficult to observe experimentally
  - Vacancy condensation followed by collapse?

Vacancy Clusters

- Clusters of 4 vacancies (each vacancy has at least two NN as vacancy)

	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

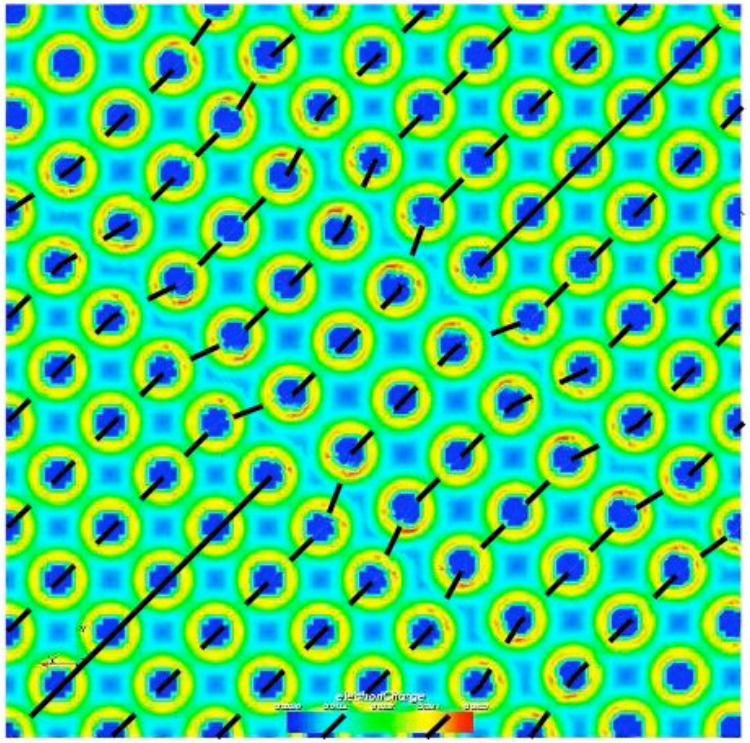
$$E_{nv}^{bind} = E_{nv}^{J} - nE_{v}^{J}$$

  - {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

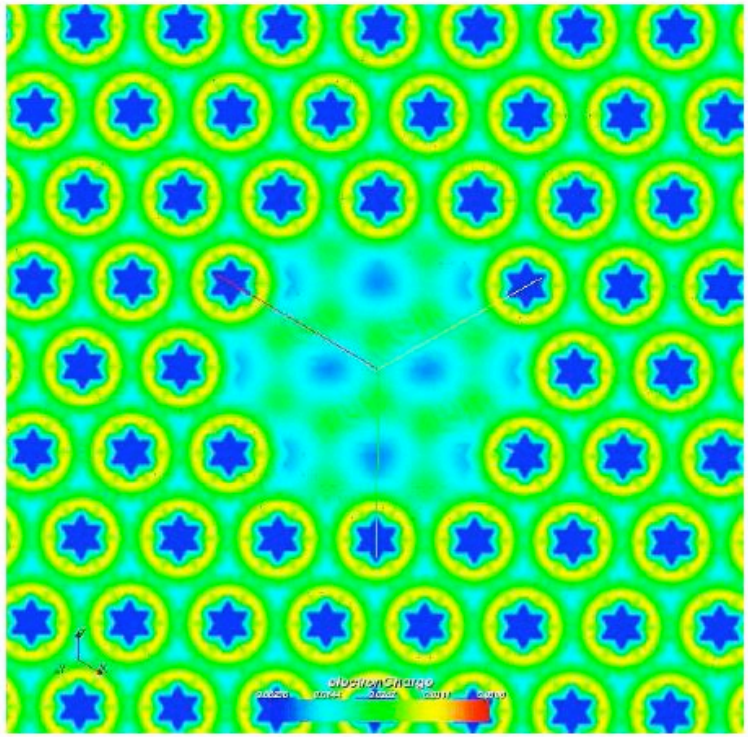
- Each cluster is energetically stable against breakup into smaller clusters
  Vacancy condensation is energetically feasible

Bi-stability of 7-vacancy cluster: prismatic loop nucleation

- 7-vacancy hexagonal cluster on a {111} plane has two stable configurations
  - Uncollapsed with binding energy -0.88 eV
  - Collapsed prismatic dislocation loop with binding energy -1.55 eV



Electron density on the (100) plane



Electron density on the (111) plane

Prismatic dislocation loops can nucleate and be stable at extremely small sizes!

Kohn-Sham Density Functional Theory

- Recall,

$$E_0 = \min_{\psi} \langle \psi | H | \psi \rangle$$

$$= \min_{\rho} \left\{ \underbrace{\min_{\psi \to \rho} \left\langle \psi \left| \frac{1}{2} \sum_i |\nabla_i \psi|^2 + \frac{1}{2} \sum_{i,j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \psi \right\rangle}_{F[\rho]} + \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + E_{ZZ} \right\}$$

Universal, independent of system!

- Introduce Orbitals
  Let ψ be the Slater determinant of the orbitals $\psi_1(\mathbf{r}_1), \psi_2(\mathbf{r}_2), \ldots \psi_N(\mathbf{r}_N)$

$$= \min_{\psi_i} \left\{ \sum_i \frac{1}{2} \int |\nabla \psi_i|^2 d\mathbf{r} + \int \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho] + \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + E_{ZZ} \right\}$$

- Traditionally,

$$\left(-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\rho, \mathbf{R}) \right) \psi_i = \lambda_i \psi_i$$

$$\rho = \sum_{i=1}^{N} |\psi_i|^2$$

$$\langle \psi_i, \psi_j \rangle = \delta_{ij}$$

Hohenberg and Kohn, Phys. Rev (1964)
Kohn and Sham, Phys. Rev (1965)

Mathematical Background

$$\min_{\psi \in X} E[\psi; \mathbf{R}]$$

$$E[\psi; \mathbf{R}] = \int_\Omega \left(\sum_{i=1}^{N} \frac{1}{2} |\nabla \psi_i|^2 + \rho \epsilon_{xc}(\rho) \right) d\mathbf{r} + J(\rho; \mathbf{R})$$

$$J(\rho; \mathbf{R}) = - \min_{\phi \in H_0^1(\mathbb{R}^3)} \left\{ \frac{1}{2} \int_\Omega |\nabla \phi|^2 d\mathbf{r} - \int_\Omega (\rho + b(\mathbf{r})) \phi \, d\mathbf{r} \right\}$$

$$X = \left\{ \psi \in H_0^1(\Omega, \mathbb{R}^N) | \langle \psi_i, \psi_j \rangle = \delta_{ij} \right\} \qquad \rho = \sum_{i=1}^{N} |\psi_i|^2$$

Proposition. E has a minimum in X

- X is closed in H^1_0
- E is lower-semicontinuous in the weak topology of X
- E is coercive in the weak topology of X

Finite Element Approximation

Theorem. Let

T_h sequence of triangulations of R^3, h -> 0

X_h restriction of X to T_h and polynomial of degree k in each triangle

$$E_h(\psi) = \begin{cases} \frac{1}{2}\|\nabla\psi\|_{L^2}^2 + E_{xc}(\rho) + J_h(\rho) & \text{if } \psi \in X_h, \\ +\infty & \text{otherwise} \end{cases}$$

$$J_h(\rho) = -\min_{\phi \in H_0^1} \begin{cases} I(\phi,\rho) = \frac{1}{2}\int_\Omega |\nabla\phi|^2 d\mathbf{r} - \int_\Omega (\rho + b(\mathbf{r}))\phi\, d\mathbf{r} & \text{if } \phi \in X_{1_h},\ \psi \in X_h, \\ +\infty & \text{otherwise,} \end{cases}$$

Then, $\lim\limits_{h\to 0} \inf\limits_X E_h = \min\limits_X E$

Proof. $E_h \xrightarrow{\Gamma} E$ in the weak topology of X

E_h is equicoercive in the weak topology of X

Theorem. $\tilde{E}_h$ as before but with quadrature of degree n

$\lim\limits_{h\to 0} \inf\limits_X \tilde{E}_h = \min\limits_X E \quad$ if $n - 2k + 3 > 0$

Simple examples

Ground state Energies of atoms (a.u)

Element	KS-DFT-FE	KS-LSD (NIST)
He	-2.833	-2.834
Li	-7.340	-7.343
C	-37.460	-37.470
N	-54.125	-54.136
O	-74.518	-74.527

Binding energy and bond length of N_2 molecule

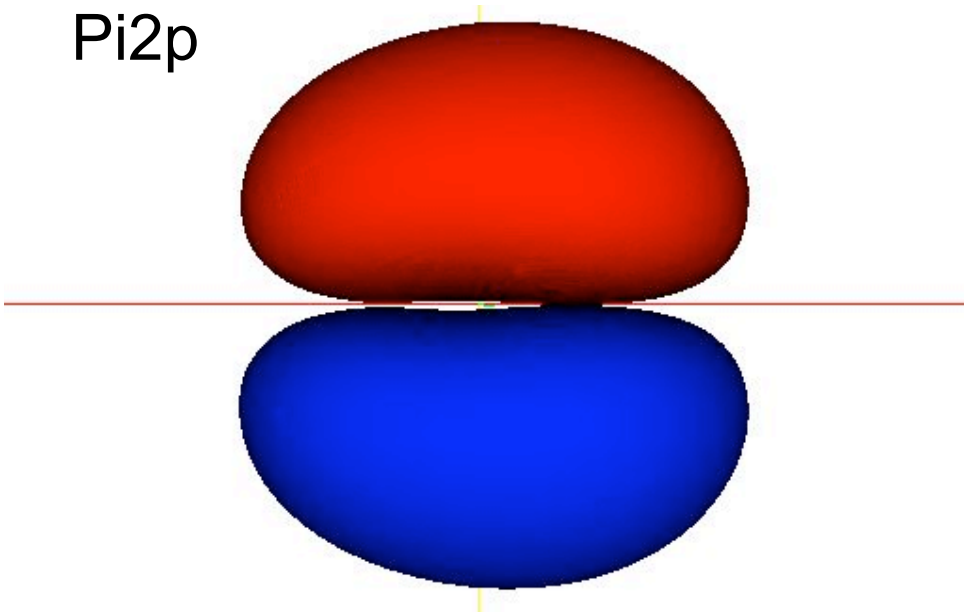
Property	KS-DFT-FE	KS-LSD (Engel et al., 2001)
Binding energy (eV)	-11.6	-11.593
Bond length (a.u.)	2.06	2.068

Binding energy and bond length of CO molecule

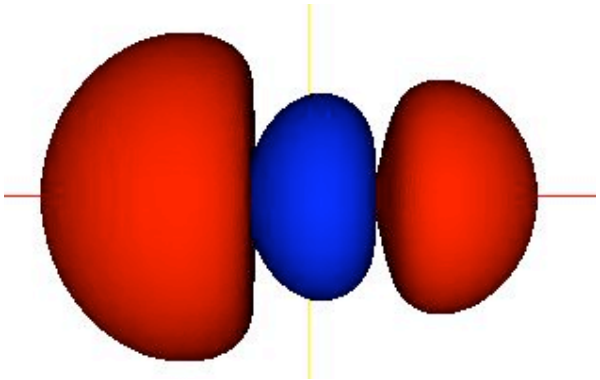
Property	KS-DFT-FE	KS-LSD (Engel et al., 2001)
Binding energy (eV)	-13.03	12.967
Bond length (a.u.)	2.08	2.128

Carbon monoxide orbitals

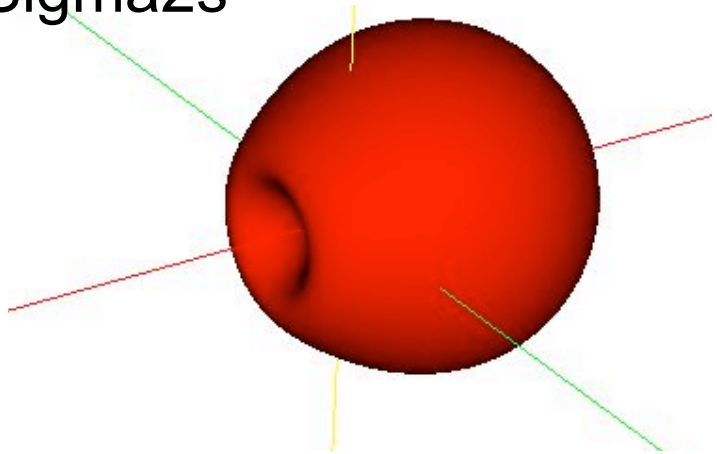
Pi2p



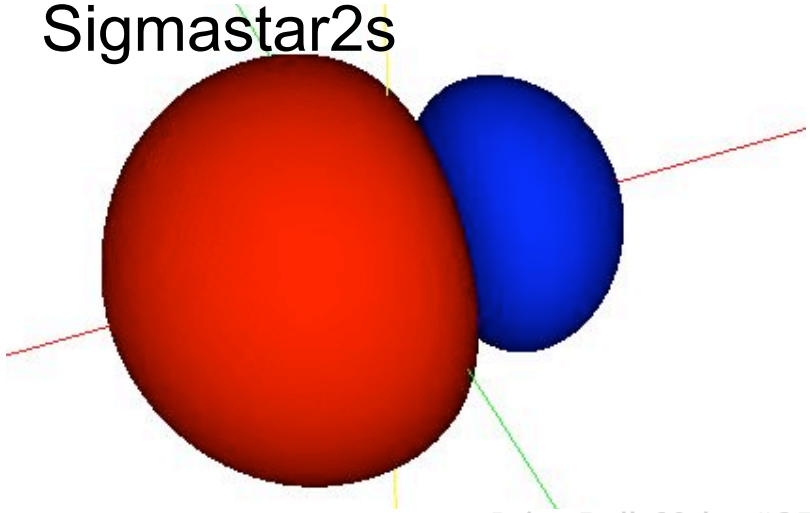
Sigma2p



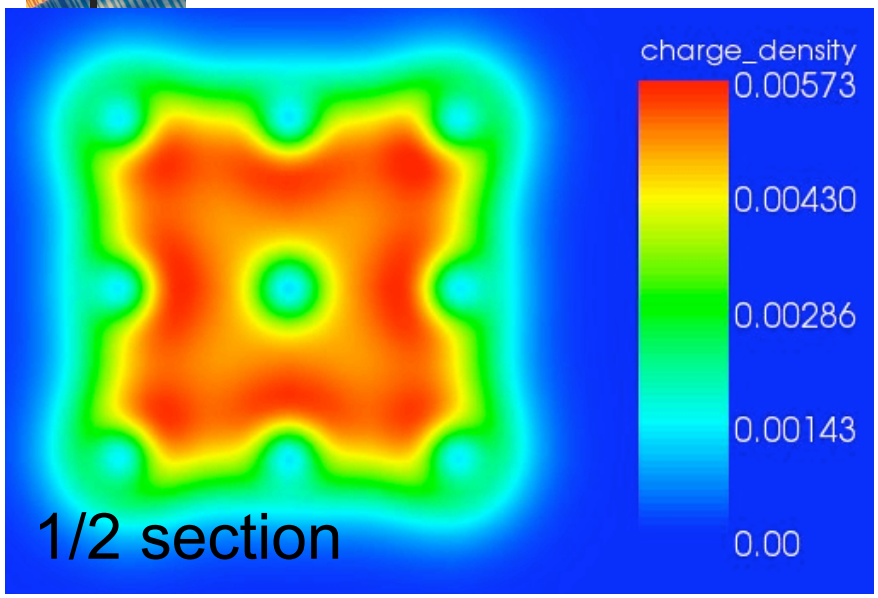
Sigma2s

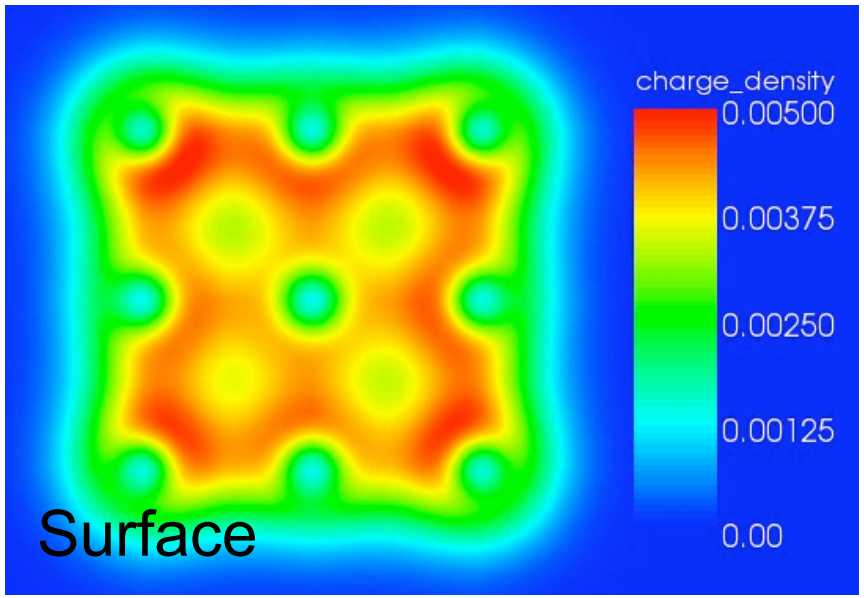


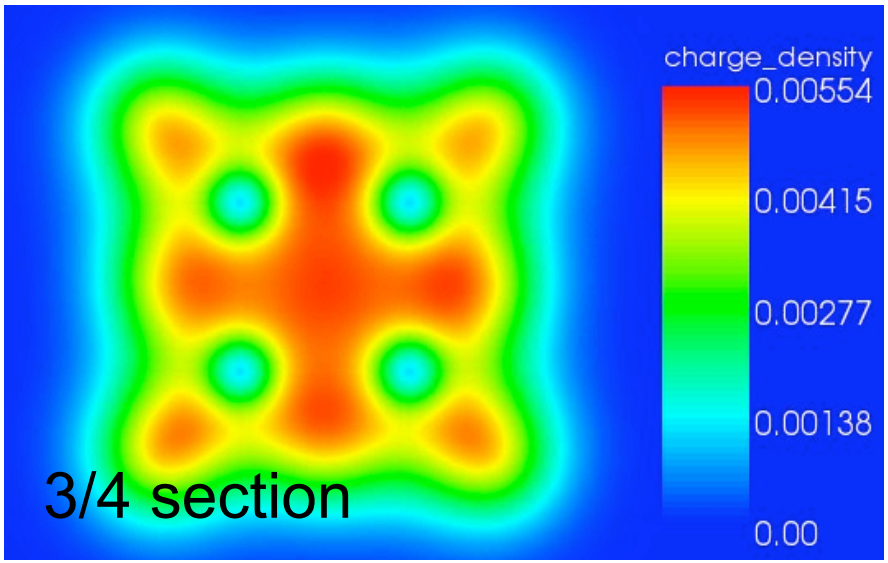
Sigmastar2s



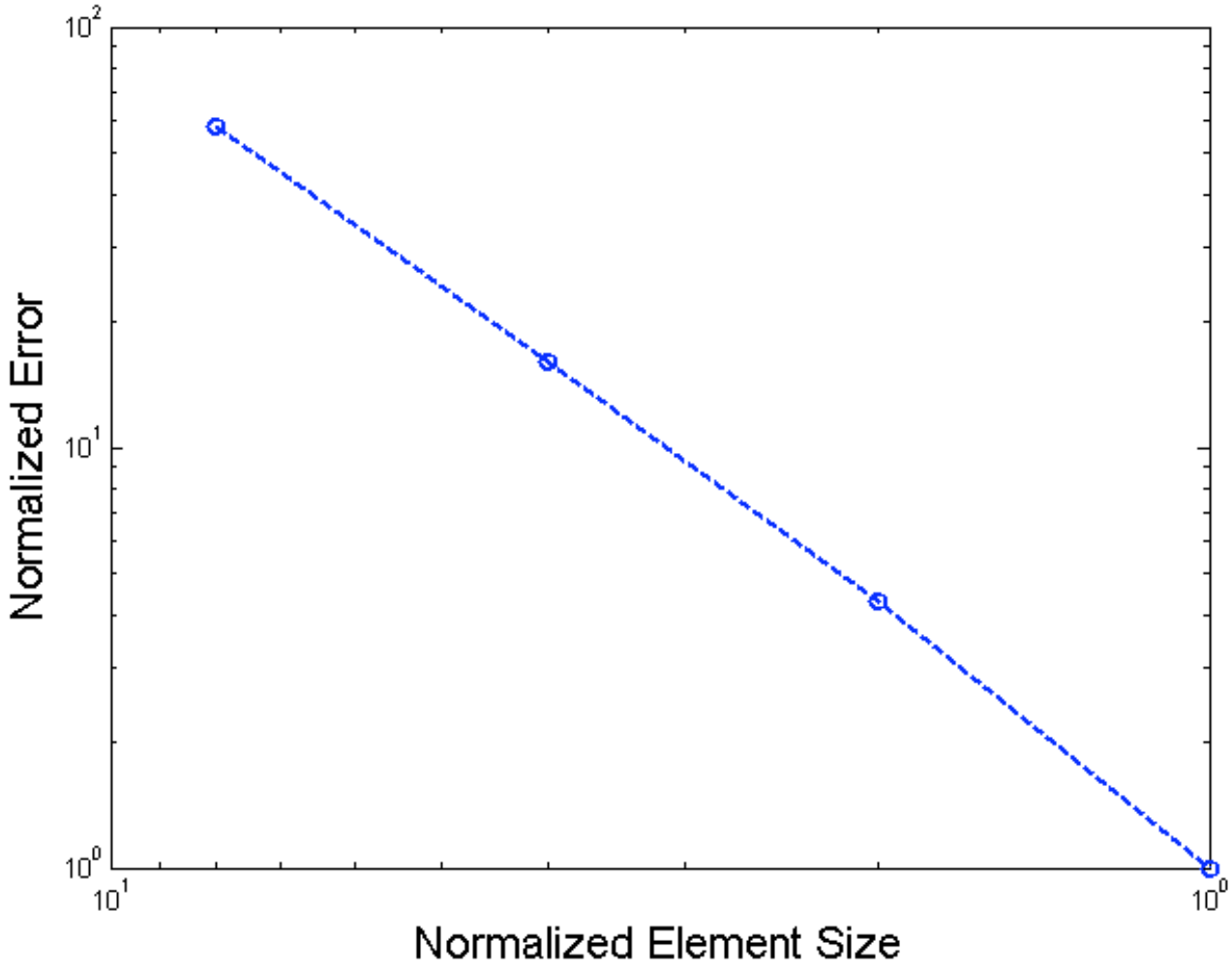
Charge density in 2x2x2 bcc Sodium clusters



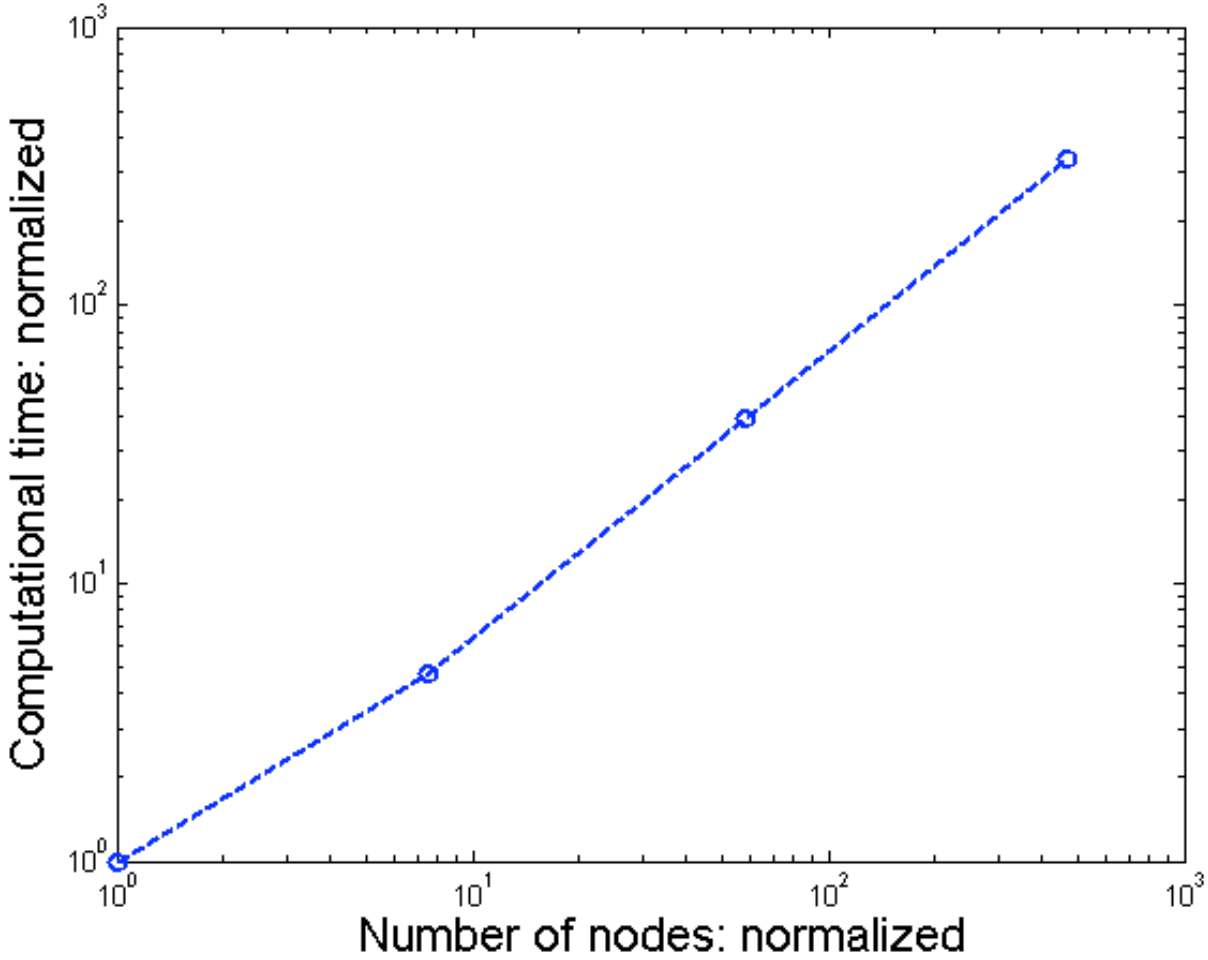




Convergence



Computational Effort



Happy Birthday!