Modeling Material Defects with the Fragment Hamiltonian Approach

Steve Valone

Los Alamos National Laboratory
Materials Science and Technology Division
Structure/Property Relationships

Co-Authors and Collaborators

Mike Baskes, UCSD/LANL

Ben Liu, Kedernath Kolluri, Rich Martin, LANL

Susan Atlas, David Dunlap, Jonathan Allen, UNM

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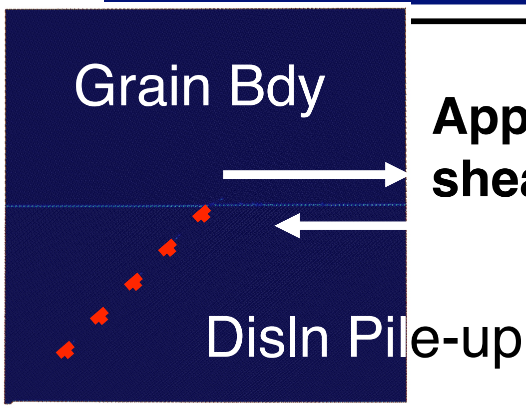
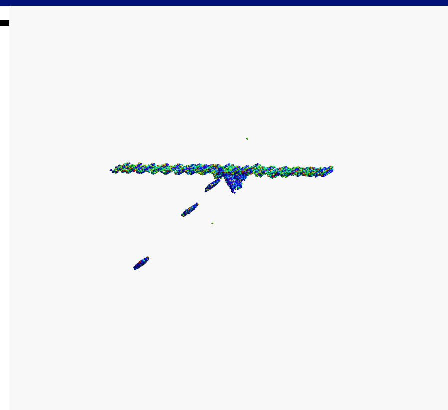
Outline

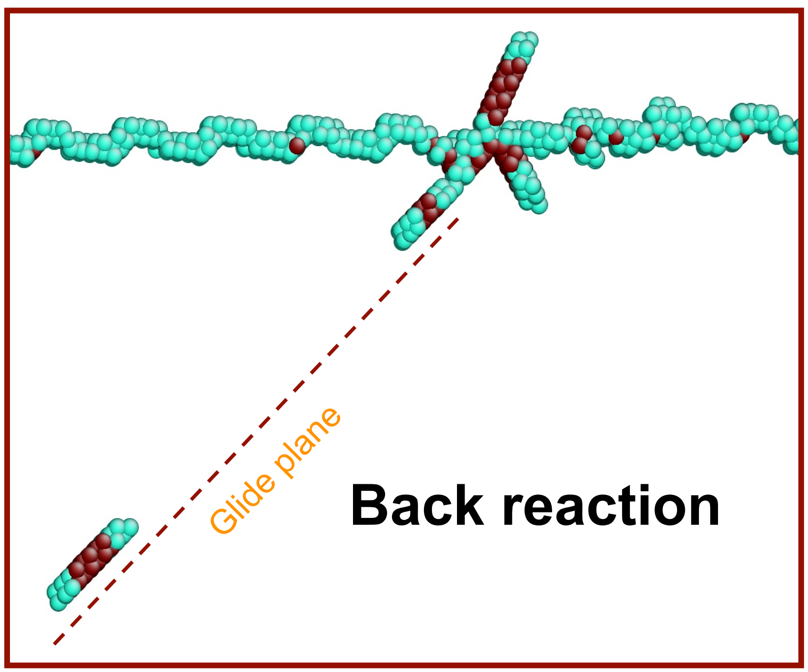
- Motivating Examples
- Refresher from tutorial
- Many-Electron View of Potential Energy Surfaces (PESs)
- Fragment Hamiltonian (IMA)
- Defect Properties
- Connections Back to Electronic Properties
- Summary Remarks

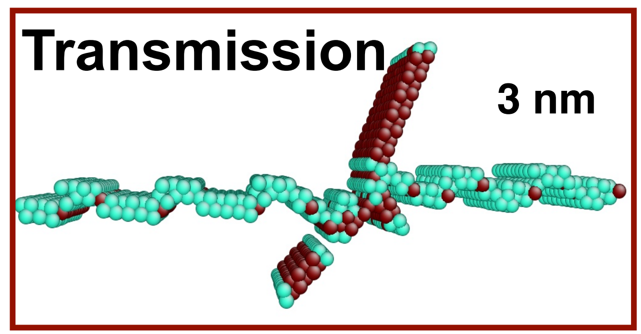
Motivation I: Materials Deformation – Dislocation Transmission

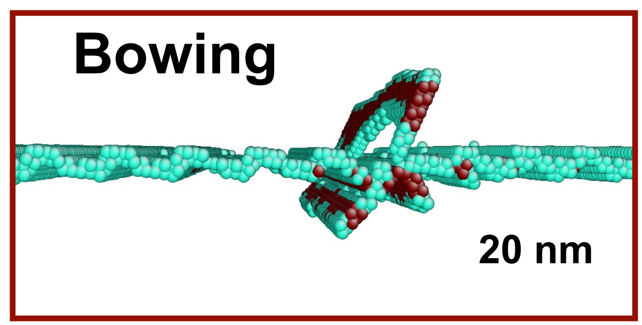




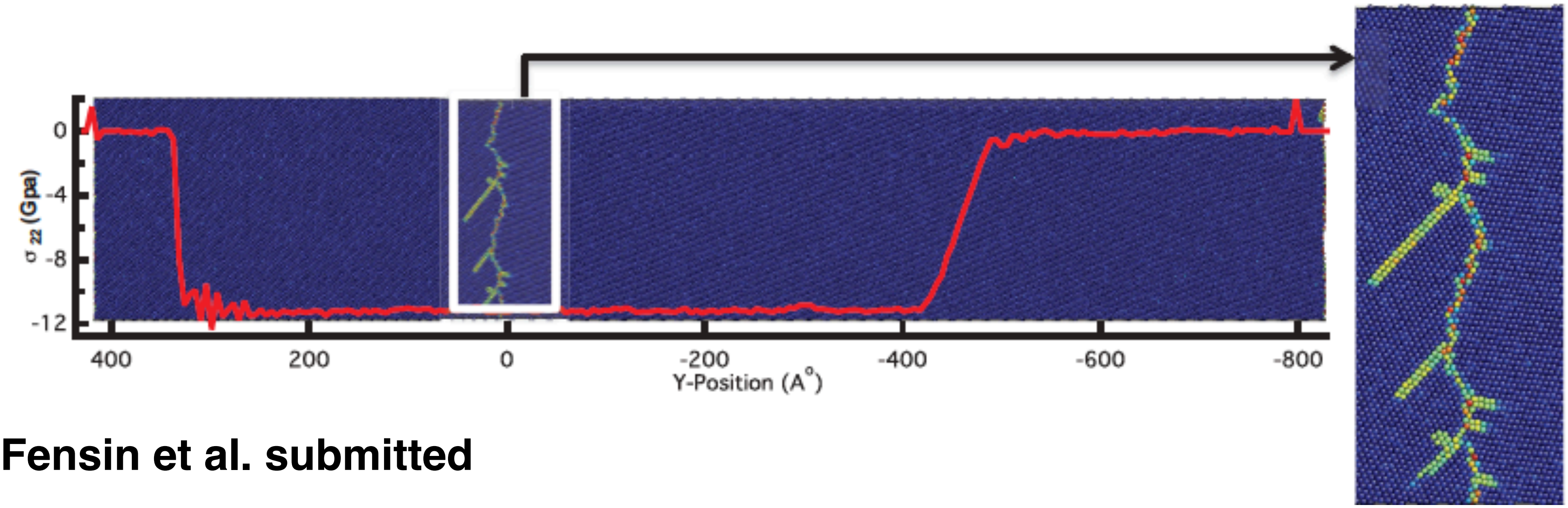
Before nucleation and transmission, similar events occur (Al)







Motivation II: Shock Deformation at Grain Boundary



Fensin et al. submitted

- **Two pieces of Cu, one smashed into the other**
  One piece has a grain boundary
  Single crystals otherwise
- **Shock wave forces Shockley partials to emit**

Metals: Embedded Atom Models

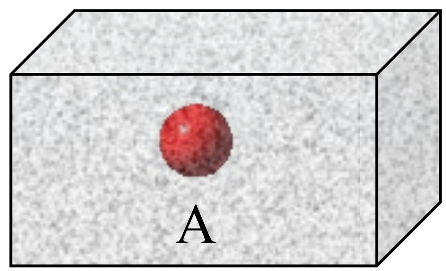
$$E = \sum_{A} \left(F_{EAM}(\bar{\rho}_A) + \tfrac{1}{2} \sum_{B \neq A} \phi_{AB}(R_{AB}) \right)$$

- **EAM energy**

$$F_{MEAM}(\bar{\rho}) = A \frac{\bar{\rho}}{\rho_0} ln \frac{\bar{\rho}}{\rho_0}$$

$$F_{F-S}(\bar{\rho}) = A \sqrt{\frac{\bar{\rho}}{\rho_0}}$$

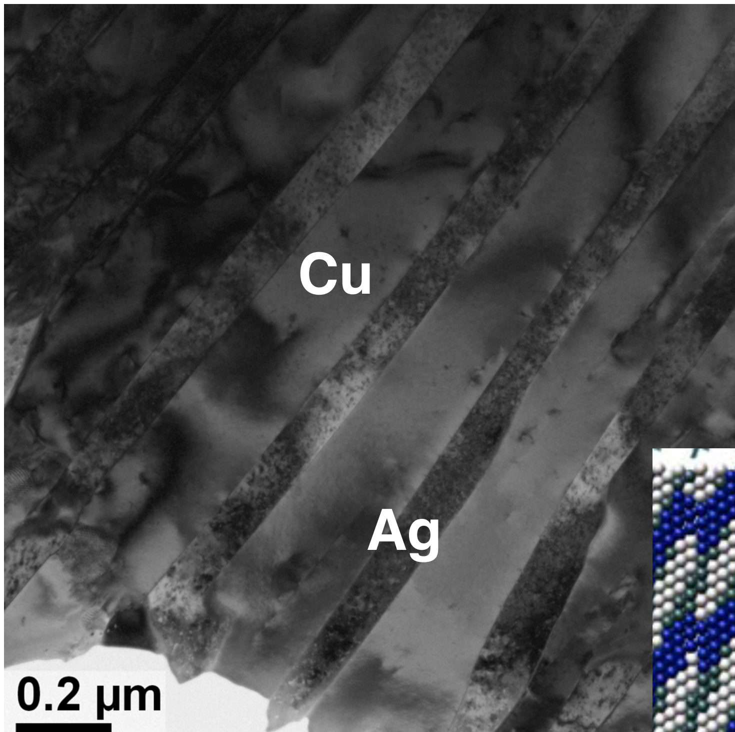
- **Embedding Function**



$$\phi(R) = \frac{2}{Z} \left\{ E^u(R) - F(\bar{\rho}^u(R)) \right\}$$

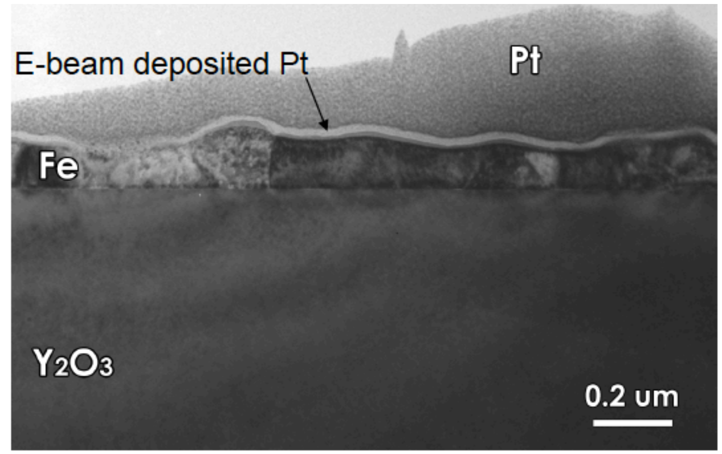
- **Pair Potential**

Motivation III: MultiLayer Materials

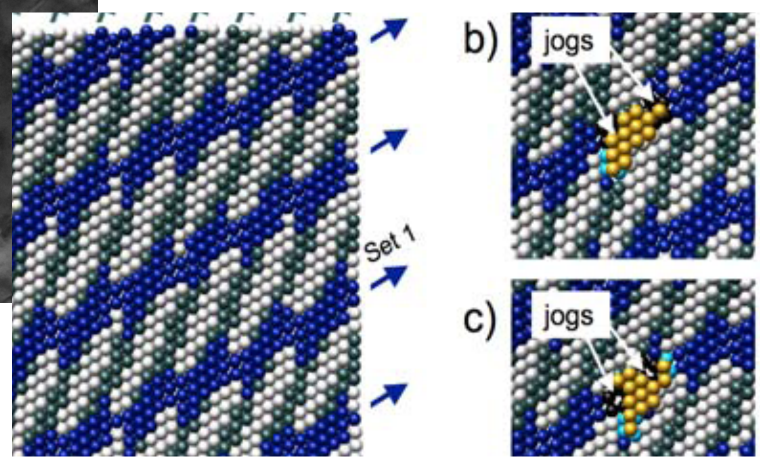


Metal-Metal Layers

Wang *et al.* 2010



Protoype Metal-Oxide Layered
Anderoglu, 2011

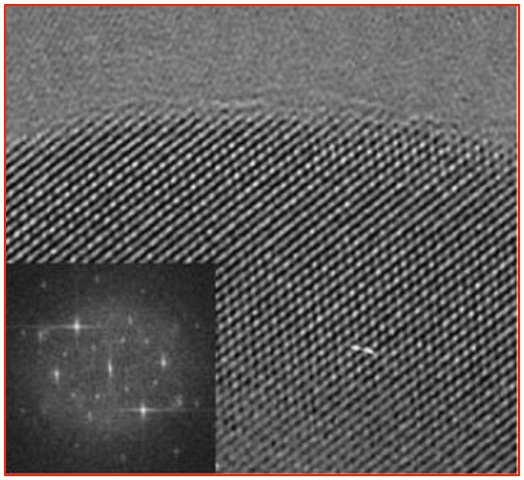


Demkowicz, 2008

Cu-Nb interface: Two sets of parallel misfit dislocations: blue atoms & gray; reconstructs

Motivation IV: Metal-Oxide Composites

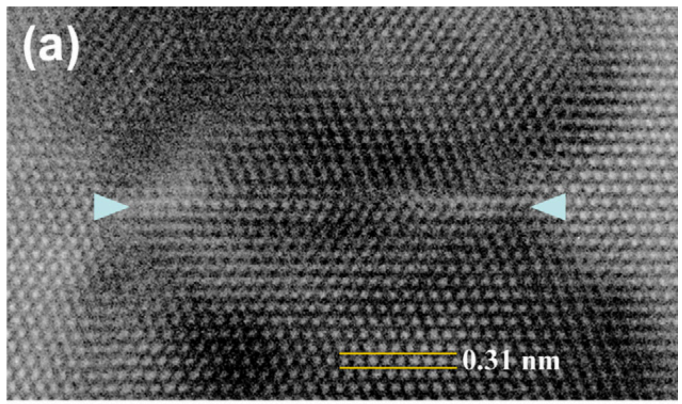
Nano-scale oxides strengthen steels



HRTEM of Fe-oxide interface in 12CrODS

Oka et al. Met Trans (2007)

Dislocations loops in ceria can be cation vacancies



HRTEM of stacking fault in ceria created by e⁻ irradiation

Yasunaga et al. Nucl Instr Meth B (2008)

Ni/NiO composites present sharp interfaces, variable oxide composition

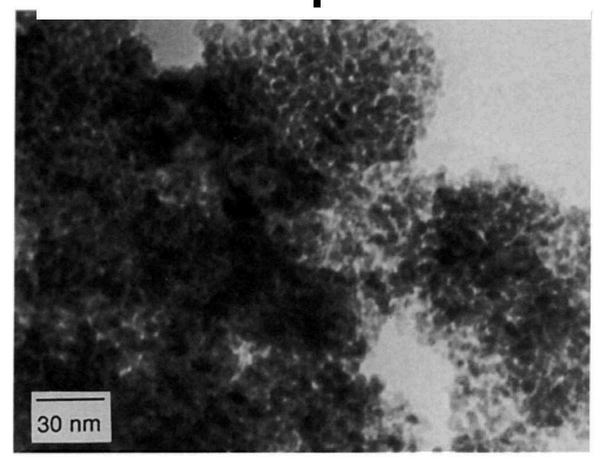


Fig. 4. Transmission electron micrograph of NiO/Ni composite fired at 300°C for 1 h in air.

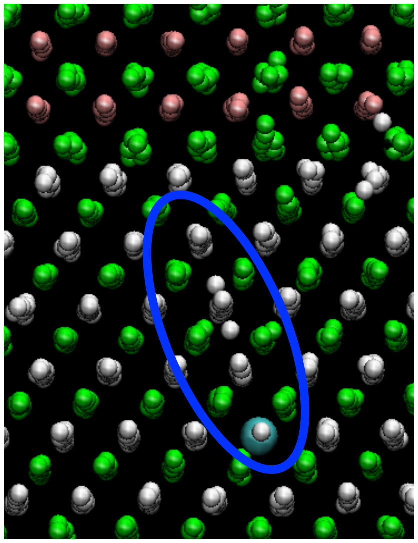
Ni/NiO nanocomposite

Liu & Anderson J Electrochem Soc (1996)

Challenge: Metals + Metal Oxides in intimate contact

- Changes in valence/oxidation state
- Multiple charge/oxidation states
- Consistent model of metals and ceramics

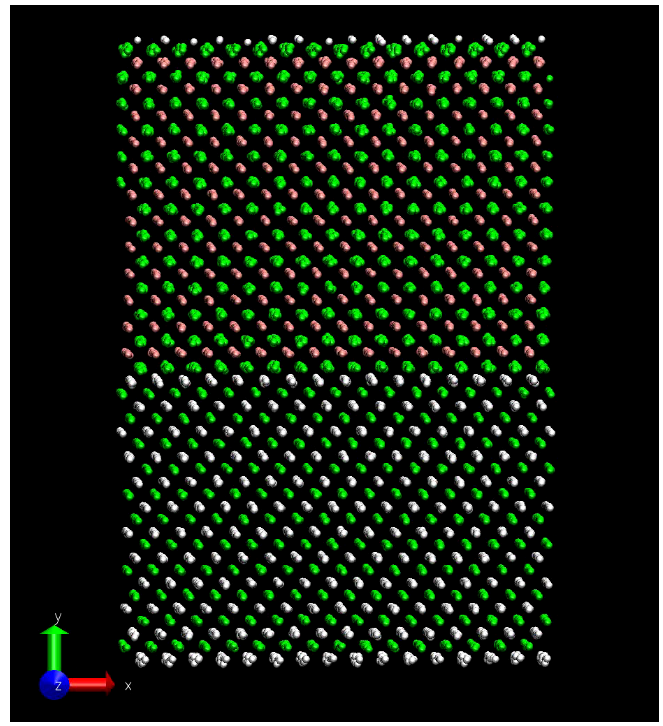
Motivation V: Radiation Damage



Oxy
Hf
Mg

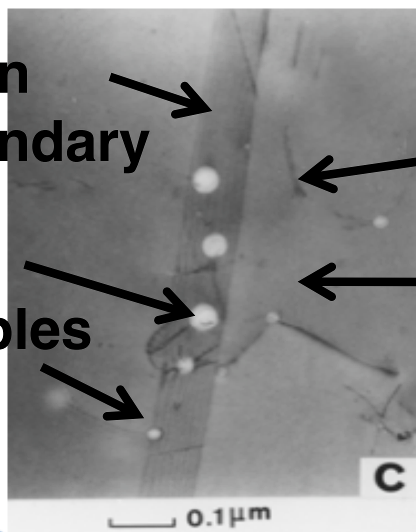
Single events in nuclear fuels

Radiation damage produces high-energy defects



grain boundary

He bubbles



dislocation

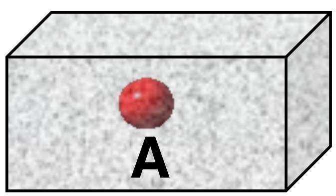
austenitic steel

Damage Accumulates into “Extended” Defects: TEM image (Wirth 2007)

Ionic Materials: Buckingham, ReaxFF, COMBS …

$$\phi_{AB}^{ionic} = A\exp\left(-R_{AB}/\rho_{AB}^{Buck}\right) - \frac{C_6}{R_{AB}^6} + \frac{q_A q_B}{\varepsilon_0 R_{AB}}$$

$$F_{IM}(q) = E_A^0 + \chi_A q + 1/2\,\eta_A q^2$$



$$E = \sum_{A}\left(F_{IM}(\bar{\rho}_A) + \tfrac{1}{2}\sum_{B\neq A} \phi_{AB}(R_{AB}) \right)$$

- **Buckingham:**
  Coulombic interactions between atoms
  Dispersion interactions
  - Constant charges
  - No bond-breaking

- **Qeq, …: Variable charges**
  χ: electronegativity ~ Fermi level
  η: hardness ~ charge transfer gap

- **Same general form as EAM**

Two Types of Materials
Two Types of Models

	Metals	Ceramics
Characteristics	• Metallic bonding • No charge transfer	• Ionic bonding • Charge transfer controlled heuristically, no physical basis
Models	EAM, MEAM, F-S …	ReaxFF, COMB, QTPIE, QEq, BETM, …

- Ionic and metallic bonding in one model
- Charge transfer and ionicity with physical basis
- Encompasses metal and ceramic models

Recall Tutorial, Interatomic Potentials: From Ab-Initio to Empirical Potentials

Electronic structure determines materials properties

Model Hamiltonian Approach

Full, Many-electron H

$\hat{H}_{\text{el}} =$

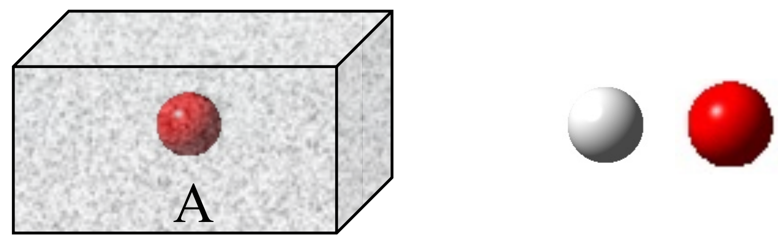
$$\sum_{e^-\text{'s } i}\left(-\frac{\Delta_i}{2}+\sum_{atoms}\frac{Z_A}{|r_i-R_A|}+\frac{1}{2}\sum_{j\neq i}\frac{1}{|r_i-r_j|}\right)$$

$+\hat{V}_{\text{NN}}$

Fragment H

Atomic granularity

$$\hat{H}_{\text{el}}\equiv\sum_{\text{A}}\left(\hat{H}_{\text{A}}+\tfrac{1}{2}\sum_{\text{B}\neq\text{A}}\hat{V}_{\text{AB}}\right)$$



$$\hat{H}_{\text{el}}\to\hat{h}_{\text{TB}}+U\hat{D}_H$$

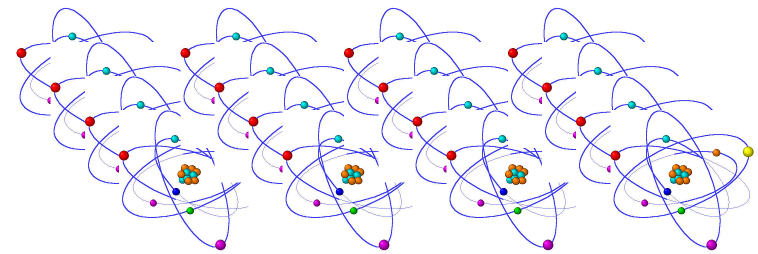
$$=-t\left(\hat{T}+\sum_{\text{A}}\hat{V}_{\text{A}}^{\text{at}}\right)+U\sum_{\text{A}}\hat{n}_{\text{A}\downarrow}\hat{n}_{\text{A}\uparrow}$$

Tight-bonding, Hubbard, DFT H's

One electron granularity

Bloch, 1928

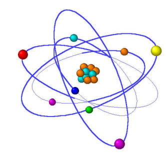
Many e⁻ Hamiltonians in Fragments

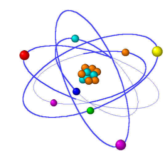


$$H_{\text{el}} = K_{\text{e}} + V_{\text{eN}} + V_{\text{ee}} + V_{\text{NN}}$$

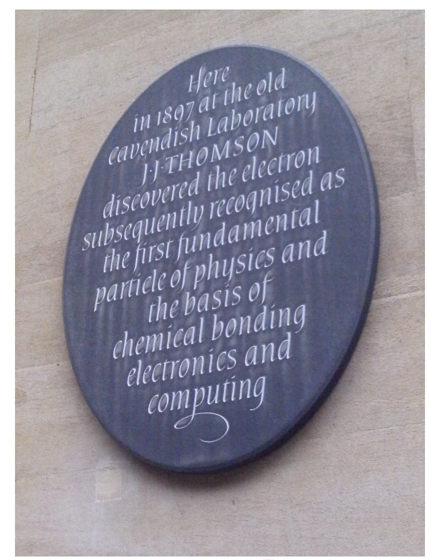
- Traditional breakdown

$$\hat{H}_{\text{el}}\psi_i = \sum_{\text{A}} \left(\hat{H}_{\text{A}}\left(Z_{\text{A}}\right) + \tfrac{1}{2}\sum_{\text{B}\neq\text{A}} \hat{V}_{\text{AB}}\left(Z_{\text{A}}, Z_{\text{B}}\right) \right) \psi_i$$



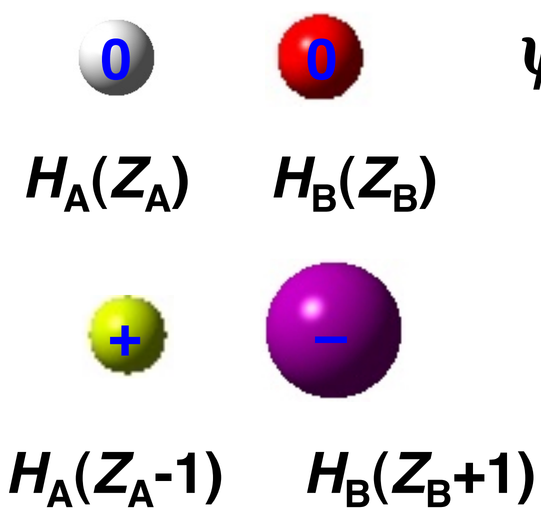


- "Atom-in-Molecule" Hamiltonian well-known
  - Moffitt (1951)
  - Always assigned number of electrons N_A equal to nuclear charge Z_A
  - Makes sense physically, but "$N_A = Z_A$" assumption problematic



Classical Valence Bond Structures I

- **Distribute electrons among fragments: Charge fluctuations**
- **Vary integer number of electrons**
  ➔ Open system
- **Superpose states with different numbers of e⁻**



$$\psi_{00} = \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)$$: **Heitler-London covalent state**

$$\psi_{+-} = \phi_B(1)\phi_B(2)$$

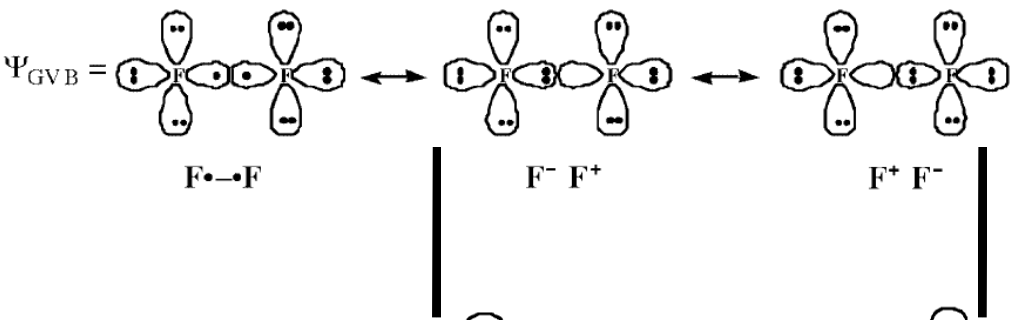
$$\psi_{-+} = \phi_A(1)\phi_A(2)$$

: **ionic states**

Note: mean-field/molecular-orbital state is an average

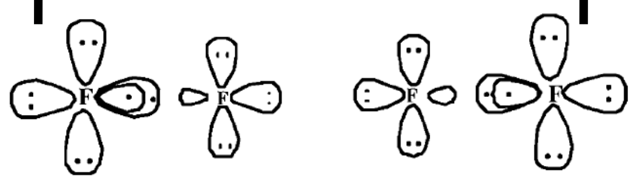
Classical Valence Bond Structures II

Other examples

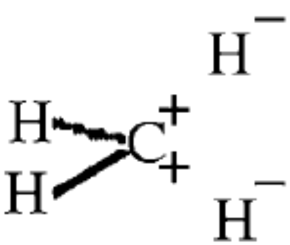


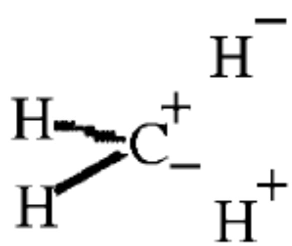
- F_2

Enhancement



- CH_4 and H_3MCl





$$\Psi_{M-Cl} = C_1\Psi_{M\cdot-\cdot Cl} + C_2\Psi_{M+Cl-} + C_3\Psi_{M-Cl+}$$

Hiberty & Shaik, et al. 2002

Lauvergnat, et al. 1996

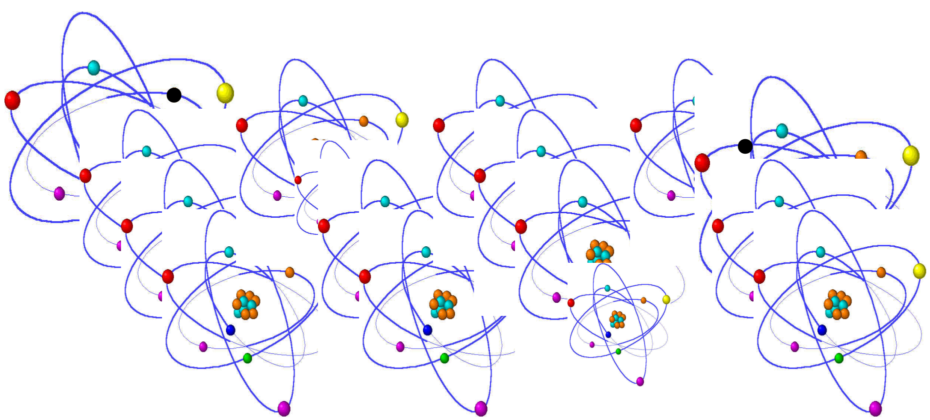
Charge Fluctuations at Fragment Operator Level

$$\hat{H}_A = \hat{H}_A(N_A)$$

Electrons 1 thru N_A assigned to A

Electrons N_A+1 thru N_A+N_B assigned to B

… N_A, N_B, … arbitrary



- **$N_A \neq Z_A$**
- **Consider Cu atoms in gas phase**
- **Fluctuations occur as gas condenses into metal Notion of $\hat{H}_A$ preserved, for the most part**
- **Similarly for pair interactions**

Description with Fragment Variables

$$\Psi \equiv \sum_i c_i \Psi_i$$

$$\Psi_A \equiv \sum_\varsigma C_{A\varsigma} \Psi_{A\varsigma}$$

$$\Psi_{A\varsigma} \equiv \sum_i \delta_{\varsigma,\varsigma_i^A} c_i \Psi_i \Big/ C_{A\varsigma}$$

$$C_{A\varsigma}^2 \equiv n_{A\varsigma} = \sum_i \delta_{\varsigma,\varsigma_i^A} c_i^2$$

cf H_2, H_3MCl molecules
Covalency = $C_{A^0}^2$

- Collect basis states (N-e⁻) and expansion coefficients according to fragment properties
- Fragment view introduces branches

  Can only define occupation numbers, not coefficients

$$\psi = \psi_A = \psi_{A^0} + \sqrt{n_+}\psi_{A^+} + \sqrt{n_-}\psi_{A^-}$$

$$\hat{H}_{A^0} \qquad \hat{H}_{A^+} \qquad \hat{H}_{A^-}$$

Fragment Variational Energy

$$\bar{E} = \frac{\langle \psi | \hat{H}_{el} | \psi \rangle}{\langle \psi | \psi \rangle}$$

$$\bar{E} \equiv \sum_{A} \left(E_A + \tfrac{1}{2} \sum_{B \neq A} V_{AB} \right)$$

$$E_A \equiv \sum_{\varsigma,\varsigma'} C_{A\varsigma'} C_{A\varsigma} H^{A}_{\varsigma'\varsigma}$$

$$= tr\ H_A \Gamma_A / tr\ \Gamma_A$$

$$V_{AB} \equiv \sum_{\varsigma,\varsigma'} C_{AB\varsigma'} C_{AB\varsigma} V^{AB}_{\varsigma'\varsigma}$$

$$= tr\ V_{AB} \Gamma_{AB} / tr\ \Gamma_{AB}$$

Essential to recognize that Ē is being modeled

- ∴ Variational energy fragments
  - Describe problem in terms of properties and states of fragments/atoms
  - Density matrix form convenient
  - Energy matrices well defined

N-e⁻ wave functions, N_A-e⁻ operators

$\psi_{A\varsigma}(N;C)$ and $\psi_{A\varsigma'}(N;C)$

$$H^{A}_{\varsigma'\varsigma} \equiv \left\langle \psi_{A\varsigma'}(N) \middle| \hat{H}_{A\varsigma'}(N_{A\varsigma'}) + \hat{H}_{A\varsigma}(N_{A\varsigma}) \middle| \psi_{A\varsigma}(N) \right\rangle / 2$$

Chemical Potential Equalization

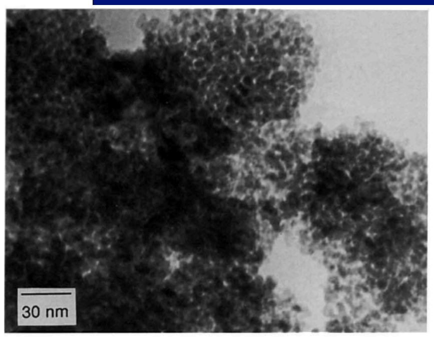


Fig. 4. Transmission electron micrograph of NiO/Ni composite fired at 300°C for 1 h in air.

Ni/NiO nanocomposite

$$\bar{E}(\underset{\sim}{q}) \equiv \min_{\underset{\sim}{c} \to \underset{\sim}{q}} \bar{E}(\underset{\sim}{c})$$

$$\psi \equiv \sum_i c_i \psi_i \qquad 0 = \sum_{\mathrm{A}} q_{\mathrm{A}}$$

$$\partial \bar{E} / \partial q_\kappa = \mathrm{tr} \sum_{\mathrm{A}} \Big(\mathrm{H_A}\, \partial \Gamma_{\mathrm{A}} / \partial q_\kappa + \partial \mathrm{H_A} / \partial q_\kappa \Gamma_{\mathrm{A}}$$

$$+ \sum_{\mathrm{B} \neq \kappa} \partial(\mathrm{V_{AB}} \Gamma_{\mathrm{AB}}) / \partial q_\kappa \Big)$$

$$\bar{E}(\underset{\sim}{q}, \underset{\sim}{\tau}) \equiv \min_{\underset{\sim}{c} \to \underset{\sim}{q}, \underset{\sim}{\tau}} \bar{E}(\underset{\sim}{c})$$

CPE critical for defect modeling

- Minimize over all q
  cf constrained search DFT
- Similarly minimize over all *q*
- Apply conservation of total charge neutrality:
  $\partial \bar{E} / \partial q_\kappa = -\mu$

- Minimize over τ too
- No comparable conservation principle known for ionicity

Charge-Dependent Site-Energy Models

A – B neutral, different ionization potentials

Quantum

$$E = E_0^{\mathrm{A}} + E_0^{\mathrm{B}} + (\mu_{\mathrm{A}} - \mu_{\mathrm{B}})\,\omega(q,d)$$
$$+A\exp\left(-d/d^{(0)}\right) - C/d^6 - q^2/d$$

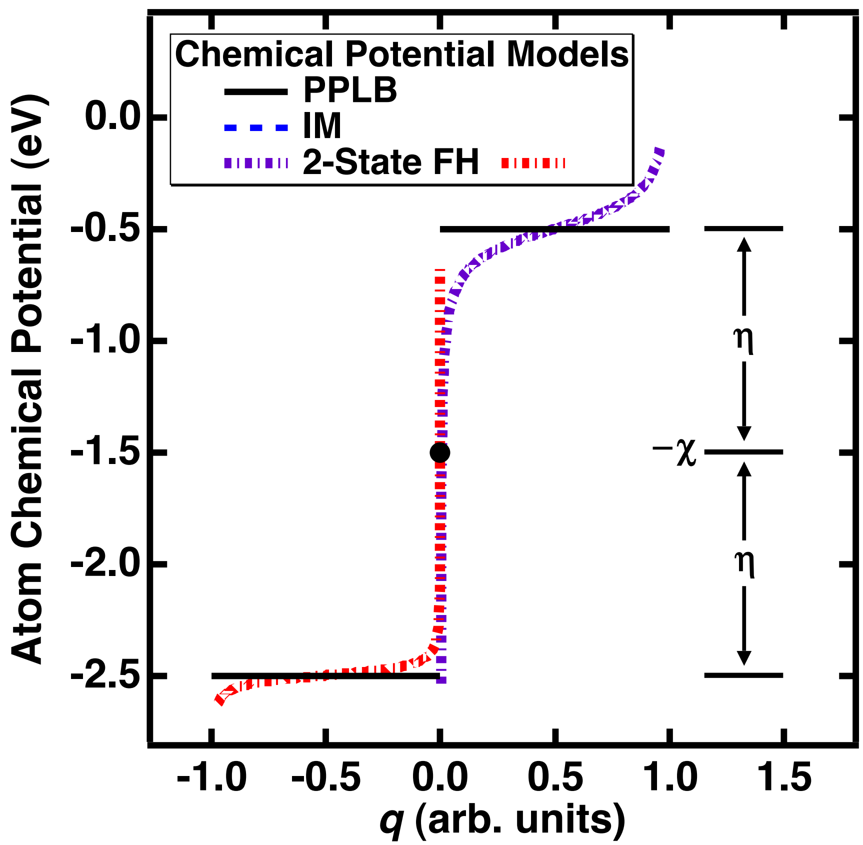
$$\omega(q,d) = \left(\sqrt{q\left(1-q_0(d)\right)} - \sqrt{q_0(d)(1-q)}\right)^2$$

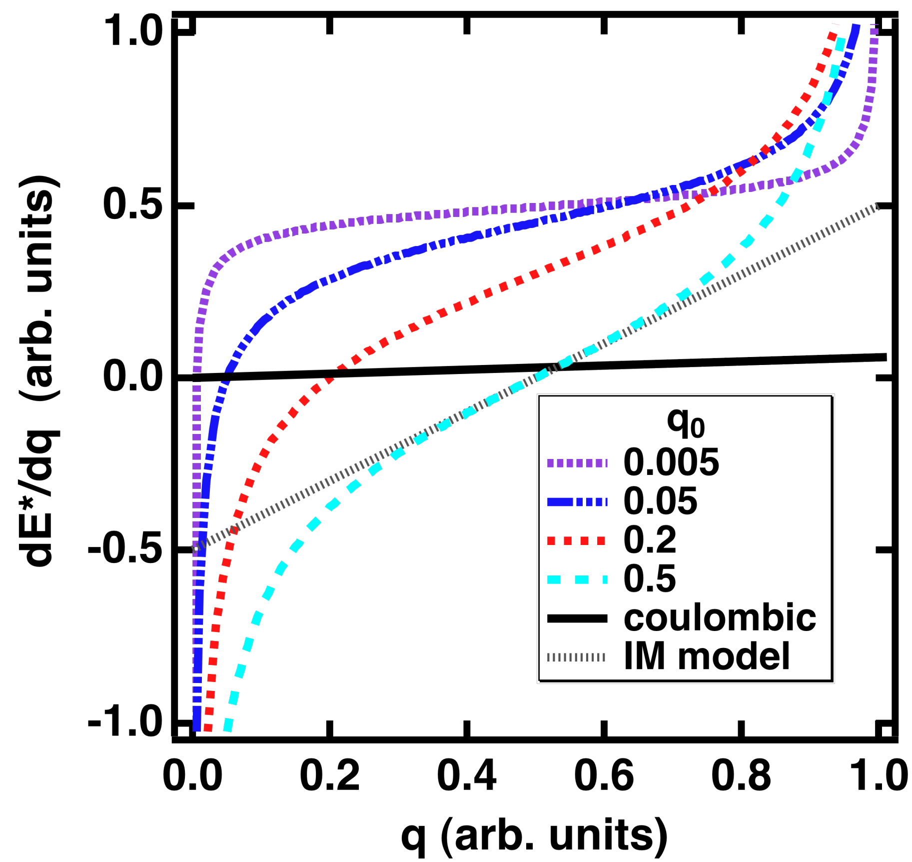
Iczkowski-Margrave: quadratic

$$E = E_0^{\mathrm{A}} + E_0^{\mathrm{B}} + (\mu_{\mathrm{A}} - \mu_{\mathrm{B}})\,q$$
$$+\frac{1}{2}(\eta_{\mathrm{A}} + \eta_{\mathrm{B}})\,q^2$$
$$+A\exp\left(-R/R^{(0)}\right) - C/R^6 - q^2/R$$

Hopping characteristics of two models lead to different charge flow properties

Chemical Potential in the FH Model

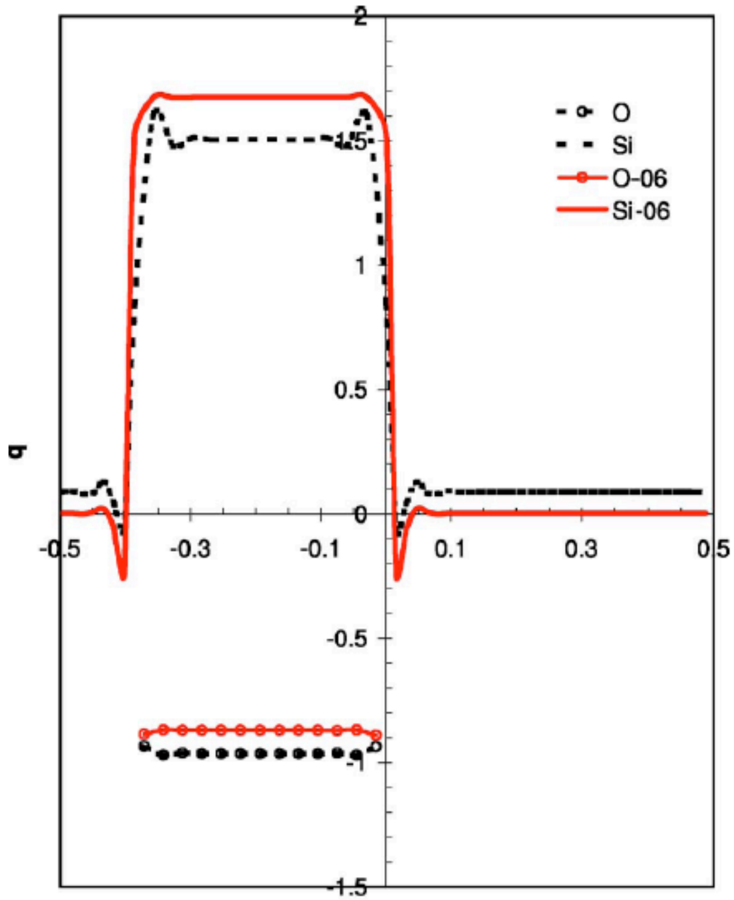




Atomic-level behavior of chemical potential varies greatly among models. PPLB is the correct limit for dissociated (gas-phase) atoms

Charge equilibration condition at crossing of black line crosses the colored curves

Charge Flow at Interfaces: Charge-Dependent Models



Charge-flow Regulation:

Development of space charge at hetero-interface

Phillpot et al.: Si/SiO_2 (PRB, 2007)

Metallic and Ceramic Composites:

Need to attenuate flow

COMBS does so by higher-order charge-dependencies

Fragment Hamiltonian (FH) Embedding Energy

Progression of variable substitutions

Fragment expansion coefficients

$$\Gamma_A(c_+,c_-)=\begin{pmatrix} c_0c_0 & c_0c_+ & c_0c_- \\ \dagger & c_+c_+ & c_+c_- \\ \dagger & \dagger & c_-c_- \end{pmatrix}_A$$

Create and annihilate atoms in particular charge states

Charge occupation numbers

$$\Gamma_A(n_+,n_-)=\begin{pmatrix} n_0 & \sqrt{n_0n_+} & \sqrt{n_0n_-} \\ \dagger & n_+ & \sqrt{n_+n_-} \\ \dagger & \dagger & n_- \end{pmatrix}_A$$

States of atoms

$$F_A = \mathrm{tr}\, H_A\Gamma_A(n_+,n_-)$$

$$H_A = H_{00}^A + \begin{pmatrix} 0 & H_{0+} & H_{0-} \\ \dagger & \mathcal{I}^* & H_{+-} \\ \dagger & \dagger & -\mathcal{E}^* \end{pmatrix}_A$$

Energy scales: Ionization, Attachment, Hopping

smv, JCTC, JPCL 2011

Net charge and Ionicity

$$q_A \equiv n_{A^+} - n_{A^-}$$

$$\tau_A \equiv n_{A^+} + n_{A^-}$$

- Each atom described by a minimum of two variables
  - Charge: Difference between n's
    Not unique: choose definition
  - "Extra" variable τ_A, ionicity: sum of n's
    $\tau_A \perp$ to q_A

$$\Gamma_A(q,\tau) = \begin{pmatrix} 1-\tau & \sqrt{(1-\tau)(\tau+q)/2} & \sqrt{(1-\tau)(\tau-q)/2} \\ \dagger & \frac{\tau+q}{2} & \frac{\sqrt{\tau^2-q^2}}{2} \\ \dagger & \dagger & \frac{\tau-q}{2} \end{pmatrix}_A$$

- Make contact with established models applying charge and "background density" (EAM, F-S)

Unified Embedding Energy

$$F_{\mathrm{FH}}(q,\tau) = F_{\mathrm{FH}}^{(gap)}(q,\tau) - F_{\mathrm{FH}}^{(hop)}(q,\tau)$$

Gap + 2e⁻ 1e⁻

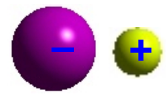
$$F_{\mathrm{FH}}^{(gap)}(q,\tau) = E_0 + \chi q + \eta\tau + W_{2e}\sqrt{\tau^2 - q^2}$$

$$F_{\mathrm{FH}}^{(hop)}(q,\tau) = W_{1e}^{+}\sqrt{(1-\tau)(\tau+q)} + W_{1e}^{-}\sqrt{(1-\tau)(\tau-q)}$$

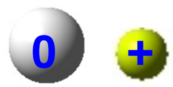
smv, JCTC, JPCL 2011

- **Arrange into two embedding energies, two variables:**
  1. Total charge fluctuations (τ)
  2. Imbalance in charge fluctuations (*q*)
- **Mulliken Electronegativity:**
  $\chi = (\mathcal{I}^* + \mathcal{E}^*)/2$
- **"Absolute Hardness":**
  $\eta = (\mathcal{I}^* - \mathcal{E}^*)/2$
  More general than Parr-Pearson
  *** means environmental influence**

Hardness and Ionicity



$$F_{\mathrm{FH}}^{(diag)}(q,\tau) = E_0 + \chi q + \eta\tau$$



Hardness 1st order in τ

- **Fragment Hamiltonian (hopping terms excluded)**
- **FH model makes hardness (gap) related to ionicity, not charge (Fermi level)**

$$E(q) = E_0 + \chi q + \eta q^2$$

Hardness 2nd order in *q*

- **Iczkowski-Margrave**

hardness ⟷ fundamental gap

Two-State Model for Hardness

$$\bar{E}_{A}(0,\tau_{A}) = E^{*}_{A^{0}} + \Delta\eta^{*}_{A}\tau_{A} + 2h^{*}_{A}\sqrt{(1-\tau_{A})\tau_{A}}$$

$$\Delta\eta^{*}_{A} = \eta^{*}_{A} + W^{2e}_{A}$$

$$h^{*}_{A} = -\left(W^{1e+}_{A} + W^{1e-}_{A}\right)/\sqrt{2}$$

- q=0 cut through embedding energy
  - 2e⁻ hopping buried in Δη
  - 1e⁻ hopping grouped together

$$v^{*}_{A}(0,\tau) \equiv \frac{\partial E_{A}(0,\tau)}{\partial \tau_{A}}$$

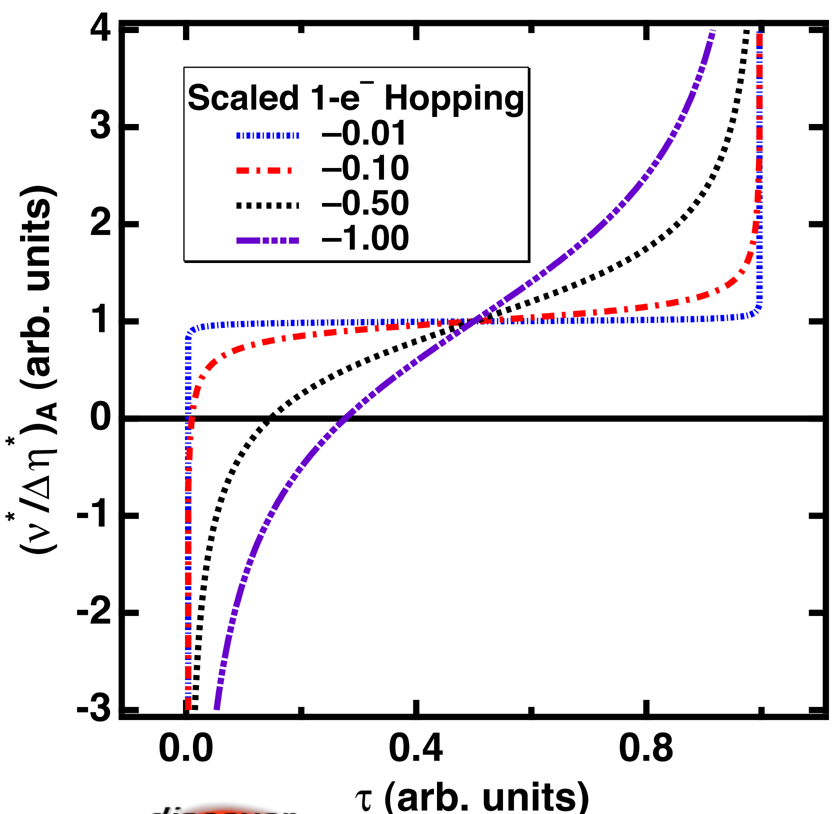
$$\equiv \left[\Delta\eta^{*} + h^{*}\frac{1-2\tau}{\sqrt{(1-\tau)\tau}}\right]_{A}$$

- Differential form of fragment hardness
- More generally, depends in *q*
- Absolute hardness appears as identifiable contribution

smv, JPCL (2011)

Limits of Ionicity Optimization

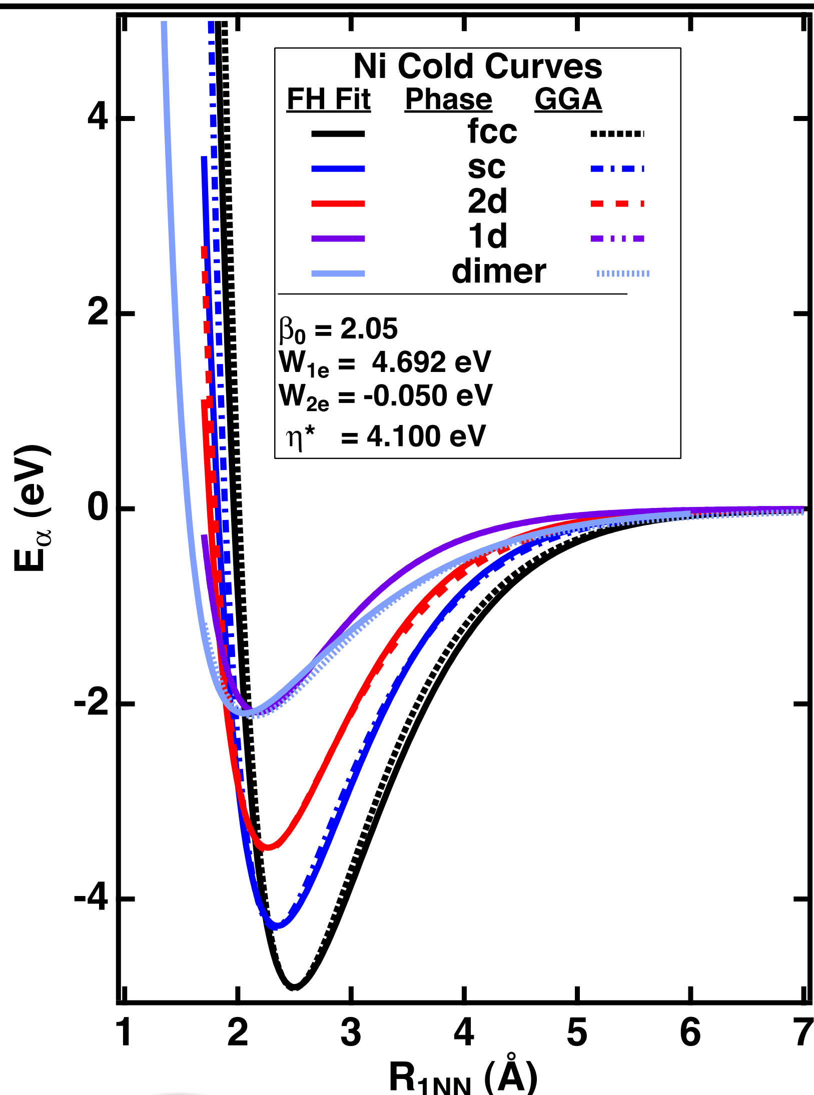
$$\tau_A = 1/2\left[1 \pm \frac{\Delta\eta^*}{\sqrt{(\Delta\eta^*)^2 + h^{*2}}}\right]_A$$



- **Optimization leads to two extremes for ionicity**
  - **Dissociation limit correct because hardness > 0**
  - **Large hopping *h** leads to "metallic-like" value of η**

smv, JPCL (2011)

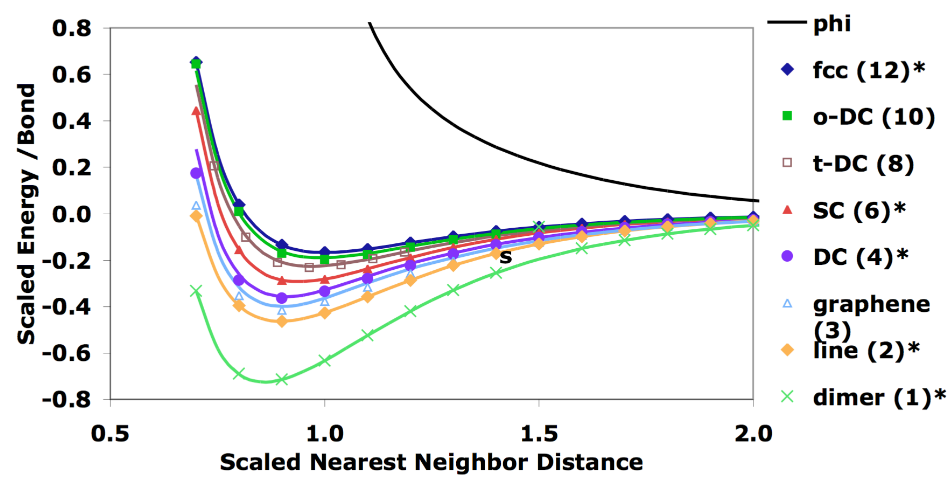
FH Embedding Energy: Nickel



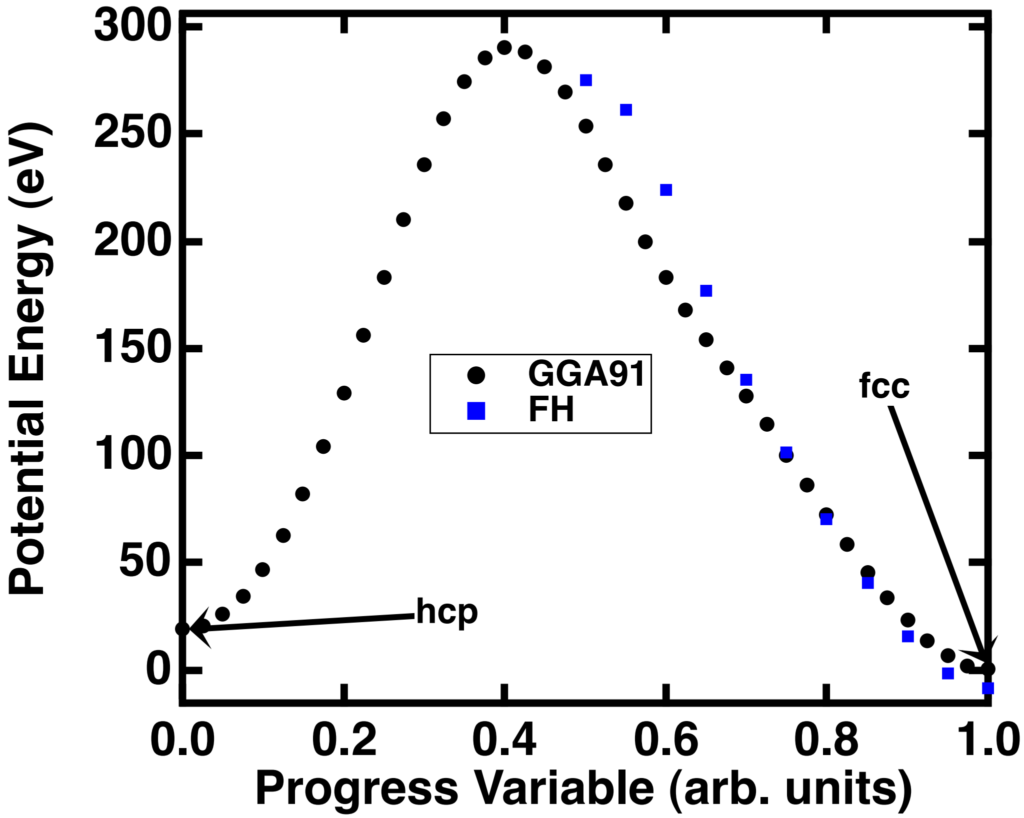
- Multiple energy-volume curves, 0 K, improve with MS-MEAM

  Baskes et al. (2007)

- Apply same strategy for FH
- Capture coordination and volume dependencies



Stacking Fault Energy: Ni



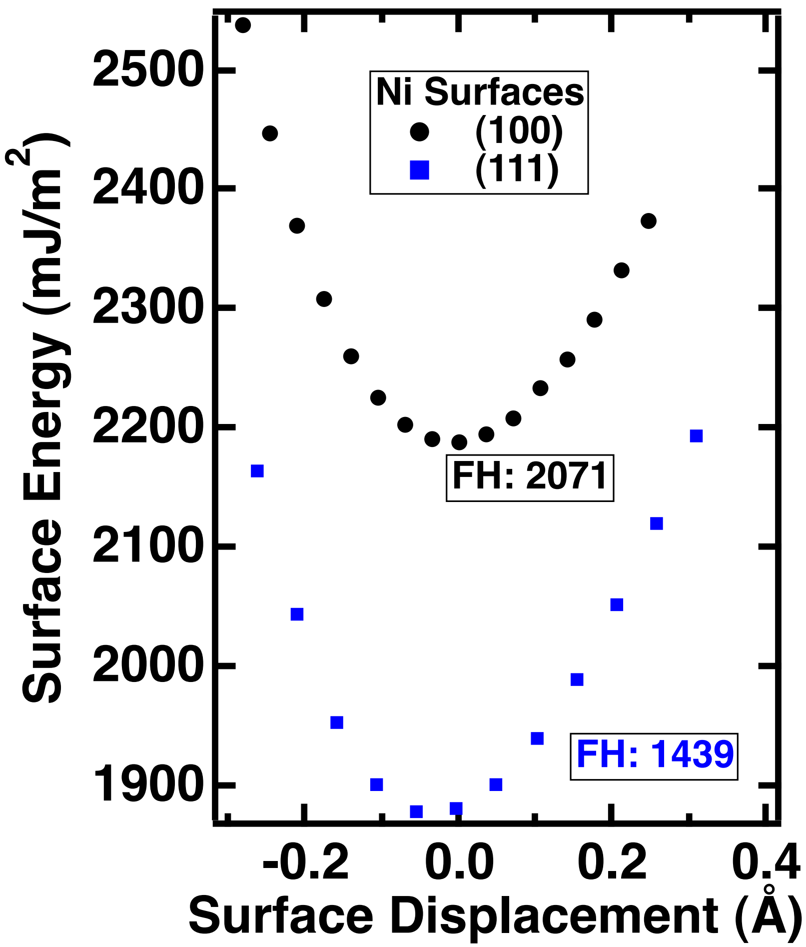
Fundamental planar defect within a material

Compare estimate from GGA calculation and FH model

Stack fault energies (mJ/m^2)

Intrinsic, relaxed GGA	Unstable EAM	FH
121	225-336	275

Surface Energy: Ni

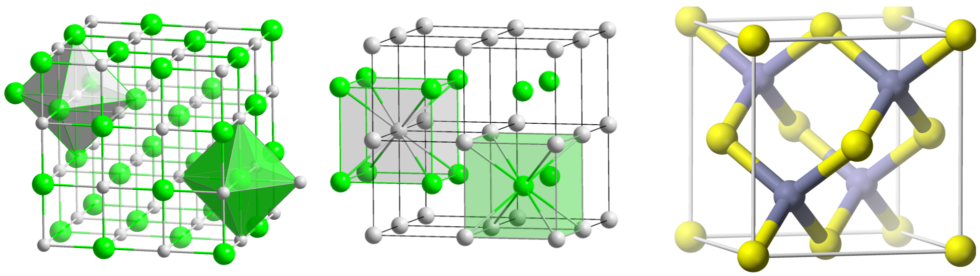


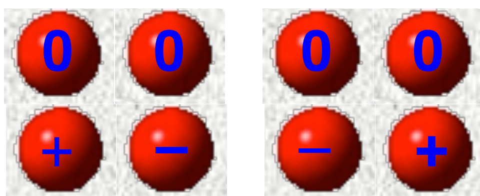
- Surfaces meet the environment
- Compare estimate from GGA calculation and FH model
- FH model gives a value that is too low compared to GGA and experiment
  "Typical"

CMIME Center for Materials at Irradiation and Mechanical Extremes

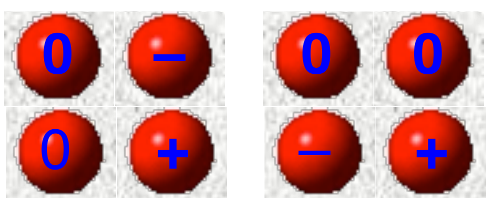
Lattice Distortions, Phase Changes

B1 B2 B3

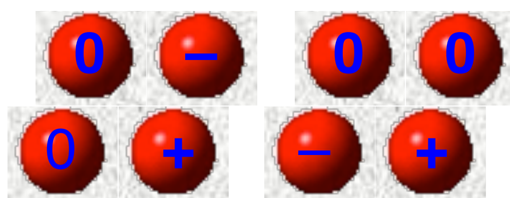




Pair-like



Three-body



shape-dependent

- Model is sensitive to different crystal structures in a way that is similar to MEAM, NMEX (Taylor), A-EAM

Sitting on cation:	L_-(1NN)	L_+(2NN)
Rocksalt	6	12
CsCl	8	6
Zincblende	4	12

$$W_A^{1e+} = -\langle A^0 \mid \hat{H}^A_{0+} \mid A^+ \rangle$$

$$\sim \frac{L_{A^+}}{\sqrt{L_{A^+}}} w_A^{1e} = \sqrt{L_{A^+}}\, w_A^{1e}$$

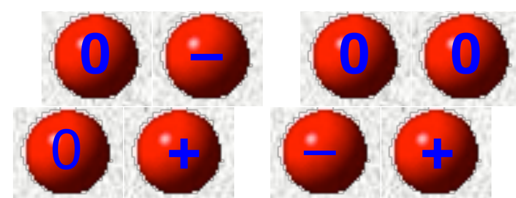
Higher-Order, Nonlinear Effects Evident in Fragment Hardness

$$W_{A}^{1e\pm} \approx \frac{\sum\limits_{B\in L_{A^{\pm}}} w_{AB}^{1e\pm}\sqrt{\tau_{B}}}{\sum\limits_{B\in L_{A^{\pm}}} \tau_{B}}$$

$$W_{A}^{2e} \approx \frac{\sum\limits_{B\in L_{A^{+}}}\sum\limits_{B'\in L_{A^{-}}} w_{BAB'}^{2e}\sqrt{\tau_{B}\tau_{B'}}}{\sum\limits_{B\in L_{A^{+}}}\tau_{B}\sum\limits_{B'\in L_{A^{-}}}\tau_{B'}}$$

$$\eta_{A}^{*} = \frac{\sum\limits_{B\in L_{A}}\left[\sum\limits_{B'\in L_{A}}\left(h_{BAB'}^{+} + h_{BAB'}^{-}\right)\sqrt{\tau_{B}\tau_{B'}} - 2h_{00}^{A}\tau_{B}\right]}{\sum\limits_{B\in L_{A}}\tau_{B}}$$

- Generalization to ligand-count argument introduces environmental effects into basics energy scales
- Shape and angular-dependencies most pronounced in hardness scale

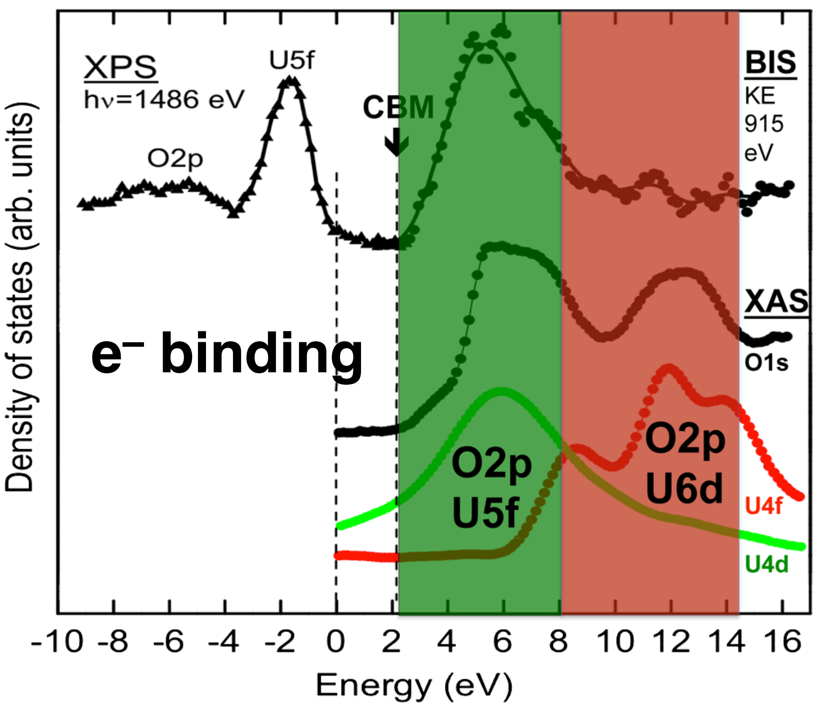


shape-dependence

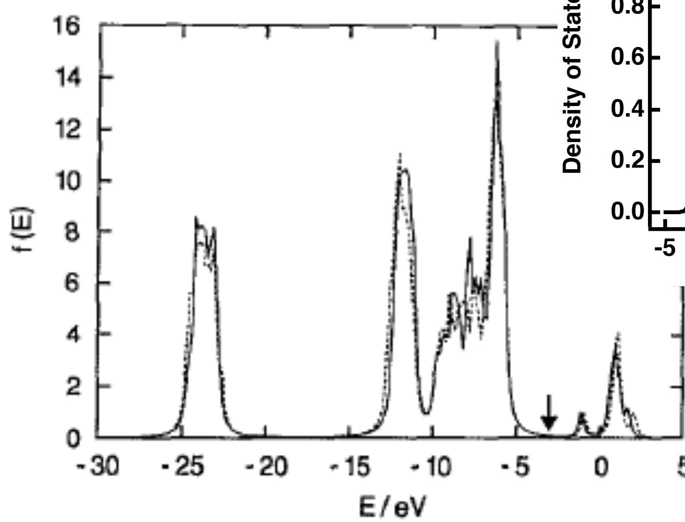
Electronic Spectra and Model Construction

$$F_{FH}(\bar{\rho}) = U_{eff} F_{FH}^{(gap)}(\bar{\rho}) - 2\left(W_{1e-} + W_{1e+}\right) F_{FH}^{(hop)}(\bar{\rho})$$

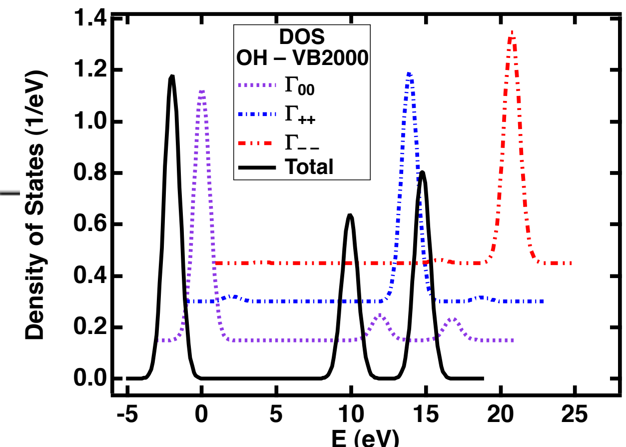
- Map peaks, occupation numbers onto FH model
- Effective hopping energies modified by coulomb interactions



XPS, BIS and XAS of UO_2
Tobin & Yu, PRL (2011)



Laasonen et al., 1993

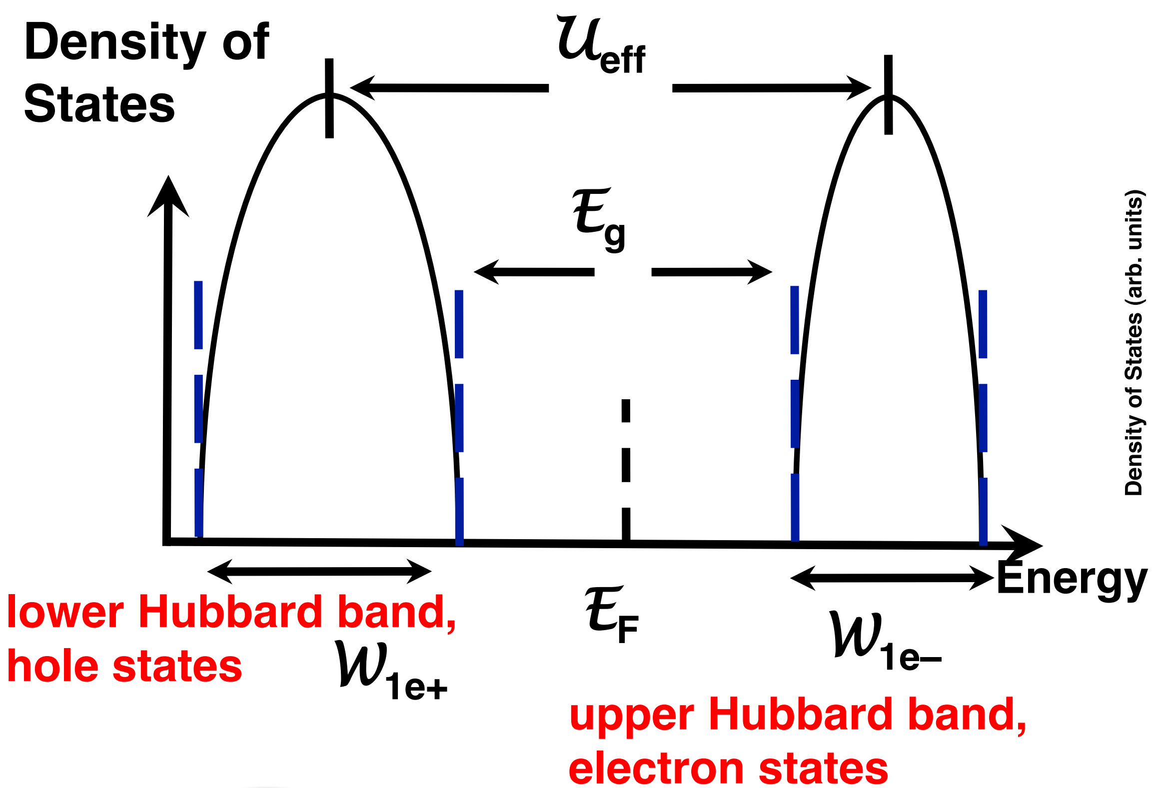


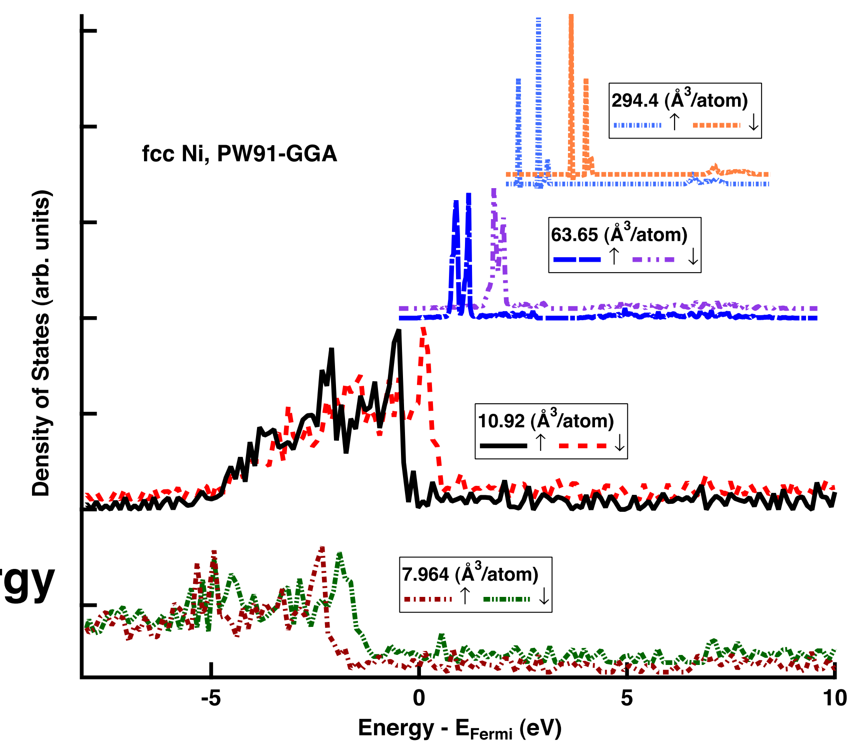
Water

FH Model and Electronic Spectra

$$F_{FH}(\bar{\rho}) = U_{eff} F_{FH}^{(gap)}(\bar{\rho})$$
$$-2\left(W_{1e-} + W_{1e+}\right) F_{FH}^{(hop)}(\bar{\rho})$$

- Need to squeeze and pull to get enough information for FH





Green Functions & Densities of State

$$\hat{L}(x)\hat{\mathrm{G}}(x,z)=\delta(x-z)$$

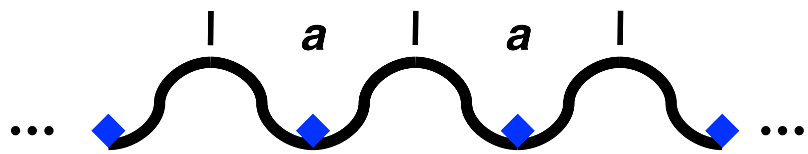
$$(z\mathrm{S}-\mathrm{H})\mathrm{G}(z)=\mathrm{I}$$

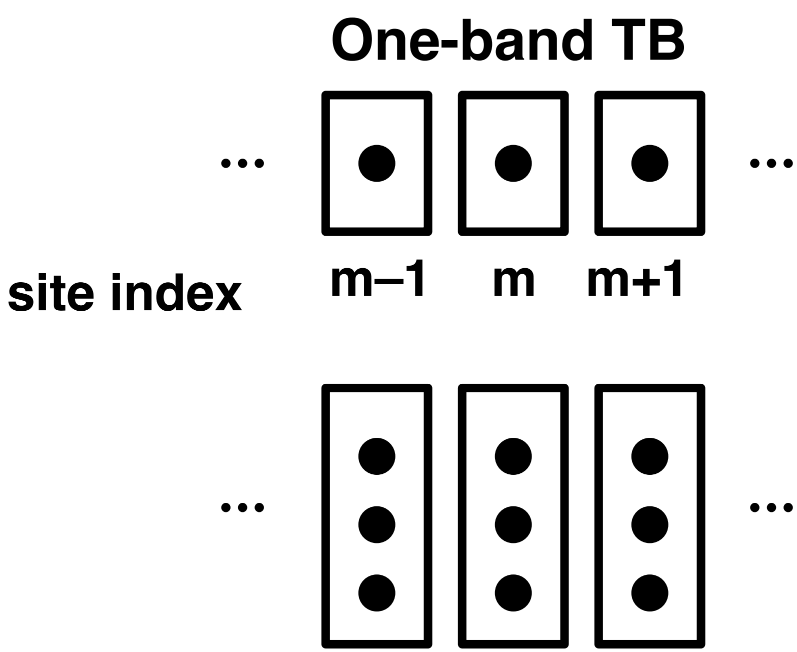
$$\Gamma(z)=-\frac{1}{\pi}\mathrm{Im}\,G(z^{+})$$

$$\rightarrow \mathrm{tr}\,\delta(zS-\mathrm{H}_{\Gamma}-\mathrm{H}_{*}-V_{\Gamma*})\Gamma$$

- **Green fcn: Inverse operator**
  - **S is the state-state overlap matrix**
  - **H is the hamiltonian matrix**
  - **G is the Green function**
  - ***z* is a complex number**
- **Green fcn perturbs system and introduces contributions from the spectrum of H**
- **Density of states (energy) Γ(*z*) is observable and computable**
  Also called Spectral Density Matrix

TB Mapping: 1D, ∞ Chain Model





3 states, 3 atoms per site → 3 bands

- **Periodic potential**

$$V(x-na)=\sum_n v(x-na)$$

- **Individual electrons move in potential**
- **Energy levels filled in successions**
- **Multiple bands (principle quantum number)**

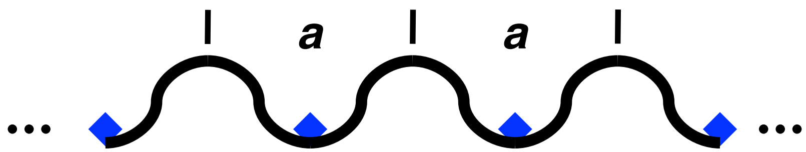
FH–to–TB Mapping

$$\Gamma_{A} = |A\rangle\langle A| \qquad \Gamma_{AB} = |B\rangle\langle A|$$

$$E = \sum_{A}\left[\sum_{\varsigma,\varsigma'} C_{A\varsigma'} C_{A\varsigma} H^{A}_{\varsigma'\varsigma} + \frac{1}{2}\sum_{B\neq A}\sum_{\varsigma,\varsigma'} C_{B\varsigma'} C_{A\varsigma} V^{AB}_{\varsigma'\varsigma}\right]$$

- AB density matrix is mixed
- Simplify H's
- Vs are interactions between fragments
- Cs are mixing coefficients

FH Model: 1D, ∞ Chain Model



$$0 = E - \epsilon_0 + 2V_{00}\cos ka$$

- One-band model

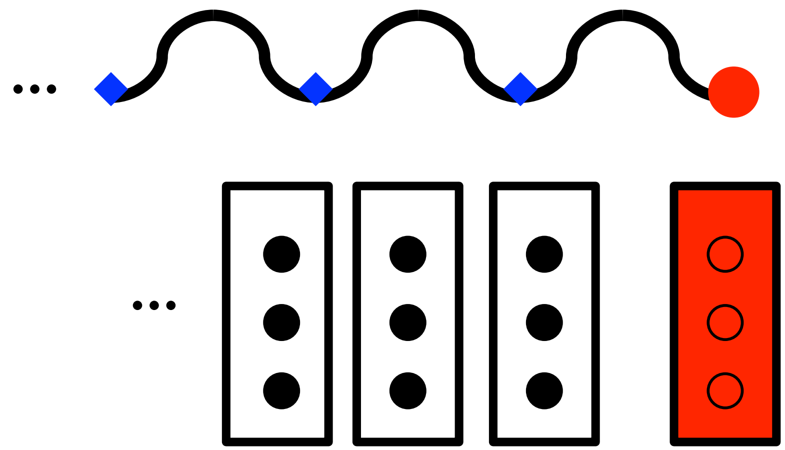
$$i\dot{C}_m^{\zeta} = \epsilon_{\zeta} C_m^{\zeta} - V_{\zeta} \bullet C_{m-1} - V_{\zeta} \bullet C_{m+1}$$

$$0 = \begin{pmatrix} E-\epsilon_+ & 0 & 0 \\ 0 & E-\epsilon_0 & 0 \\ 0 & 0 & E-\epsilon_- \end{pmatrix} + 2\begin{pmatrix} V_{++} & V_{+0} & V_{+-} \\ V_{0+} & V_{00} & V_{0-} \\ V_{-+} & V_{-0} & V_{--} \end{pmatrix}\cos k$$

- Three-state FH model maps onto three-band Tight-Binding Model
- Charge index maps to band index

w/ Dunlap and Allen

FH Model: 1D Semi-∞ Chain



- Defect: Truncate ∞-chain to get semi-∞ chain
- End atom is a "surface" atom

$$G_{\mathrm{TB}}^{1-band}(z) \approx \frac{z \pm \left(z^2 - 4W^2\right)^{1/2}}{2W^2}$$

$$G \approx G_{\mathrm{atom}} + G_{\mathrm{atom}} V G V G$$

but with matrices

Green fcn estimate: Isolated atom+chain "unperturbed", add to chain

Dyson Equation or Perturbation Expansion

$$G^{(n+1)} = G^{(n)} + G^{(n)} V^{(n+1)} G^{(n+1)}$$

Impurity atom + "Environment"

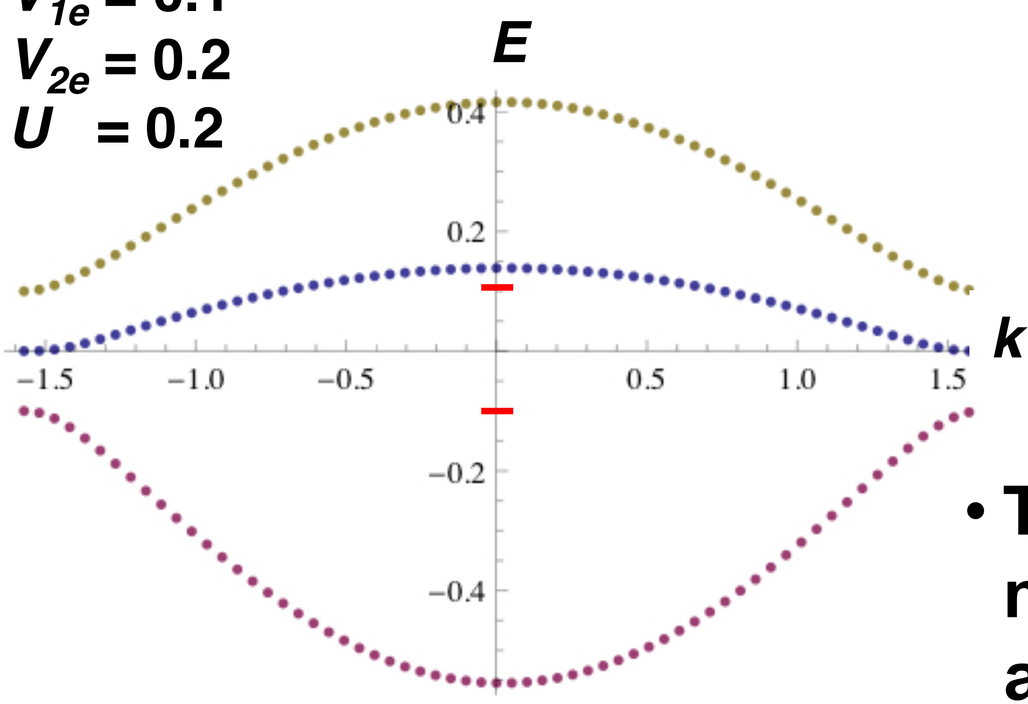
Anderson, Kondo, Huang & Carter

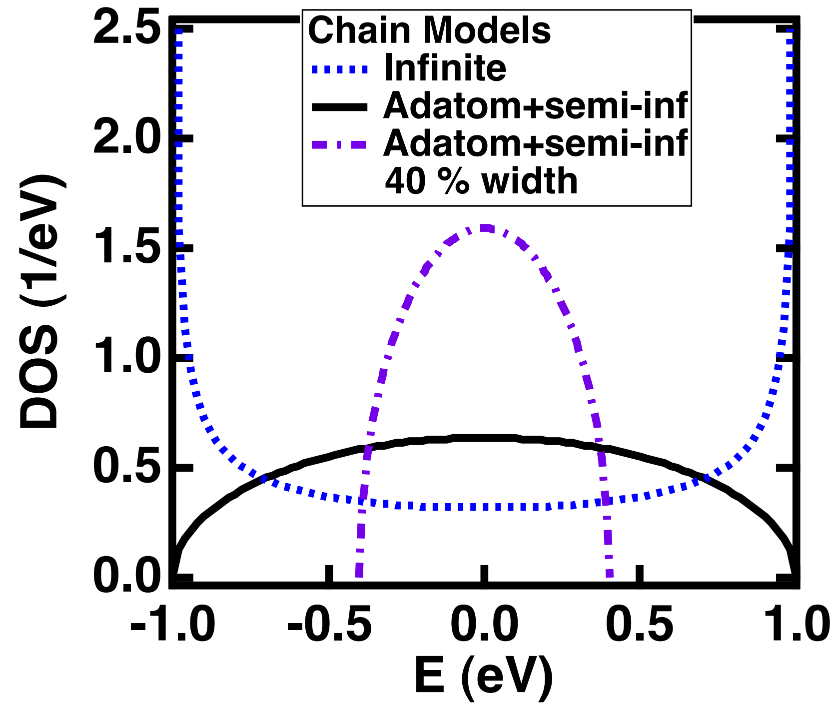
FH Chain Model Density of States

Band Structure

1D-∞ Chain FH Model

$V_{1e} = 0.1$
$V_{2e} = 0.2$
$U = 0.2$



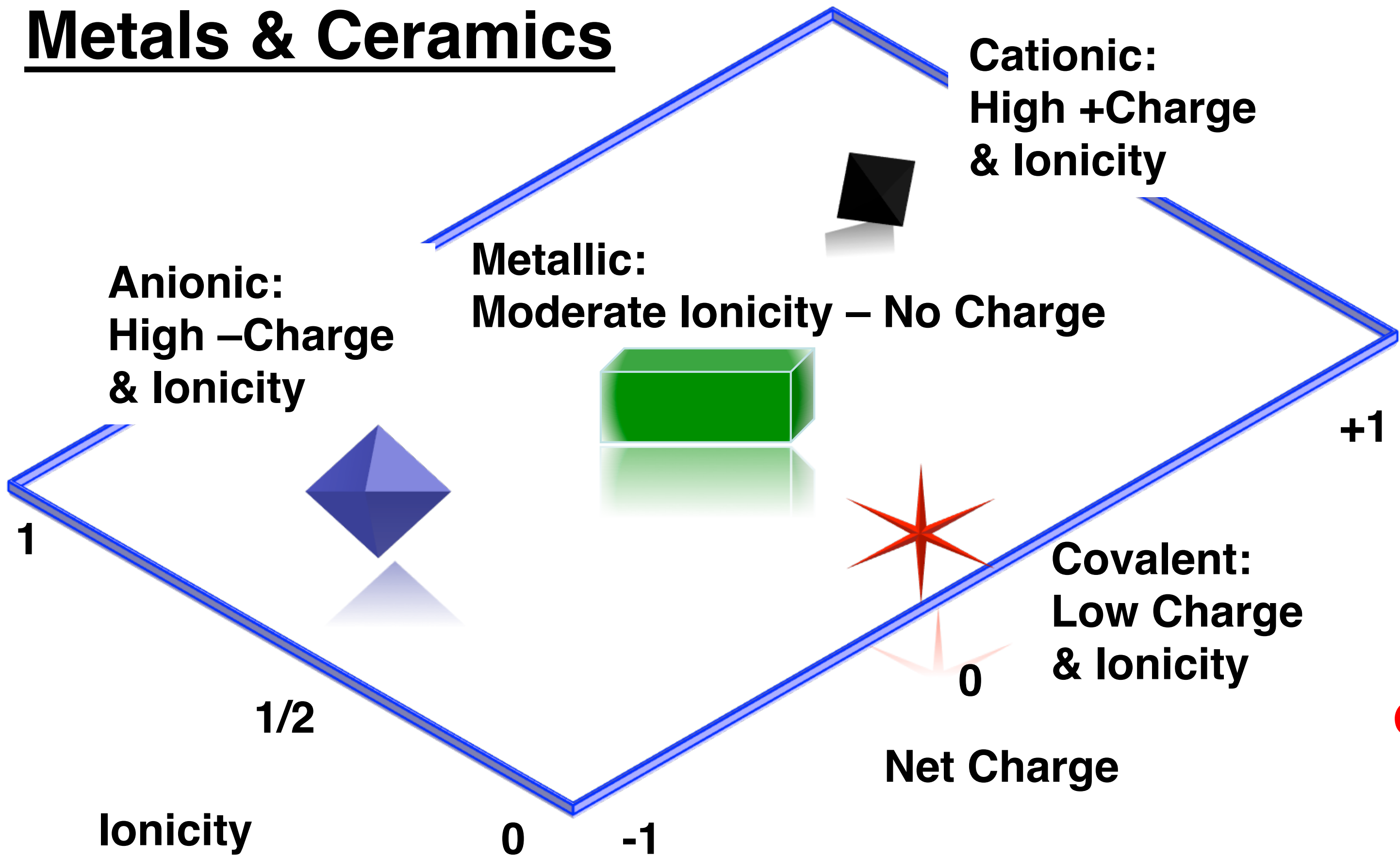


- Trying to answer question of metal-insulator transition in an *atomistic* model

cf Lieb & Wu, Gross

Unified Model of Bonding

Metals & Ceramics



Ionicity orthogonal to net charge

Summary

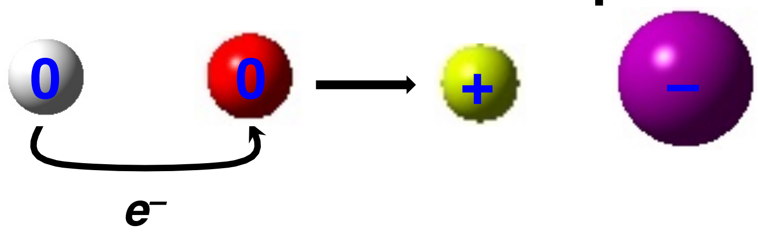
- **Fragment Hamiltonian based on rigorous 1st principles**
  - **Unifies models with oxides and metals**
  - **States of ATOMs need at least two variables, *q* and τ**
  - **Maps onto multi-band tight-binding, with charge-excitation gap, hopping, different variable dependencies cf Hubbard**
- **Defect properties computed by charge equilibration, perturbation techniques**
- **Fragmentation in QM introduces branches and nonlinearities, approach to multi-scale modeling**

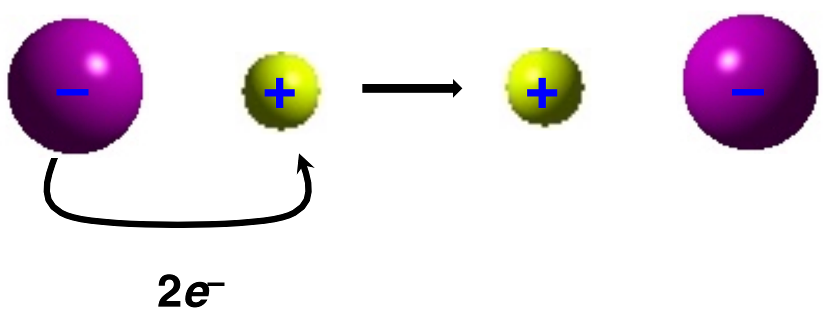
Mathematical Issues:

Pseudo-inverses & Transformations (q ↔ C ↔ c)
Branches and singularities
Solution Methodologies, model H and large-scale opt

Both 1e⁻ and 2e⁻ Hopping Contribute

One-electron hop:





Two-electron hop:

- Charge flow controlled by "hopping" contributions
  Both energies and functional dependencies important
  Two Flavors of hops
- Hopping will contribute to differential forms of fragment hardness
- Hopping still occurs in metals, but the net charge is zero
  – Delocalization

Comparison to Hubbard Model

$$h_i = \sum_{\mu,\nu} T_{ii}^{\mu\nu} c_{i\mu}^{+} c_{i\nu}$$

Isolated-Atom Limit

Three-state approximation

$$\begin{pmatrix} 0 & H_{0+} & H_{0-} \\ \dagger & \mathcal{I}^* & H_{+-} \\ \dagger & \dagger & -\mathcal{E}^* \end{pmatrix}_A \quad \begin{pmatrix} c_0c_0 & c_0c_+ & c_0c_- \\ \dagger & c_+c_+ & c_+c_- \\ \dagger & \dagger & c_-c_- \end{pmatrix}_A$$

Hubbard ('64, '65) | **FH Model**

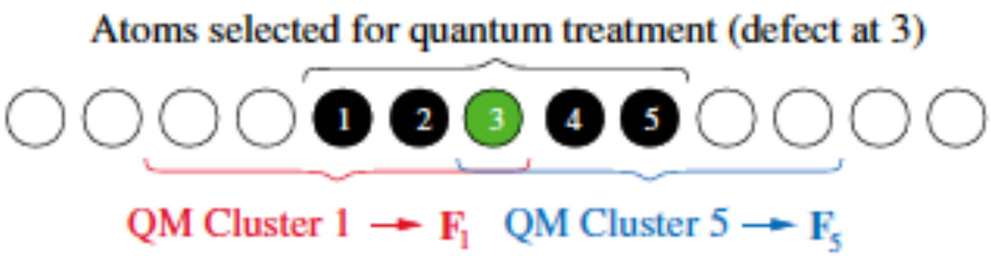
$\#\ e^-$	Energy	μ	μ	Energy	State
0	0			$\mathcal{I}^*$	+
		$\mathcal{T}_o$	$-\mathcal{I}^*$		
1	$\mathcal{T}_o$			0	0
		$\mathcal{T}_o+\mathcal{U}$	$-\mathcal{E}^*$		
2	$2\,\mathcal{T}_o+\mathcal{U}$			$-\mathcal{E}^*$	−

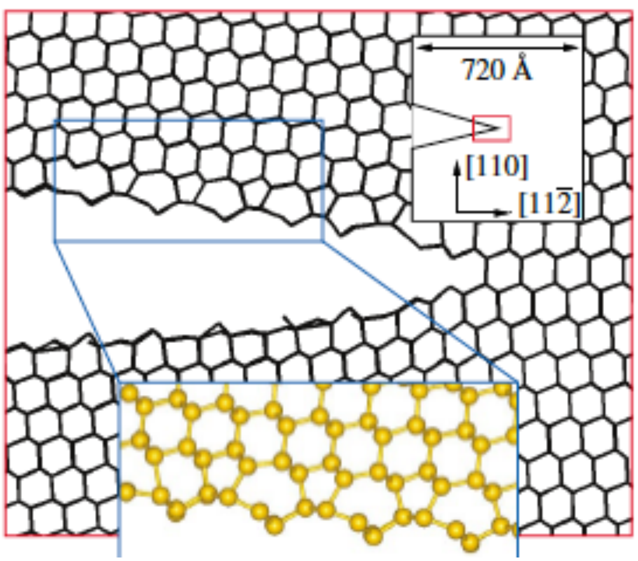
Hartree-Fock H | **Full H**

Start w/ isolated cations. Fill to neutrals. Fill to anions.

Refresher I: Csanyi Tutorial

Decomposition Strategies





Csanyi *et al.* PRL 2004

Functional Forms

Gaussian Approximation Potls

$$E = \sum_{i}^{\text{atoms}} \varepsilon(\{\mathbf{r}_{ij}\}),$$

Assumes adiabatic ground-state

Bartok *et al.* PRL 2010

Break system into different regions modeled differently
Couple classical and quantum mechanics
Time scale issues