Multiscale Challenges In Many Fields
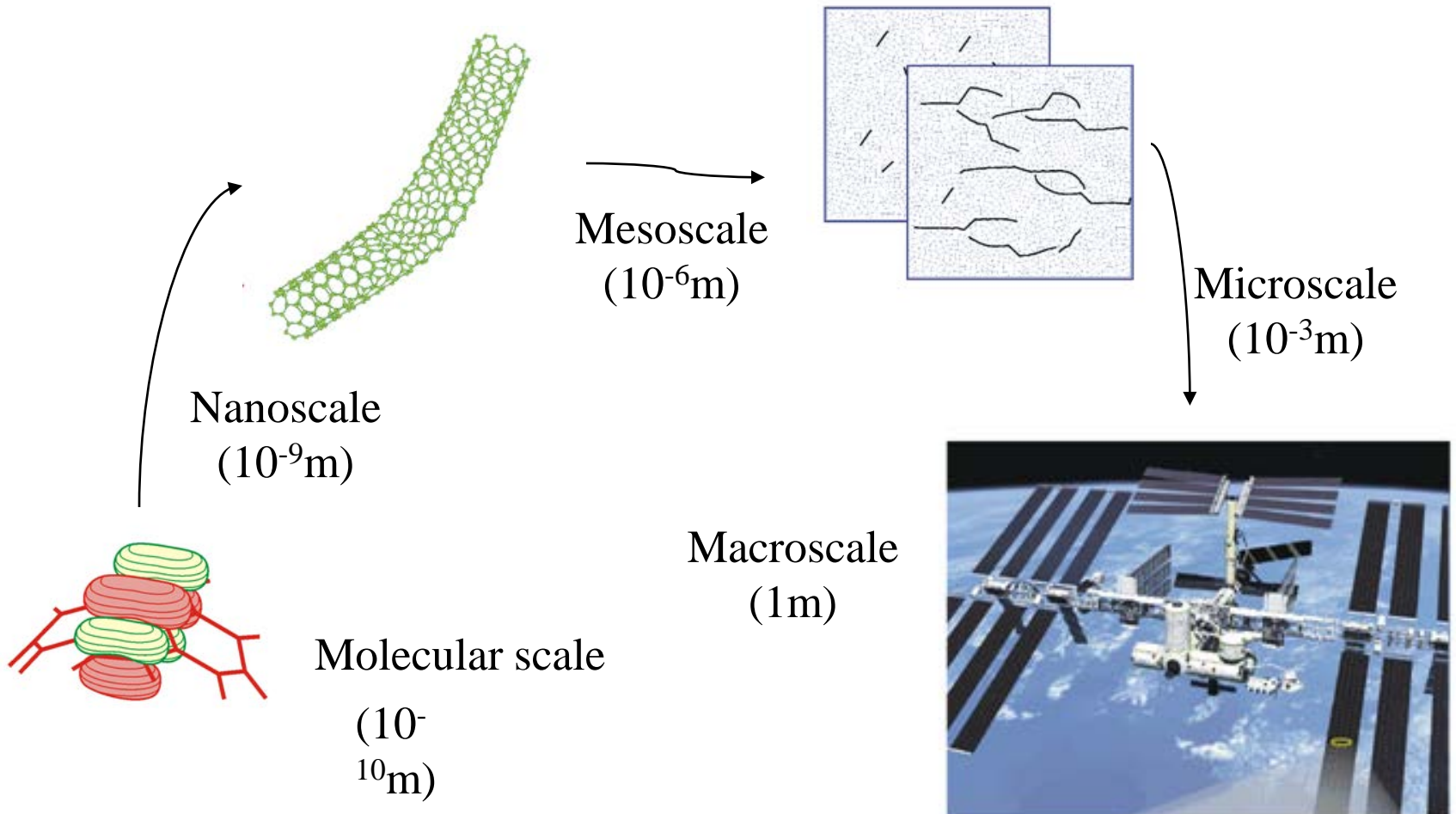
- Physics and Materials

  Semiconductors, Metals, …

- Chemistry

- Mechanics

- Biology

- Medical

- …

Physical length scales (from bottom to top)

Mesoscale
(10^{-6}m)

Microscale
(10^{-3}m)

Nanoscale
(10^{-9}m)

Macroscale
(1m)

Molecular scale

(10^{-10}m)

A variety of interesting phenomena/systems

Brittle or ductile behavior of solids (mechanical properties)

1. Embrittlement of Molybdenum Disilicide (PN model + DFT)
2. Nano-indentation of Silicon (QC method + TBA)
3. Piezoelectric response of Lead Titanate (QC method + DFT)
4. Dislocations in Aluminum and Silicon (SDPN model + DFT)
5. Brittle fracture of Silicon (MAAD + TBA)

Corrosion and catalysis (chemistry inside solids and on surfaces)

1. Hydrogen-induced embrittlement of Aluminum (SDPN model + DFT)
2. Ordering in Carbon-enriched Si surfaces (DFT + Potts model)
3. Reactivity of Molybdenum-oxide surfaces (DFT + KMC)
4. Role of geometry in catalytic efficiency of microchannels (LBE)
5. Impurity-induced embrittlement of metal alloys (OF-DFT + EAM)

Biologically-related processes

1. Optical response of DNA bases and aminoacids (CHARMM+TD DFT)
2. Rotary motion in ATPase (CHARMM + DFTB)
3. Electron localization in DNA nanowires (DFTB + KG)

Sequential vs. Concurrent

Sequential:

Knowledge learned at one length or time scale is passed on as input parameters to the next length or time scale, without explicit treatments of the coupling within the boundary region.

Concurrent ("handshake"):

Seamless coupling in the boundary region is treated explicitly.

Sequential Multiscale Modeling of Film Growth

- ## Calculations of activation barriers within DFT:
  - Vienna *ab initio* simulation package (VASP)
    Hafner, et al., '94-96.
  - "Climbing Image Nudged Elastic Band" (NEB)
    Jonsson et al., '98-00.

- ## Kinetic Monte Carlo simulations of growth:
  - Physically realistic growth conditions
    Voter, '86
    Metiu, Lu, & Zhang, '92.

- ## Continuum: classical nucleation theory & elasticity.
  Ultimate Goal: Theory with Predictive Power!

See Karsten Reuter, *First-Principles Kinetic Monte Carlo Simulations for Heterogeneous Catalysis: Concepts, Status and Frontiers*, in Modeling Heterogeneous Catalytic Reactions: From the Molecular Process to the Technical System, O. Deutschmann (Ed.), Wiley-VCH, Weinberg (2009).

Concurrent Multiscale Modeling

Courtesy:

Prof. Gang Lu, *Cal State Northridge*
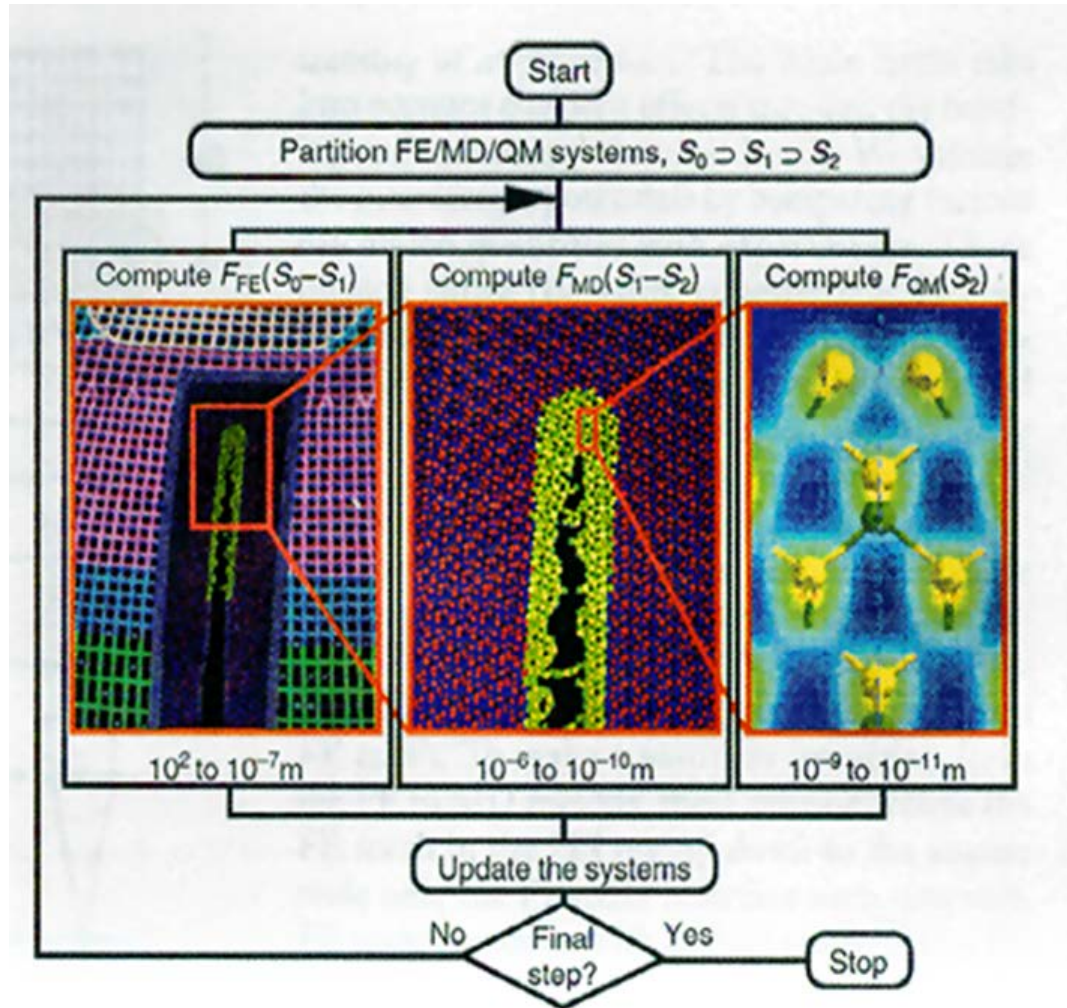**Prof. Tim Kaxiras,** *Harvard*

Crack Propagation in Si

modeled by

MAAD (**M**acroscopic **A**tomistic
**A**b initio **D**ynamics)

Macroscopic Atomistic *ab* initio Dynamics

- Finite elements (FE), molecular dynamics (MD), and tight binding (TB) all used in a single MAAD calculation

- Atomistics used to resolve features of interest (crack)

- Continuum used to extend size of domain

Why is Multiscale Modeling Difficult?

- Wave reflection at MD/FE interface
- Larger length scales (FE) cannot represent wave lengths typically found at smaller length scales (MD)
- Also due to energy conserving formulations for both MD and FEM
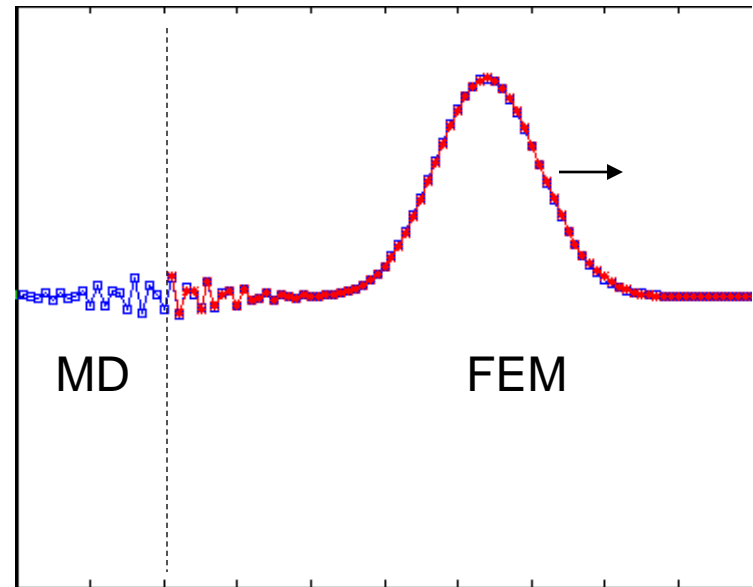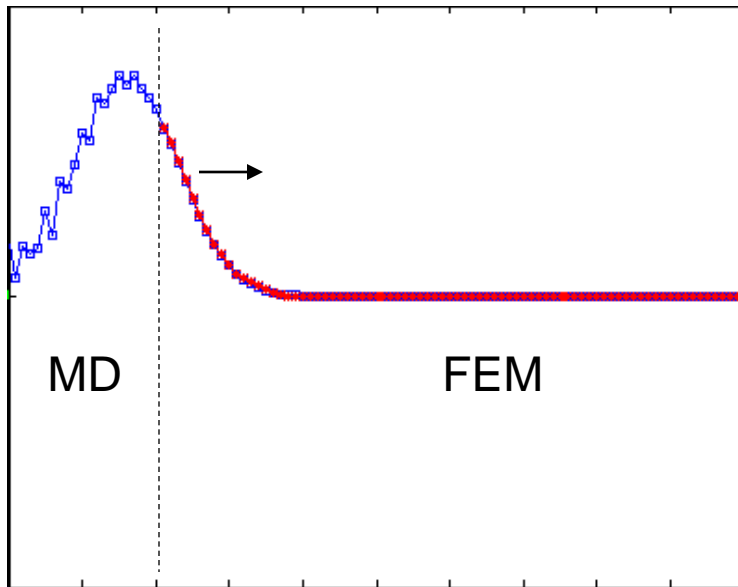
Concurrent Multiscale Methods

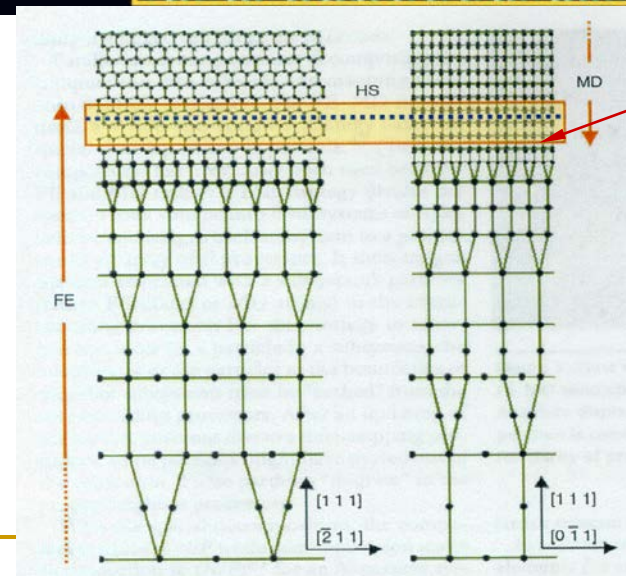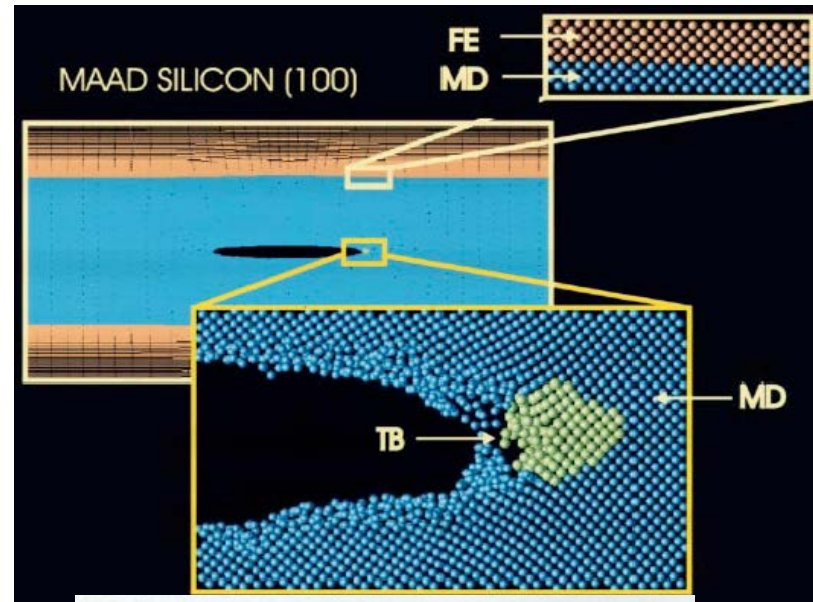- ## Multiscale issues:

  - numerical issues:
    - the finite elements are meshed down to the atomistic scale in handshake regions.
    - Time step is governed by the smallest element in the mesh. Time step will be too small for continuum region and many time steps will be wasted.

  - physical issue:
    - Pathological wave reflection. The wavelength emitted by MD region is considerably smaller than that which can be captured by the continuum FE region. Wave reflection occurs at the interface between the MD and FE regions.

MAAD: Concurrent Coupling of Length Scales

- Scales are coupled in "handshake" regions

- Finite element mesh graded down to atomic lattice in the overlap region

- **Total Hamiltonian** is energy in each domain, plus overlap regions

Handshake at MD/FE interface

$$H_{Tot} = H_{FE}\left(\mathbf{u}, \dot{\mathbf{u}}\right) + H_{FE/MD}\left(\mathbf{u}, \dot{\mathbf{u}}, \mathbf{r}, \dot{\mathbf{r}}\right)$$
$$+ H_{MD}\left(\mathbf{r}, \dot{\mathbf{r}}\right) + H_{MD/TB}\left(\mathbf{r}, \dot{\mathbf{r}}\right)$$
$$+ H_{TB}\left(\mathbf{r}, \dot{\mathbf{r}}\right)$$

Broughton, et al, *PRB* **60(4)** (1999).

Nakano et al, *Comput. In Sci. and Eng*., **3(4)** (2001).

No reflection of stress waves: seamless coupling across boundaries

Stress waves pass from MD to FE
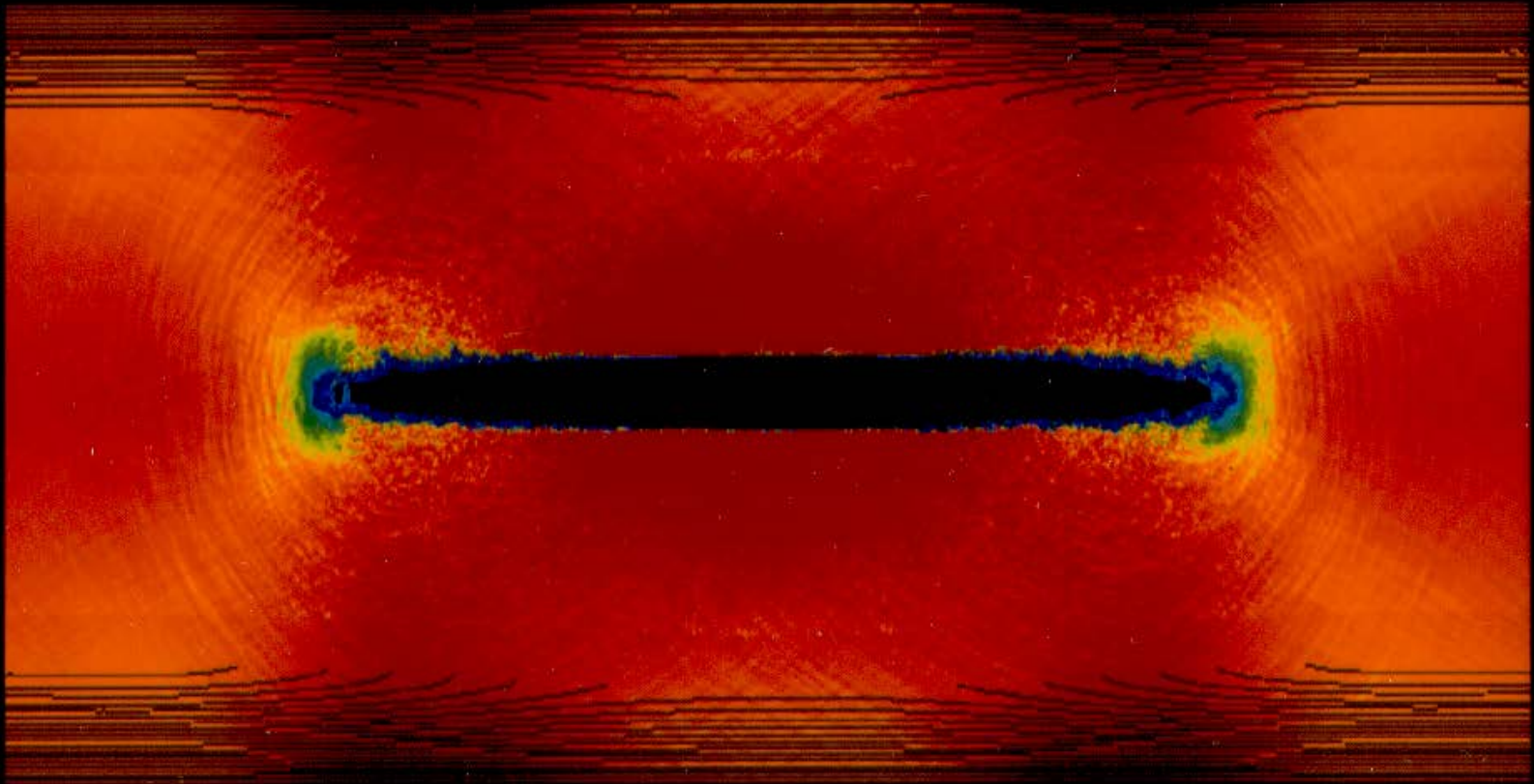
F. Abraham, J. Broughton, N. Bernstein, E. Kaxiras (Computers in Phys, 1998)

Impurities and Mechanical Responses

Metal alloys: change from ductile to brittle behavior induced by chemical impurities

brittle fracture in "hostile" environment (moisture)
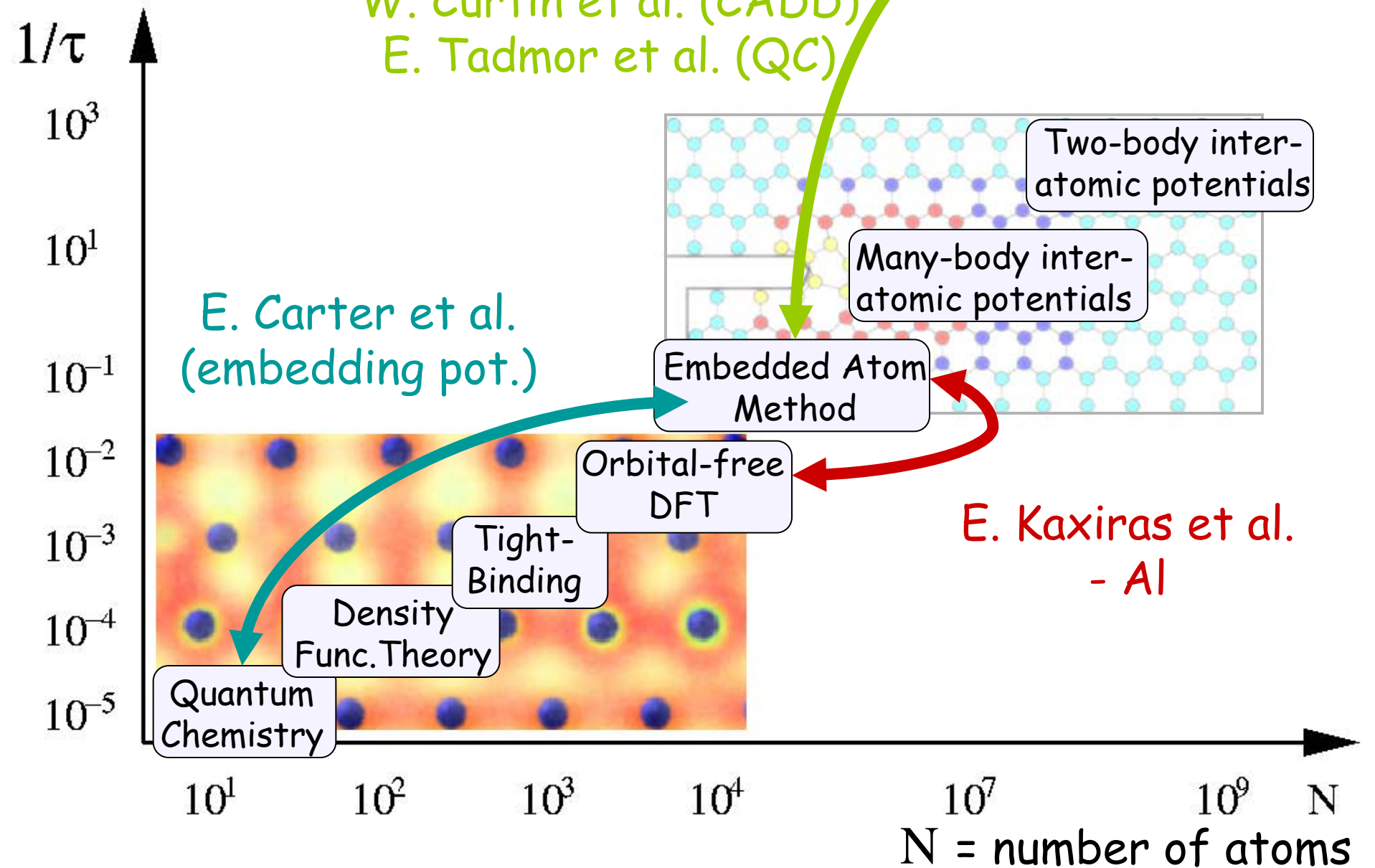
Semiconductors vs Metals

Semiconductors: electrons are largely localized, tight-binding

Metals: electrons are largely delocalized, embedded-atom method (EAM)

τ = time step/atom (sec)

CONTINUUM

$1/\tau$

10^3

10^1

10^{-1}

10^{-2}

10^{-3}

10^{-4}

10^{-5}

W. Curtin et al. (CADD)
E. Tadmor et al. (QC)

E. Carter et al.
(embedding pot.)

Two-body inter-
atomic potentials

Many-body inter-
atomic potentials

Embedded Atom
Method

Orbital-free
DFT

Tight-
Binding

Density
Func.Theory

Quantum
Chemistry

E. Kaxiras et al.
- Al

10^1 10^2 10^3 10^4 10^7 10^9 N

N = number of atoms

Orbital-Free DFT
(handle delocalized nature of metallic electrons)

$$E'\big[V, \rho\big] = \tilde{T}_s\big[\rho\big] + E_{ext}\big[V, \rho\big] + E_H\big[\rho\big] + E_{XC}\big[\rho\big]$$

- Eliminates $O(N^3)$ orthogonalization
- Eliminates $O(N^2)$ memory requirement
- Truly $O(N)$ method in real space
- Closer to Hohenberg-Kohn DFT picture

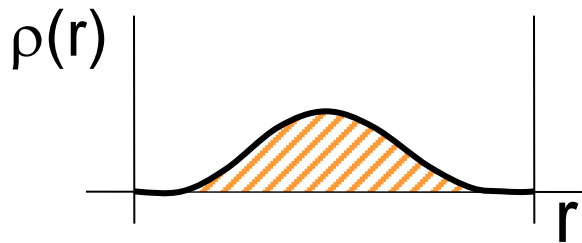# Approximate Kinetic Enegry Functional T$_s$[ρ]

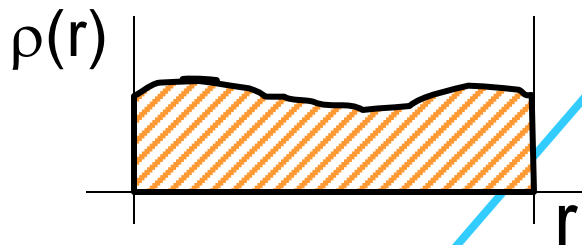KEF's: Wang, Govind, Carter, PRB **58** (1998); **60** (1999)

ρ(r)
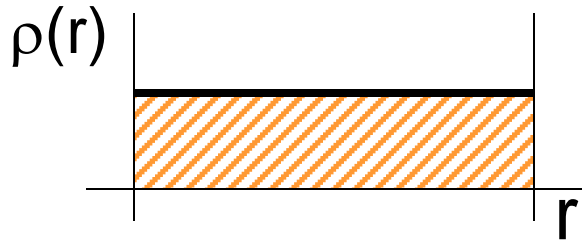
Uniform e⁻ gas (Thomas-Fermi):

$$E\left[\rho_0\right] = C\int \rho^{5/3}dr$$

ρ(r)

Single Orbital (von Weizsacker):

$$E\left[\rho_0\right] = \int \sqrt{\rho}\left(-\frac{1}{2}\nabla^2\right)\sqrt{\rho}dr$$
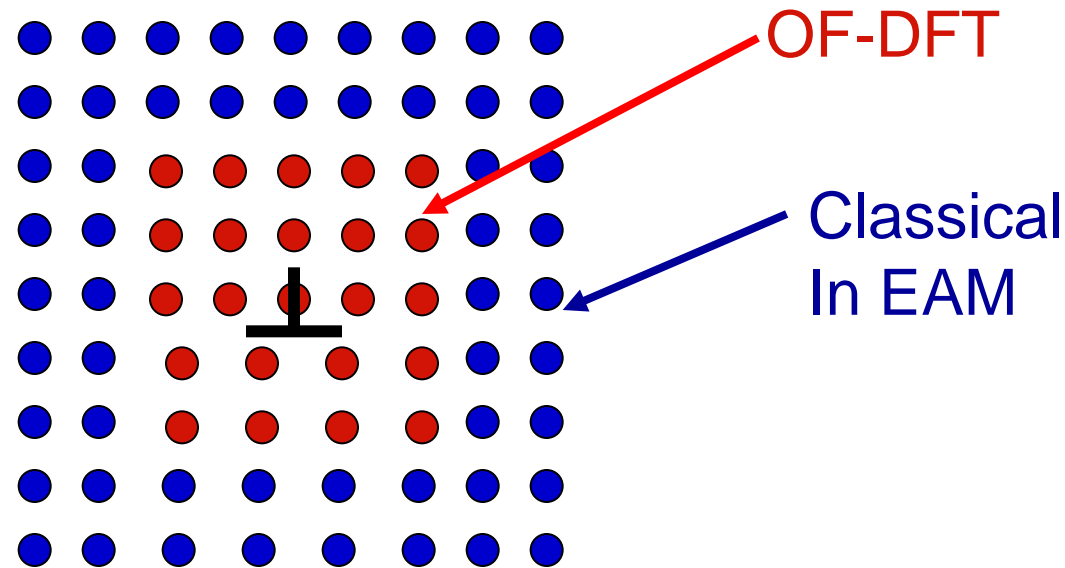
ρ(r)

Linear Response (Lindhard):

$$\delta V \rightarrow \delta\rho\left(q\right) = \chi_{Lind}\left(q\right)\delta V\left(q\right)$$

$$\tilde{T}_s\left[\rho\right] = C\int \rho^{5/3}dr + \int \sqrt{\rho}\left(-\frac{1}{2}\nabla\right)\sqrt{\rho}dr + \int dr\int dr'f\left(\rho\left(r\right)\right)K\left(r-r'\right)g\left(\rho\left(r'\right)\right)$$

OF-DFT in Multiscale Simulations

OF-DFT

Classical
In EAM

- Boundary conditions for $\rho(r)$ only
- Coupling to classical atomistics:
  - Embedded-Atom Method (EAM)
    - designed for simple metals
    - based on DFT arguments

Empirical atomistic simulations for metals

Energy functional with Embedded Atom Method (EAM):

$$V_{tot}[\mathbf{R}_i] = \sum_{i=1}^{N} G\left[\sum_{j \neq i}^{N} \rho\left(\left|R_{ij}\right|\right)\right] + \frac{1}{2}\sum_{j \neq i}^{N} \phi\left(\left|R_{ij}\right|\right)$$

G: embedding functional $\qquad \rho$: electron charge density

ϕ : pair potential $\qquad \mathbf{R}_{ij}$: interatomic distance

Empirical: G & ϕ fitted to experimental data

Theory: fitted to *ab* initio results

References on EAM:

MS Daw and MI Baskes, Phys. Rev. Lett. 50, 1285 (1983).
MS Daw and MI Baskes, Phys. Rev. B 29, 6443 (1984).
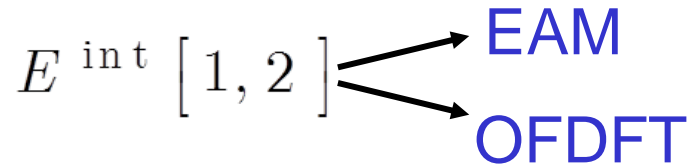SM Foiles, MI Baskes, and MS Daw, Phys. Rev. B 33, 7983 (1986).

Coupling Formalism
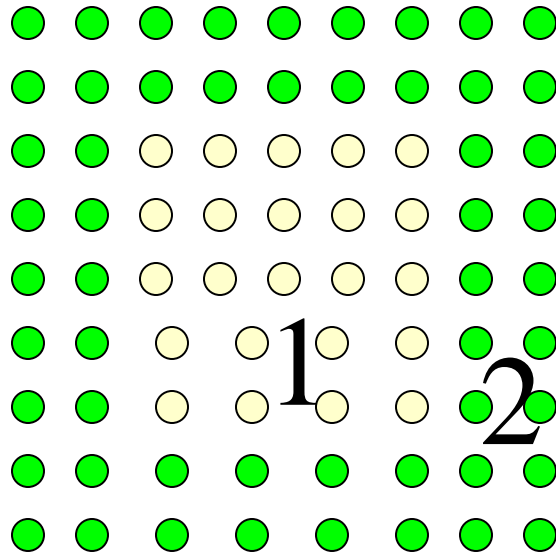
$$E\left[1+2\right] = E^{DFT}\left[1\right] + E^{EAM}\left[2\right] + E^{\text{int}}\left[1,2\right]$$

$$E^{\text{int}}\left[1,2\right] \equiv E\left[1+2\right] - E\left[1\right] - E\left[2\right]$$

How to Calculate the interaction energy

$$E^{\text{int}}[1, 2]$$

EAM

OFDFT

$$E^{\text{int},EAM}[1, 2] = E^{EAM}[1+2] - E^{EAM}[1] - E^{EAM}[2]$$

$$E[1+2] = E^{DFT}[1] + E^{EAM}[2] + (E^{EAM}[1+2] - E^{EAM}[1] - E^{EAM}[2])$$

$$= E^{DFT}[1] + E^{EAM}[1+2] - E^{EAM}[1]$$

cluster cal.

Forces on EAM (R^2) atoms:

$$\mathbf{F}[\mathbf{R}_2] \equiv -\frac{\partial E[1+2]}{\partial \mathbf{R}_2} = -\frac{\partial E^{EAM}[1+2]}{\partial \mathbf{R}_2}$$

EAM atoms *see* DFT atoms as if they were EAM atoms:
Good for coupling!

Forces on DFT atoms (R^1): contributions from all three terms.
Error in forces can be reduced by using force-matching EAM
Potentials (e.g. Ercolessi & Adams, '94)

QM-based Multiscale Modeling for Catalysis

- **QM/MM method:** atomistic modeling coupling QM simulation of a reactive region **(region I)** with MM modeling of surrounding non-reactive region **(region II).**

"MM" = classical atomistic modeling; orders of magnitude cheaper than QM modeling

- **QCDFT method:** Continuum-to-atomistic quantum modeling simulates material properties from electrons to finite elements.
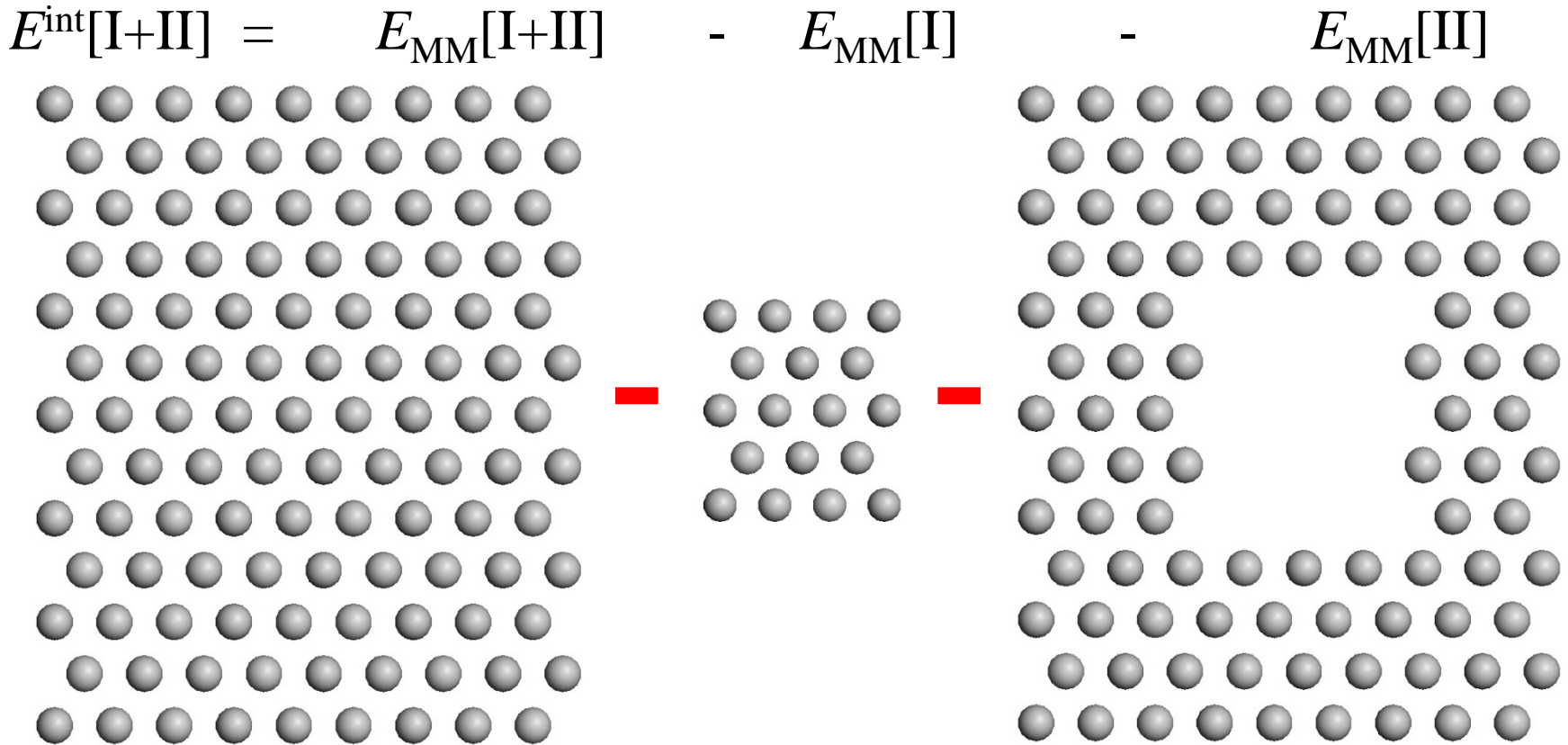

$$E^{\text{tot}}[\text{I}+\text{II}] \quad = \quad E_{\text{QM}}[\text{I}] \quad + \quad E_{\text{MM}}[\text{II}] \quad + \quad E^{\text{int}}[\text{I, II}]$$
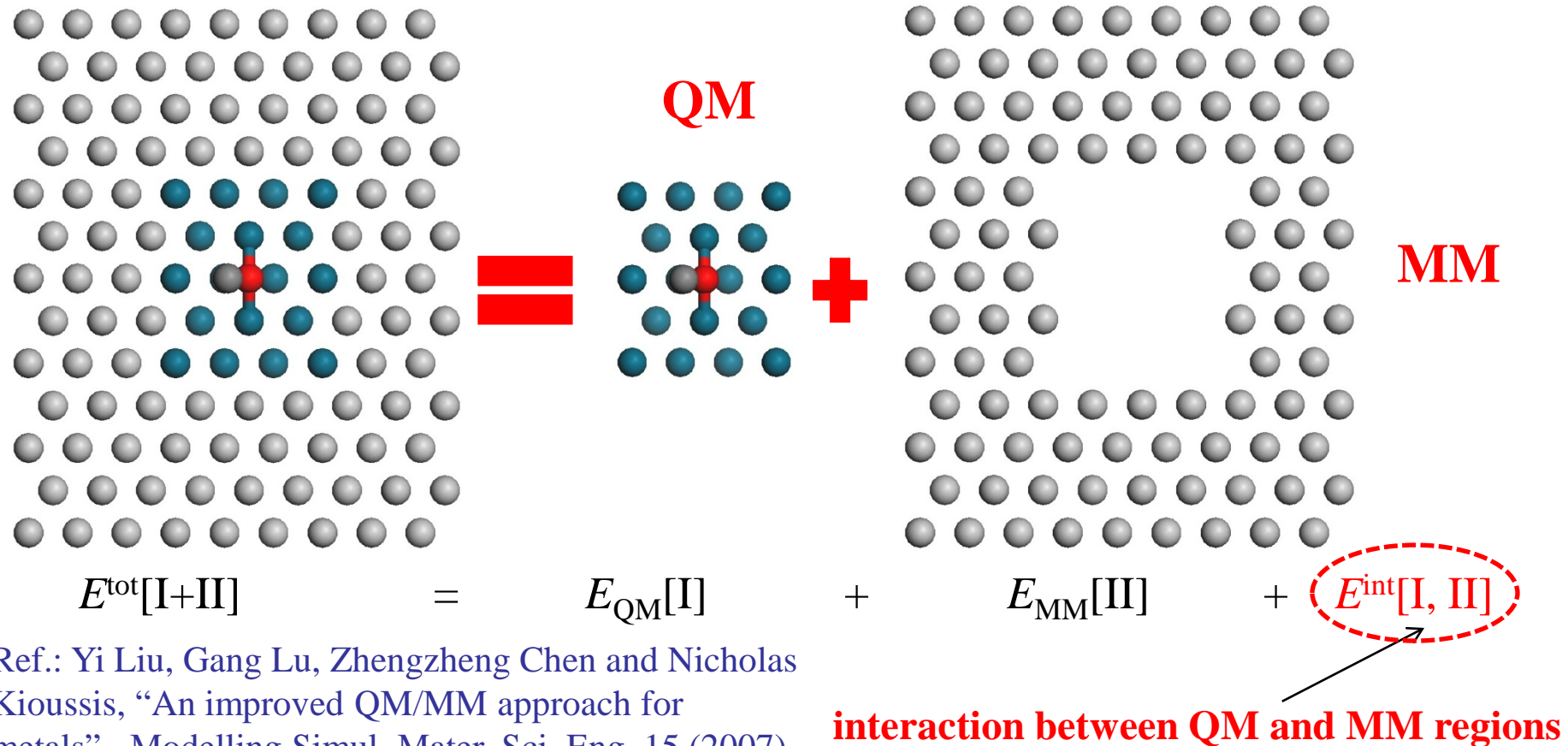
Ref.: Yi Liu, Gang Lu, Zhengzheng Chen and Nicholas Kioussis, "An improved QM/MM approach for metals", Modelling Simul. Mater. Sci. Eng. 15 (2007) 275–284

interaction between QM and MM regions

E^{int}[I,II] can be calculated at different levels depending on the problem at hand; For example,

(I) E^{int}[I, II] calculated at MM level:

$$E^{\text{int}}[\text{I+II}] \quad = \quad E_{\text{MM}}[\text{I+II}] \quad - \quad E_{\text{MM}}[\text{I}] \quad - \quad E_{\text{MM}}[\text{II}]$$

- Efficient methods have been developed to correct for possible coupling errors (*Liu et al, Model. Simul. Mater. Sci. Engin. 2007*).
- **Advantage:** simplicity and efficiency. If high quality interatomic potentials are available, this method could be an excellent choice.

Energy formulation: OFDFT-based QM/MM Method

The energy of entire QM/MM system:

$$E_{tot}[\vec{R}_1 + \vec{R}_2] = E_{DFT}[\vec{R}_1] + E_{MM}[\vec{R}_2] + E_{OFDFT}^{\text{int}}[\vec{R}_1, \vec{R}_2]$$

(II) OFDFT used to calculate the interaction energy

$$E_{OFDFT}^{\text{int}}[\vec{R}_1, \vec{R}_2] = E_{OFDFT}[\vec{R}_1 + \vec{R}_2] - E_{OFDFT}[\vec{R}_1] - E_{OFDFT}[\vec{R}_2]$$

The GS energy is given by minimizing the energy functional w.r.t. ρ_1

$$E_{tot} = E_{MM}[\vec{R}_2] + \min_{\rho_1}\left[E_{DFT}[\rho_1] + E_{OFDFT}[\rho^{tot} = \rho_1 + \rho_2] - E_{OFDFT}[\rho_1] - E_{OFDFT}[\rho_2] \right]$$

$$\rho_{tot}(\vec{r}) = \rho_1(\vec{r}) + \rho_2(\vec{r})$$
$$\rho_2(\vec{r}) = \sum_{j \in II} \rho^{at}(\vec{r} - \vec{R}_2^j)$$

$\rho_1(\vec{r})$: degree of freedom

More accurate than the first method, it involves OFDFT approximation.

(III) Constrained Minimization QM/MM Method

potentially more accurate and versatile; doesn't rely on interatomic potential or OFDFT

Aim: Charge density of ***QM region*** is self-consistently determined, which converges to the "bulk-like" charge density ρ_0 at QM/MM boundary layers Ω_B.

Performing constrained minimization of total energy functional in QM region with constraint:

$$C = \frac{1}{2} \iint \frac{[\rho(\vec{r}) - \rho_0(\vec{r})][\rho(\vec{r}') - \rho_0(\vec{r}')]}{|\vec{r} - \vec{r}'|} d\vec{r} \, d\vec{r}' = 0 \qquad \rho_0(\vec{r} \in \Omega_B) = \sum_{i \in I} \rho^{at}(\vec{r} - \vec{R}_i)$$

Introducing a Lagrange multiplier λ associated with C, by minimizing total energy yields a constraint potential:

$$v_c(\vec{r} \in \Omega_B) = \lambda \int \frac{\rho(\vec{r}') - \rho_0(\vec{r}')}{|\vec{r} - \vec{r}'|} dr'$$

which is then added to original KS Hamiltonian of QM region:

$$H'_{KS}[I] = H_{KS}[\rho(\vec{r})] + v_c(\vec{r} \in \Omega_B)$$

$H'_{KS}[I]$ is self-consistently determined for region I
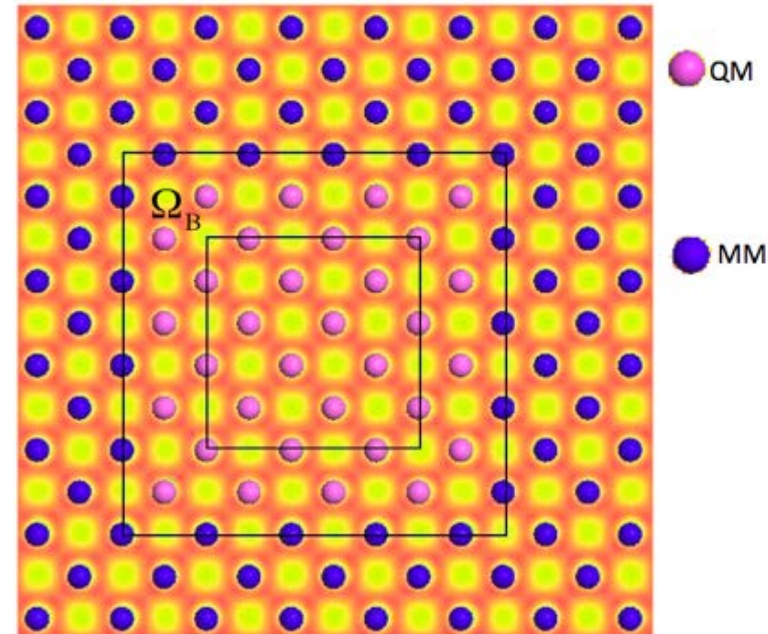
Self-Consistent DFT Embedding Method

Calculating interaction energy quantum mechanically (if satisfactory interatomic potentials are unavailable)

Open circle: DFT atoms
Filled circle: MM atoms
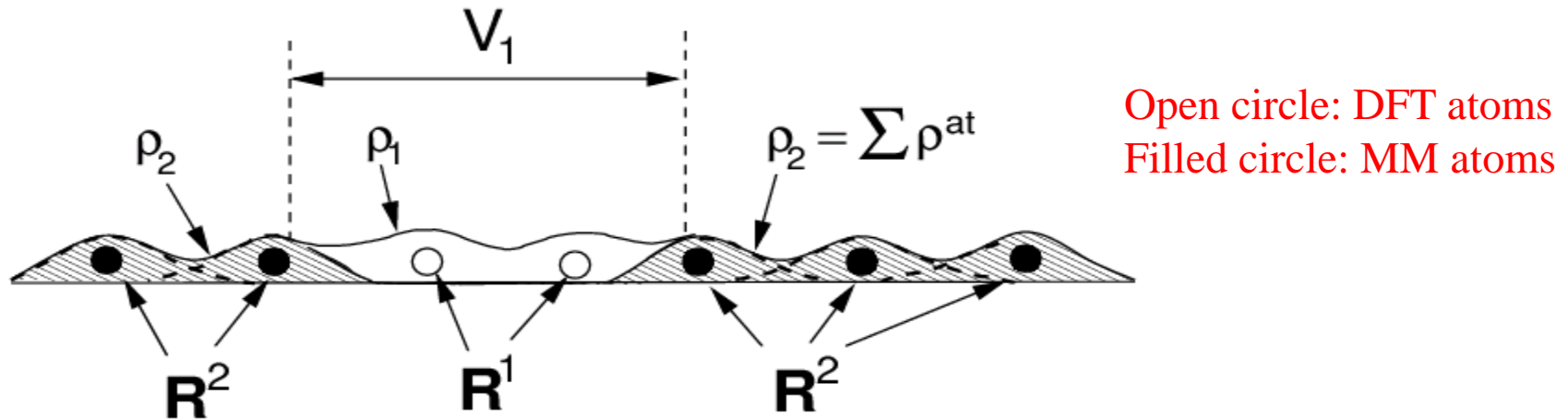
FIG. 1: An illustration of the partitioning of the system according to the second coupling method.

Attach ρ^{at} and pseudopotential to each MM atom $\mathbf{R_2}$

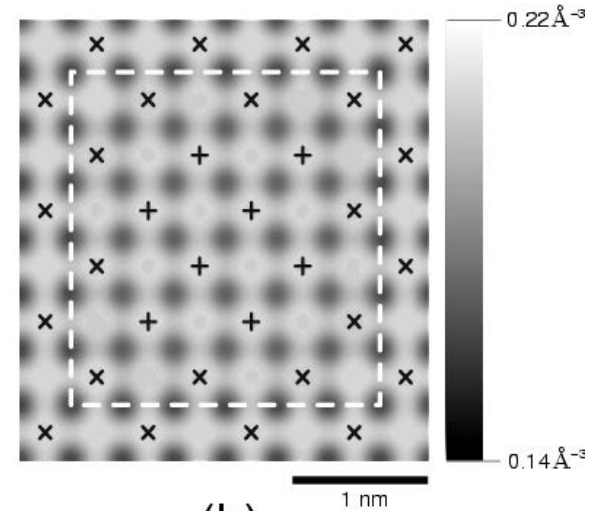Both constructed *a priori*; ρ_2 =superposition of ρ^{at}

Goal: self-consistently determine ρ_1 in the presence of ρ_2

Ref: Nicholas Choly, Gang Lu, Weinan E and Efthimios Kaxiras, "Multiscale simulations in simple metals: a density-functional based methodology", Phys. Rev. B 71, 094101 (2005).

(a)

(b)

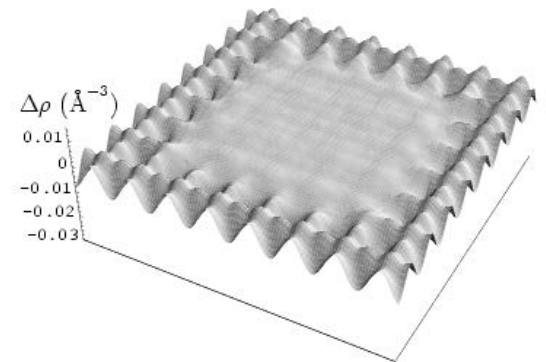0.22 Å⁻³

0.14 Å⁻³

1 nm

(c)

(d)

~20%
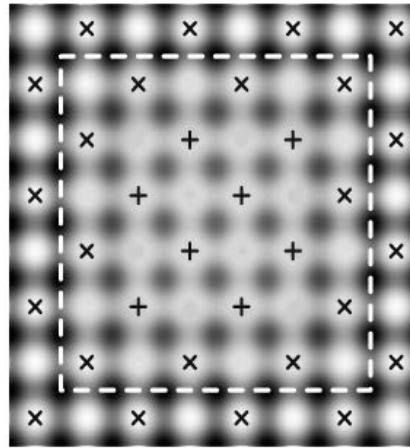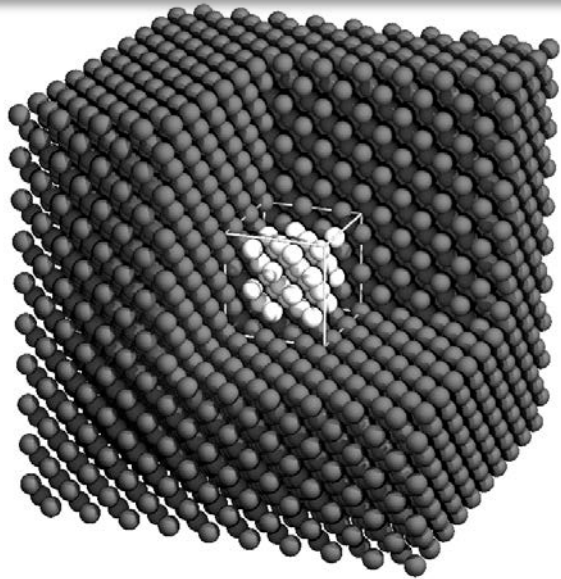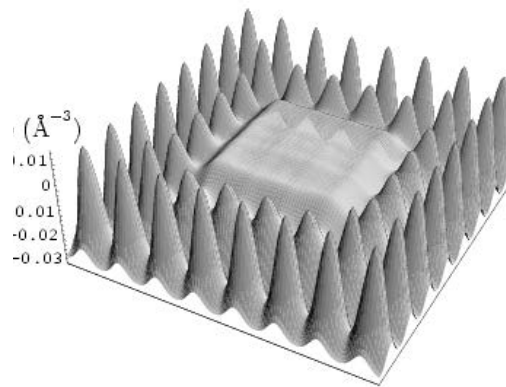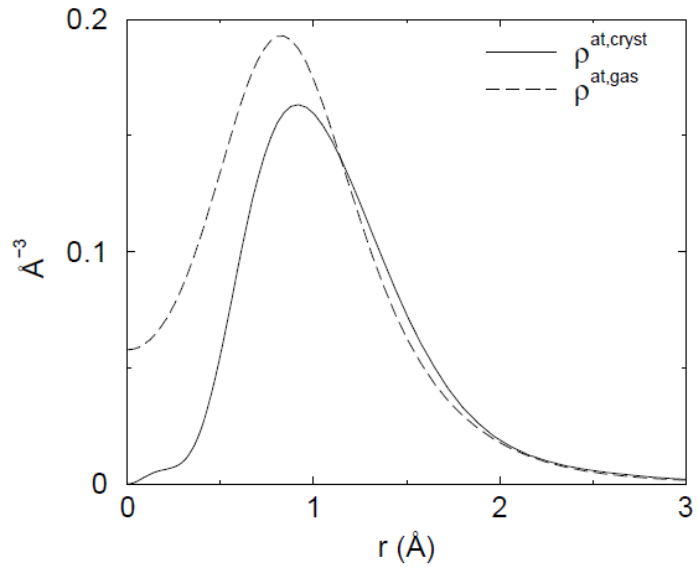
<5%

Issues with OF-DFT:

Systems where it is applicable: simple metal alloys
e.g. Al-Mg and Al-Li alloys

Need local pseudopotentials – few elements:
- Na, K, Rb, Cs, Mg, Al, Ga, In, Tl, Sn, Pb, Li, some transition metals
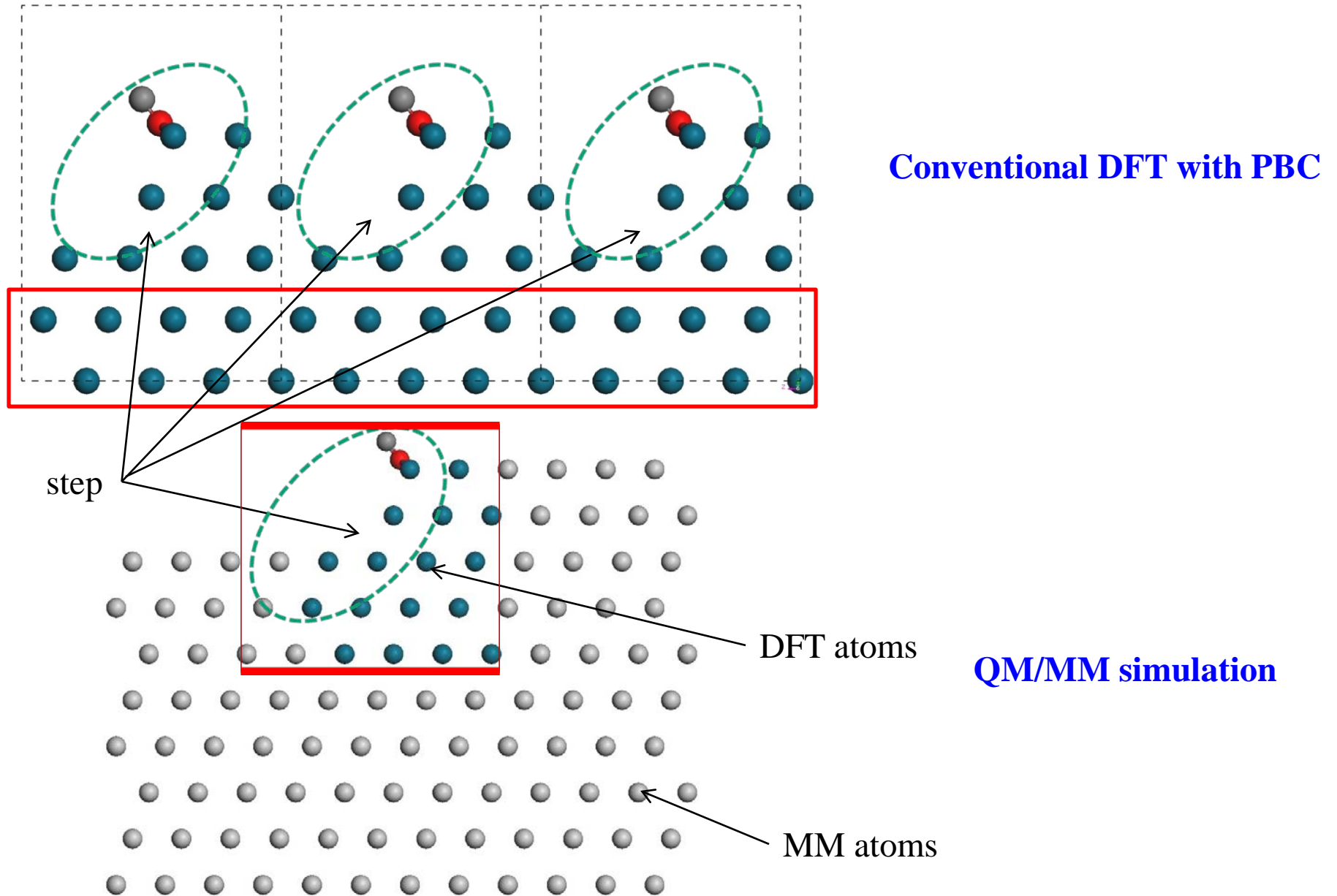- Recent progress in local pseudopotentials for any type of element (Carter *et al*.)

A variety of ***numerical/computational*** issues

(a) N. Choly and E. Kaxiras, Solid State Comm. (2002)

(b) N. Choly and E. Kaxiras, Phys. Rev. B (2003)

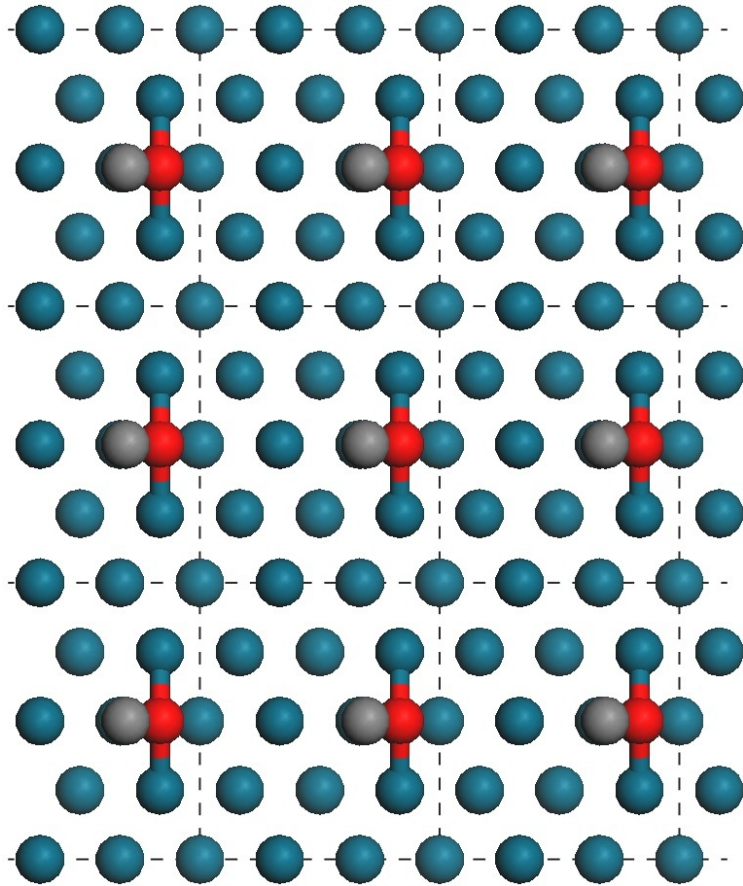# Some ideas to simulate more realistic systems with QM/MM

QM/MM Modeling of Surface Steps

Conventional DFT with PBC
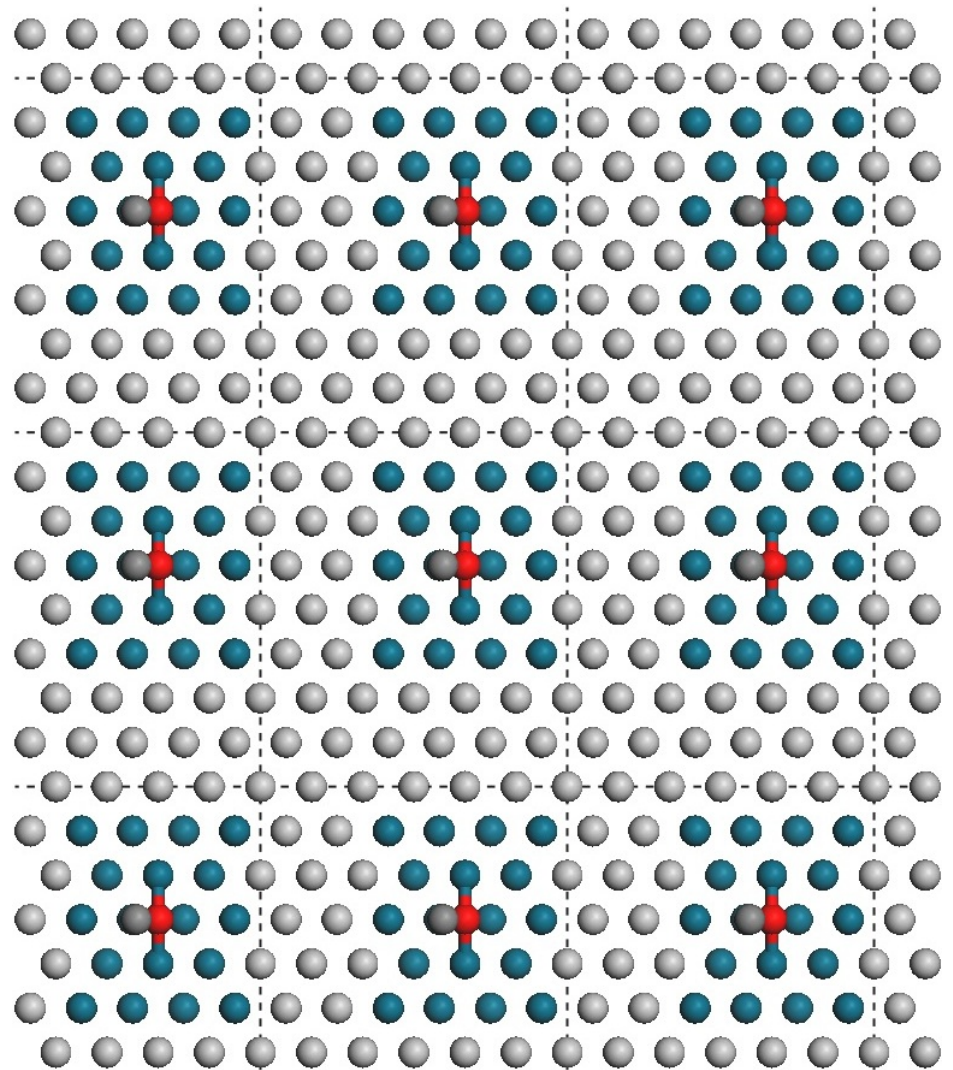
step

DFT atoms

QM/MM simulation

MM atoms

QM/MM Modeling of Coverage

CO adsorption on Pd (111) surface

QM simulation with PBC

QM/MM simulation with PBC

Much higher and unrealistic coverage

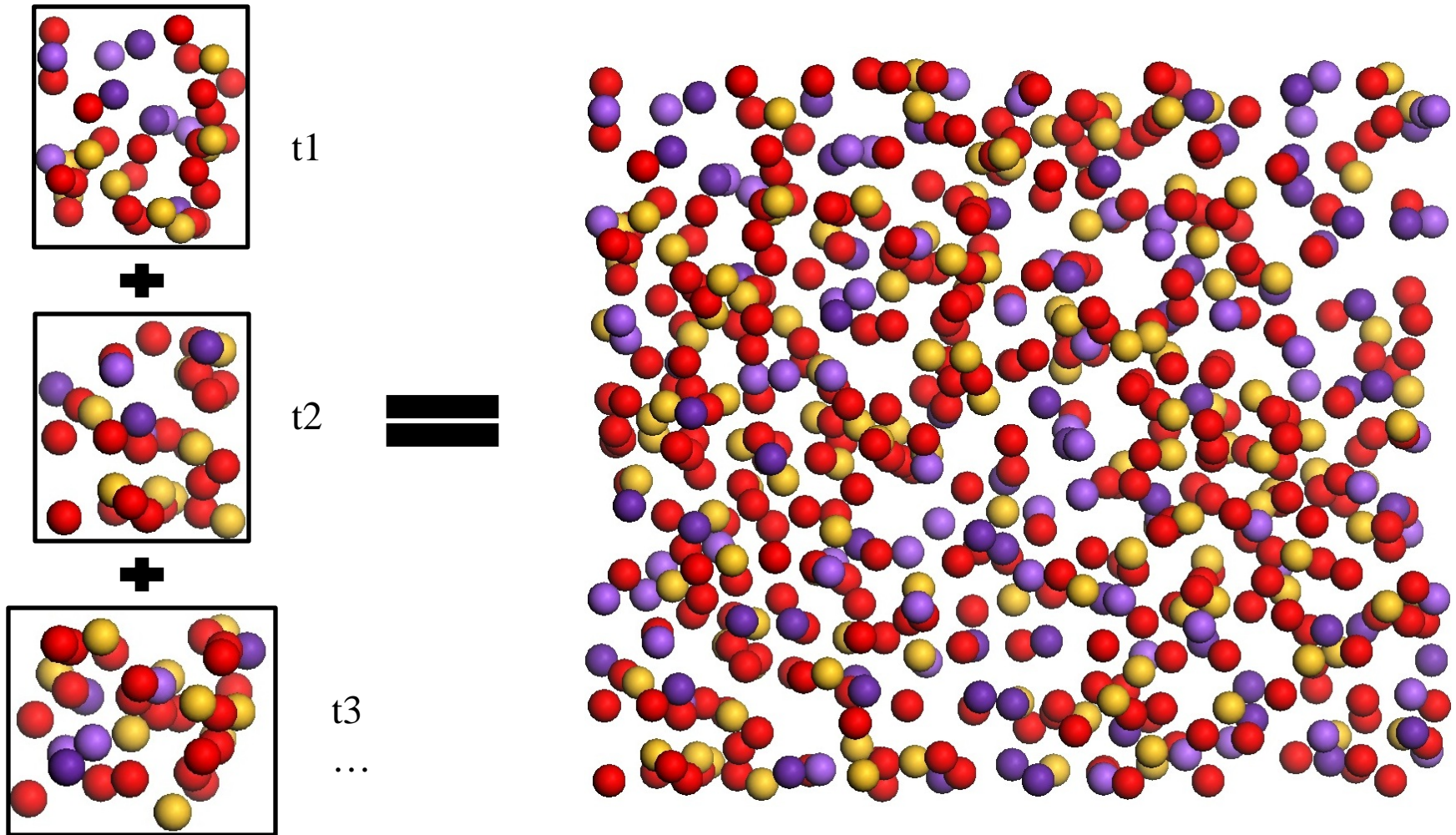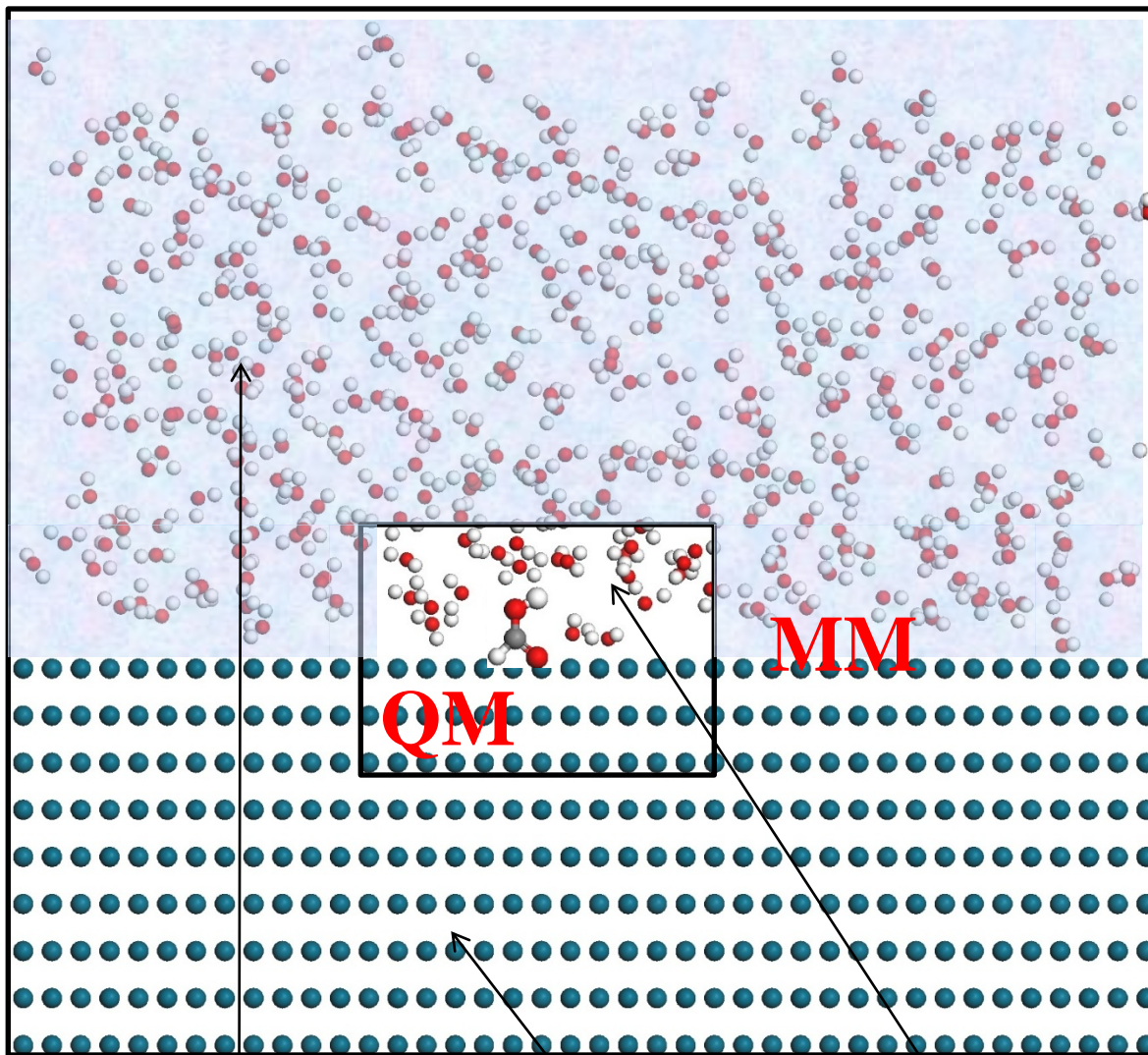**Realistic coverage**

CO adsorption on Pd (111) surface
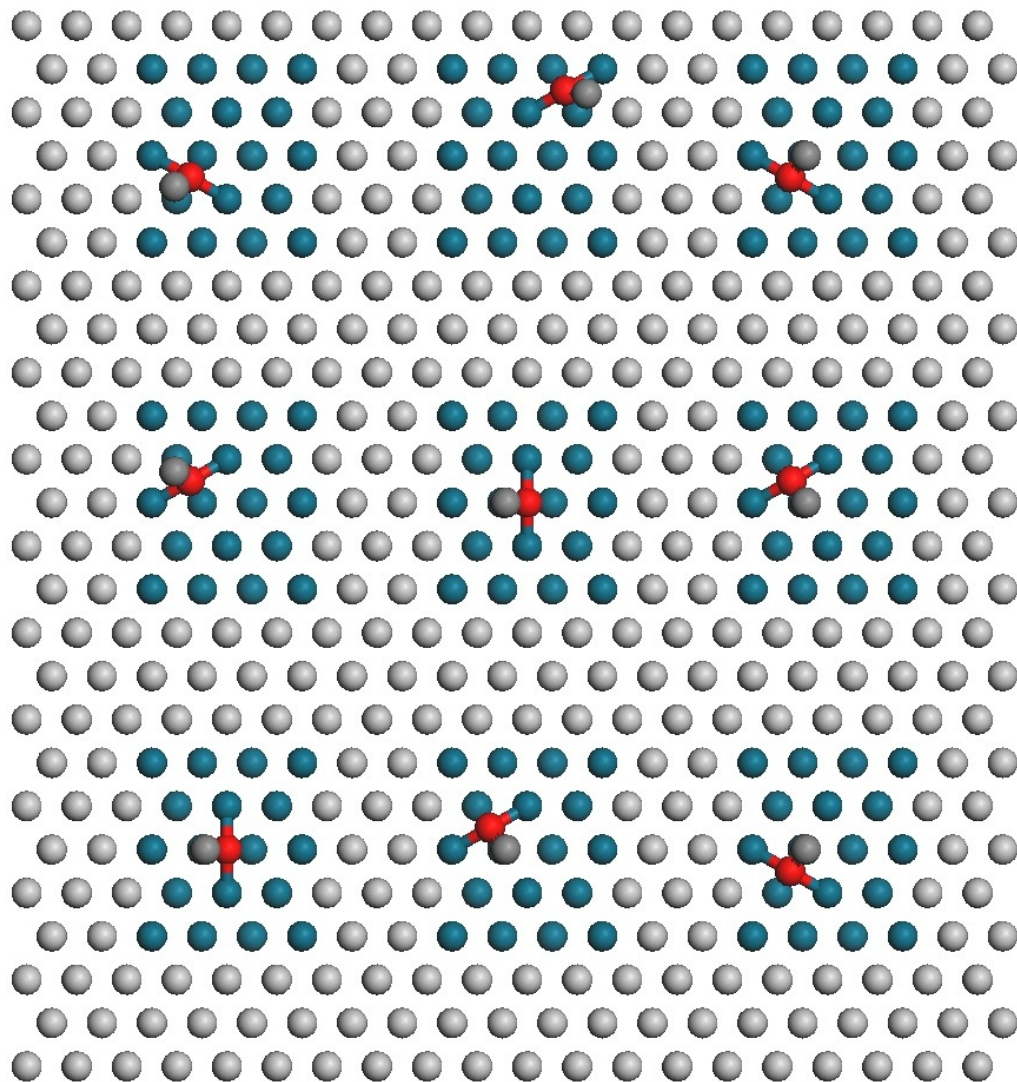
1 MM region + multiple QM regions in parallel:
different molecular configurations and adsorption sites

Multiscale Modeling of Bulk Metallic Glasses (BMG)

- **Ab initio MD simulations of small unit cell (a few hundred atoms) – "liquid quench technique"**
- **Ab initio MD snapshots to construct larger scale BMG samples**

Multiscale Modeling of Formic Acid Oxidation in Solution

Water medium treated by continuum solvation model with a smooth dielectric function:

$$\varepsilon(\rho(r)) = 1 + \frac{\varepsilon_\infty - 1}{2}\left[1 + \frac{1 - (\rho(r)/\rho_0)^{2\beta}}{1 + (\rho(r)/\rho_0)^{2\beta}}\right]$$

- $\rho(r)$: charge density of water
- ε_∞: 78.36 for water at 300 K
- ρ_0 and β are parameters fitted to experiments

Poisson equation:

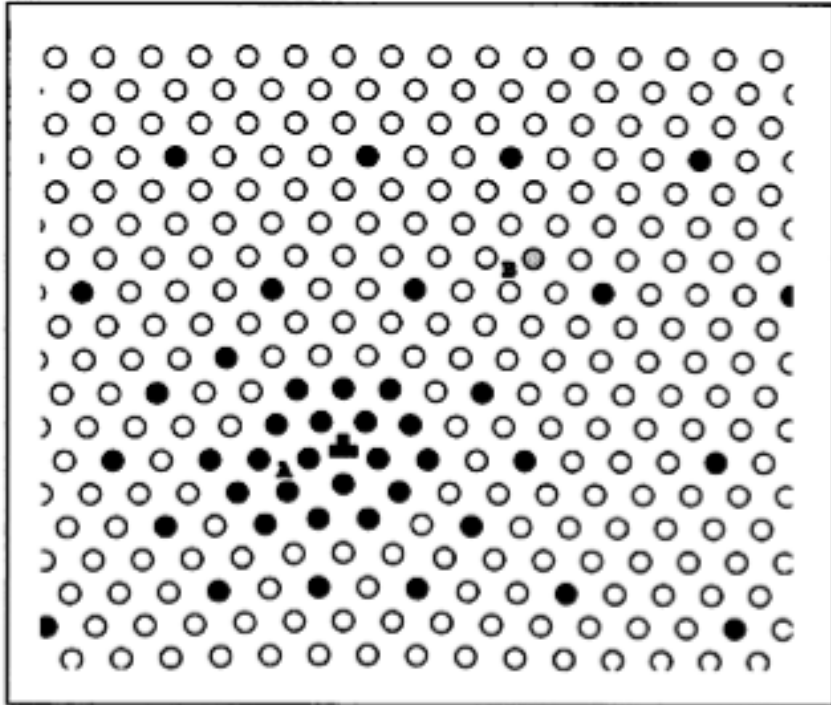$$\nabla^2 V_{sol}(r) = -4\pi\varepsilon_0\varepsilon(\rho(r))\rho(r)$$

$$H_{KS}[I] + V_{sol}$$

Potential from water medium

water medium   **Pd surface**   **water molecules**

MM   **QM**

Quasicontinuum (QC) Method

(Tadmor, et al. '96, Shenoy, et al. '99)

Most of the atomistic processes of interest occur in very small spatial domains, while the vast majority of the materials behaves according to continuum theories.
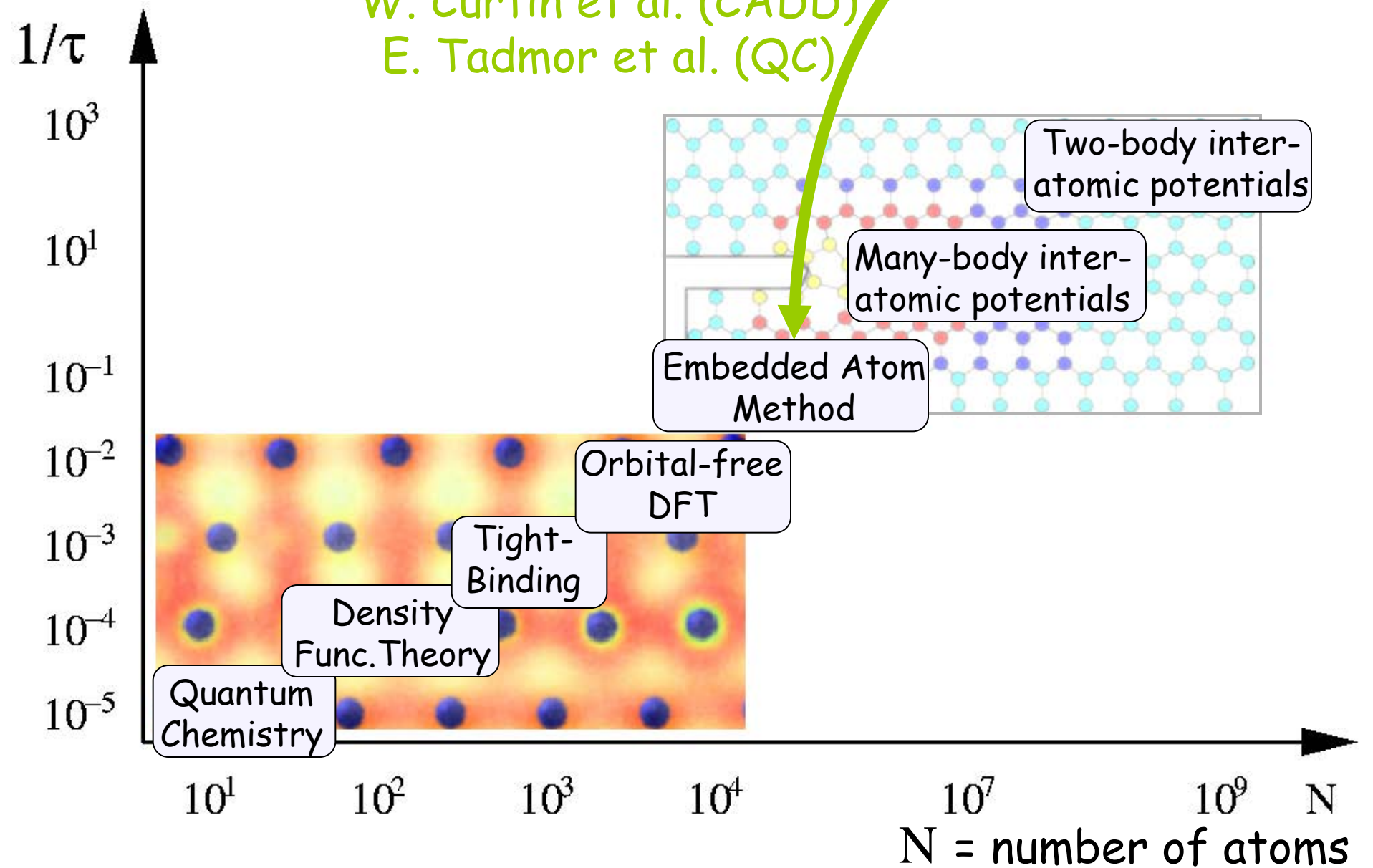

Key ideas behind QC:

• A small subset of atoms ("**repatoms**") with varying density is selected to represent the energetics of the entire system.

   - near defect core: more repatoms;
   - less deformed region: fewer repatoms

• The representative atoms are adaptively updated as deformation evolves.

τ = time step/atom (sec)

CONTINUUM

W. Curtin et al. (CADD)
E. Tadmor et al. (QC)

$1/\tau$

10^3

10^1

10^{-1}

10^{-2}

10^{-3}

10^{-4}

10^{-5}

Two-body inter-atomic potentials

Many-body inter-atomic potentials

Embedded Atom Method

Orbital-free DFT

Tight-Binding

Density Func. Theory

Quantum Chemistry

10^1 10^2 10^3 10^4 10^7 10^9 N

N = number of atoms

Quasicontinuum Method (continued)

Two types of repatoms in QC:

Local atoms: its energy depends only on deformation gradient $\mathbf{F}$ in its vicinity

Non-local atoms: energy depends on own position and neighbors (as in full atomistic calculations based on classical interatomic potentials.)

In QC formulation, non-local atoms are treated by full atomistic calculations based on classical potentials.
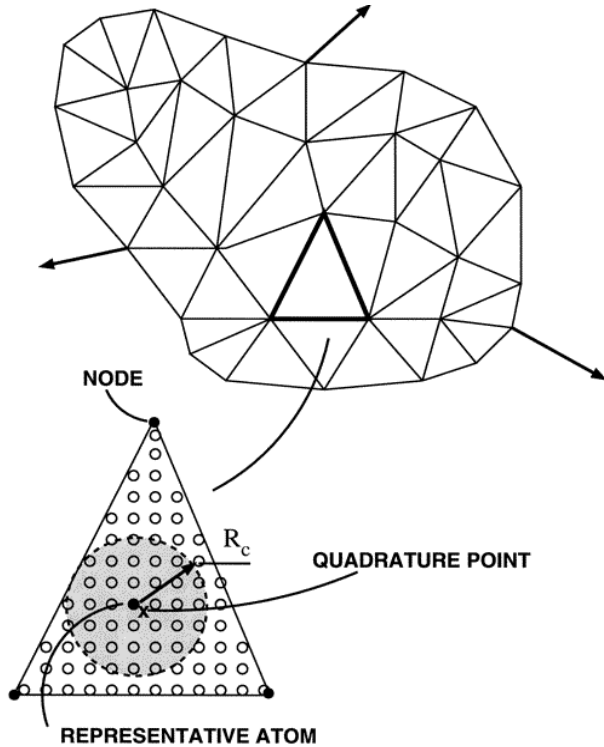
Two reasons why classical simulations as opposed to DFT calculations are used:
• Too expensive to treat all non-local atoms with DFT.
• No prescription as how DFT is coupled to local QC atoms directly.
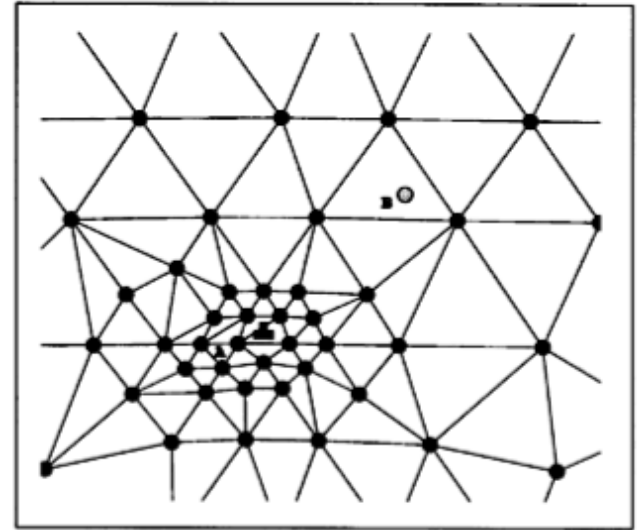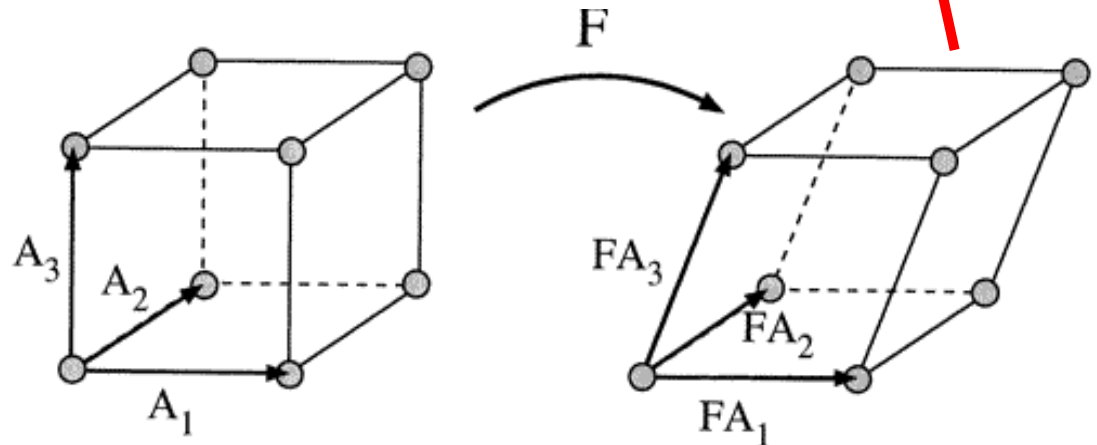
Local quasicontinuum method

Energy of each element can be calculated by using **Cauchy-Born Rule** (deformation gradient F is the same everywhere within the same element.)

$$E_{tot} = \sum_{j=1}^{N_{atom}} E_j^{atom} \approx \sum_{i=1}^{N_{element}} n_i \overline{E_i}$$
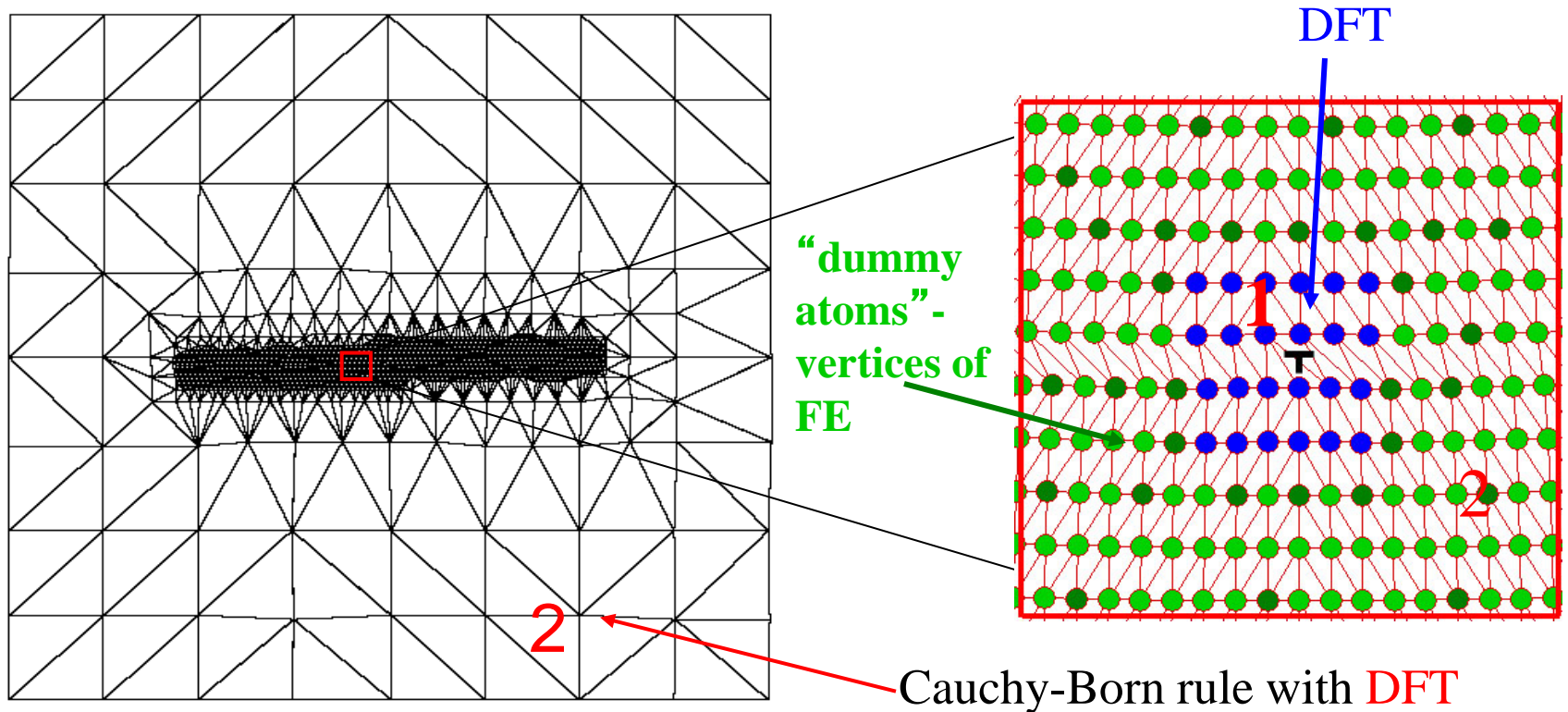
$$N_{element} \ll N_{atom}$$

atom. cal.

NODE

QUADRATURE POINT

R_c

REPRESENTATIVE ATOM

Deformation gradient tensor at the repatom is F.

Lattice vectors $\mathbf{A_i} \longrightarrow F\mathbf{A_i}$

F

A_3 A_2 A_1

FA_3 FA_2 FA_1

Tadmor et al. 1996

Quasicontinuum DFT (QC DFT) method: nucleation of dislocations in thin films

Lu et al. PRB (2006); Peng et al. PRB (2008)

DFT

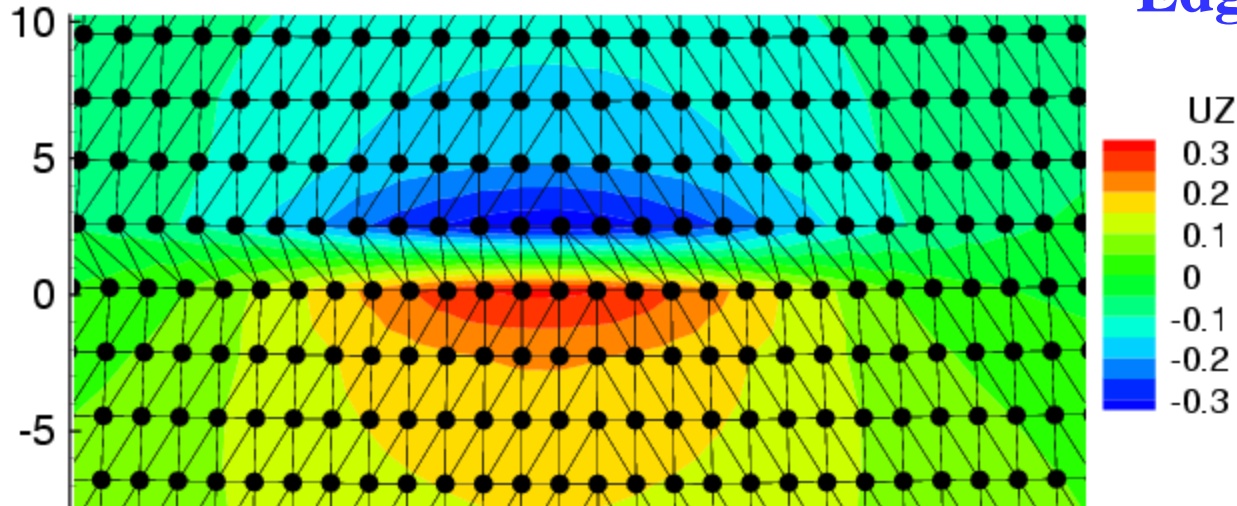"dummy atoms"- vertices of FE

Cauchy-Born rule with DFT

• All QM processes contained in region 1 treated with DFT

• Region 1 connected to finite-element region (region 2) **directly**

• Energy in FE region (region 2) calculated by DFT with Cauchy-Born rule

QM/MM

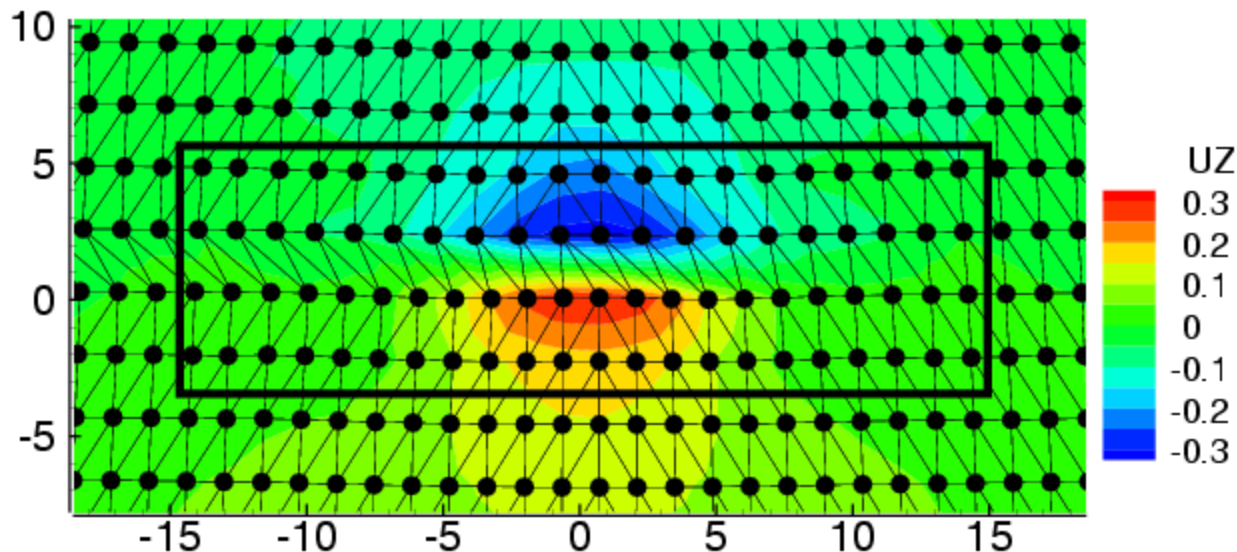# Coupling the Quasi-Continuum to DFT
[G. Lu, E. Tadmor and EK, Phys Rev B 73, 024108 (2006)]

Edge dislocation in Al
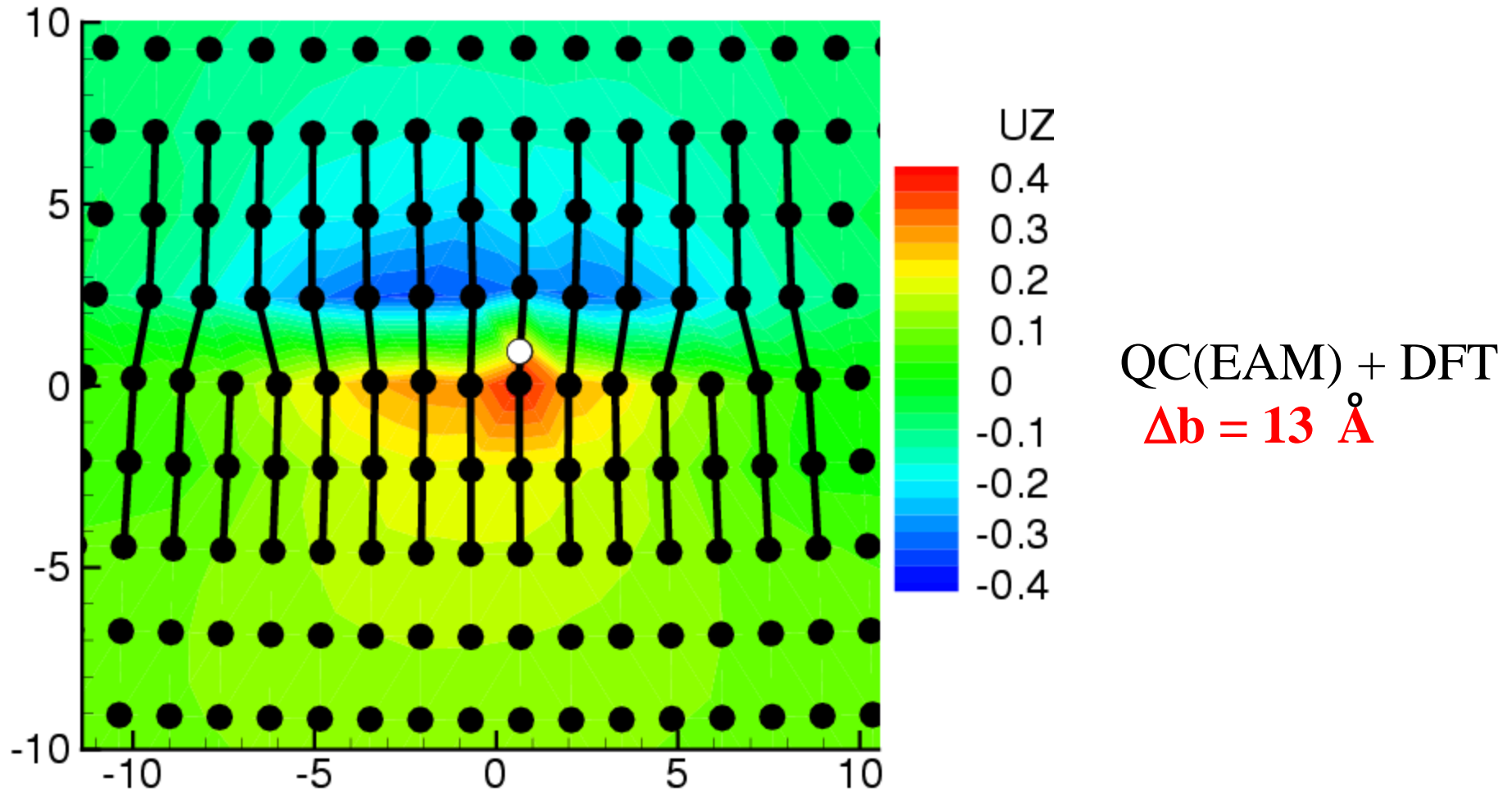
QC only (EAM)
$\Delta b = 15.4 \text{ Å}$

QC(EAM) + DFT
$\Delta b = 5.6 \text{ Å}$
(expt. 5.5 Å)

Edge dislocation in Al with H impurities

QC(EAM) + DFT

$\Delta b = 13$ Å

- **Hydrogen (open circle) lowers stacking fault energy:** wider dislocation consistent with H-embrittlement by enhanced local plasticity mechanism