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CMIME Update on Metal-Metal Oxide Atomistic Models

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Capability Gap: Multiple Material Types with One Model

Nano-scale oxides
strengthen steels

*Oka et al. Met
Trans (2007)*

HRTEM of Fe-oxide
interface in 12CrODS

Aguilar & Anderoglu

Phillpot et al.: Si/SiO₂
(PRB, 2007)

General model that
reduces to models for
metals and ceramics

Target Applications: Metal/Metal Oxide Composites

- Corrosion:
Fuel-cladding interactions
ODS Cladding
- Oxide layer growth and Properties

NiO scale on Ni:
Rhines & Wolf 1970
Mitchell & Hirth
2008

Metals

- Metallic bonding
- No charge transfer

EAM, MEAM, F-S,
COMB3, ...

Covalent

- Angular bonding
- No charge transfer

Tersoff, ReaxFF,
COMB, BETM, ...

Ceramics

- Ionic bonding
- Charge transfer controlled
heuristically, no physical basis

ReaxFF, COMB, QTPIE,
QEq, BETM, ...

Motivation: STEM-EELS: Fe-TiO₂

Iron influences titanium valence states near interface

Aguiar

Approach: Model valence states directly

Many e⁻ Hamiltonians in Fragments

$$\hat{H}_{\text{el}} \psi_i = \sum_A \left(\hat{H}_A(\mathbf{z}_A) + \frac{1}{2} \sum_{B \neq A} \hat{V}_{AB}(\mathbf{z}_A, \mathbf{z}_B) \right) \psi_i$$

- Objects defined by Hamiltonians
- “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**

$$|AB\rangle = C_0 |A^0 B^0\rangle + C_+ |A^+ B^-\rangle + C_- |A^- B^+\rangle$$

Pauling, 1929, Slater 1931, Mulliken, 1934

Fragment Hamiltonian (FH) Model as a Model Hamiltonian

Fragment:

$$E_A = \text{tr } H_A \Gamma_A (C_+, C_0, C_-)$$

H matrix

$$H_A = H_{00}^A + \left(\text{Diagram of three atoms with red arrows indicating interactions} \right)_{A_i}$$

States of atoms paramount

Density Matrix

$$\Gamma_A (C_+, C_0, C_-) = |A\rangle\langle A| = \begin{pmatrix} C_+ C_+ & C_0 C_+ & C_+ C_- \\ \dagger & C_0 C_0 & C_0 C_- \\ \dagger & \dagger & C_- C_- \end{pmatrix}_A$$

Fragment – Fragment:

$$V_{AB} = V_{00}^{AB} + \begin{pmatrix} V_{++} - V_{00} & V_{0+} & V_{+-} \\ \dagger & 0 & V_{0-} \\ \dagger & \dagger & V_{--} - V_{00} \end{pmatrix}_{AB}$$

Recovers energy scales:
Ionization, Attachment,
Gaps, Hopping

$$\mu_A = -(\mathcal{I}_A + \mathcal{E}_A)/2$$

$$U_A = (\mathcal{I}_A - \mathcal{E}_A)/2$$

Fragment
CP &
Gaps

$$\Gamma_{AB} (C_+, C_0, C_-) = (|B\rangle\langle A| + |A\rangle\langle B|)/2$$

Approach I: Empirical Atomistic Modeling

$$E = \sum_A \left(F_A + \frac{1}{2} \sum_{B \neq A} \phi_{AB}(R_{AB}) \right)$$

$F_A^{metal} = \text{fcn of val. } e^- \text{ density}$

$F_A^{ionic} = \text{polynomial in charge}$

$\phi_{AB}^{metal} = \text{Short - Range Pair}$

$\phi_{AB}^{ionic} = \text{Buckingham + Electrostatic}$

- Basic Paradigms the Same: Site Energies + Site-Site Interactions
- Site: Embedding/Fragment/Atom Completely different physical origins for metals and ceramics
- Site-Site: Pair potentials, 3-body terms
- Only ceramics models are “variational”

Derive from common point of view

Unified Embedding Energy: Background- ρ and charge q

$$F_{\text{FH}}(\bar{\rho}_+, \bar{\rho}_-) = F_{\text{FH}}^{(\text{gap})}(\bar{\rho}_+, \bar{\rho}_-) - F_{\text{FH}}^{(\text{hop})}(\bar{\rho}_+, \bar{\rho}_-)$$

Two background densities,
anion & cation

$$F_{\text{FH}}^{(\text{gap})} \rightarrow \text{Gaps, chem. potl., hops}$$

$$F_{\text{FH}}^{(1e-\text{hop})} \rightarrow \begin{array}{l} \text{neutral} \leftrightarrow \text{anion} \\ \text{neutral} \leftrightarrow \text{cation} \end{array}$$

smv, JCTC, JPCL 2011

- Embedding energies

$$q \equiv \frac{\bar{\rho}_+^2 - \bar{\rho}_-^2}{1 + \bar{\rho}_+^2 + \bar{\rho}_-^2}$$

- Mulliken Electronegativity:

$$\mu = -(I + \mathcal{E})/2$$

- Fragment Hardness, Local

“Hubbard U”:

$$U = I - \mathcal{E}$$

$$F_{\text{F-S}}(\tau) \sim (W_{1e}^+ + W_{1e}^-) \sqrt{\bar{\rho}}$$

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

Hardness/gap 2nd order in q

Embedding for Elements: Ni

$$F_{\text{FH}}(\bar{\rho}_+ = \bar{\rho}_-) = F_{\text{FH}}^{(\text{gap})}(\bar{\rho}_+ = \bar{\rho}_-) - F_{\text{FH}}^{(\text{hop})}(\bar{\rho}_+ = \bar{\rho}_-)$$

Gap + 2e⁻

1e⁻

- Get 3d structures
- Have difficulty with 2d and 1d

FH Ni: Metallic Character

- Keep some notion of concept from solid state physics
- Qualitative match
- Still need other properties to conclude material is “metallic”

Ni Elastic Constants, Defects, Surfaces

- Same theme:
Get 3d structures
Have difficulty with 2d and 1d
- C_{11} , C_{44} good; C_{12} off as expected
- Vacancy formation energy good

Josh

Lattice Distortions, Phase Changes, Defects

- FH model sensitive to different crystal structures (neighbors, deformations), similar to MEAM, NMEX (Taylor), A-EAM, COMBS

Need dimensional dependence, shape changes

$$U_A^* (h_{BAB'}^+, h_{BAB'}^-, \tau_B, \tau_{B'})$$

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

First Principles Route to Ionicity

- Decompose density from e.g. DFT
- Fit to form from FH theory
- Good agreement with Bader analysis for charge q

$$\rho_A = \rho_{A^0} + C_{A^+}^2 (\rho_{A^+} - \rho_{A^0}) + C_{A^-}^2 (\rho_{A^-} - \rho_{A^0})$$

$x \rightarrow$

$$q_A = C_{A^+}^2 - C_{A^-}^2$$

$$\tau_A = C_{A^+}^2 + C_{A^-}^2$$

Pilania

Gaps and Metallicity Appear in FH: Be Densities of States

1d Chain

2-D Square

- Gaps open and close in e-structure calculations
- Mirror these essential features in FH model

Pilania

Approach II (with UNM): Model H

$$\bar{E} \approx \sum_A \sum_{\zeta} \left(\varepsilon_{A\zeta A\zeta} C_{A\zeta}^\dagger C_{A\zeta} + \frac{1}{2} \sum_{B \neq K} \sum_{\zeta, \zeta'} V_{A\zeta B\zeta'} C_{A\zeta}^\dagger C_{B\zeta'} \right)$$

$$EC_{A\zeta} = \varepsilon_{A\zeta A\zeta} C_{A\zeta} + \frac{1}{2} \sum_{B \neq K} \sum_{\zeta, \zeta'} V_{A\zeta B\zeta'} C_{B\zeta'}$$

• Structure of tight-binding H, but FH means something different

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

$$\rightarrow \text{tr} \delta(zS - H_\Gamma - H_* - V_{\Gamma*}) \Gamma$$

- Green fcn introduces contributions from the spectrum of H
- Density of states (energy) $\Gamma(z)$ observable and computable
- “Spectral Density Matrix”

- Related to vast knowledge, data of electron spectroscopy, electronic structure calculations
- Not used in typical atomic-scale models

Model Hamiltonian Form: 1D, ∞ Chain

TB

1-band: $E(k) = E_0 + 2V \cos ka$

FH analog

3-bands: 3 states per site

$$0 = \left| E(k) - \left(\tilde{E}_0 + 2\tilde{V} \cos ka \right) \right|$$

- Periodic potential

$$V(x) = \sum_m v(x - ma)$$

- Individual electrons move in potential
- Fill e^- levels successively (fermionic)
- Multiple bands:
Integer charges replace principle quantum number as band index
- States of **fragments**

FH Model for 1D, Periodic, ∞ Chain: Gap Closure

For 1D chain

- Multiband TB: metal or insulator depending on filling
- Hubbard model: No gap closure unless $U \rightarrow 0$
cf Lieb & Wu, 1968
- **Atomistic FH model:** Gaps open, close with “local U ” and hopping

$$\begin{aligned} I &= 2 & V_{00} &= -0.5 \\ \mathcal{E} &= 1 & V_{+-} &= -0.0 \end{aligned}$$

FH DOS

Near Future: Link FH Model & Electron Spectroscopy

$$|AB\rangle = C_0 |A^0 B^0\rangle \\ + C_+ |A^+ B^-\rangle \\ + C_- |A^- B^+\rangle$$

Wave fcn

FH & PES (from Hüfner, 1994)

$$|\text{Ni}^{+2}\text{O}^{-2}\rangle, |\text{Ni}^{+1}\text{O}^{-1}\rangle, |\text{Ni}^0\text{O}^0\rangle \\ |d^8 L\rangle, |d^9 L^{-1}\rangle, |d^{10} L^{-2}\rangle$$

NiO mimicked by NiO_6^{10-} :

H matrix

$$H_{\text{Ni}} + H_{\text{O}} = \begin{pmatrix} 0 & T\sqrt{2} & 0 \\ T\sqrt{2} & \Delta & T\sqrt{2} \\ 0 & T\sqrt{2} & 2\Delta + U_{dd} \end{pmatrix}_{dL}$$

$$T \sim 2 \text{ eV}, \Delta \sim 5 \text{ eV}, \\ U_{dd} \sim 8 \text{ eV}$$

Matters for structural problems

**Mitchell & Hirth, 2008
Model of scale growth**

Other Applications: Charge Separation

Time Evolution in Composite Materials Electromechanics Grand Challenge

Plasma-Material Interactions

Umstadter,
Doerner, Tynan
2009

Topological
Properties

jqi.umd.edu

Solar Cells from Composite Materials

Charge separation at interfaces

Achermann
et al. 2004

Summary: FH Model Potentials

- FH Model for atomic scale
 - States of ATOMs, rather than states of e^- s
 - Unify models for oxides and metals
 - Ni model developed, applied to surfaces, stacking fault E, paper about to be submitted
- Introduce local Hubbard energy or chemical hardness
 - Some connection to 3-band tight-binding model
 - Gaps and gap closure in an atomistic model
- Apply FH model to NiO based on Ni, O

References

- [1] RP Iczkowski and JL Margrave, J Am Chem Soc **83**, 3547 (1961).
- [2] HO Pritchard and FH Sumner, Proc Roy Soc, London A **235**, 136 (1956).
- [3] JP Perdew, RG Parr, M Levy, JL Balduz, Jr, Phys Rev Lett **49**, 1691 (1982).
- [4] SM Valone and SR Atlas, J Chem Phys **120**, 7262 (2004).
- [5] SM Valone, J Li, and S Jindal, IJQC **108**, 1452 (2008).
- [6] RP Feynman, Statistical Mechanics: A Set of Lectures, (Addison-Wesley, Reading MA, 1998), Ch. 2
- [7] SM Valone, J Chem Theory Comput **7**, 2253 (2011)
- [8] SM Valone, J Phys Chem Lett **2**, 2618 (2011)

Talk outline – method development talks

1. 25-30 minute talks (leave 10-15 minutes for discussion).
2. State the **gap** in capability that your project is trying to fill.
3. State the **application** of the method you are developing to CMIME research (present and future).
4. Describe your **approach**, highlighting the qualifications of the team working with you.
5. Highlight the “*what’s new*” aspect in your approach as well as capabilities of your method.
6. Give examples of applications of your method to CMIME.
7. Show a list of publications (published or accepted) directly related to this project (Do not show your other CMIME publications that are NOT directly related to this project).
8. Indicate future plans for this method development project. **(i) complete and publish work in the current grant period (through July 2014), and (ii) a vision for next 5 years (if there is a call for renewal proposal, what will you propose?).**
9. Indicate other applications of your method, e.g., any spin-off projects not funded by CMIME where the method may be used (be specific).

FH Gives Unified Model of Bonding

Metals & Ceramics

Model Hamiltonian Approach

Full, Many-electron $\hat{H}$

$$\hat{H}_{\text{el}} = \sum_{\mathbf{e}^- \mathbf{s}} \left(T_i + \sum_{\text{atoms } A} V_{iA} + \frac{1}{2} \sum_{j \neq i} V_{ij} \right) + \hat{V}_{\text{NN}}$$

$$\begin{aligned} \hat{H}_{\text{el}} &\rightarrow \hat{h}_{\text{TB}} + U \hat{D}_H \\ &= - \sum_{R_A \neq R_B, \sigma} t(R_A - R_B) \hat{c}_{R_A, \sigma}^\dagger \hat{c}_{R_B, \sigma} \end{aligned}$$

$$+ U \sum_A \hat{n}_{A\downarrow} \hat{n}_{A\uparrow}$$

Gebhard

Tight-bonding, Hubbard, DFT H's
One-electron granularity

Fragment $\hat{H}$

Atomic granularity

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

$$E = \sum_A \left(F + \frac{1}{2} \sum_{B \neq A} \phi_{AB} \right)$$

Missing Element: Charge Fluctuations on Operators

- Distribute electrons among fragments: Charge fluctuations
- Vary integer number of electrons assigned to fragments
→ Open system
- Superpose states with different numbers of e^- on sites

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

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

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

: ionic states

Note: mean-field/molecular orbital state is an average of ψ_{00} , ψ_{+-} and ψ_{-+}

Metals: Embedded Atom Models

$$E = \sum_A \left(F_{EAM}(\bar{\rho}_A) + \frac{1}{2} \sum_{B \neq A} \phi_{AB}(R_{AB}) \right) \quad \bullet \text{ EAM energy}$$

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

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

- Embedding Function

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

- Pair Potential

FH Density Matrix for Diatomic: Chemical Potential and Charge Equilibration

Chemical Potential (dE/dq): Varies greatly among models. PPLB is correct limit for dissociated (gas-phase) atoms. IM is linear.

Attenuate charge flows: Crossing of black line with colored curves

BeO Chain

BeO 2-D Square Lattice

FCC Ni