Computational design of materials for photo- and electro-catalytic water splitting

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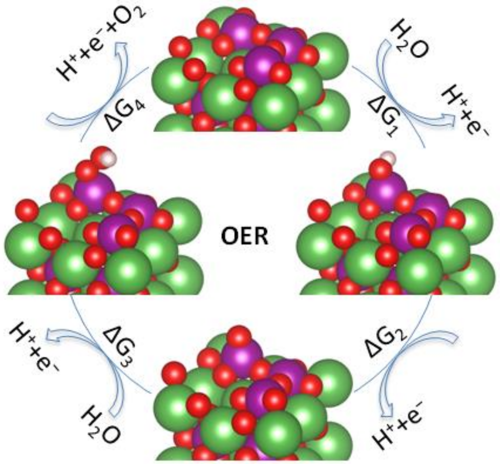
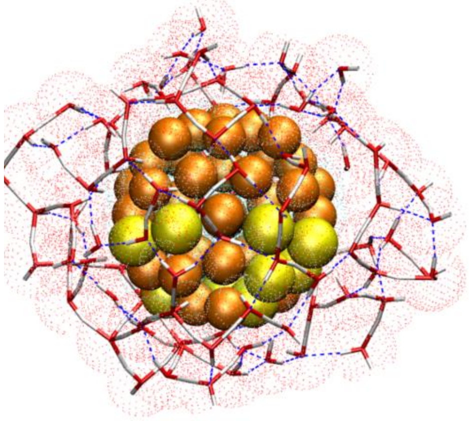
ICYS 9/18/17

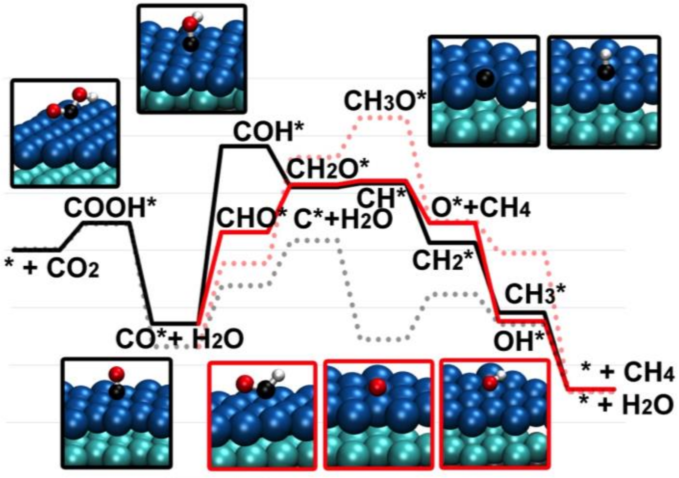
Research Areas

Electro- and Photo-catalysis

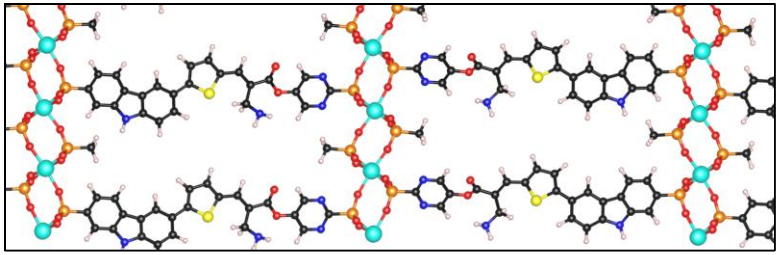


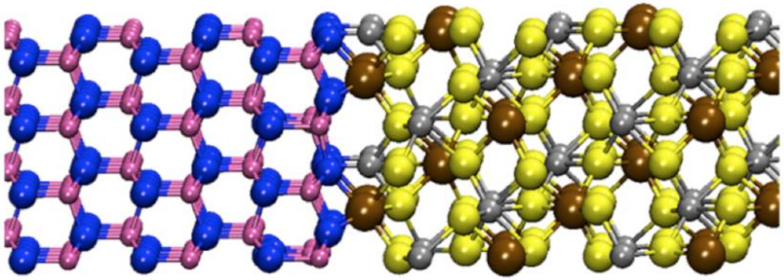


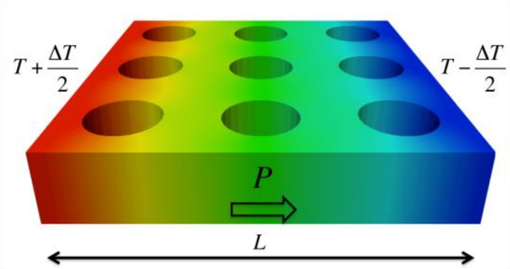
CO_2 Capture & Conversion



Photovoltaics







Thermoelectrics

Method Development

Outline

- Introduction & Motivation
- Computational Methods
- Catalyst/Water Interfaces
    - Electrochemical OER on Perovskite Oxides
    - Overall photocatalytic H_2O splitting on CoO
    - Au/Cu Nanoparticles in H_2O

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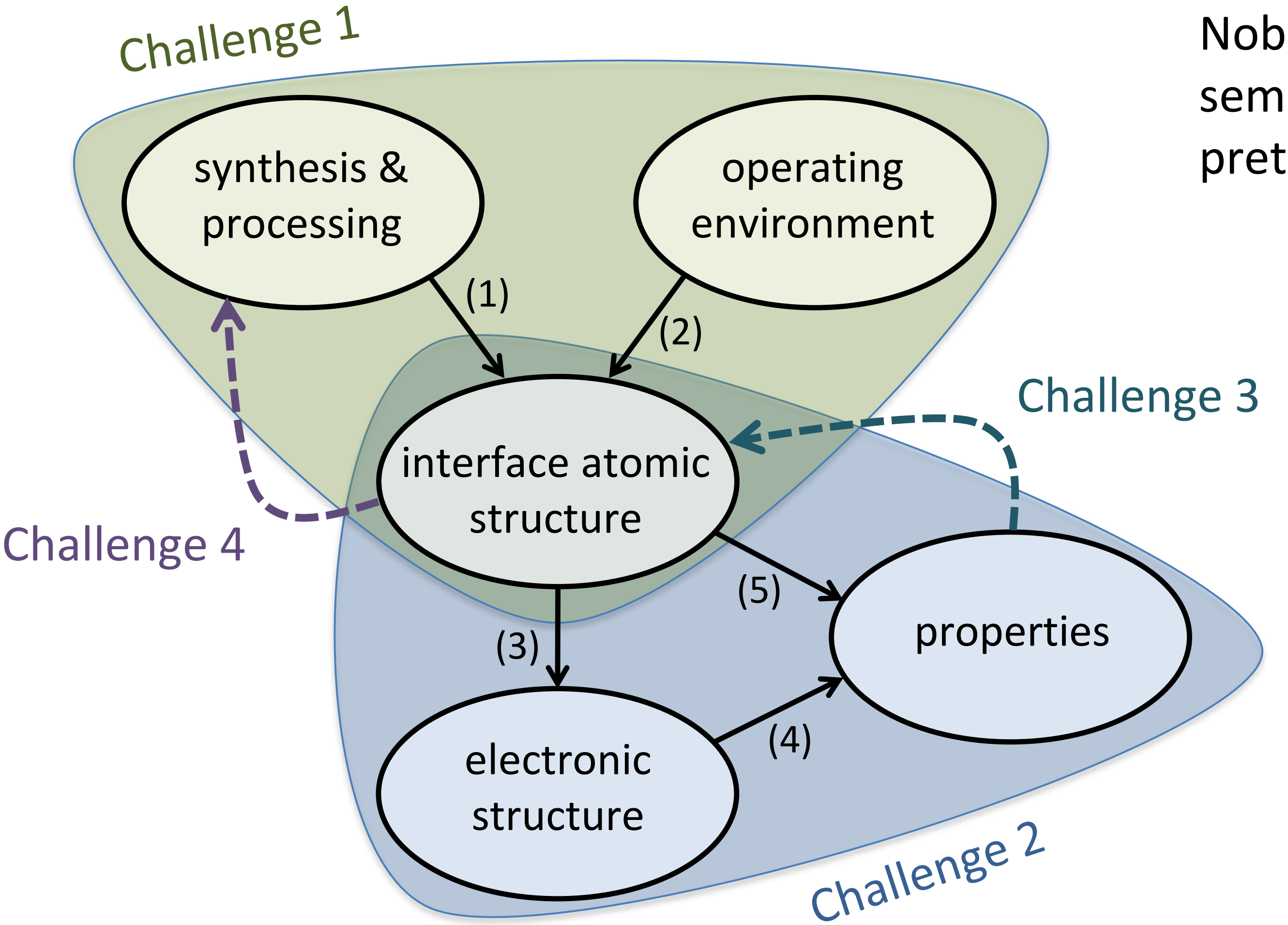
Fundamental challenges for design of energy storage & conversion materials systems

- Design of new *materials* with optimized properties
  - light absorption
  - electronic/ionic carrier mobility
  - thermal transport
  - catalytic activity
  - stability (lifetime)
- Design of new *heterostructures* to control or optimize transport across interfaces (device level)
  - Electrocatalysts (batteries, fuel cells, electrolyzers)
  - Photocatalysts
  - Photovoltaics
  - Thermoelectrics
- Design of new *processes* for control/reproducibility

“The Interface is the Device”

-- Herbert Cromer
Nobel laureate,
semiconductor physicist,
pretty smart guy



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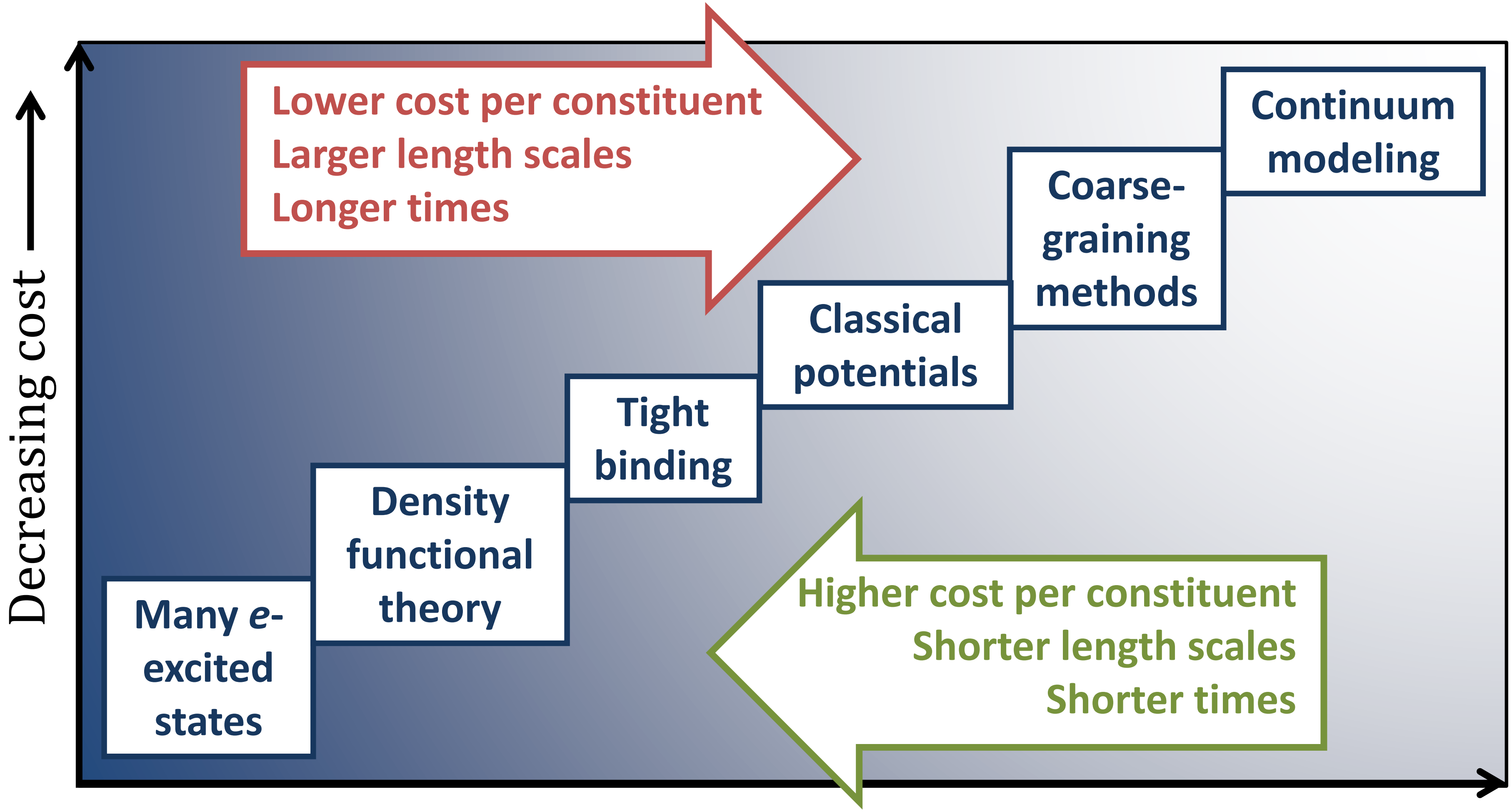
Computational Methods



Lower cost per constituent
Larger length scales
Longer times

Many *e*-excited states

Density functional theory

Tight binding

Classical potentials

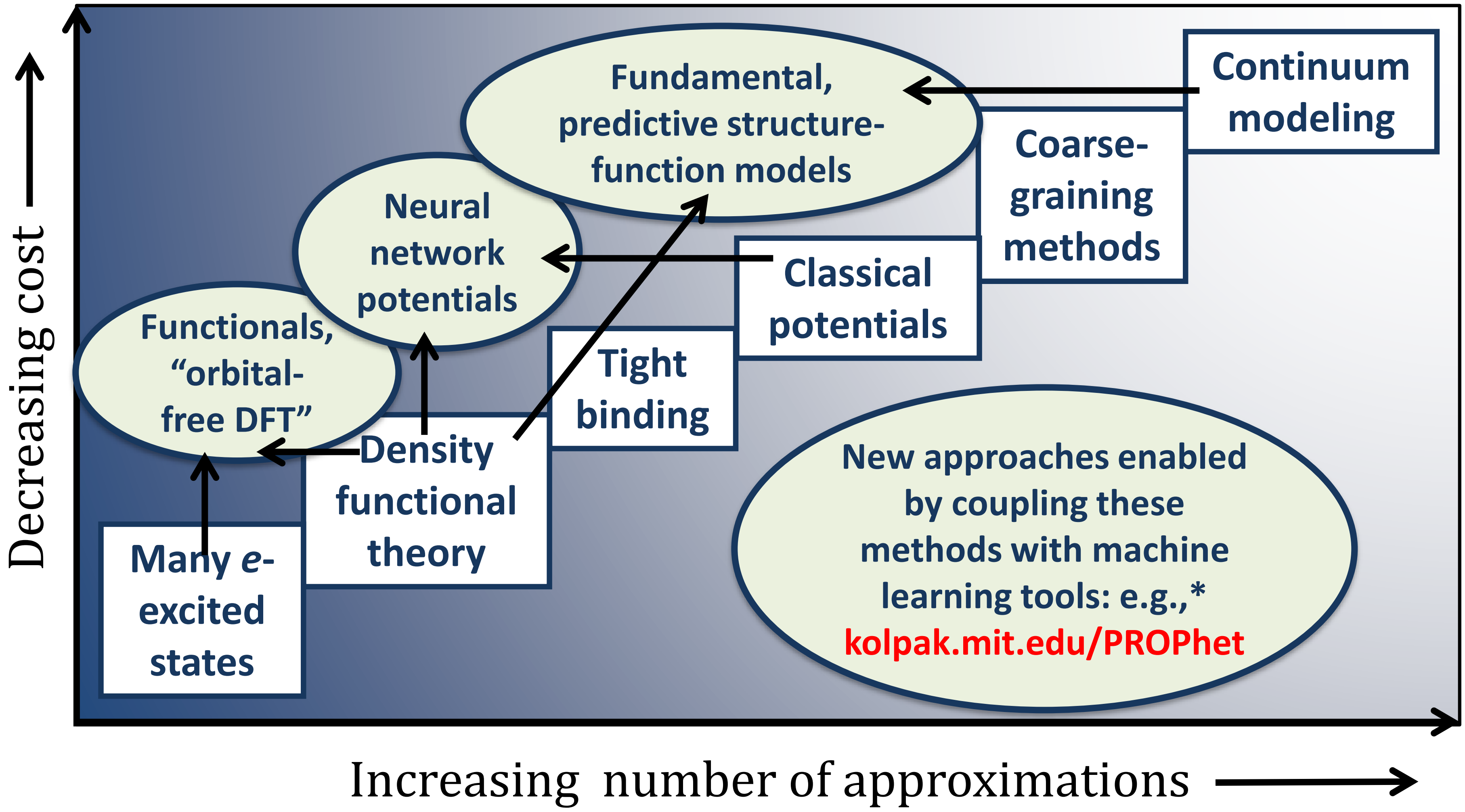
Coarse-graining methods

Continuum modeling

Higher cost per constituent
Shorter length scales
Shorter times

Increasing number of approximations

Computational Methods



*Kolb, Lentz, Kolpak, Sci. Rep. 7, 1192 (2017)

Density functional theory (DFT)

$$HY = EY$$

$$Y(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N)$$

wavefunction: 3N variables

Walter Kohn

Won the Nobel prize in 1964 for the formulation of DFT

$$r(\mathbf{r}) = \mathop{\text{å}}\limits_{i}^{N} \left|y_{n\mathbf{k}}(\mathbf{r})\right|^2$$

electron density: 3 variables

Basic idea: In the ground state, all aspects of the electronic structure of a system of interacting electrons in an “external” potential (due to the nuclei) are determined by $\rho(\mathbf{r})$.

The energy functional

$$E[\rho] = T_s[\rho] + V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \frac{e^2}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|r - r'|}d\mathbf{r}d\mathbf{r}' + E_{XC}[\rho]$$

Kinetic energy of a homogeneous, non-interacting electron gas

Energy due to the external potential

Hartree energy

Exchange-correlation energy (*i.e.*, everything we don’t know)

- Interacting part of the electronic kinetic energy
- Exchange energy (Pauli exclusion)
- Correlation energy (Coulomb repulsion; overall symmetry/spin)
- Self-interaction correction

The Kohn-Sham equations

We can write the electron density in terms of a set of one-electron orbitals (Kohn-Sham orbitals):

$$\rho\left(\mathbf{r}\right)=\sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$$

Then solve a set of equations (the Kohn-Sham equations) for a non-interacting electron in an effective potential, V^{eff}:

$$\left(-\tfrac{1}{2}\nabla^2+V^{\text{eff}}\left(\mathbf{r}\right)\right)\psi_i\left(\mathbf{r}\right)=\varepsilon_i\psi_i\left(\mathbf{r}\right)$$

Take the functional derivative of the energy with respect to $\psi_i^*(\mathbf{r})$ to obtain the Kohn-Sham orbitals that minimize the total energy.

The exchange-correlation energy

In principle, **DFT is an exact formulation with no approximations**.

One can find exact solutions to the Schrodinger equation as long as one knows the form of the potential:

$$V^{\mathrm{eff}}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \frac{e^2}{2}\int \frac{\rho(\mathbf{r})\,d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} + V_{XC}\left[\rho(\mathbf{r})\right]$$

Just one minor problem: V_{xc} is not known!

Approximations are necessary

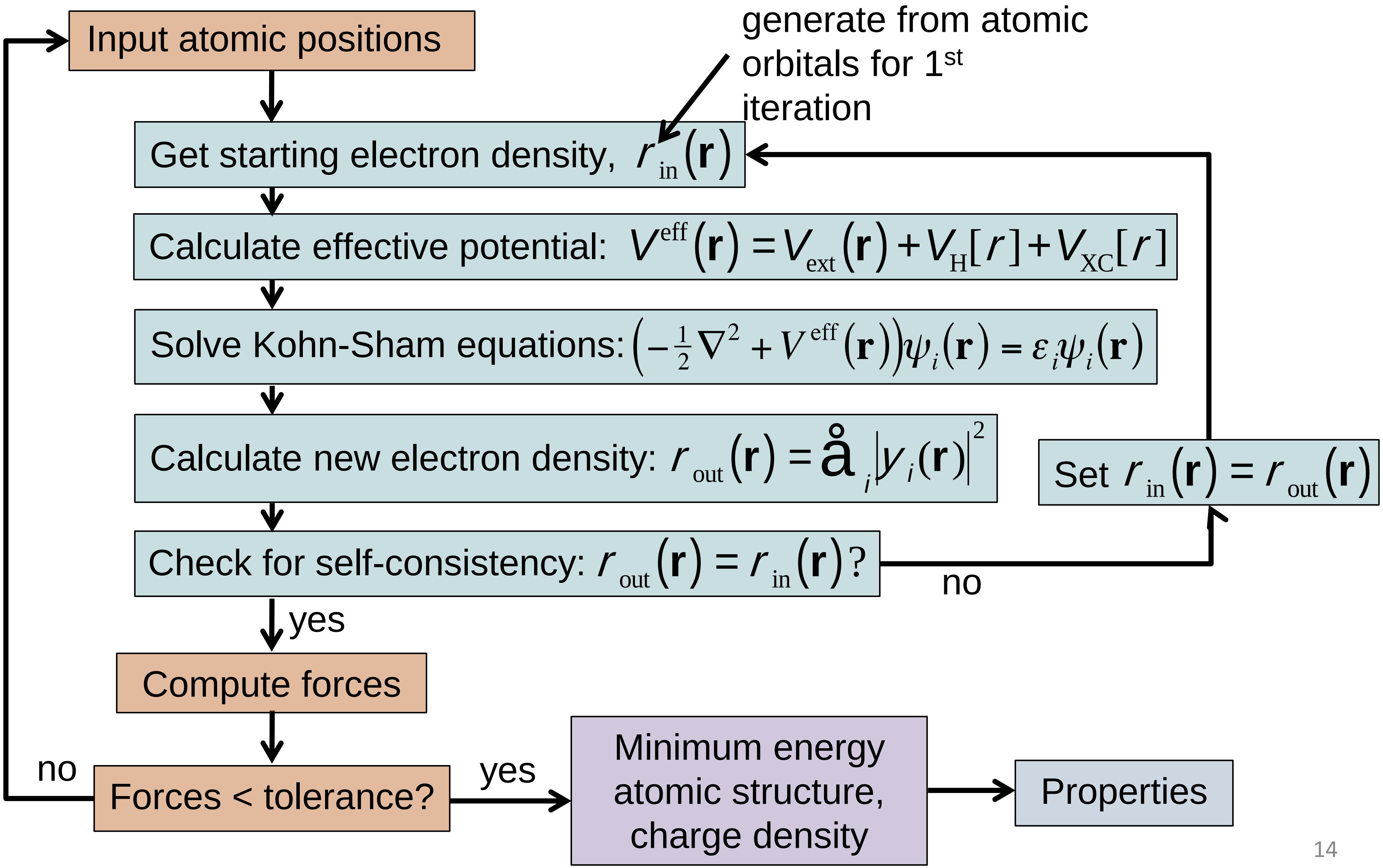
LDA

GGA

“meta”-GGAs

hybrids

Solving the Kohn-Sham equations



Input atomic positions

generate from atomic orbitals for 1st iteration

Get starting electron density, $\rho_{\text{in}}(\mathbf{r})$

Calculate effective potential: $V^{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}[\rho] + V_{\text{XC}}[\rho]$

Solve Kohn-Sham equations: $\left(-\tfrac{1}{2}\nabla^2 + V^{\text{eff}}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$

Calculate new electron density: $\rho_{\text{out}}(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$

Set $\rho_{\text{in}}(\mathbf{r}) = \rho_{\text{out}}(\mathbf{r})$

Check for self-consistency: $\rho_{\text{out}}(\mathbf{r}) = \rho_{\text{in}}(\mathbf{r})?$

no

yes

Compute forces

no

Forces < tolerance?

yes

Minimum energy atomic structure, charge density

Properties

Key challenges & possible solutions

Exchange-correlation functional → cannot get important properties such as band gap correctly

Better V_{XC} approximations

Improved computational resources

Size and number of systems → limited to small, often idealized systems

Improved computational resources

New methods to link DFT to MD → e.g., Neural Network Potentials!

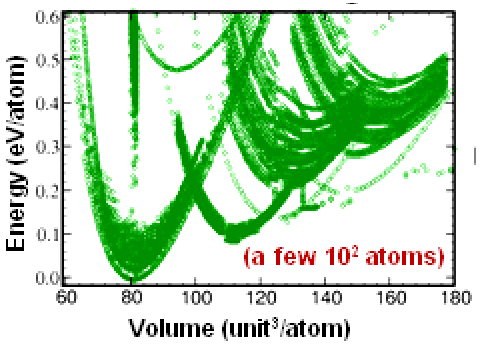
Smarter approaches for choosing structures/systems

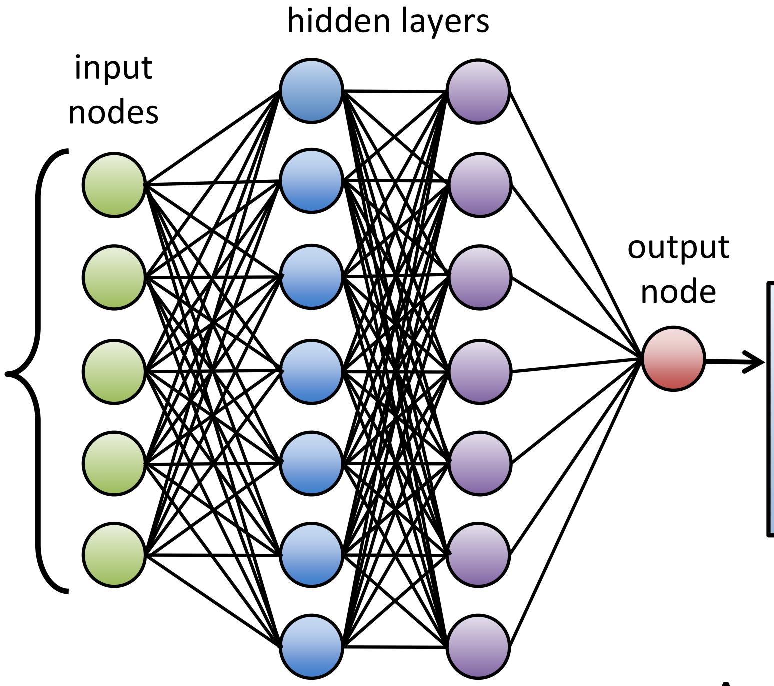
Development of new, general predictive models

Interpolating flexible & accurate analytical potentials from DFT data

signals (input)

Reference data (e.g., DFT)





response (output)

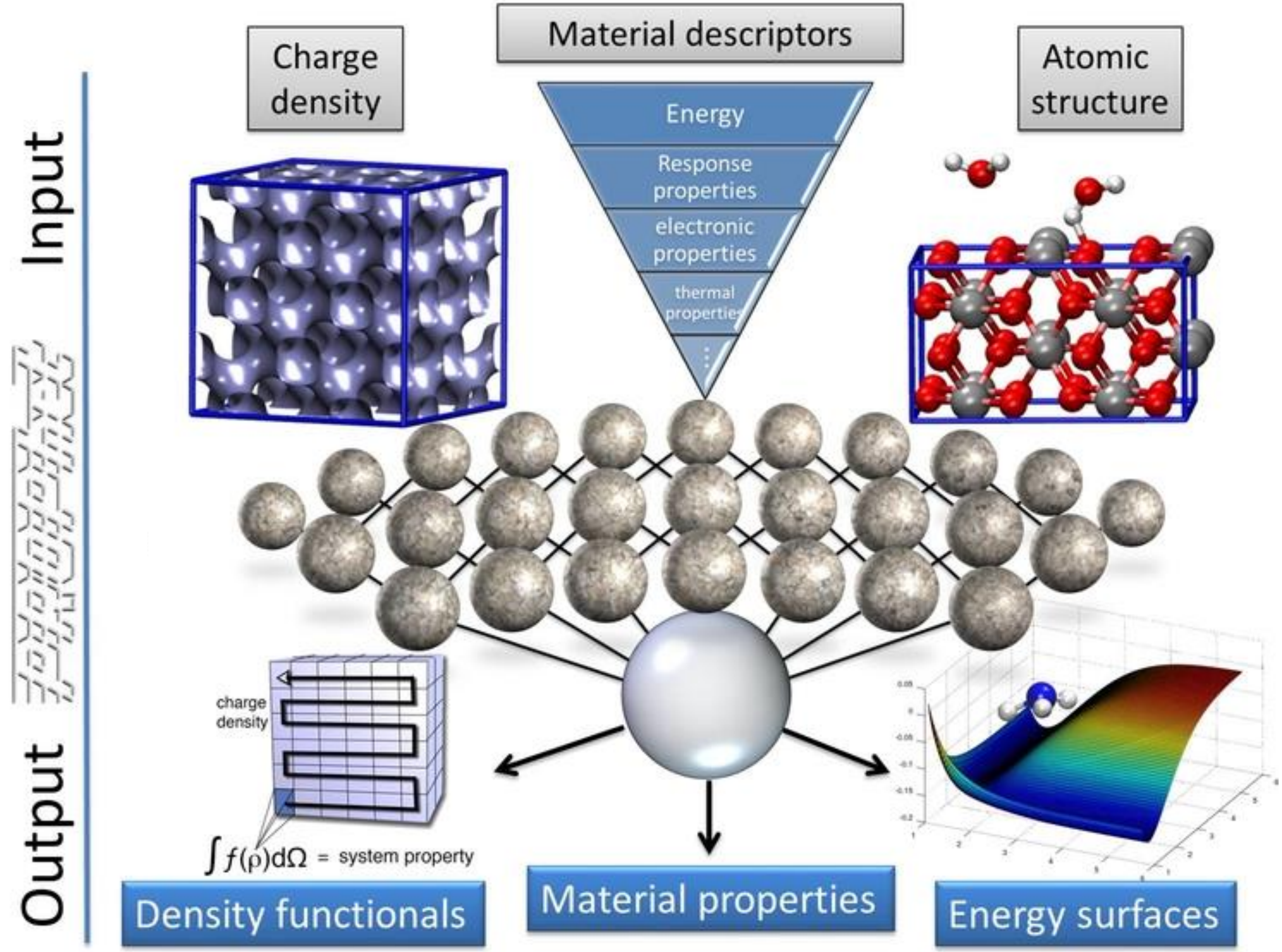
Highly flexible & accurate classical atomic potentials

Quantum mechanical description of atom structure and energy in a wide range of environments.

activation function (no imposed functional form)

Analytical potentials enable modeling of large, complex systems with DFT accuracy!

PROPerty Prophet (PROPhet)



Kolb, Lentz, Kolpak, Sci. Rep. 7, 1192 (2017)

www.kolpak.mit.edu/PROPhet

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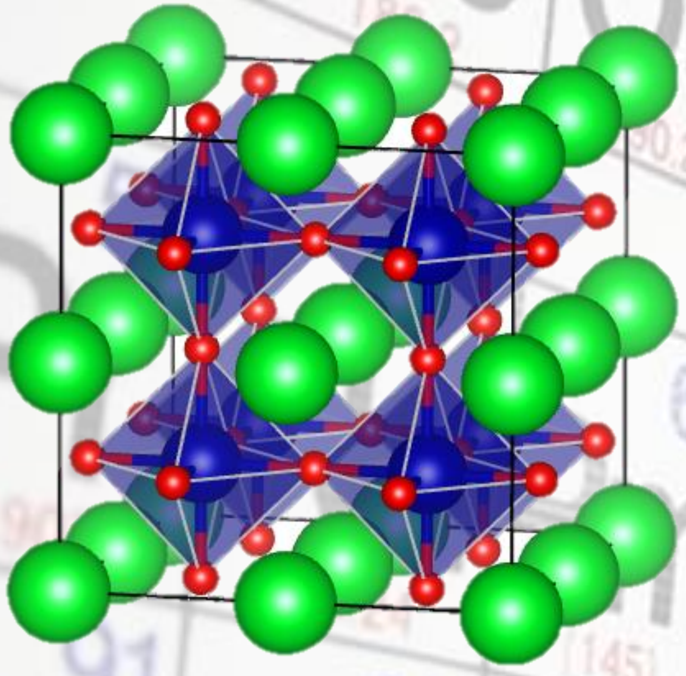
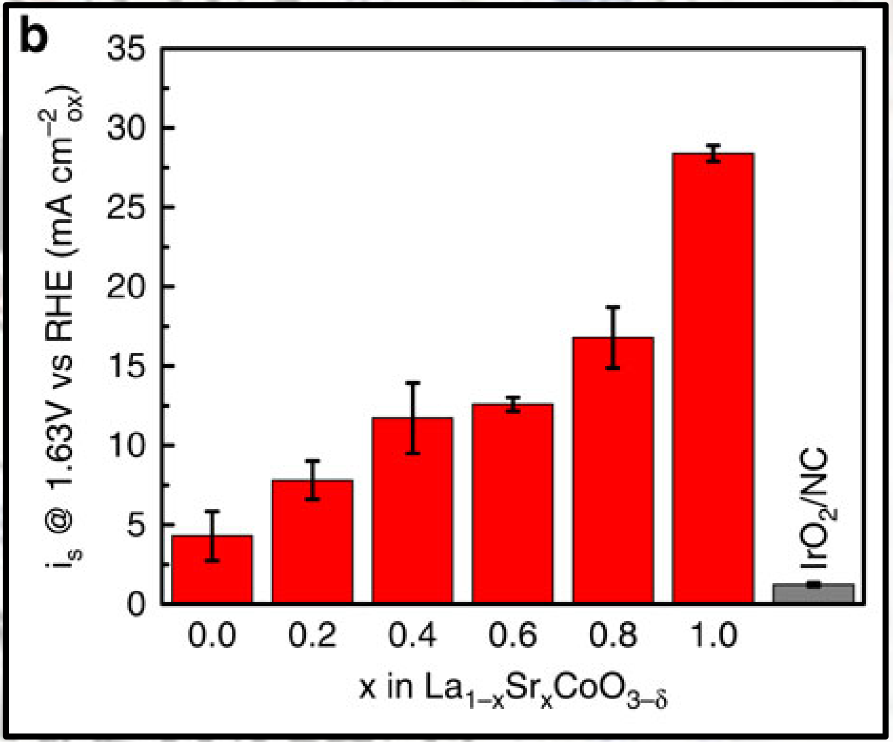
Perovskite oxides as OER/ORR catalysts

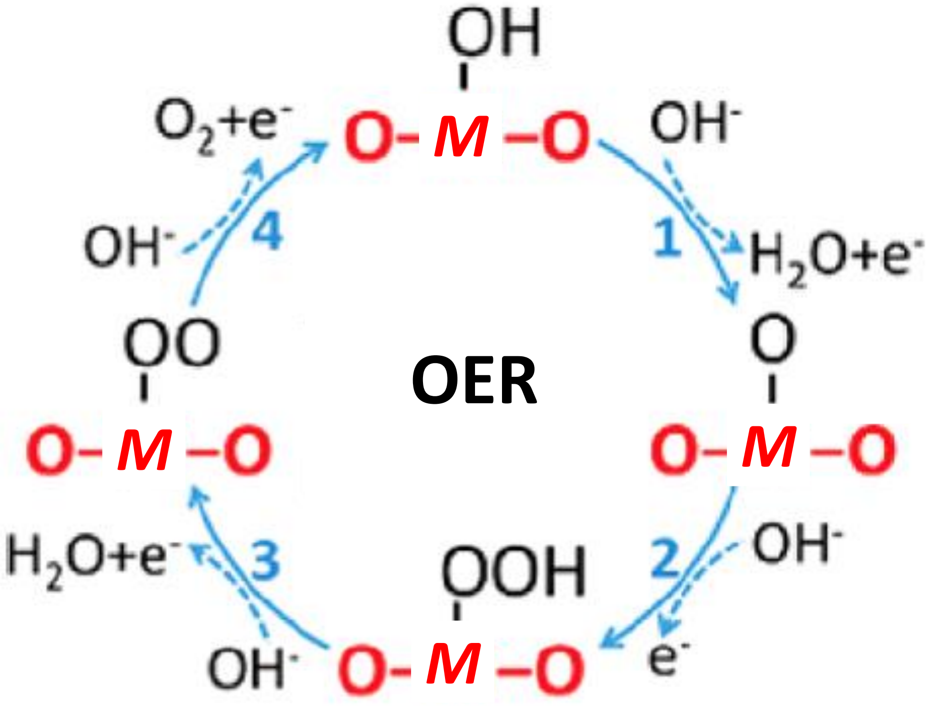
ABO_3





Mefford, Rong, et al, Kolpak, Stephenson, *Nature Comm. 7*, **2016**

Electrocatalytic Water Splitting



OER pathway via the Adsorbate Evolution Mechanism (AEM) under alkaline conditions

Overall:

$H_2O(l) = H_2(g) + 1/2O_2(g)$
$\Delta G^o = 1.23$ eV

Cathode:

$2H_2O(l)+2e^- = H_2(g) + 2OH^-$
Oxygen reduction (ORR)

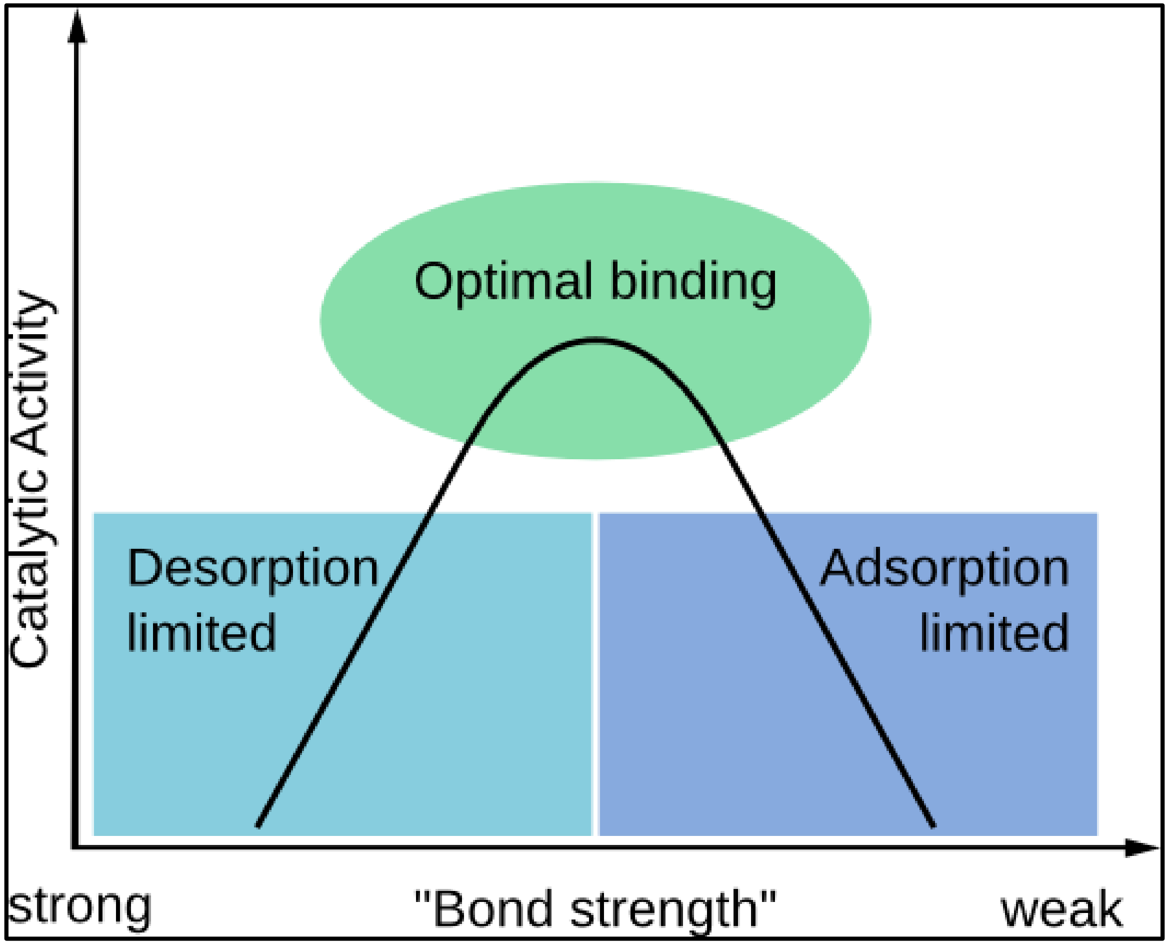
Anode:

$4OH^- = O_2(g) + 2H_2O(l)+4e^-$
Oxygen evolution (OER)

Applied potential:

$E_{ext} = 1.23\text{ V} + \eta$
$\eta = \eta_{anode} + \eta_{cathode} + \eta_{solv} + \ldots$

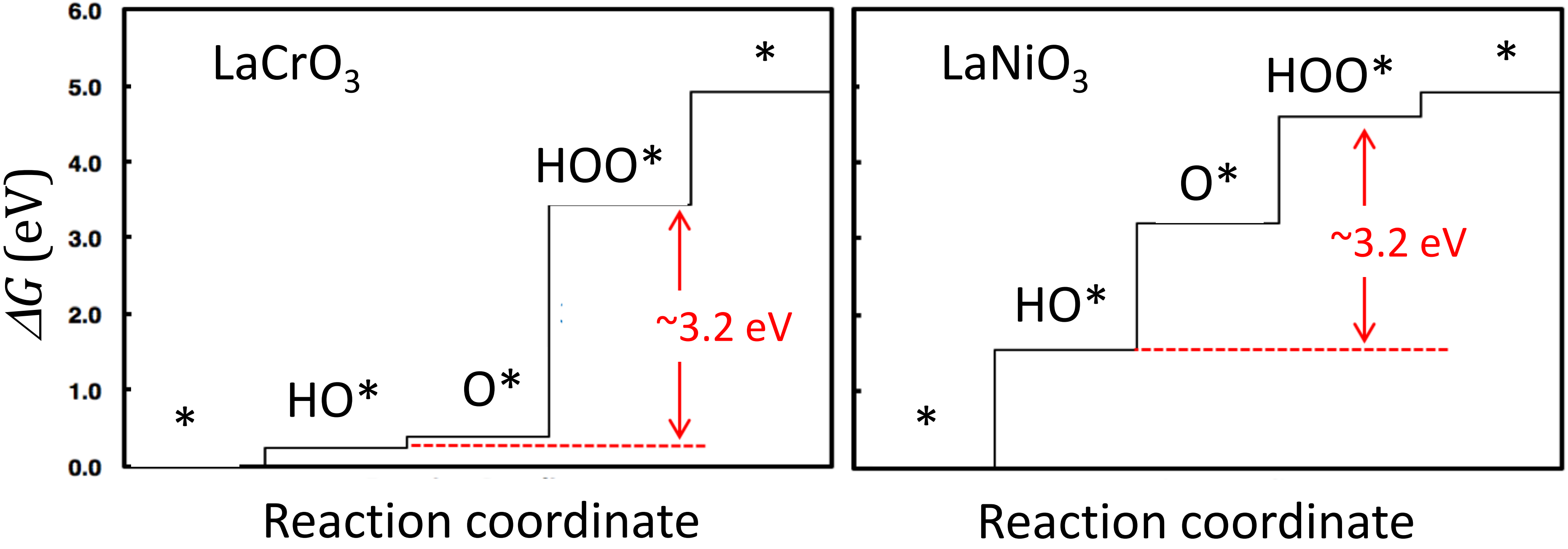
Sabatier’s principle and volcano plots



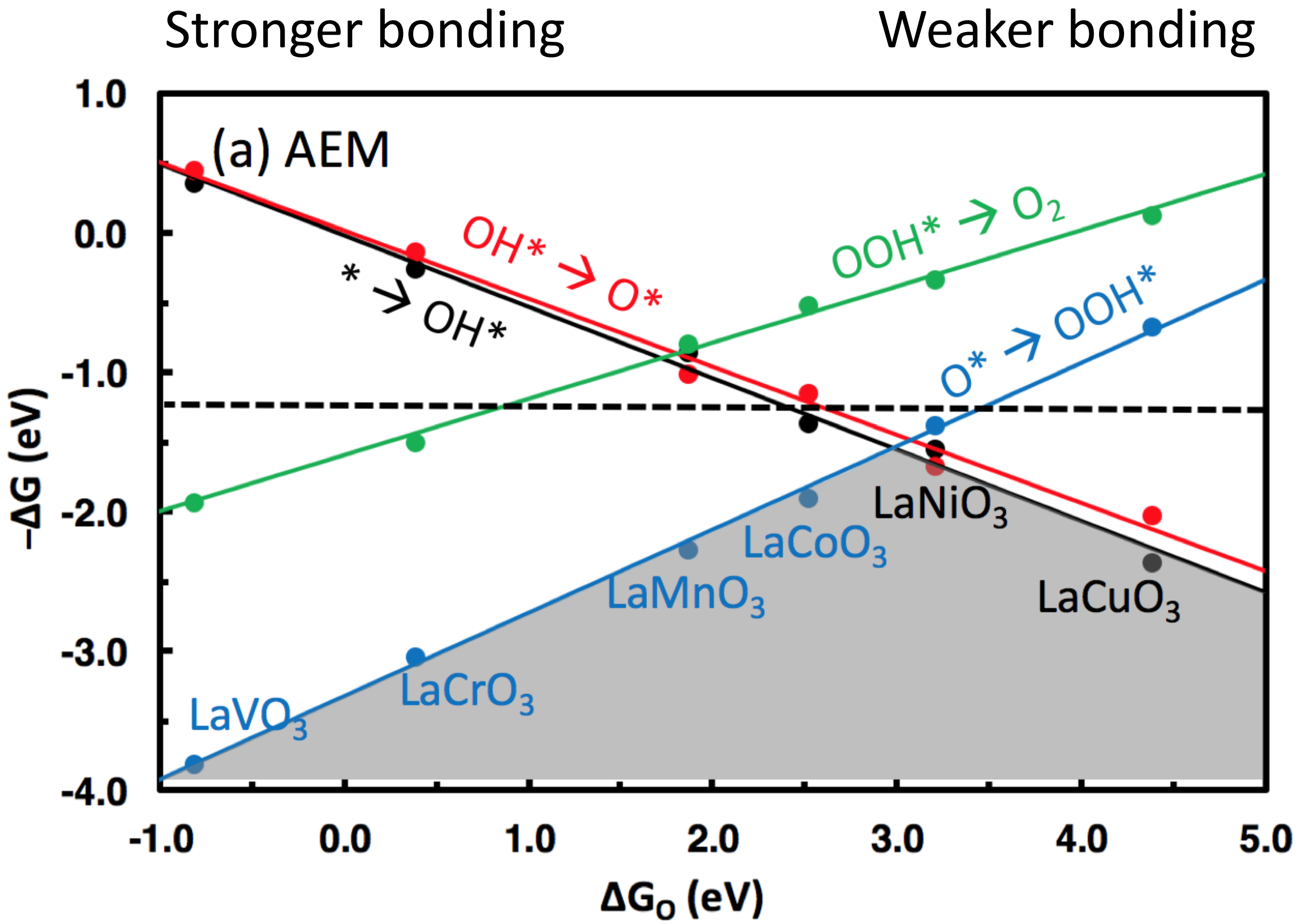
Scaling relationships for OER on LaMO$_3$

$* + H_2O_{(l)} \rightarrow OH^* + H^+ + e^-$	ΔG_{HO^*}
$OH^* \rightarrow O^* + H^+ + e^-$	ΔG_{O^*}
$O^* + H_2O_{(l)} \rightarrow OOH^* + H^+ + e^-$	ΔG_{HOO^*}
$OOH^* \rightarrow O_{2(g)} + H^+ + e^-$	ΔG_{*}

$\Delta G_{HOO^*} - \Delta G_{HO^*} \sim 3.2$ eV for all AMO_3 → ideal is 2.46 eV



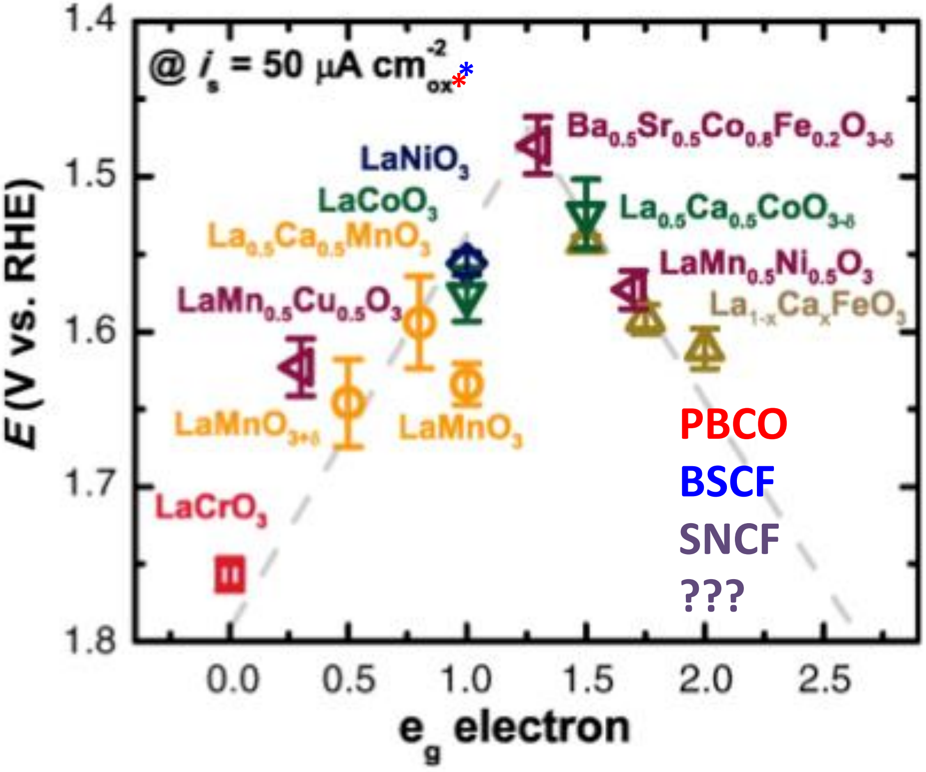
OER activity volcano plot LaMO$_3$



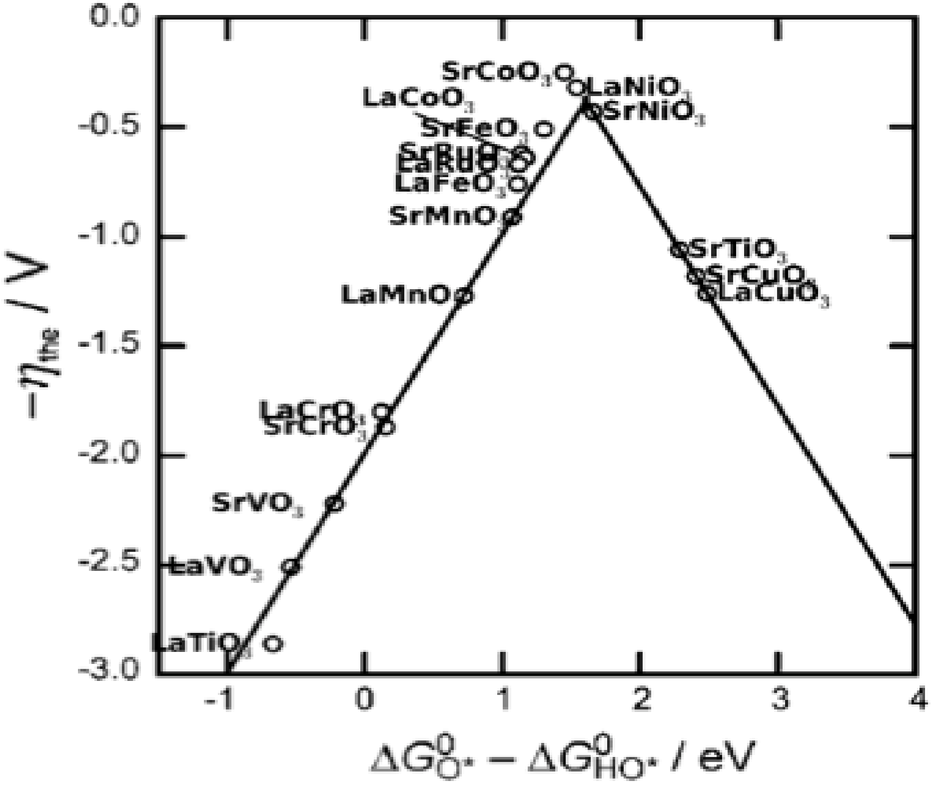
Problem: What about BSCF, PBCO, LSCF? Weaker bonding than LaNiO$_3$, but higher experimental activity!

Descriptor-activity relationships

Suntivich* et al., *Science*, 2011



Man et al., *ChemCatChem*, 2011

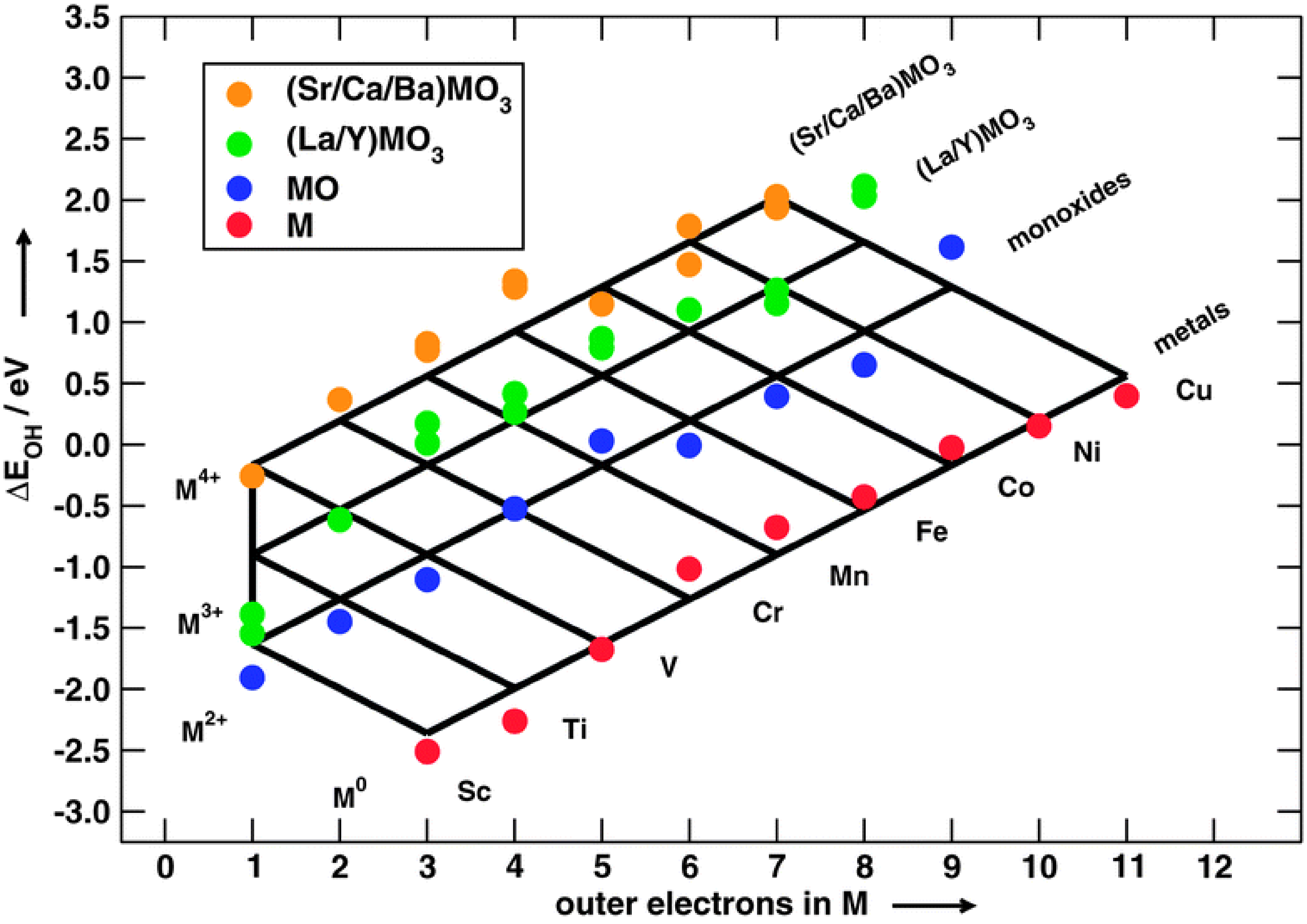


Volcano plots of activity vs descriptor

- e_g filling
- *d*-band center
- O *p*-band center

Grimaud et al, *Nat. Comm.*, 2013
Yagi et al, *Nat. Comm.*, 2015
Zhu et al, *Angew. Chem.*, 2015

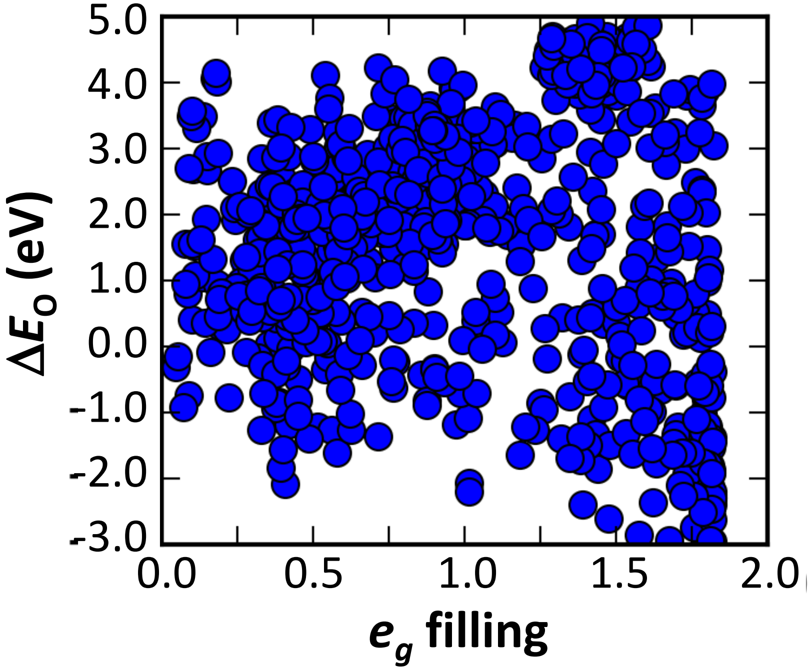
Different trends for different classes

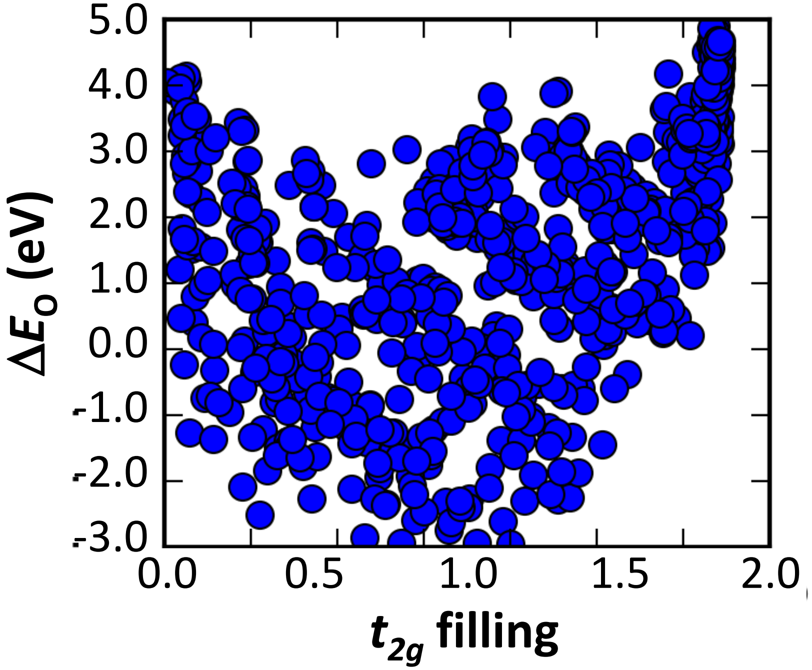


Calle-Vallejo, et al., Chem. Sci. 4,1245 (2013)

High throughput screening with DFT

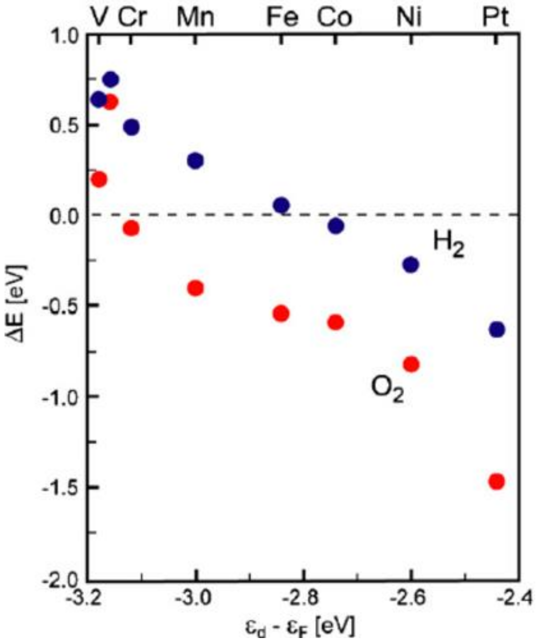
- Used DFT to compute bulk electronic structure and oxygen adsorption energies(ΔE_O) on “ideal” slabs for around 800 (La,Sr)(*M*,*M’*)O_3 perovskite compositions

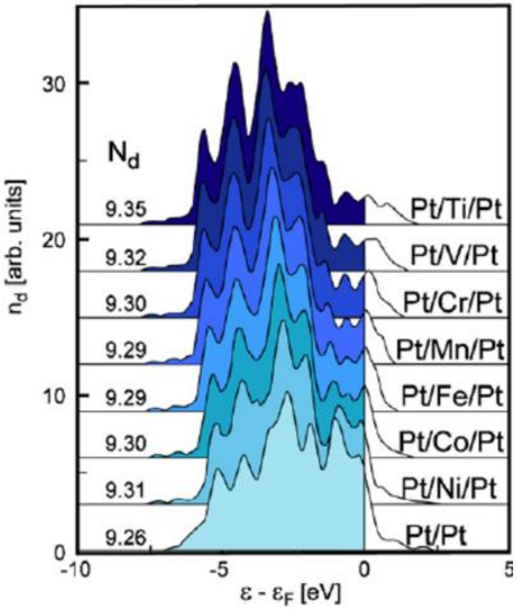




- That doesn’t look like a trend…

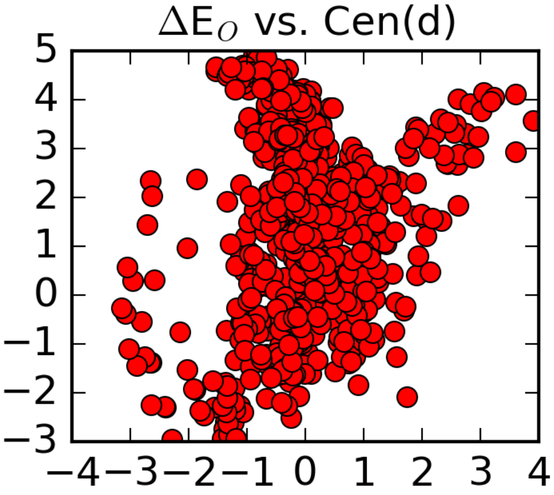
d-band center as a descriptor?

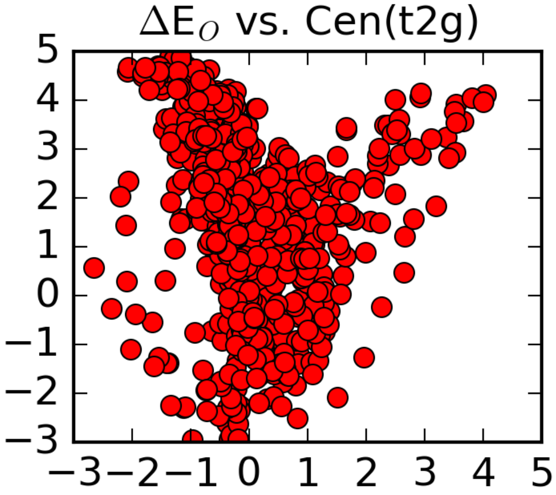


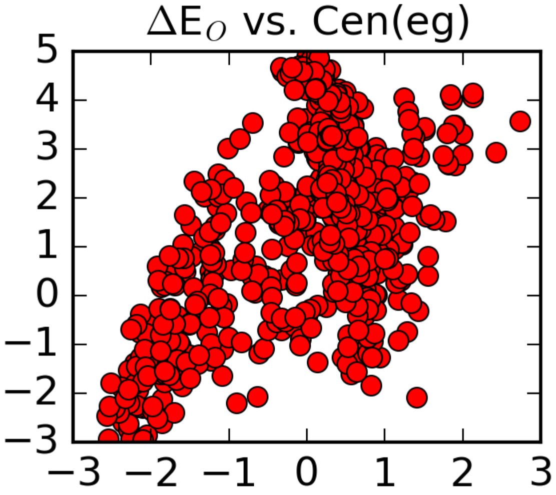


The *d*-band center is a good descriptor for O adsorption on metals... But not very good for oxides (but we already know this)

Norskov et al., *Nat. Chem.*, 2009

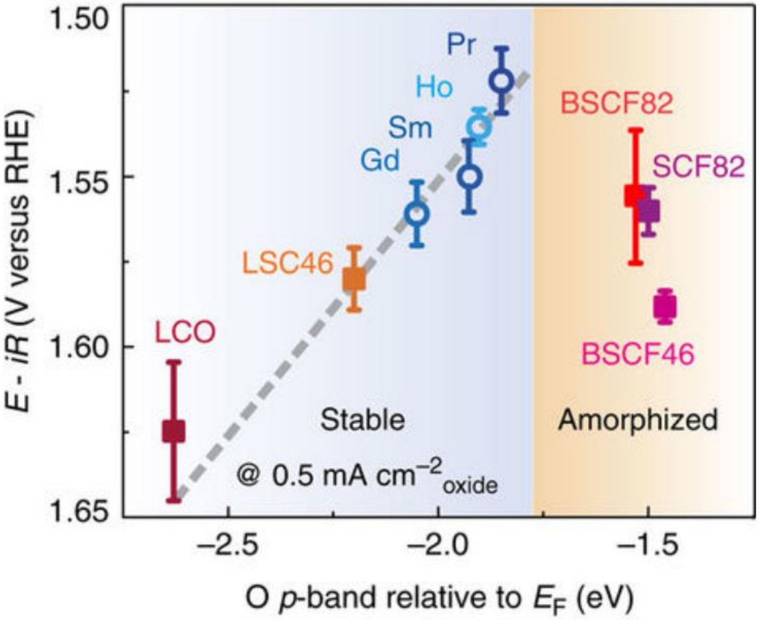


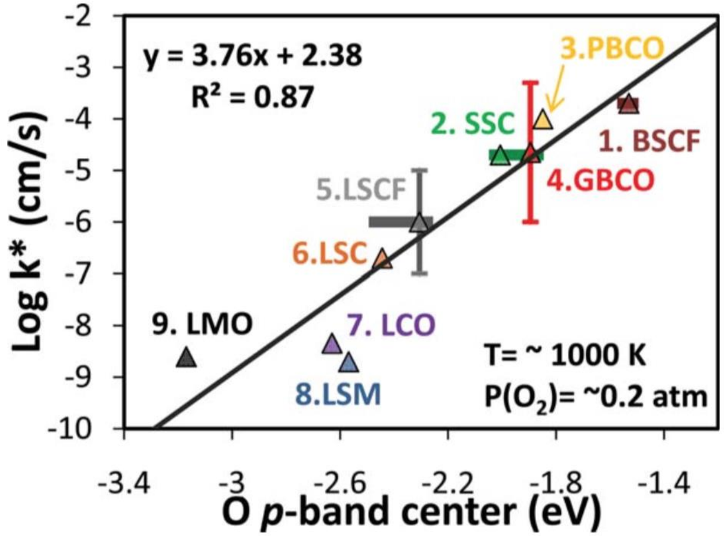




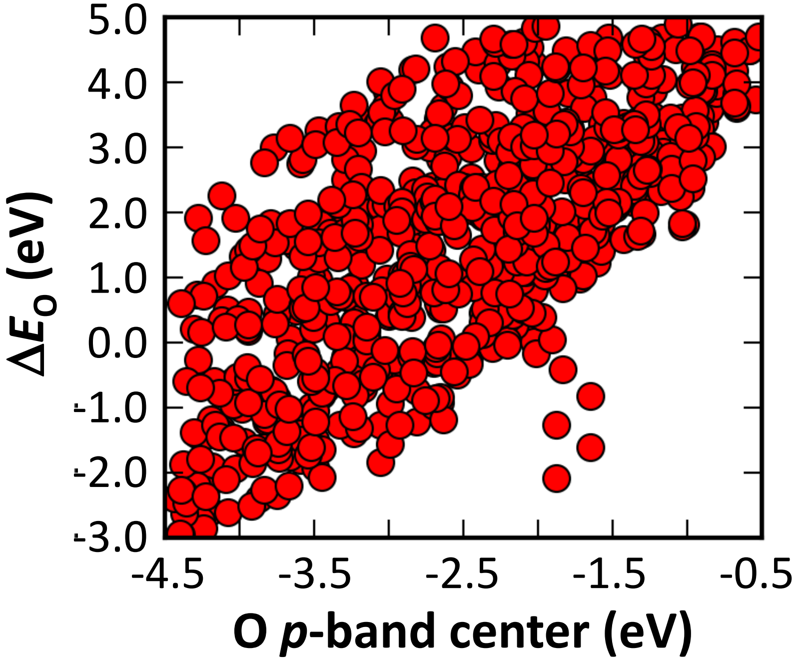
What about O *p*-band center?

Grimaud et al, *Nat. Comm.*, 2013

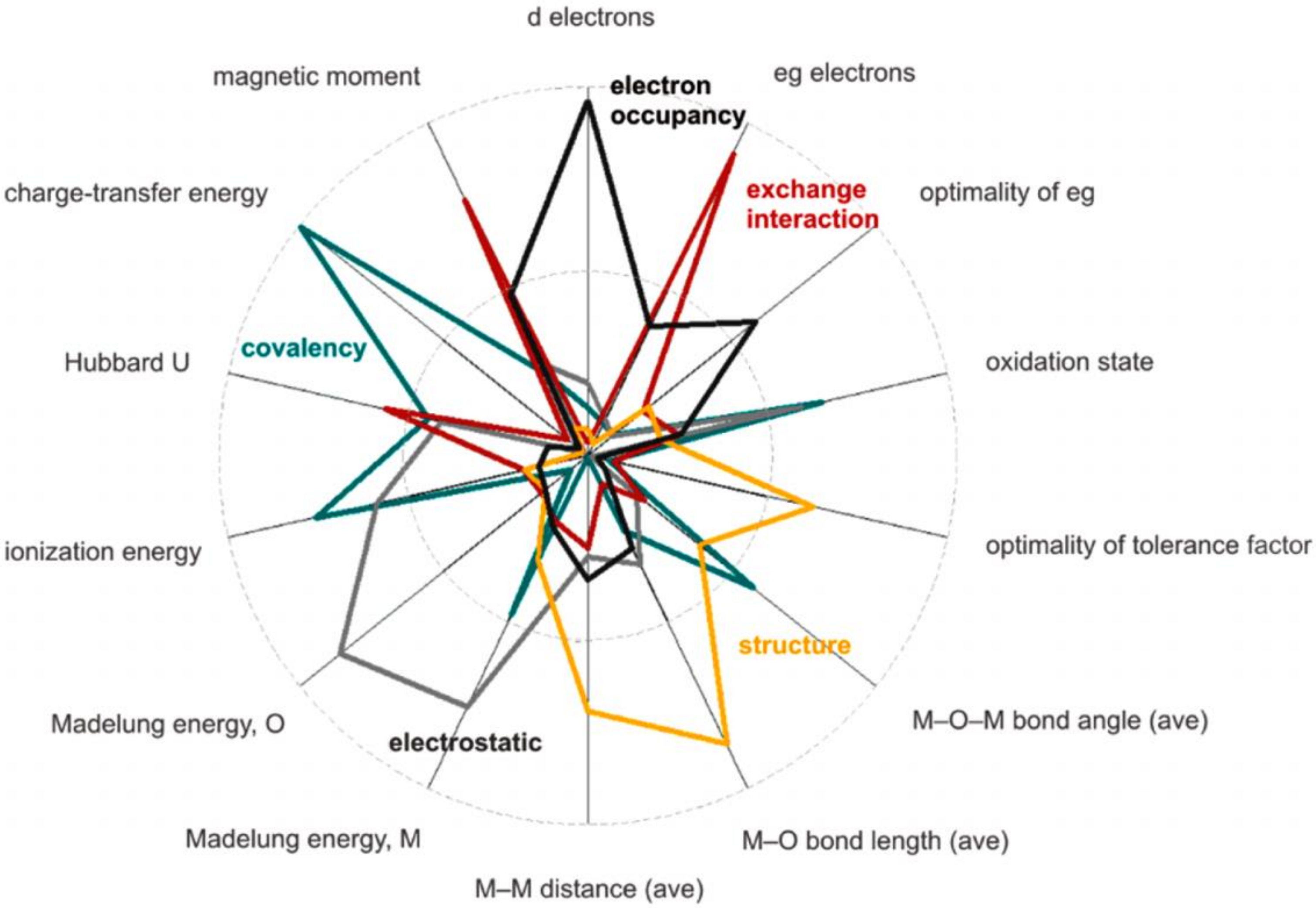




DFT results for ~ 800 (La,Sr)(*M*,*M'*)O_3 perovskites

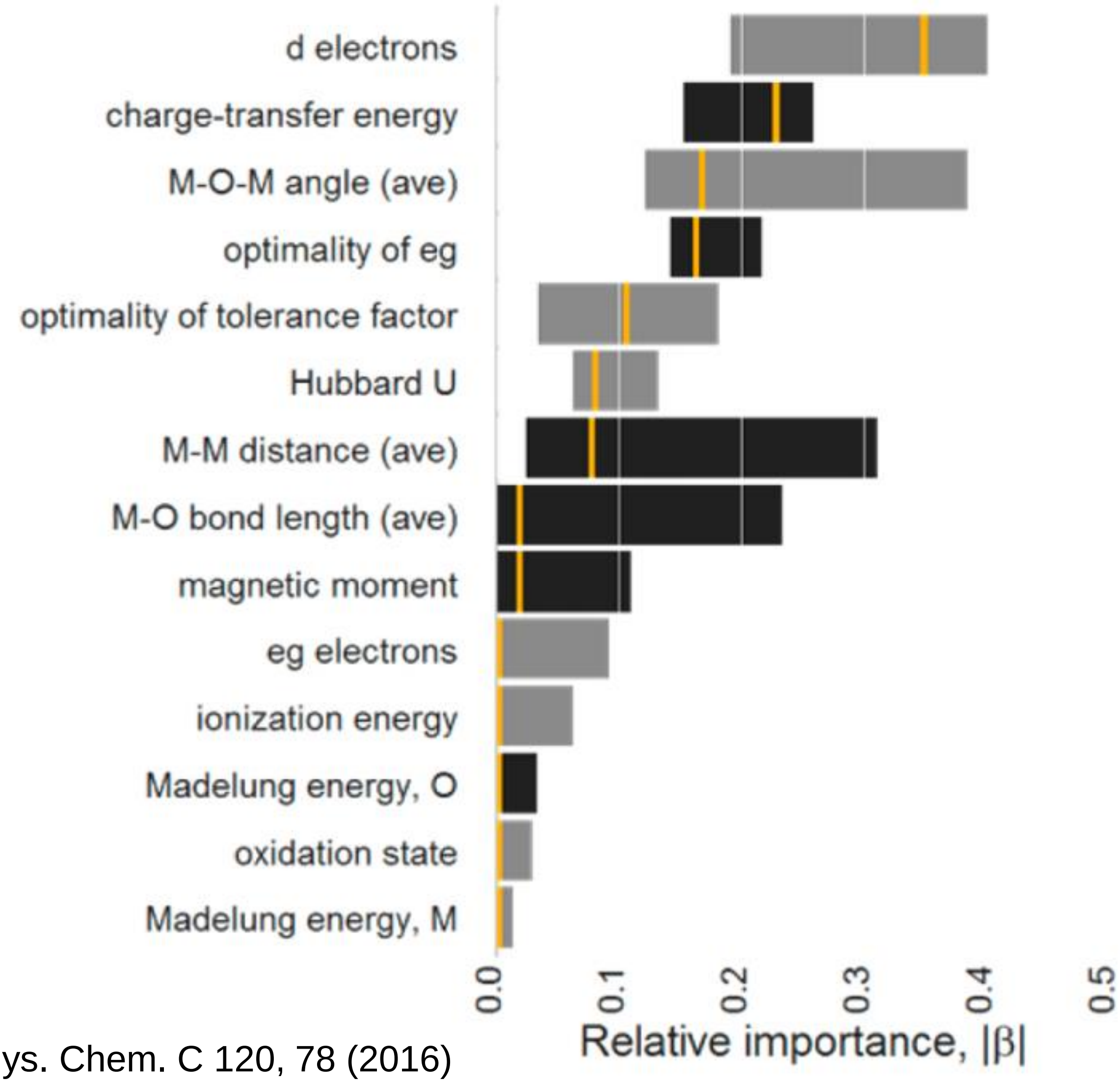


More complex descriptors



Hongi, et al., J. Phys. Chem. C 120, 78 (2016)

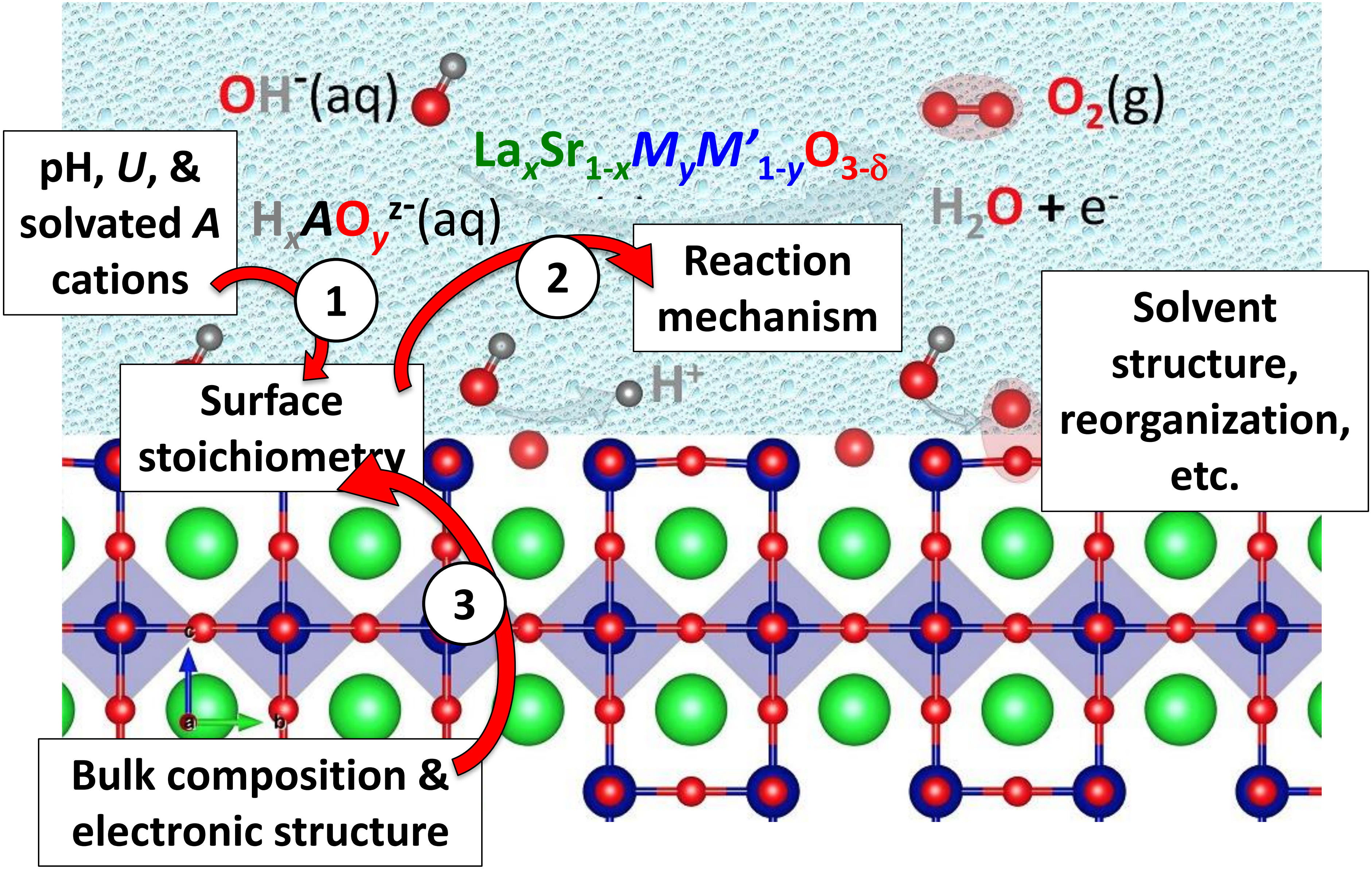
More complex descriptors



Hongi, et al., J. Phys. Chem. C 120, 78 (2016)

Why can’t we do better with descriptors?

Why can't we do better with descriptors?



pH, *U*, & solvated *A* cations

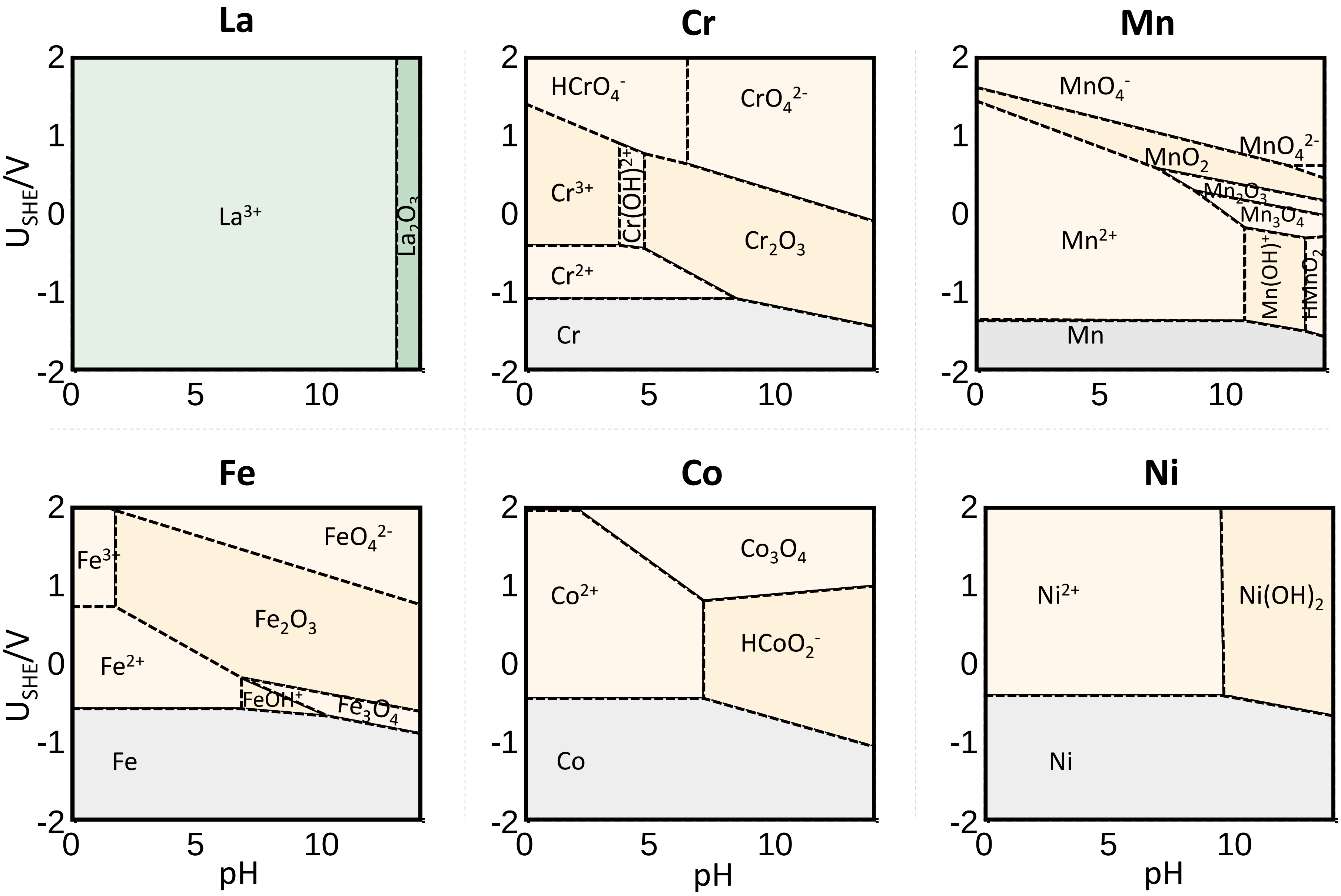
Reaction mechanism

Surface stoichiometry

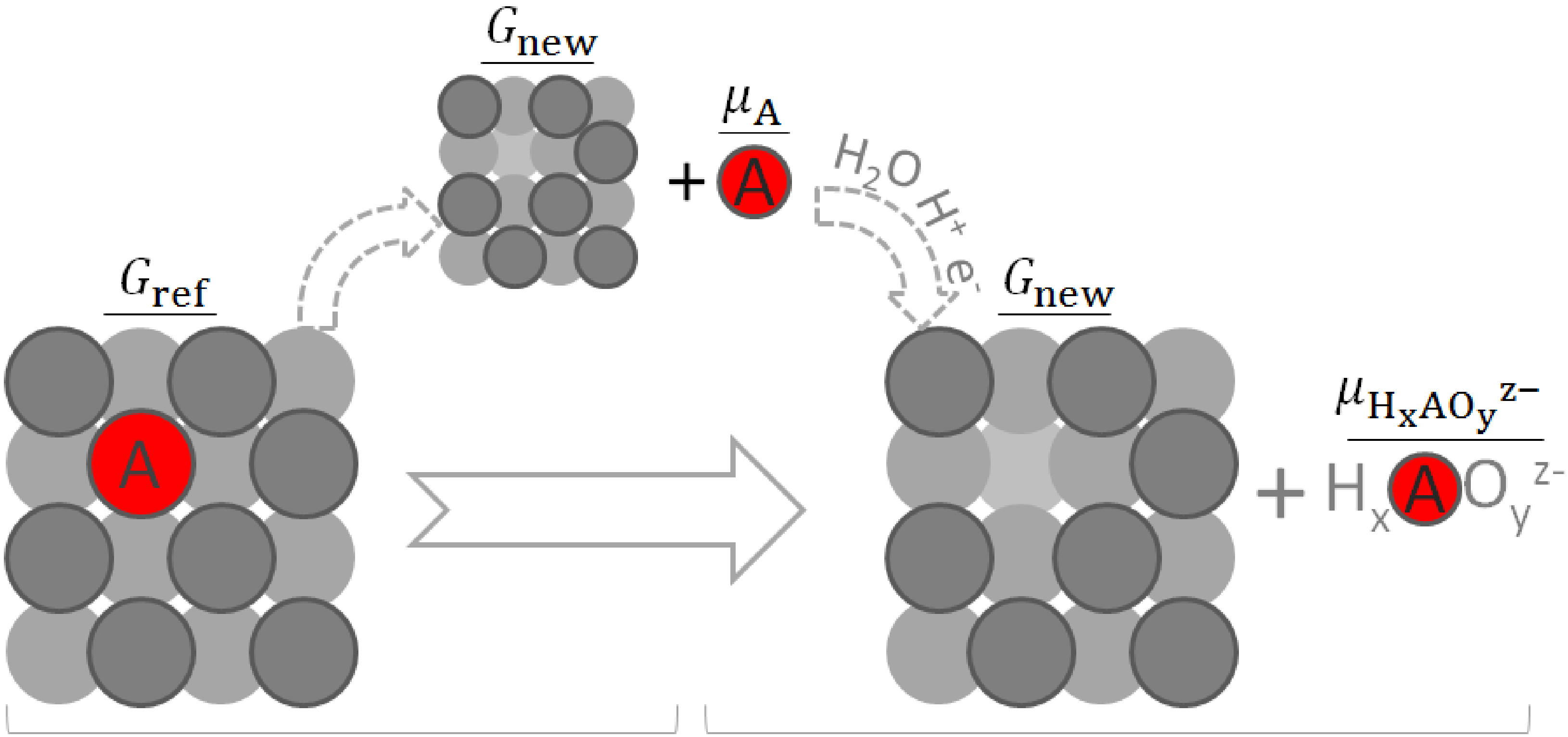
Solvent structure, reorganization, etc.

Bulk composition & electronic structure

Role of solvated cations on surface chemistry?



Modeling surface reconstruction in oxides in aqueous electrochemical environments



$$\Delta G_{\mathrm{vac}} = G_{\mathrm{new}} + \mu_{\mathrm{A}} - G_{\mathrm{ref}}$$

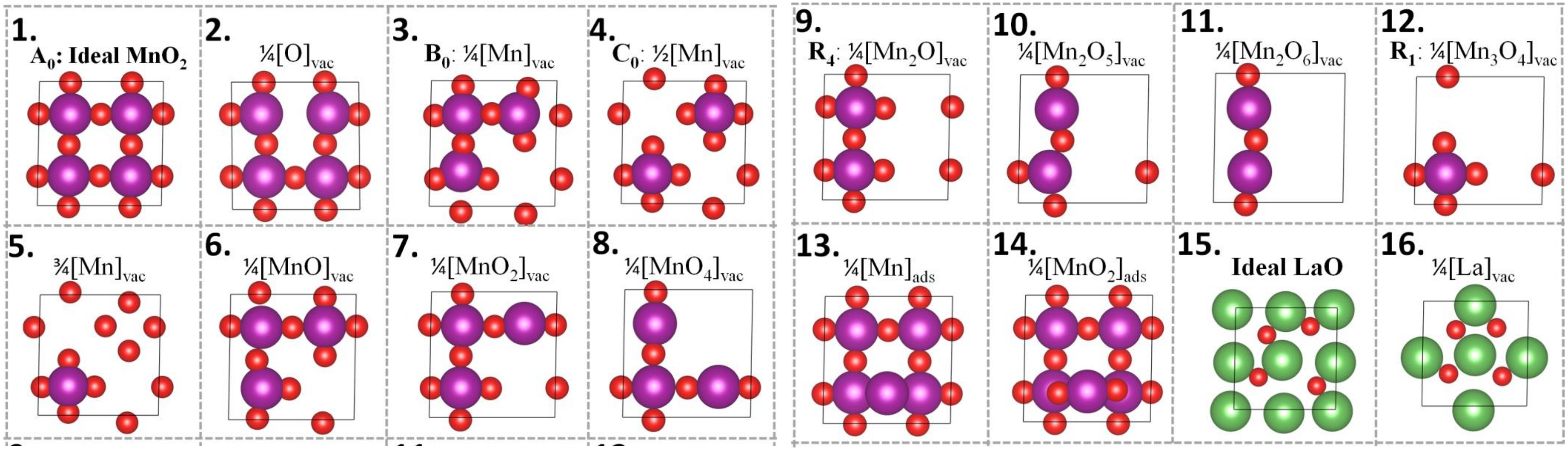
$$\boldsymbol{\Delta G_2} = \mu_{\mathrm{H_xAO_y}^{\mathrm{z-}}} - \mu_{\mathrm{A}} - \sum n_{\mathrm{i}}\mu_{\mathrm{i}}$$

$$\Delta G = \Delta G_{\mathrm{vac}} + \boldsymbol{\Delta G_2}$$

The structure/stoichiometry phase space

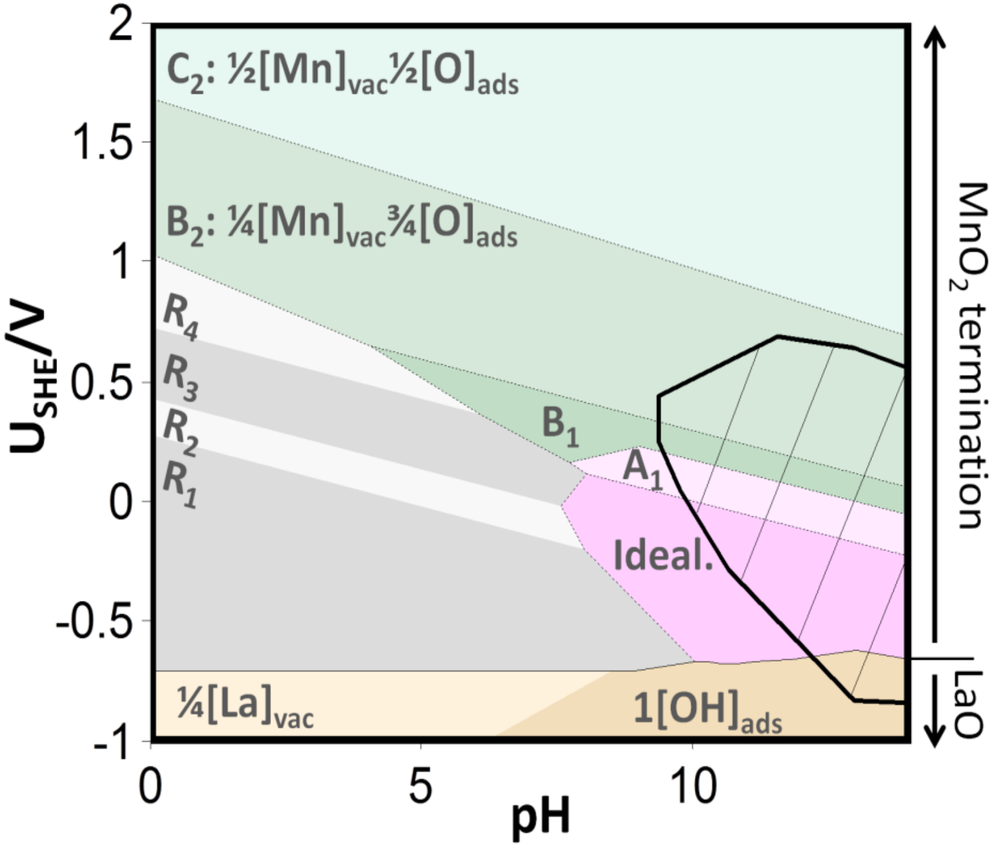
Critical considerations:

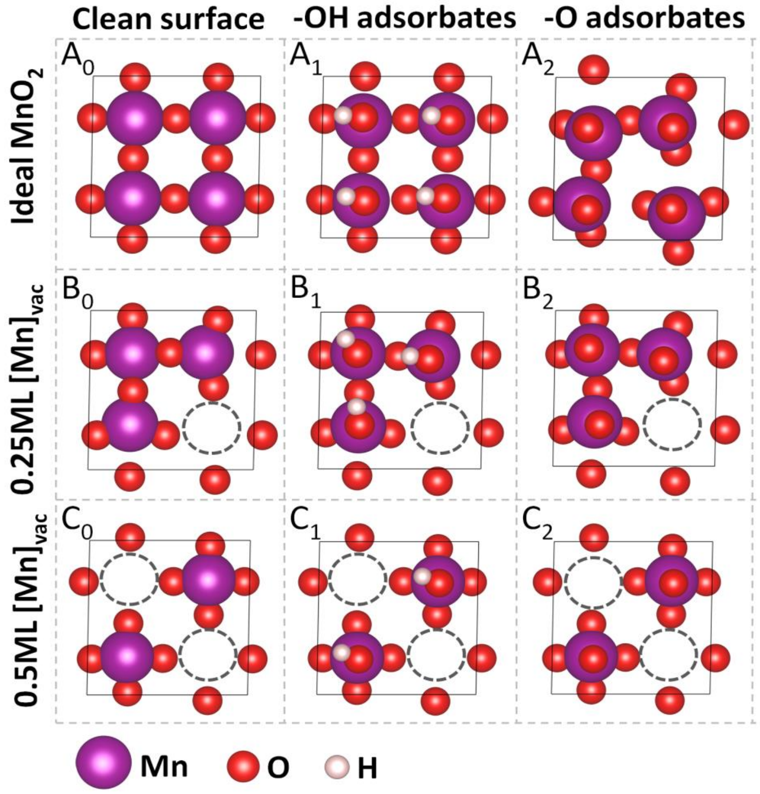
- Non-ideal surface structure and composition
- Depends on applied potential, pH, and solvated cations



- Cation vacancies and adsorbates, and oxygen vacancies
- *B*O_2 vs *A*O-based surface termination
- OER/ORR reaction intermediate adsorbates (-O, -OH, -OOH)
- Different concentrations of reconstructions/adsorbates

Surface phase diagram for $LaMnO_3$

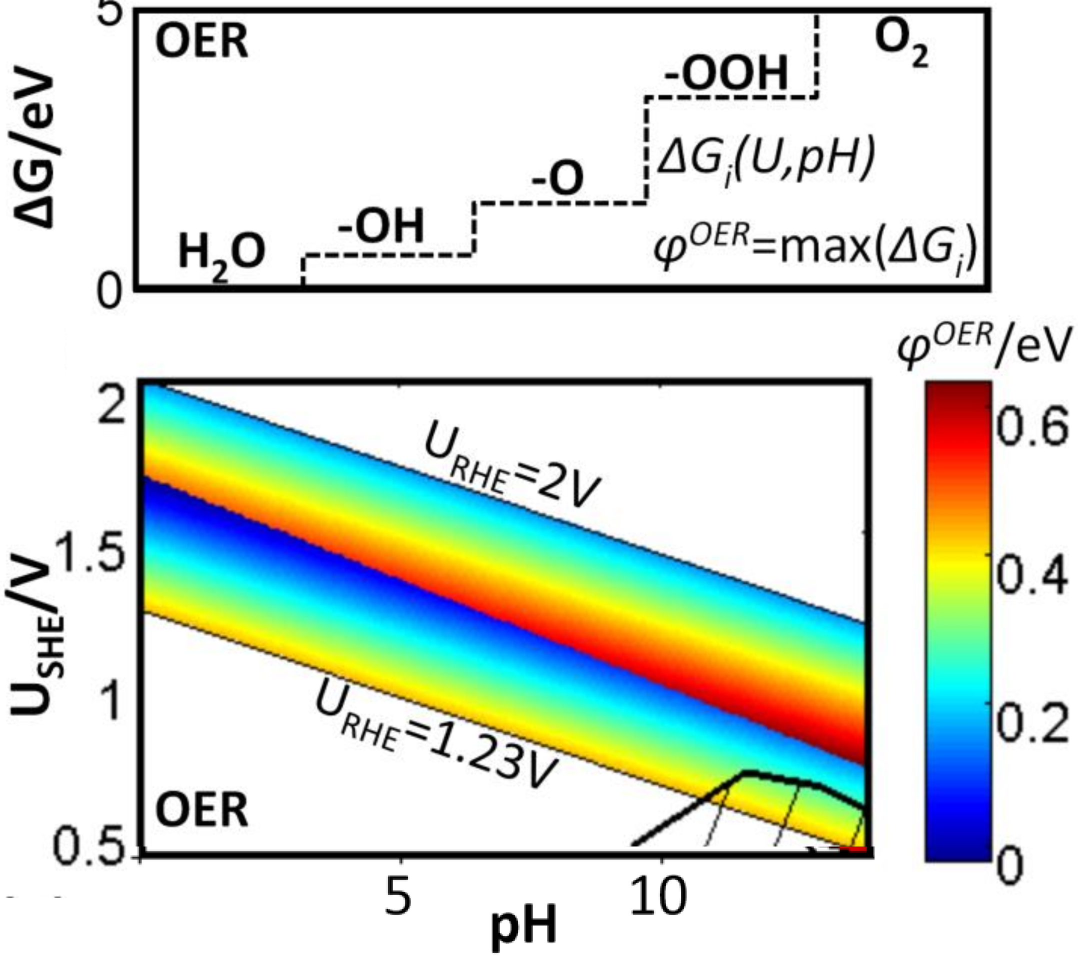




The stable surface phase is strongly influenced by the **difference in the oxidation state of the surface and solvated Mn cations.**

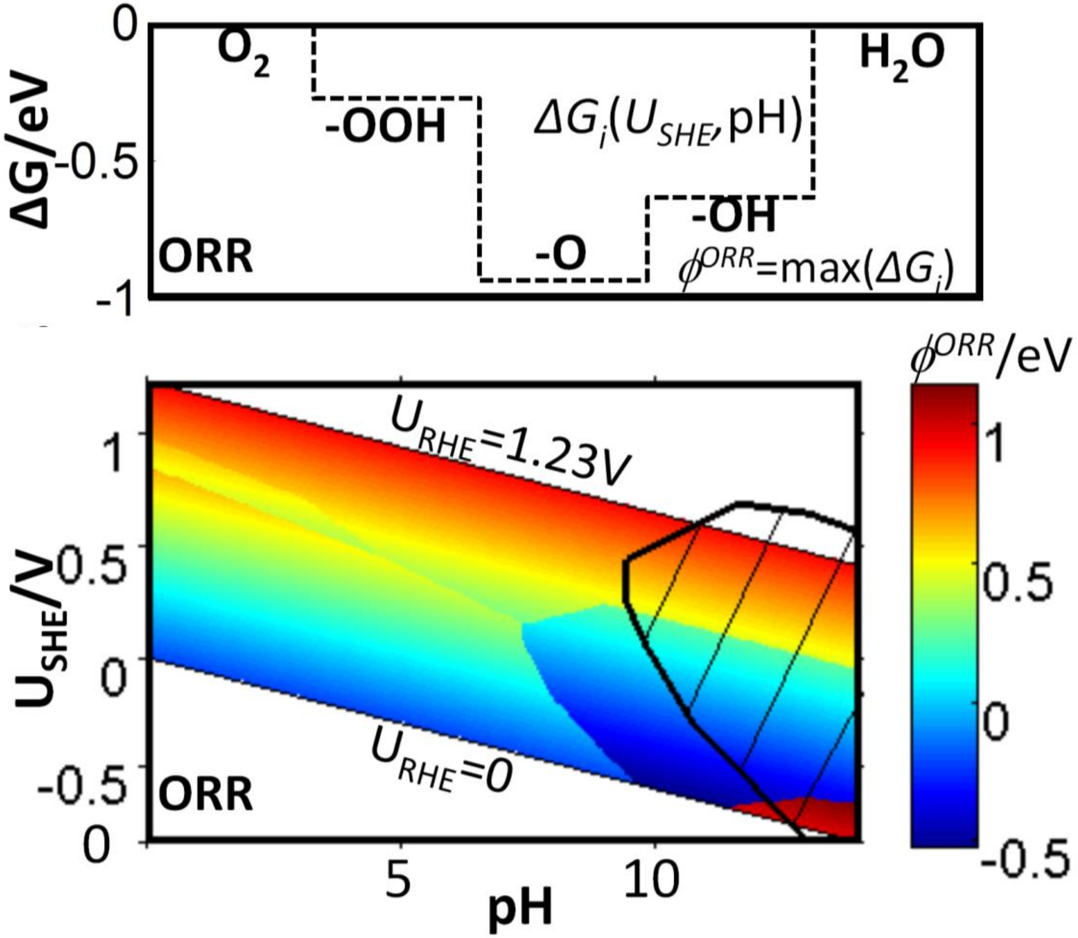
Rong & Kolpak, *JPCL* (2015)

Surface-dependent OER activity



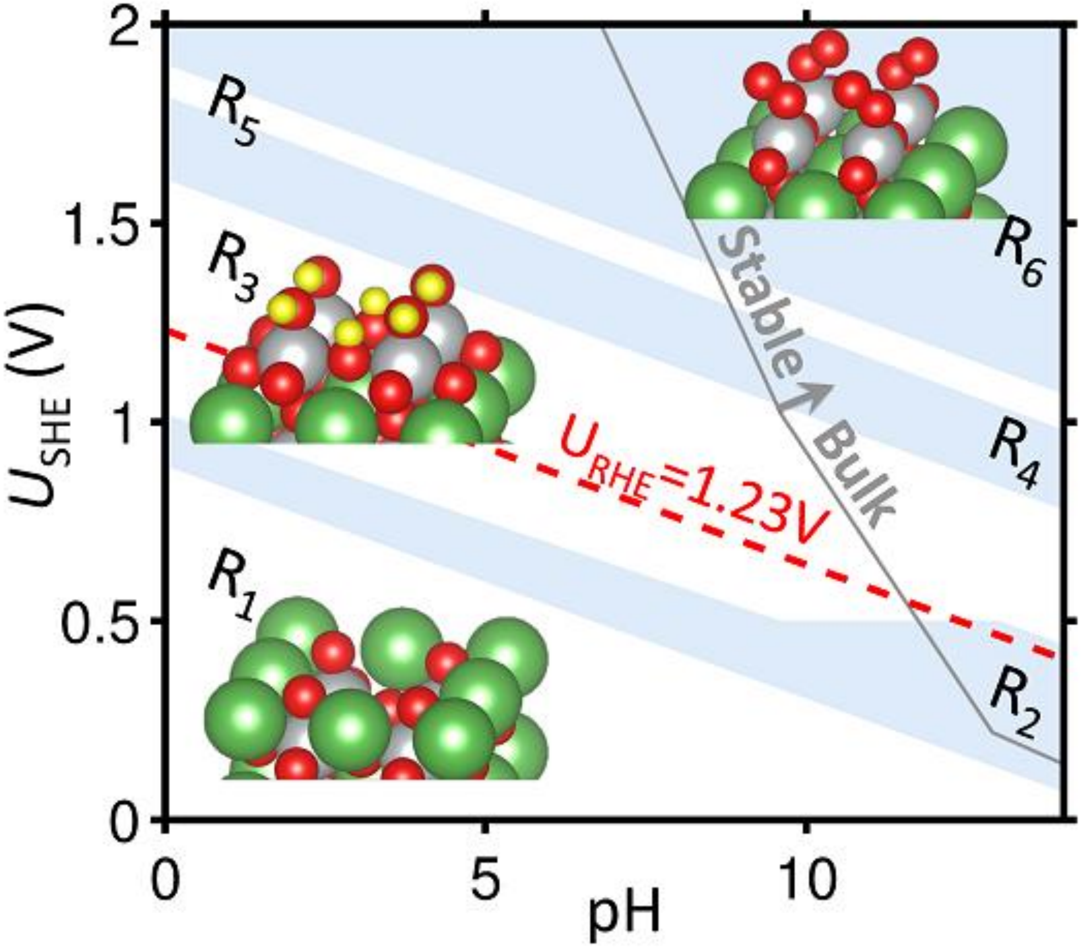
Rong & Kolpak, *JPCL* (2015)

Surface-dependent ORR activity



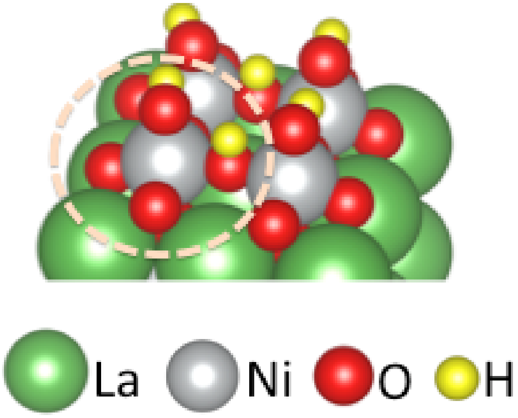
Rong & Kolpak, *JPCL* (2015)

Surface phase diagram of $LaNiO_3$



Stable surface for OER:

$1[OH]_{ads} + ½[H]_{ads}$



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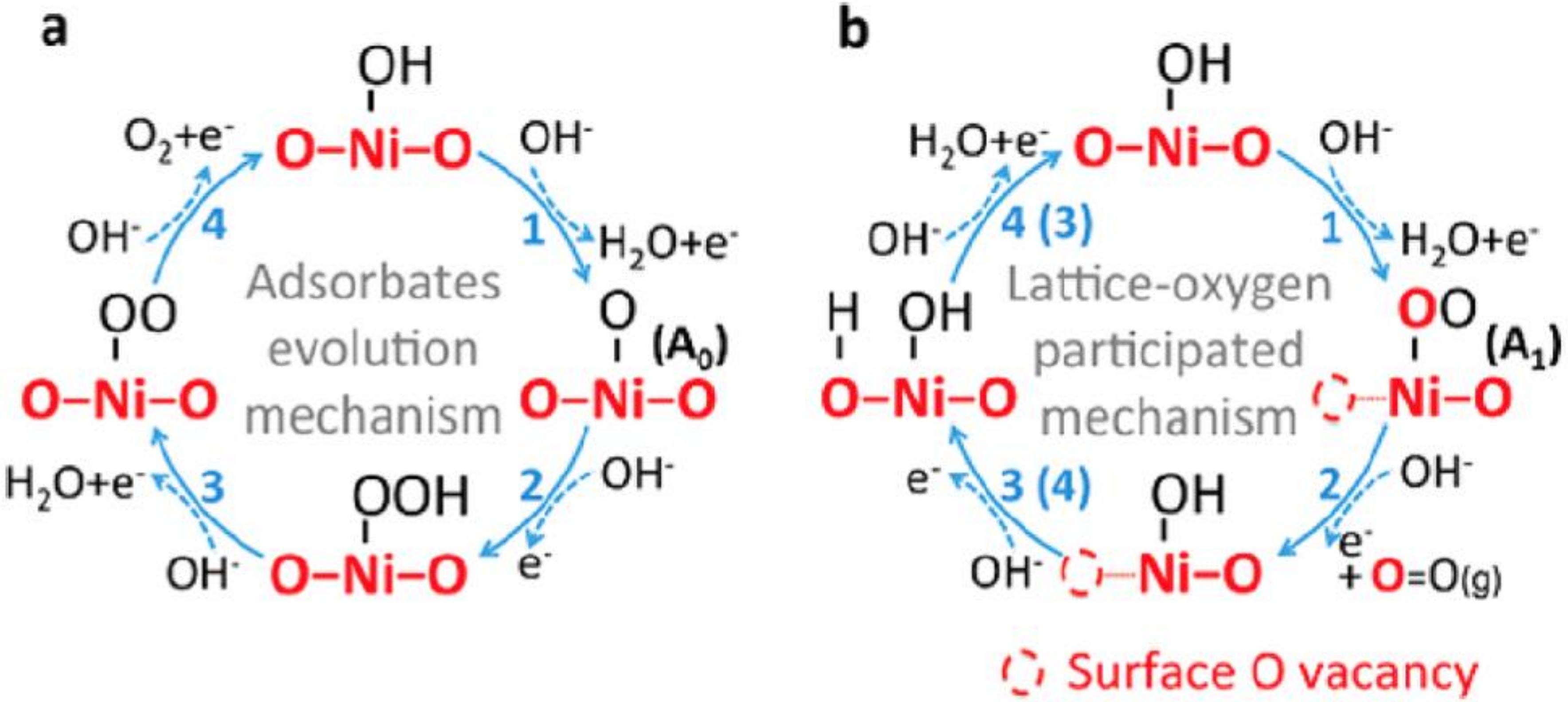
OER takes place on the protonated NiO_2 terminated surface; the computed overpotenial is 0.70 V (experiment: 0.35 V). Is the reaction mechanism different?

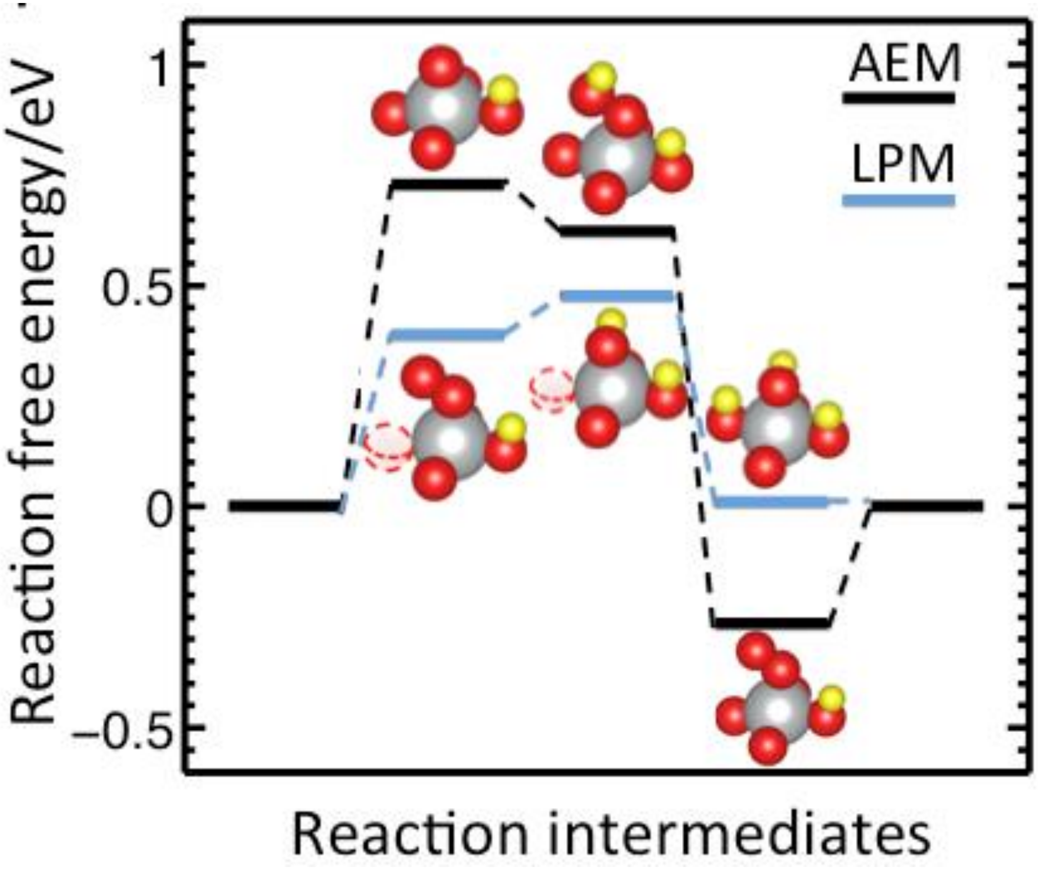
Proposed mechanism on $LaNiO_3$

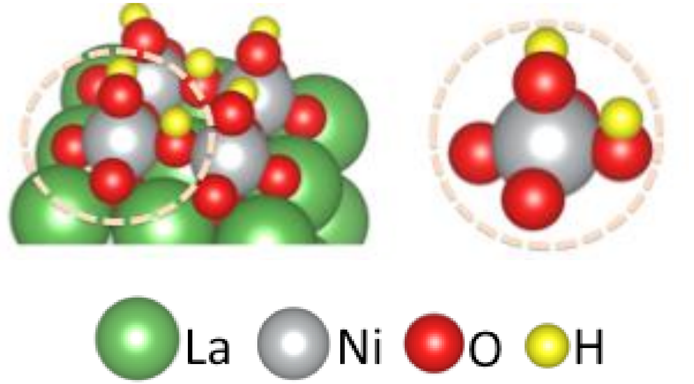


Computed free energies of intermediates to determine limiting steps and predict which pathway is most likely to occur at lowest potential.

Considered many possible intermediates and pathways.

Comparison of AEM and LOM



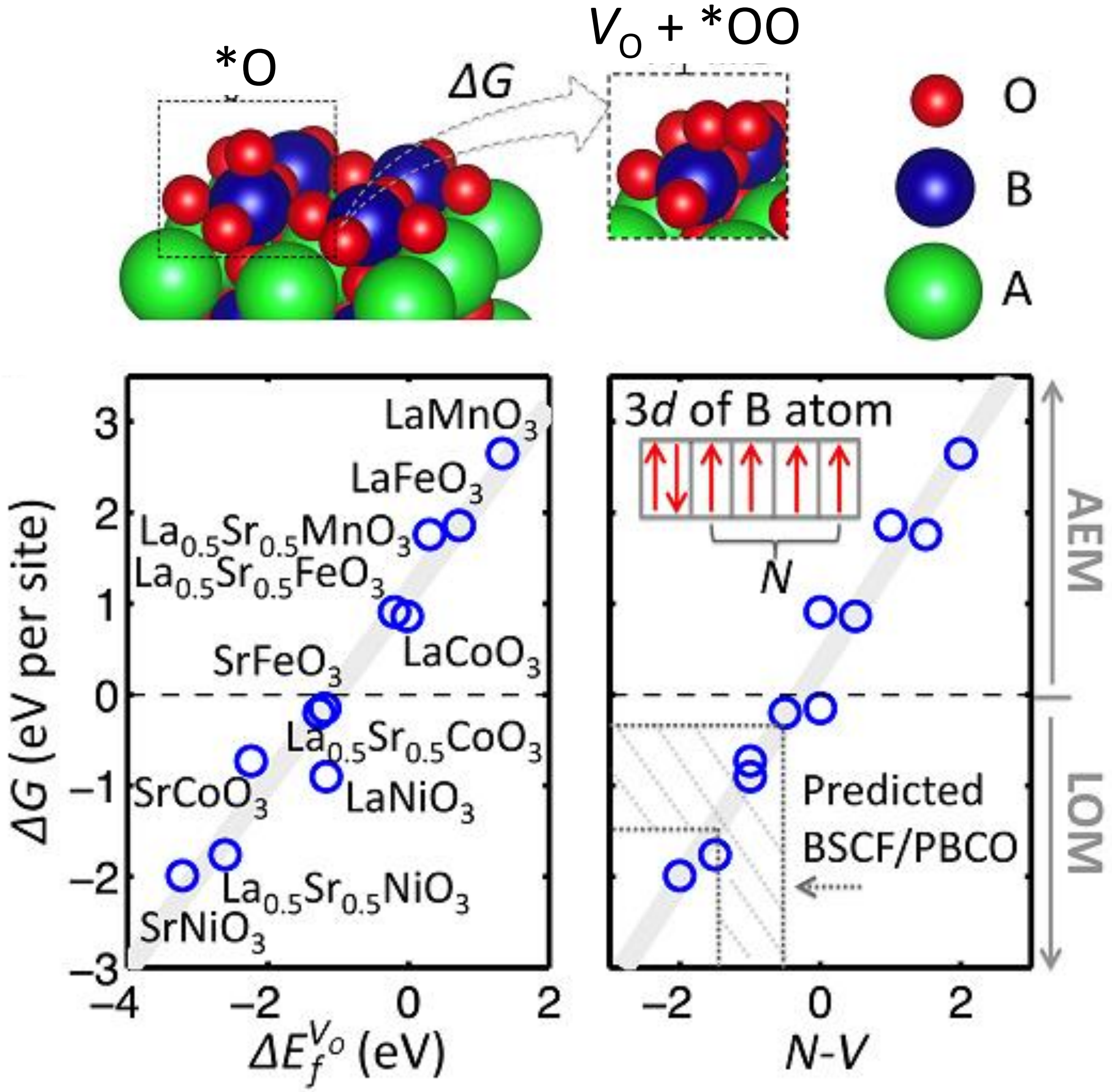


The mechanism in which lattice oxygen participates in the reaction has a much lower energy barrier

Overpotential in good agreement with experiment!

Rong & Kolpak, *ACS Catal.* (2016)

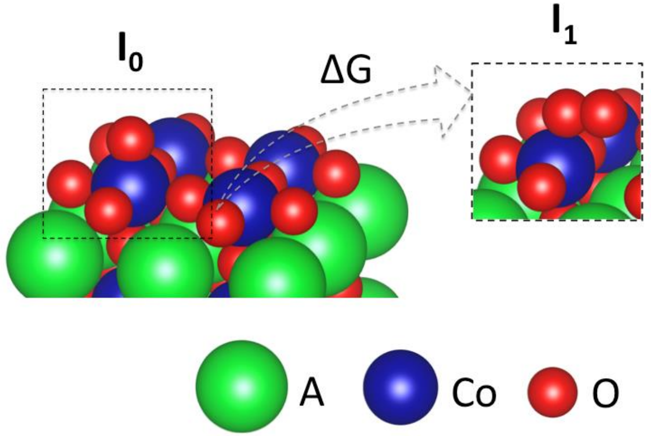
Reaction mechanism relation to stability

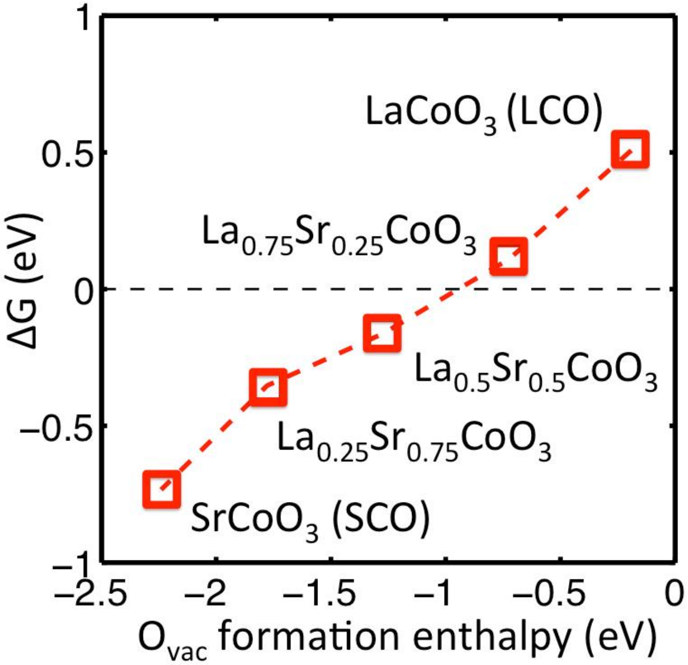


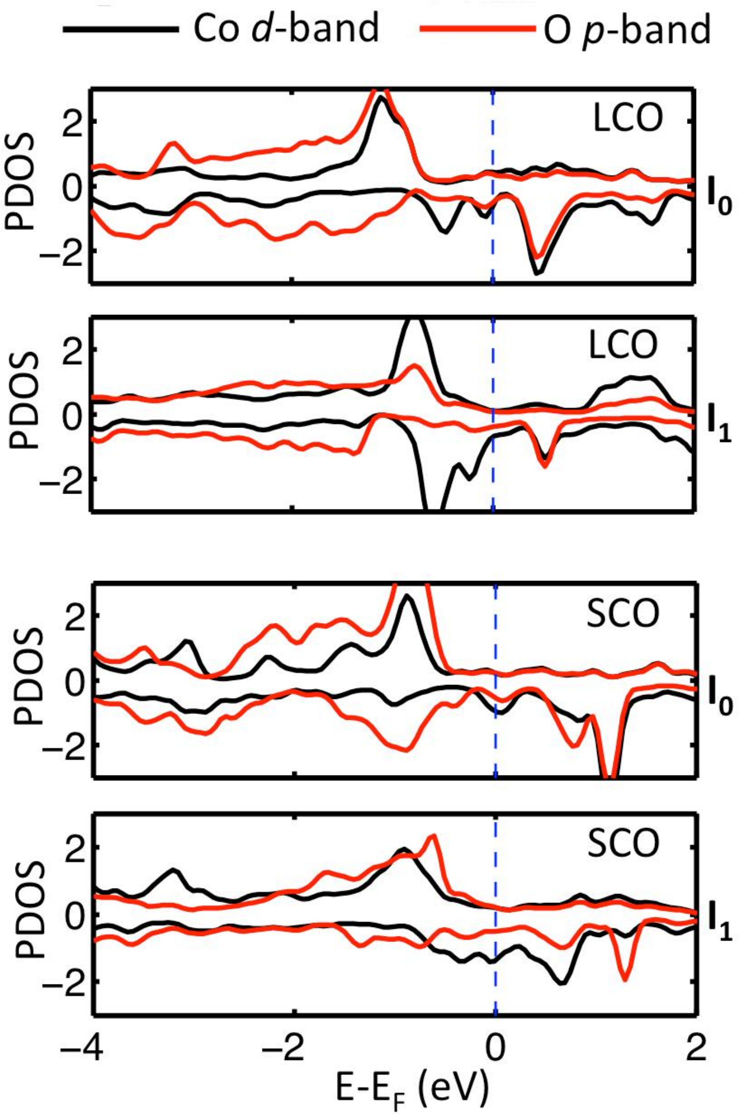
- Preferred mechanism governed by energy difference between *O and V_O + *OO (ΔG)
- ΔG linearly related to bulk oxygen vacancy formation energy (ΔE_f^{VO}) → **stability**
- ΔG and ΔE_f^{VO} linearly related to difference between occupation of isolated and bulk B site cation (*N*-*V*) → **electronic structure (“descriptor”)**

Rong & Kolpak, *ACS Catal.* (2016)

Comparison of mechanisms for $La_{1-x}Sr_xCoO_{3-\delta}$







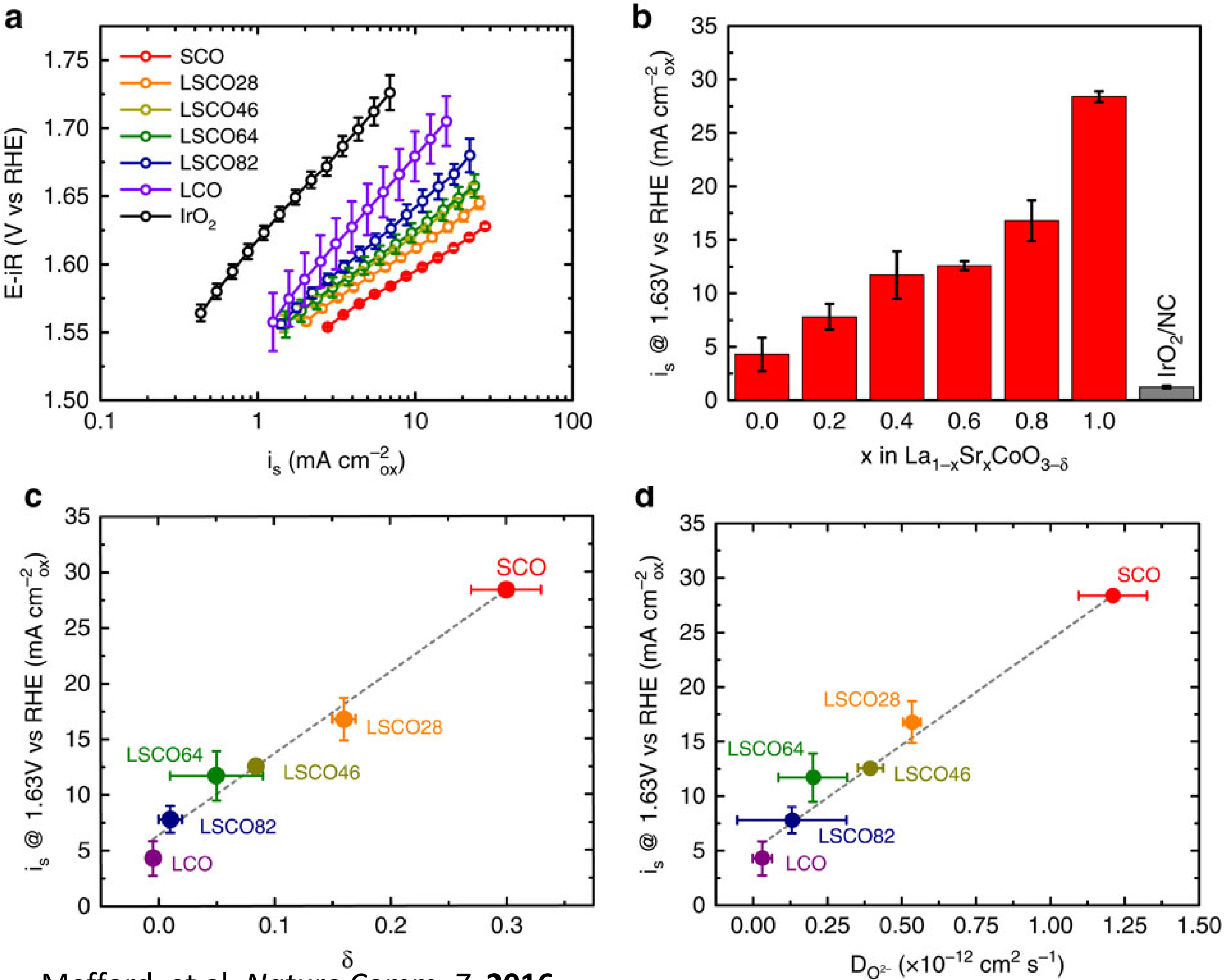
Ovac+OO shows Less overlap of bonding states (less stable)

Ovac +OO* shows strong overlap of bonding, less overlap of antibonding states (more stable)

Mefford, et al, *Nature Comm. 7*, **2016**

Grimaud et al, *Nat. Chem. 9*, **2017**

Experimental Data: Increasing efficiency for $La_{1-x}Sr_xCoO_{3-\delta}$ with increasing Sr content



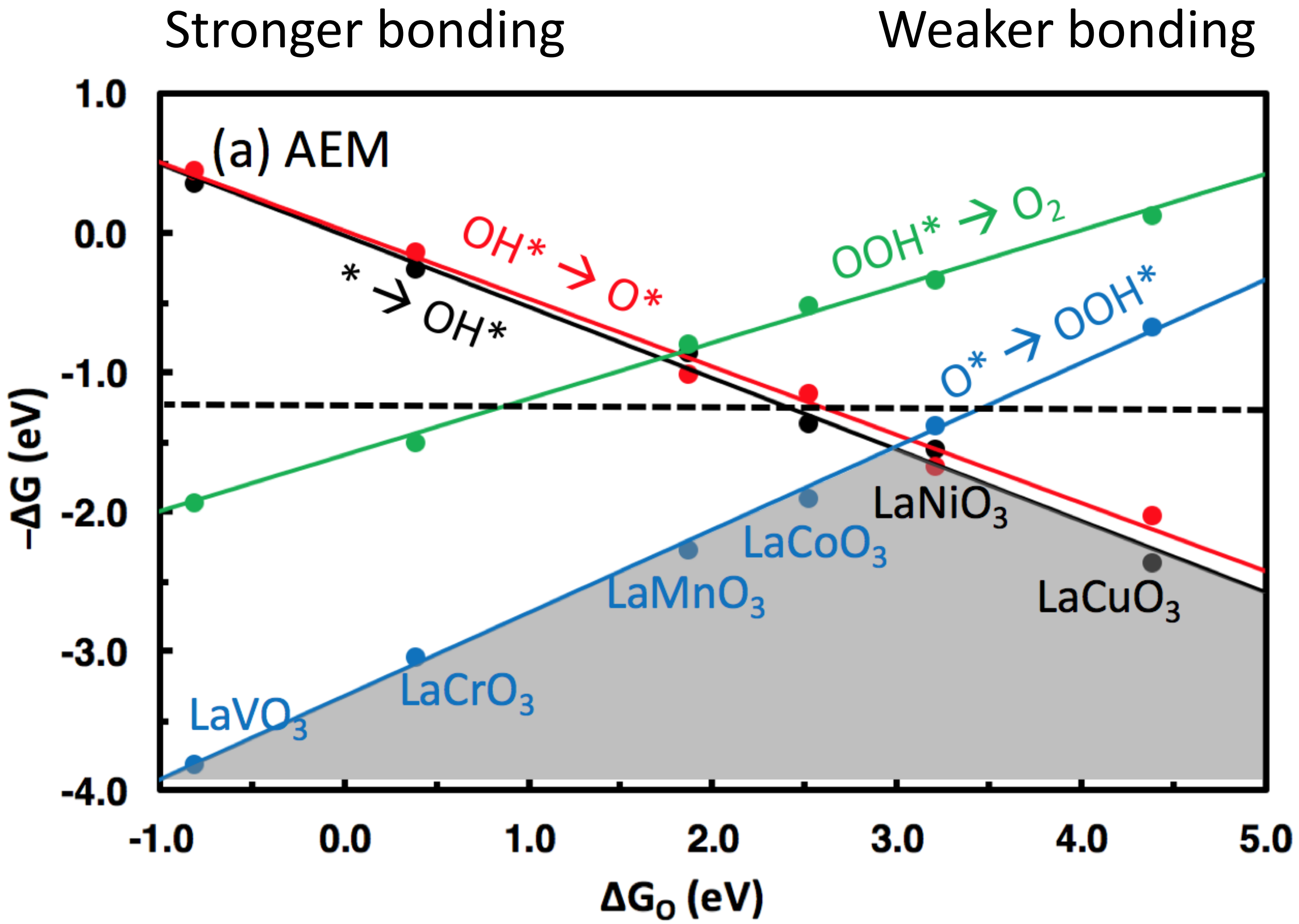
Mefford, et al, *Nature Comm. 7*, **2016**

Experiments show increasing activity with increasing bulk O vacancy concentration and O diffusion rate.

^{18}O isotope labeling experiments also show O lattice participation in LSCO.

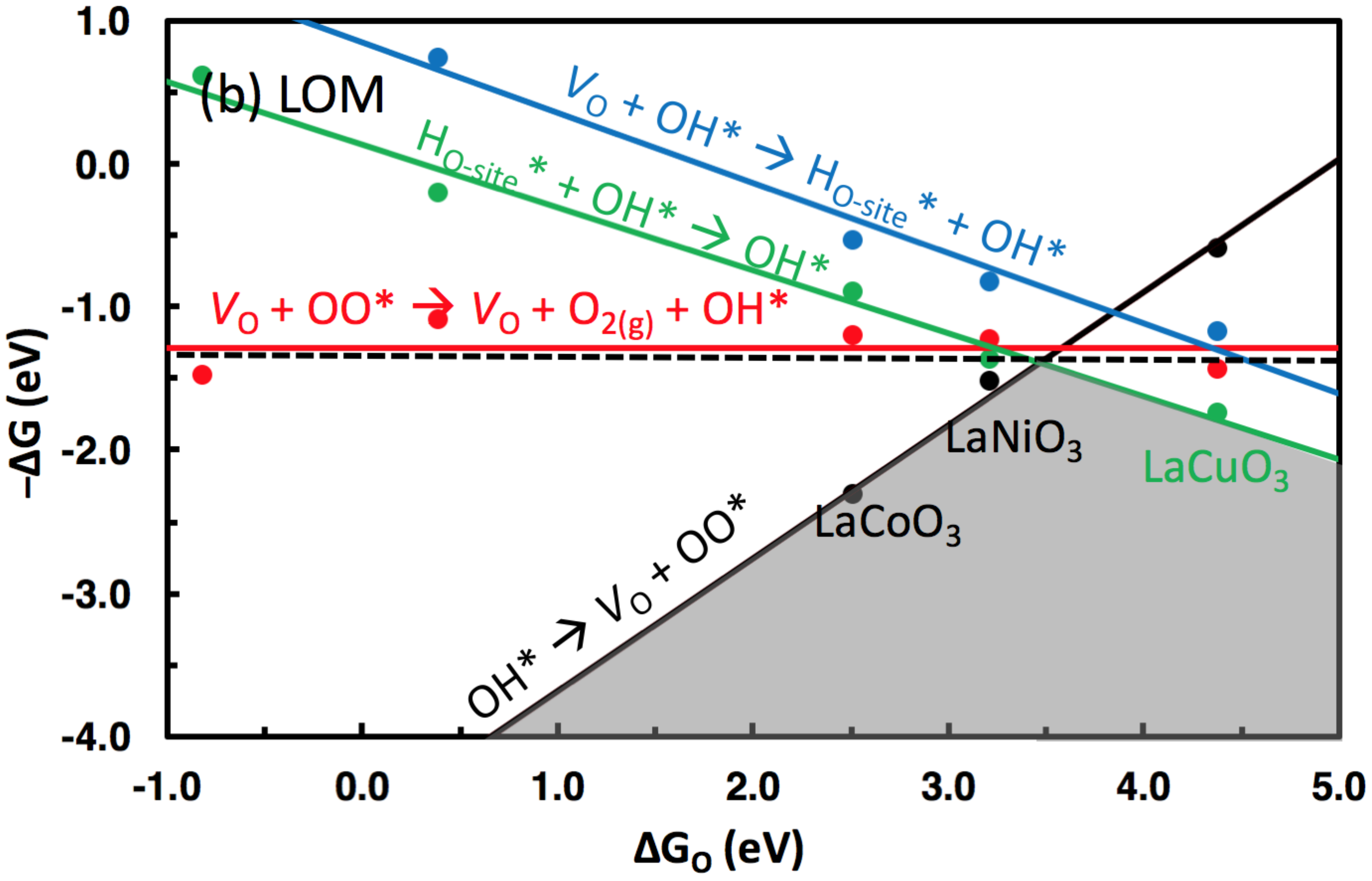
Grimaud et al*, Nat. Chem. 9*, **2017**

OER activity volcano plot for AEM

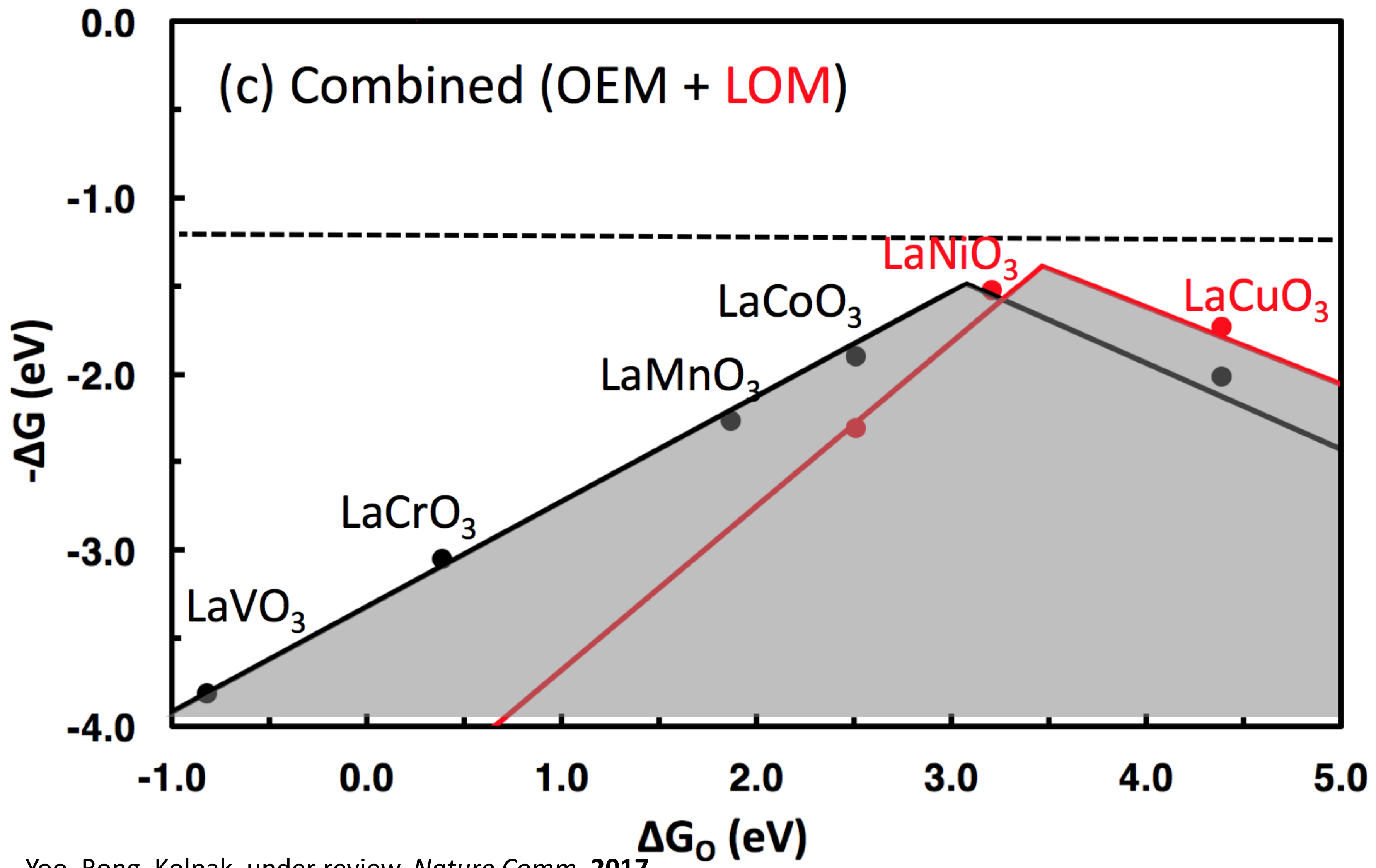


Problem: But what about BSCF, PBCO, LSCF? Weaker bonding than $LaNiO_3$, but higher experimental activity!

OER activity volcano plot for LOM

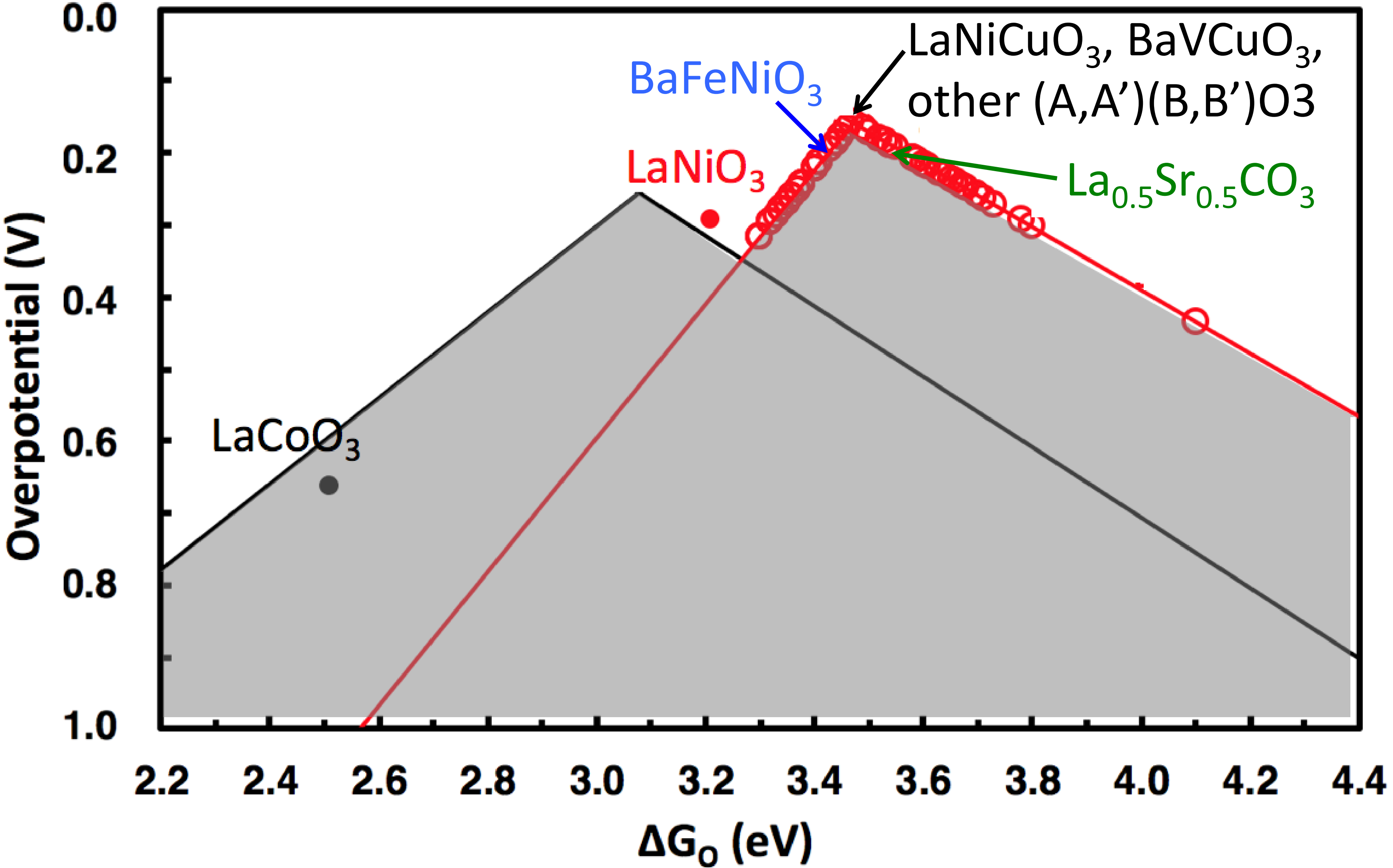


New OER volcano plot for perovskite oxides



Yoo, Rong, Kolpak, under review, *Nature Comm.* **2017**

Room for new materials at the top!



Yoo, Rong, Kolpak, under review, *Nature Comm.* **2017**

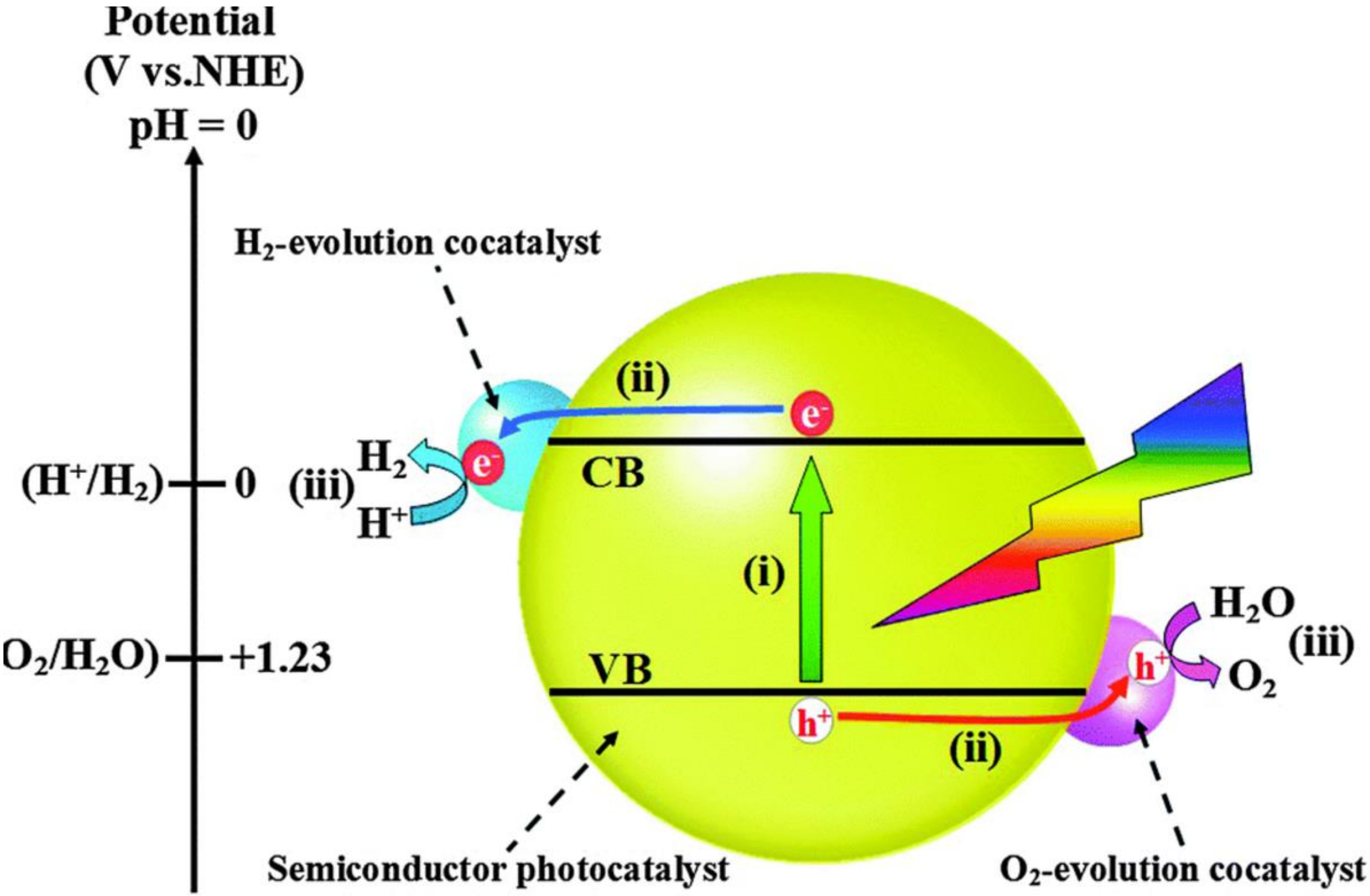
Conclusions (OER on Perovskites)

- Surface structure & stoichiometry is highly sensitive to the environment (and the components of the bulk).
- Free energies of reaction steps vary substantially depending on surface structure & stoichiometry.
- Reaction mechanism is material dependent & strongly correlated to stability
- Bulk oxygen *p*-band center, metal *d*-band center, e_g fillings, etc, are not good activity descriptors!
- Is there a good bulk activity descriptor? Most likely, but it's complicated!
- Bulk properties + environment → surface structure & stoichiometry → reaction mechanism & stability → activity & lifetime (performance)

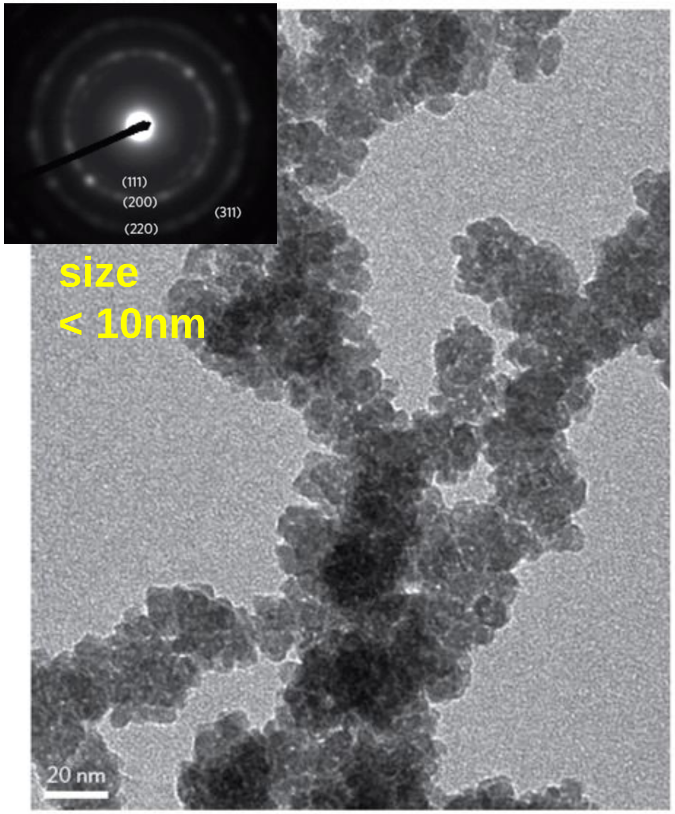
Outline

- Introduction & Motivation
- Computational Methods
- Catalyst/Water Interfaces
  - Electrochemical OER on Perovskite Oxides
  - Overall photocatalytic H_2O splitting on CoO
  - Au/Cu Nanoparticles in H_2O

Photocatalytic water splitting

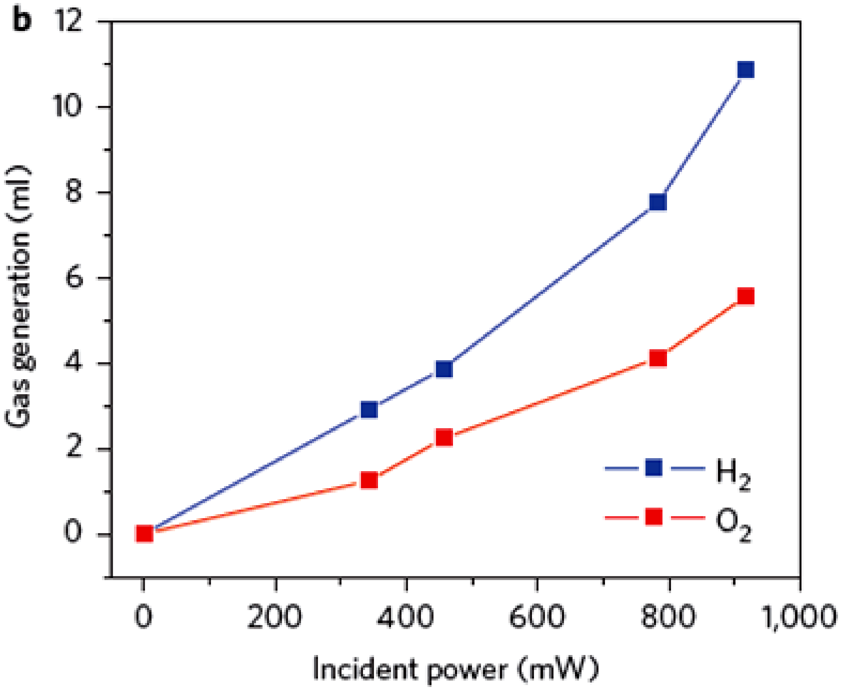


Overall photocatalytic water splitting with CoO nanoparticles



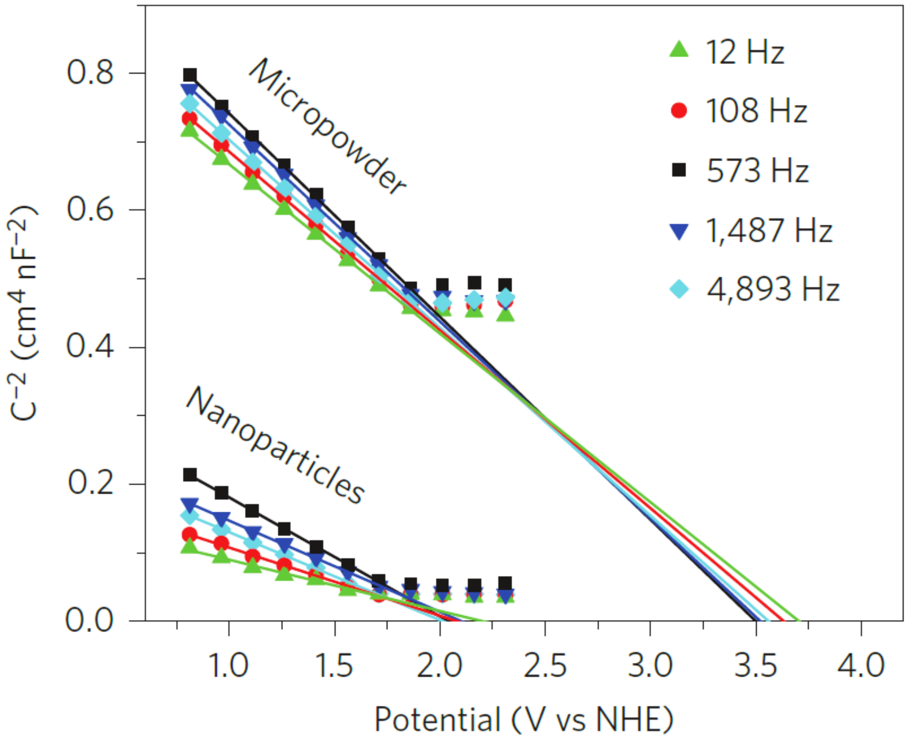
CoO nanoparticles show overall water splitting with a high efficiency (~5%)

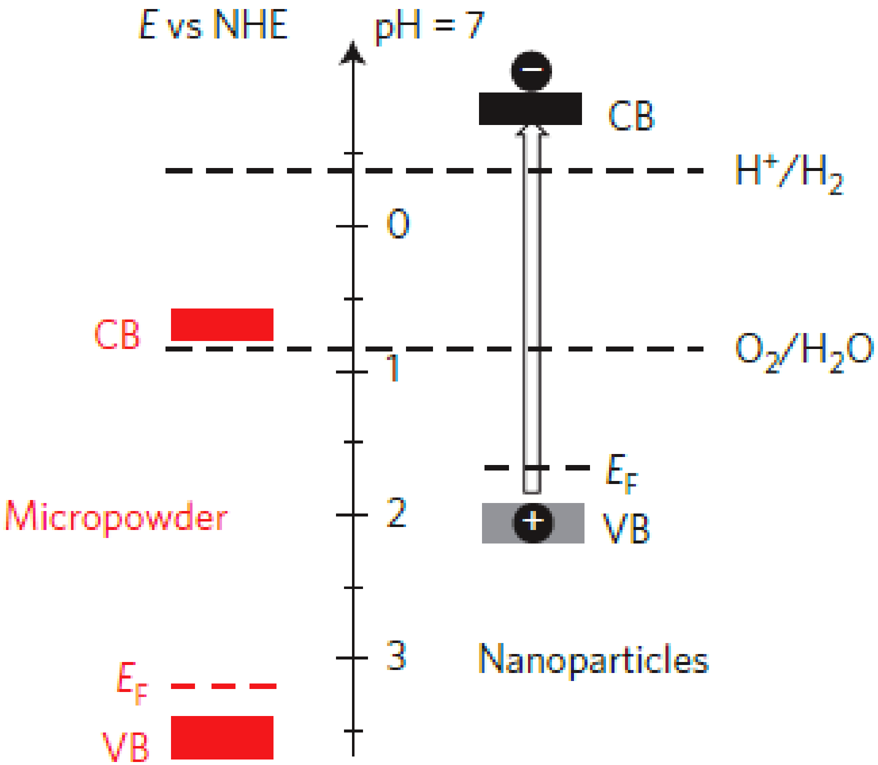
L. Liao et al, Nature nanotech., 9, 69 (2014)



1. No applied potential
2. No co-catalyst
3. No apparent change in pH (~6.9) (stoichiometric generation of H_2 and O_2)
4. No photocatalytic activity on CoO micropowder

Overall photocatalytic water splitting with CoO nanoparticles

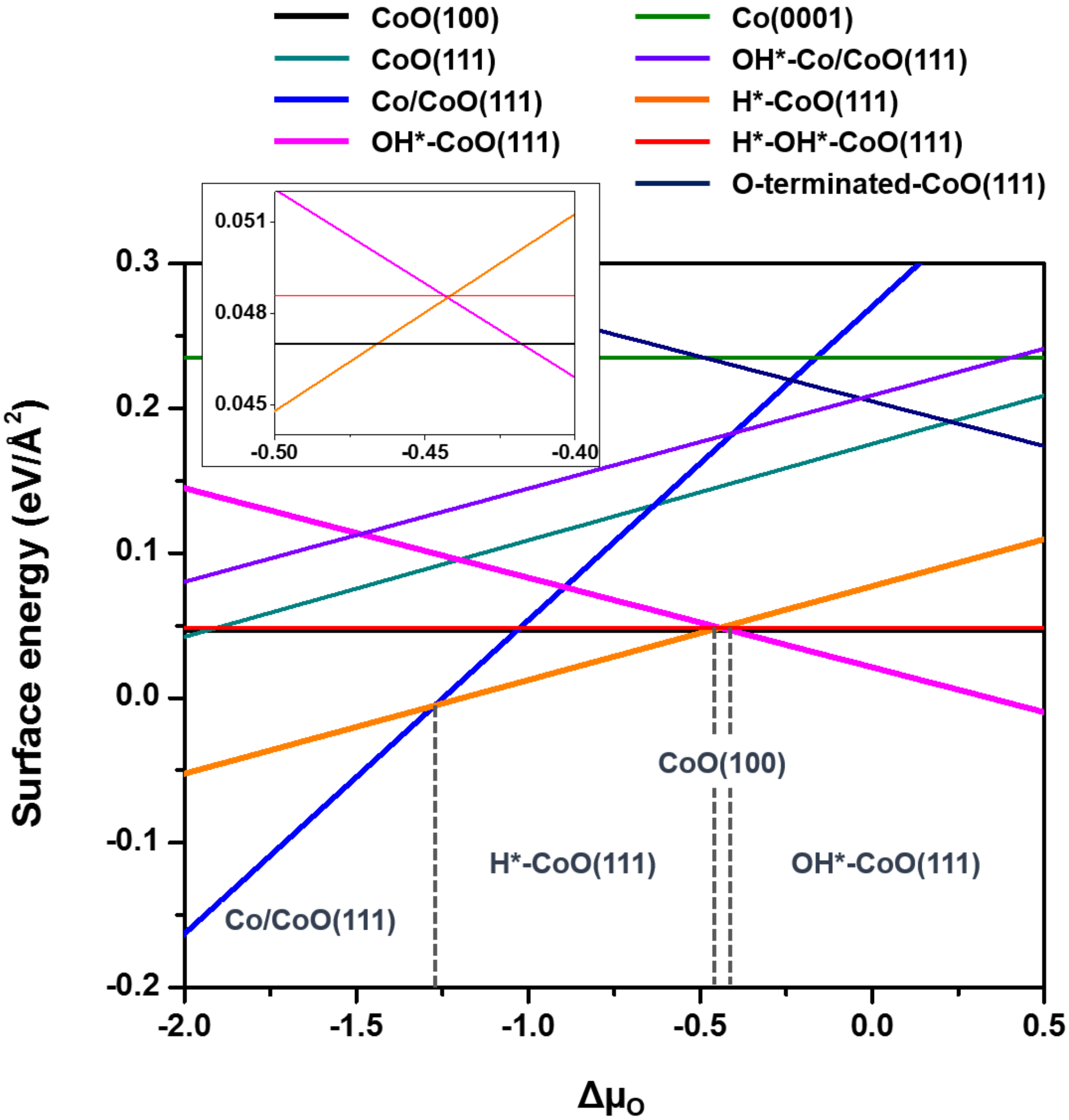




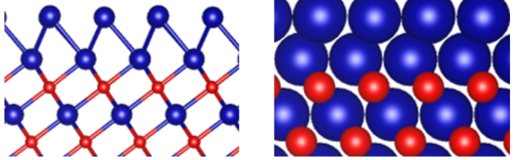
- No difference in band gap (no quantum confinement effect)
- Upward band shift for nanoparticles → band gap spans water redox potentials

L. Liao et al, Nature nanotech., 9, 69 (2014)

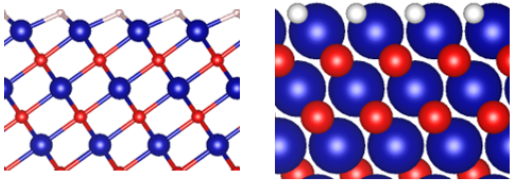
Thermodynamically stable CoO surfaces



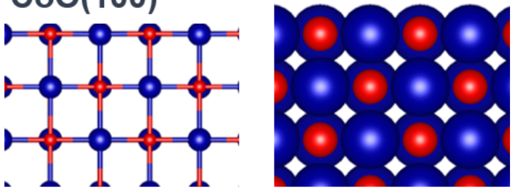
Co/CoO(111)



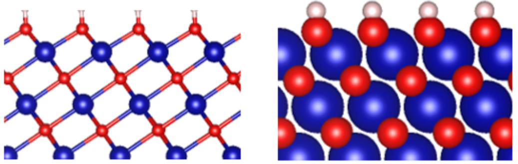
H*-CoO(111)



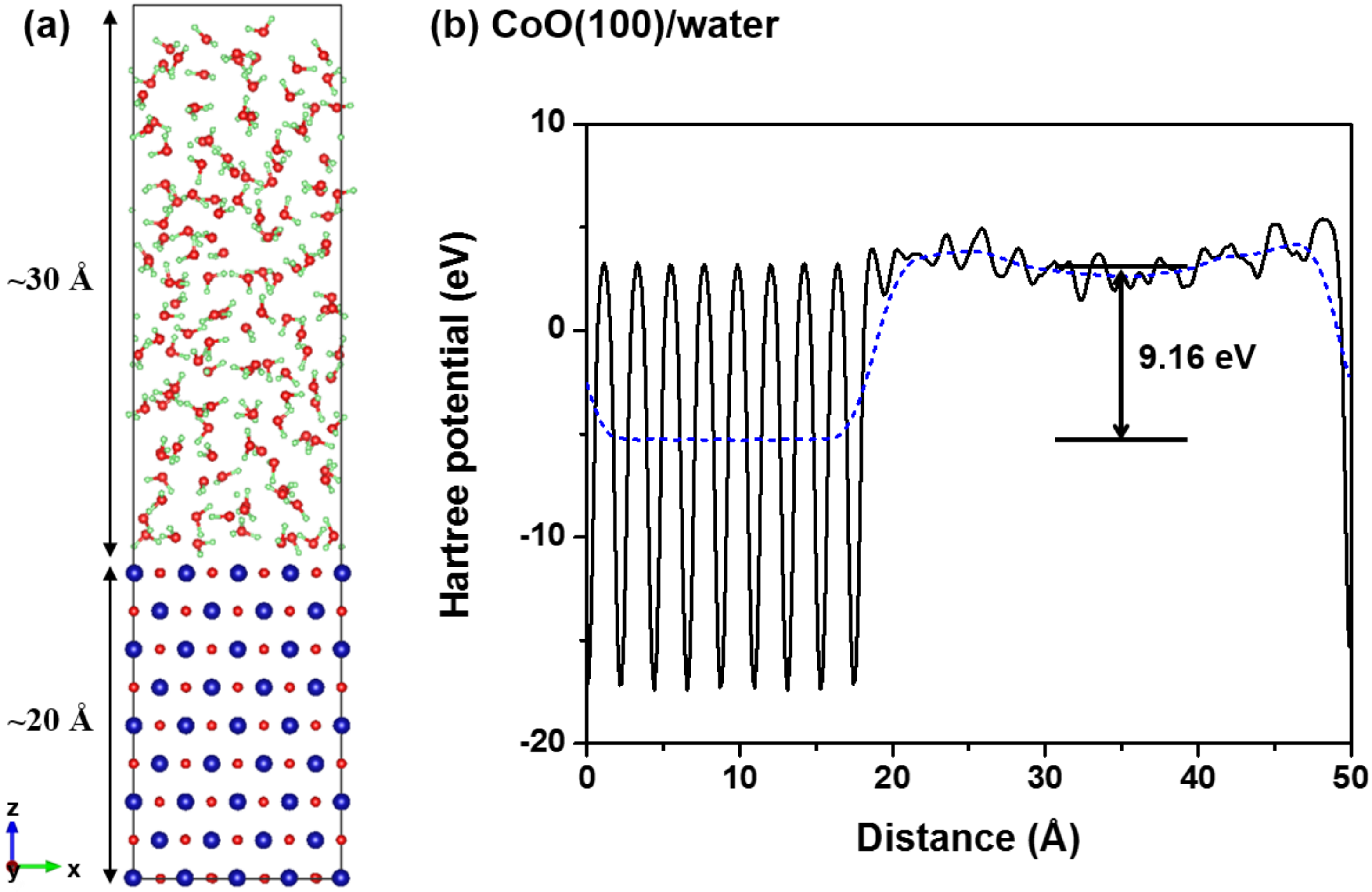
CoO(100)



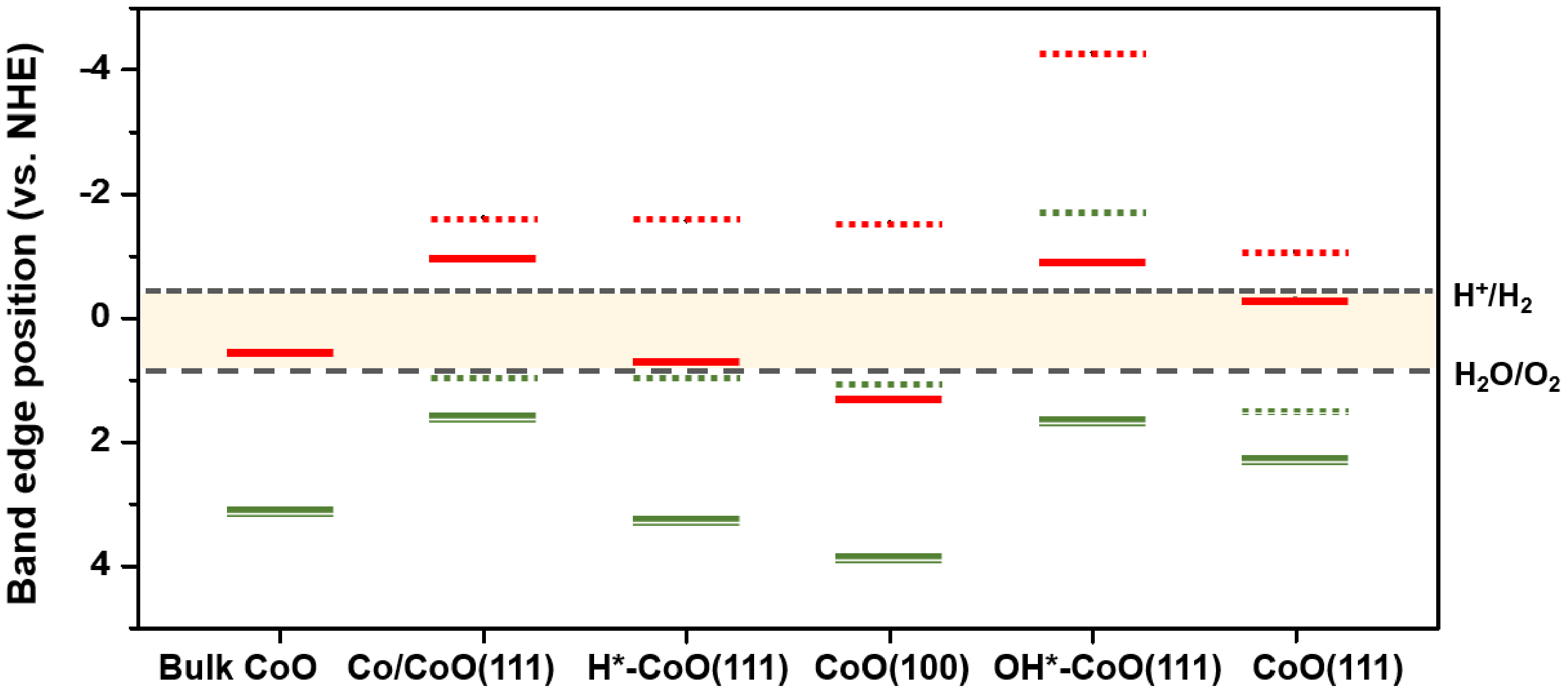
OH*-CoO(111)



Influence of explicit water on CoO band edges



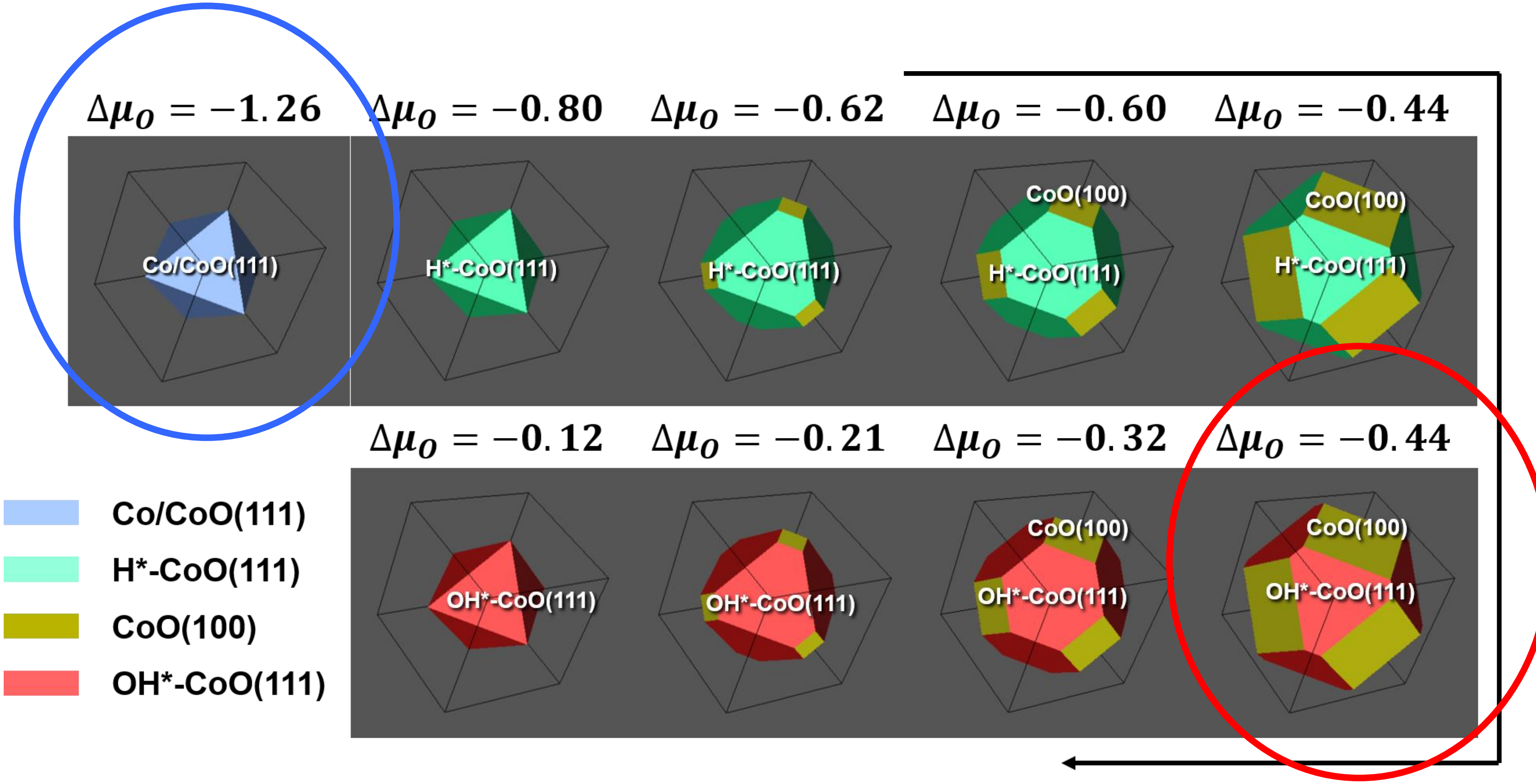
Influence of explicit water on CoO band edges



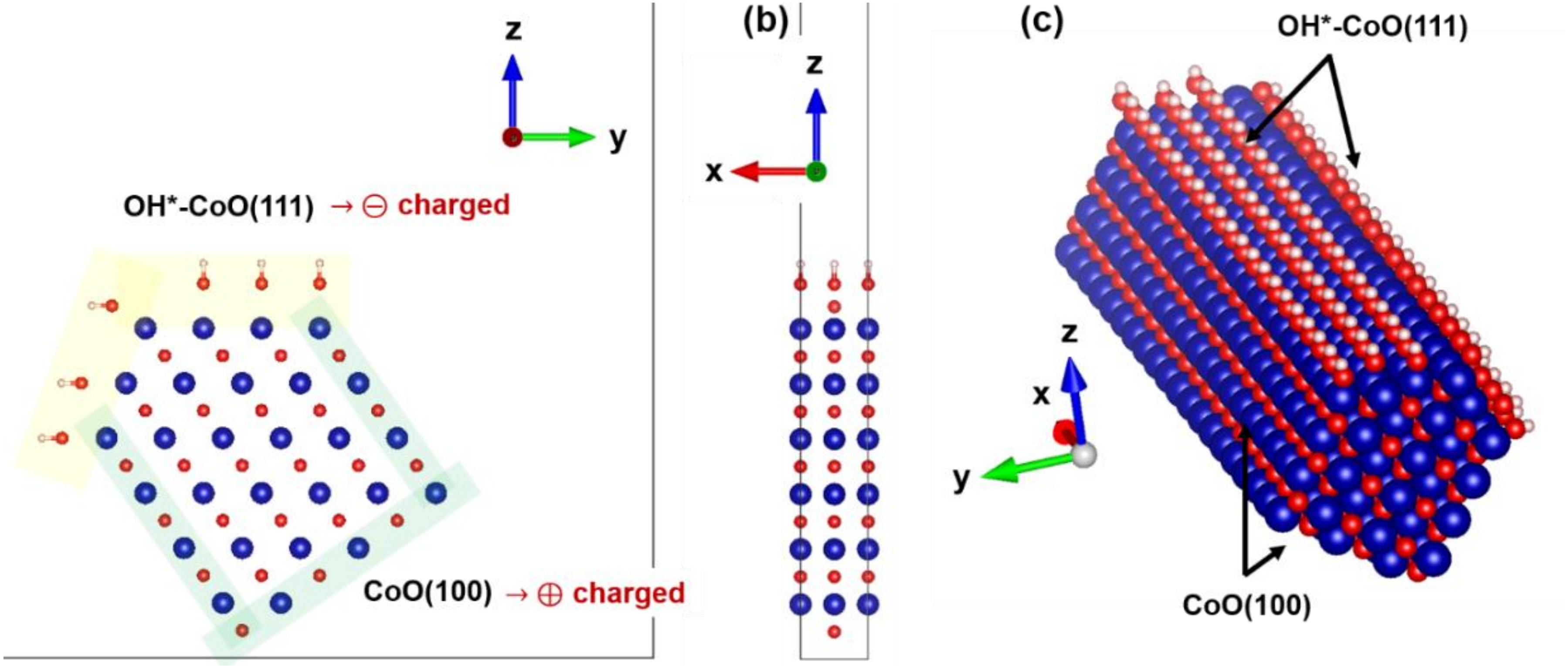
Band edges shift significantly with explicit water due to:

- Charge transfer/surface dipole modification
- CoO changes from AFM to non-magnetic ground state

CoO nanoparticle morphology vs conditions

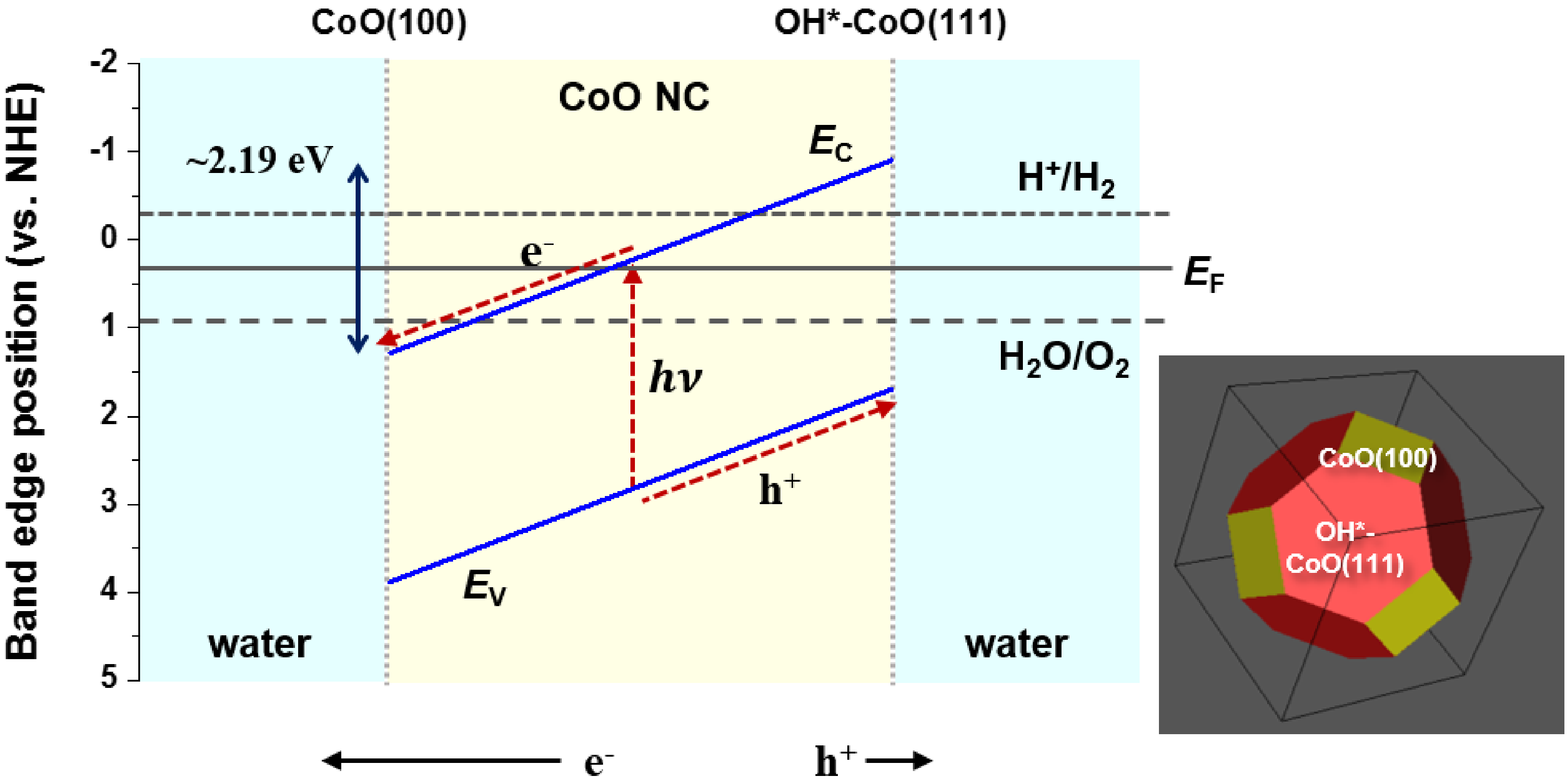


Charge separation in CoO nanoparticles

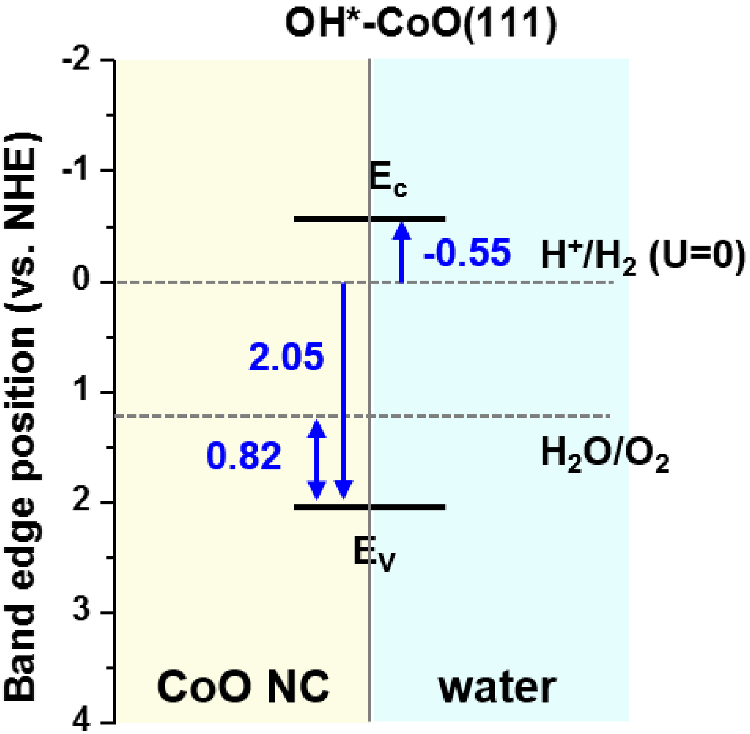


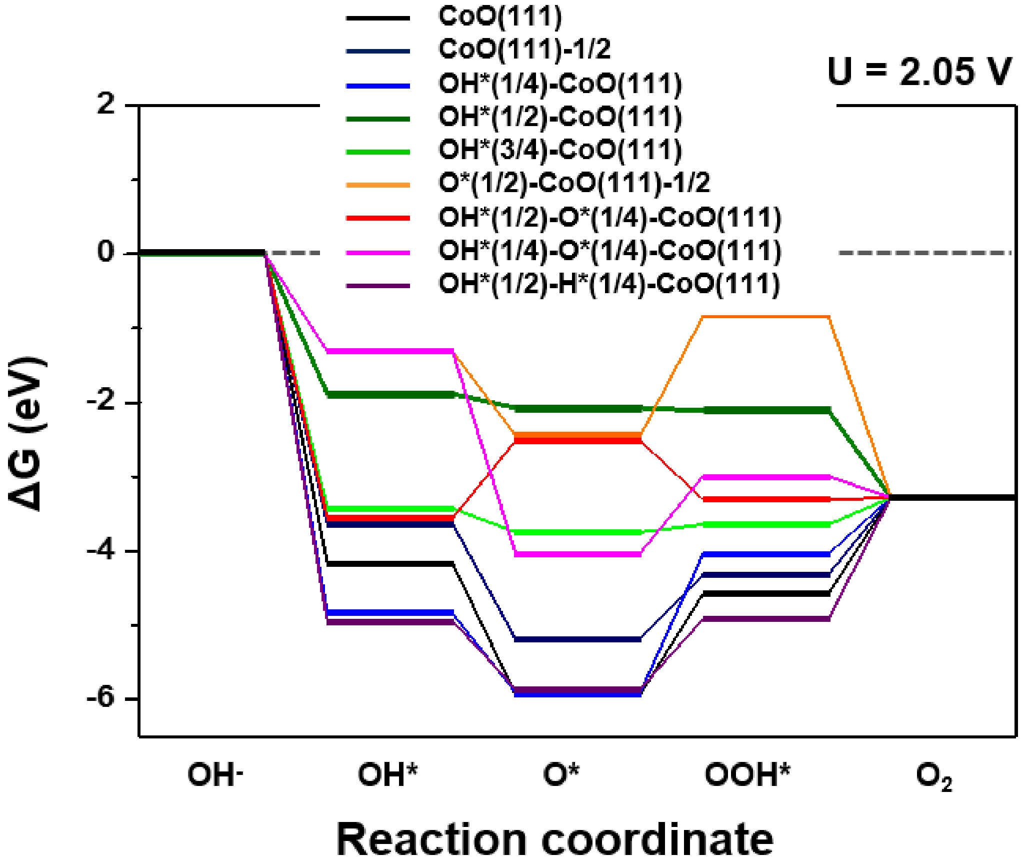
- Surface charge on each facet is similar to that on the isolated slabs → same band edge positions
- Built-in potential → excited e^- go to the CoO(100) surface, while excited h^+ go to the OH*-CoO(111) surface

Charge separation in CoO nanoparticles



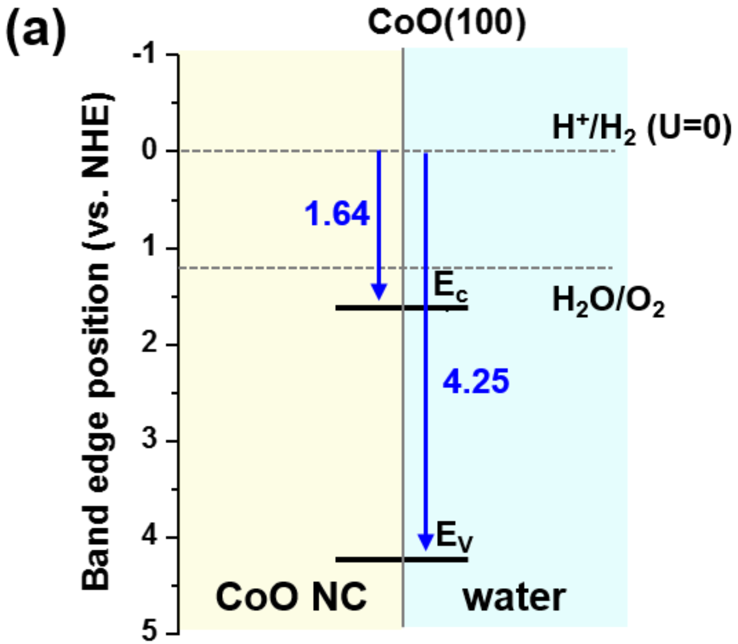
OER on the OH*-CoO(111) facets

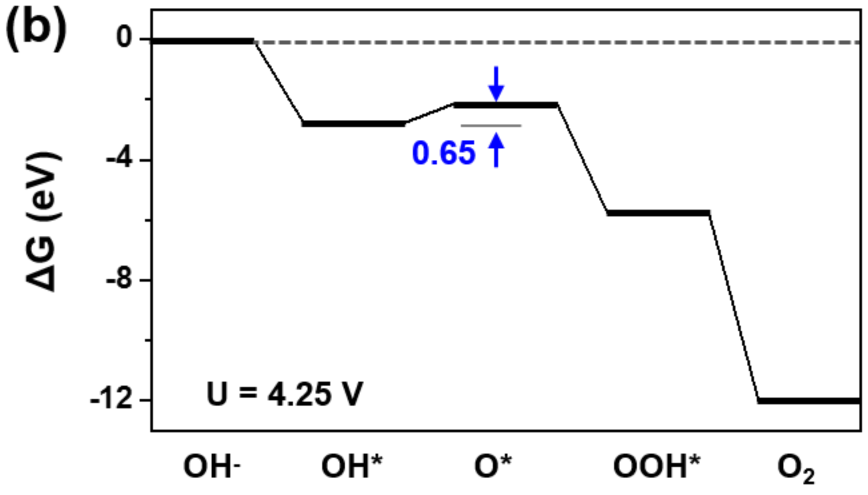


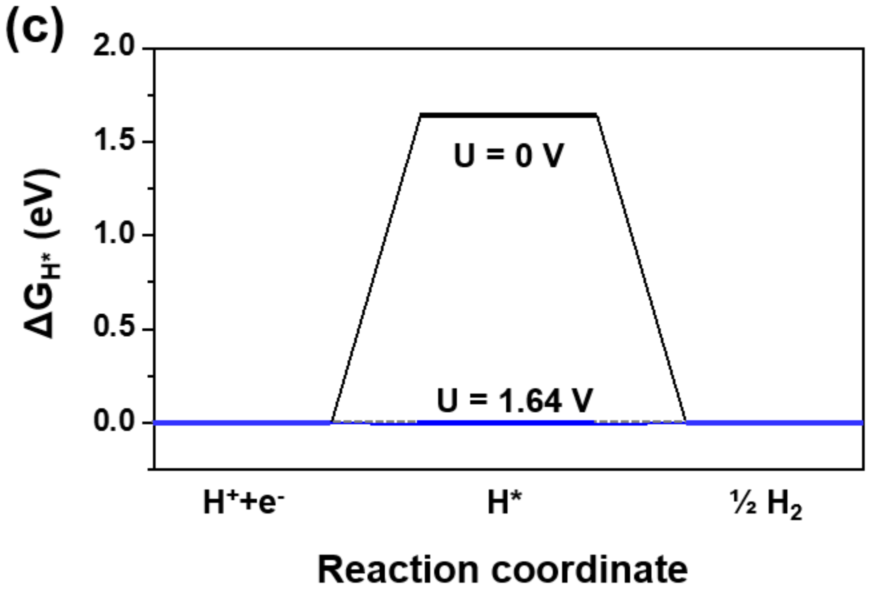


- Under photo-induced potential, OER can occur without additional applied potential for ½ OH coverage (dark green)
- No overpotential for HER on this surface either

HER on the CoO(100) facet







- Under photo-induced, no overpotential for HER, but OER requires an additional 0.65 V

Summary (Photocatalytic Water Splitting)

- Environment dependent surface structure and particle morphology
- Relative energies of surface phases are not sensitive to inclusion of liquid water in calculation
- Band edges are extremely sensitive to explicit inclusion of liquid water in calculation!
- Built-in potential due to band edges at different surfaces → efficient separation of photogenerated charges
- HER and OER primarily occur on different facets
- Relevant metric for feasibility of overal PC water splitting: Do the photoexcited carriers have sufficient energy to overcome highest barrier to HER/OER on relevant surface?

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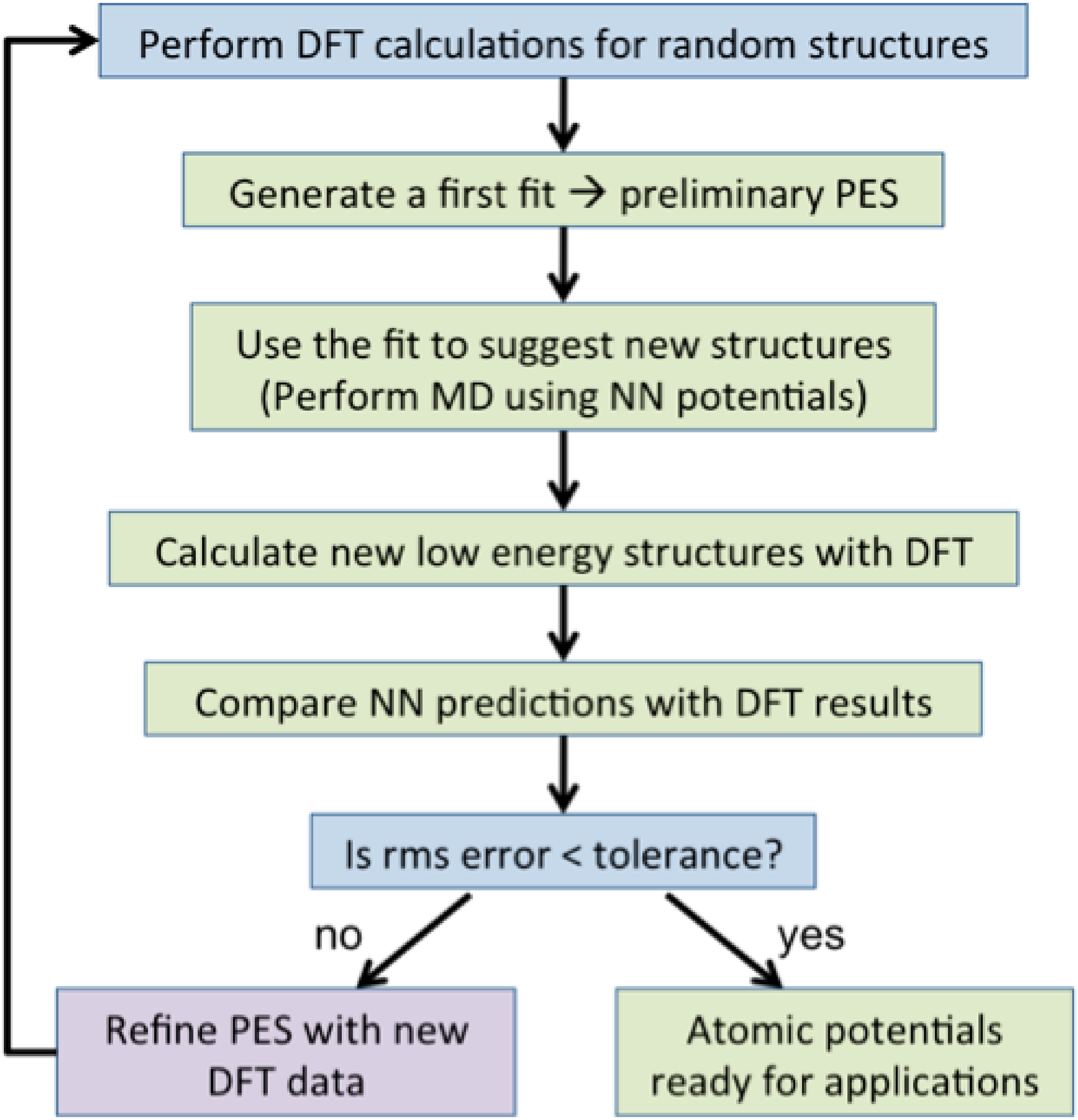
Gold-copper alloy nanoparticles for electrochemical CO_2 reduction

- How does the composition depend on synthesis conditions?
- How are different species distributed within the nanoparticle?
- How does the presence of explicit H_2O molecules affect the nanoparticle surface structure, composition, and morphology?
- How does the surface composition, etc., affect catalytic activity?

    - Need many atoms (large structures, many water molecules)
    - Need to perform many calculations (different compositions, atom arrangements, etc.)
    - Also need to include electronic effects…

Iterative procedure for constructing NNPs



Perform DFT calculations for random structures

Generate a first fit → preliminary PES

Use the fit to suggest new structures
(Perform MD using NN potentials)

Calculate new low energy structures with DFT

Compare NN predictions with DFT results

Is rms error < tolerance?

no

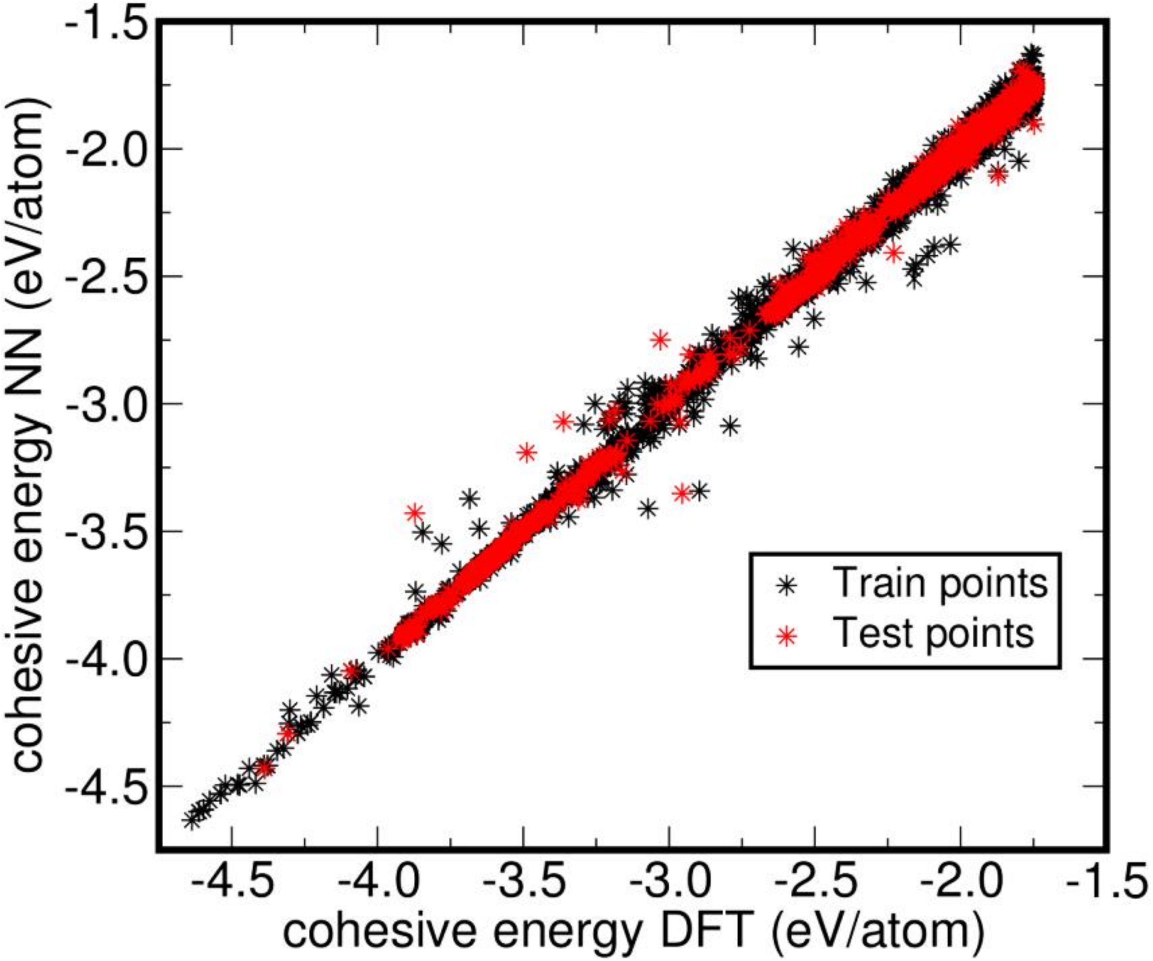
yes

Refine PES with new DFT data

Atomic potentials ready for applications

The accuracy and applicability of a NNP is ultimately governed by the quality and phase space of the input data set!

NN training for the Au/Cu/O/H system



Au/Cu/O/H Structures:

Ideal and distorted structures:
clusters, bulk structures,
surface slabs and molecules

Training data set ≈ 20,000
Test data set ≈ 2,000

Train (Test) Errors (meV/atom)
Energy RMSEs = **8.21 (12.45)**
Energy MAEs = **5.96 (6.04)**

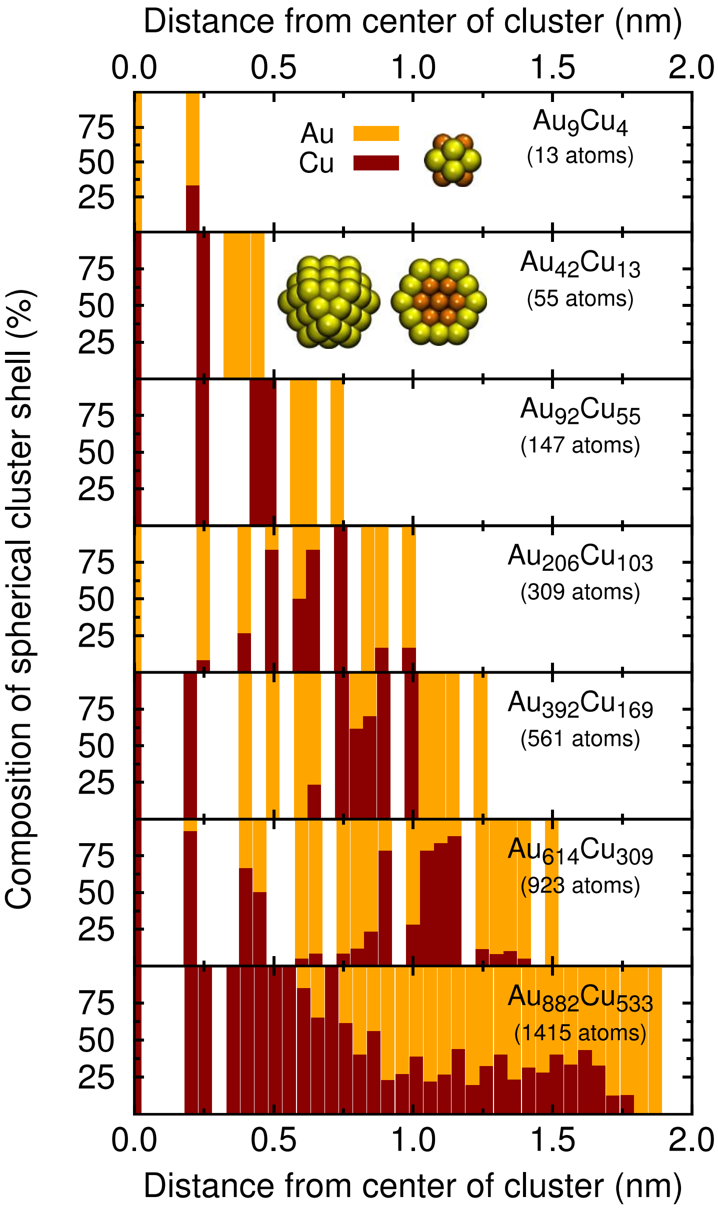
NNP code:

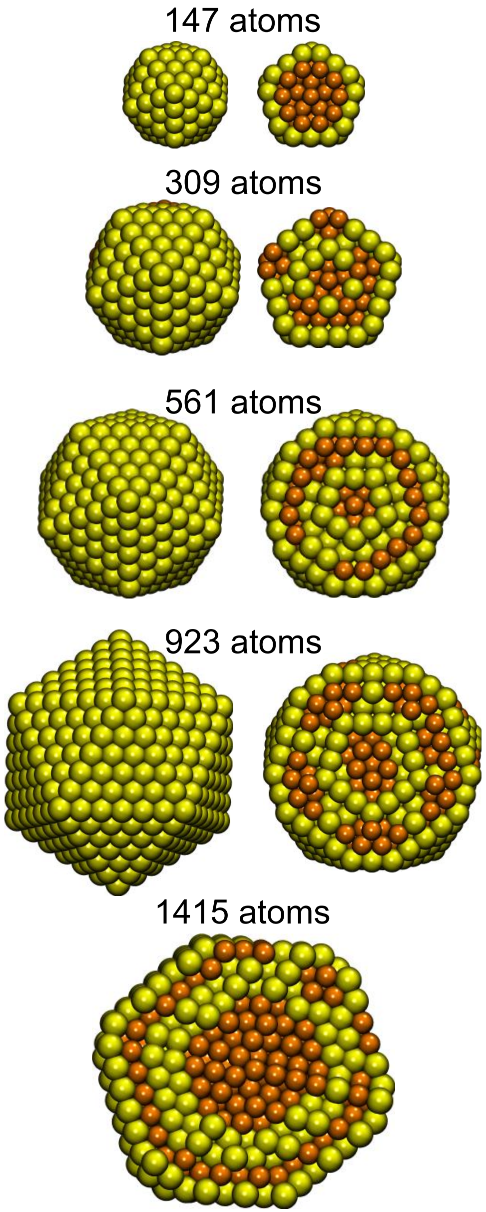
Artrith & Urban., *Comp. Mat. Sci.* 114, 135 (2016).

http://ann.atomistic.net

N. Artrith and A. M. Kolpak, *Nano Letters* **14**, 2670 (2014).
N. Artrith and A. M. Kolpak, *Comp. Mater. Sci.* **110**, 20 (2015).

Optimized composition and ordering

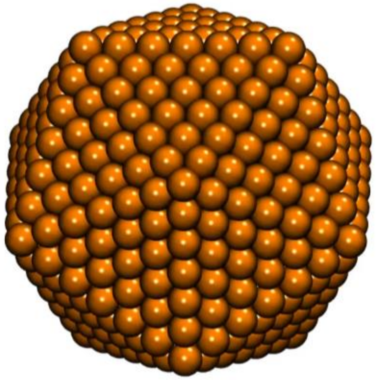


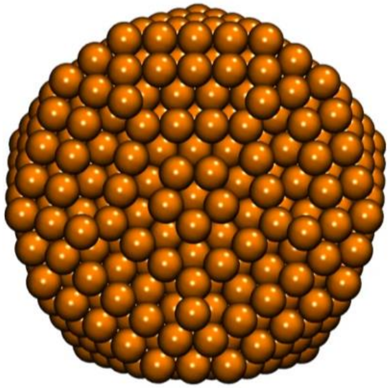


MC Annealing:

T= 5,000-300 K

Cluster 923 atoms

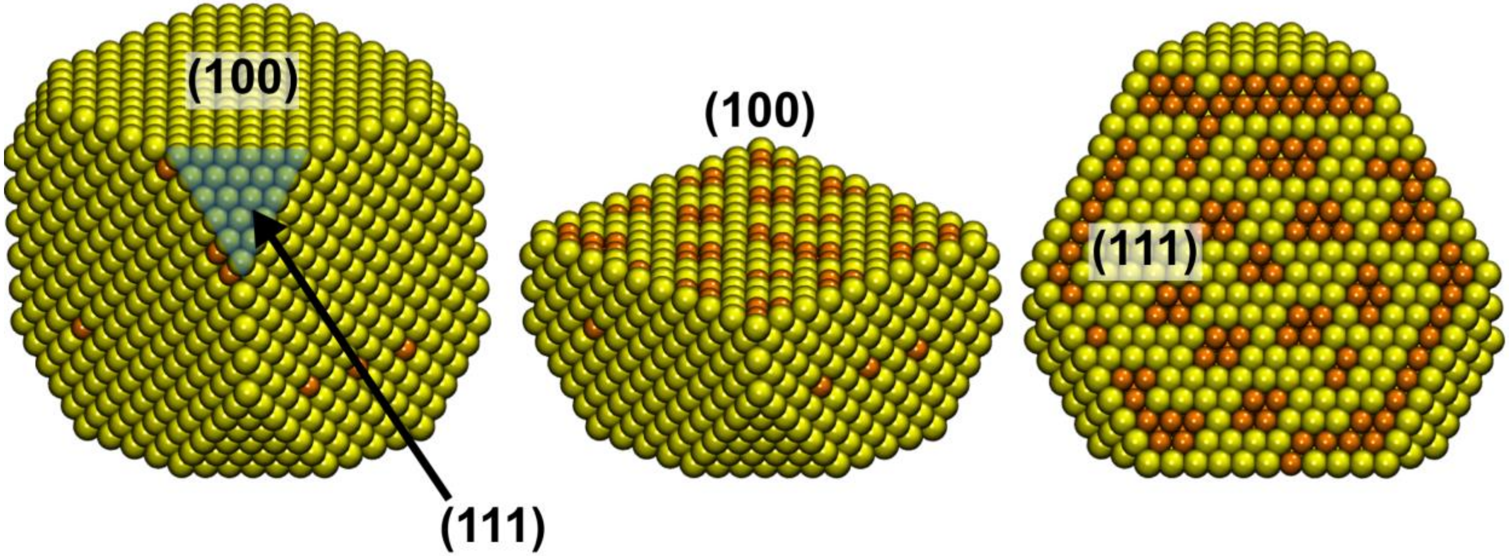


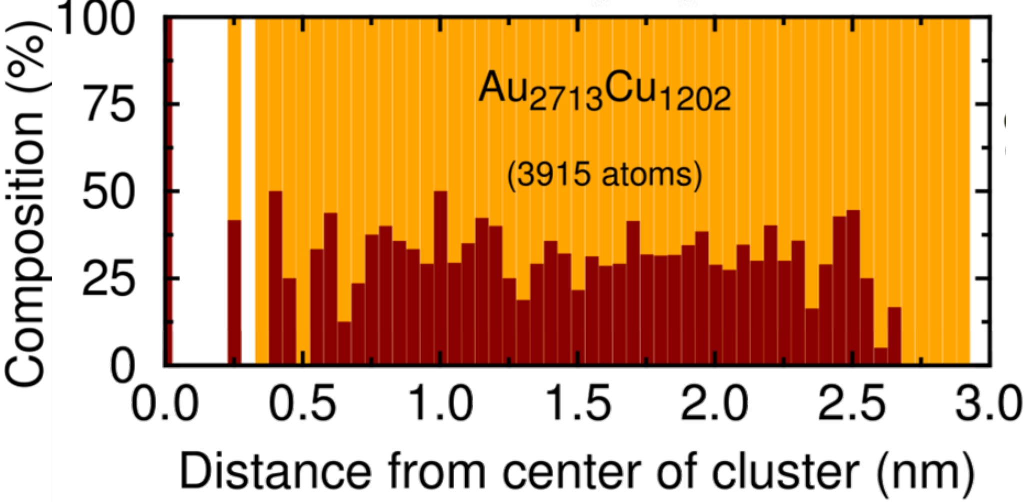


Cross-section

Cluster 923 atoms

Au/Cu nanoparticle composition and atomic distribution (in vacuum)

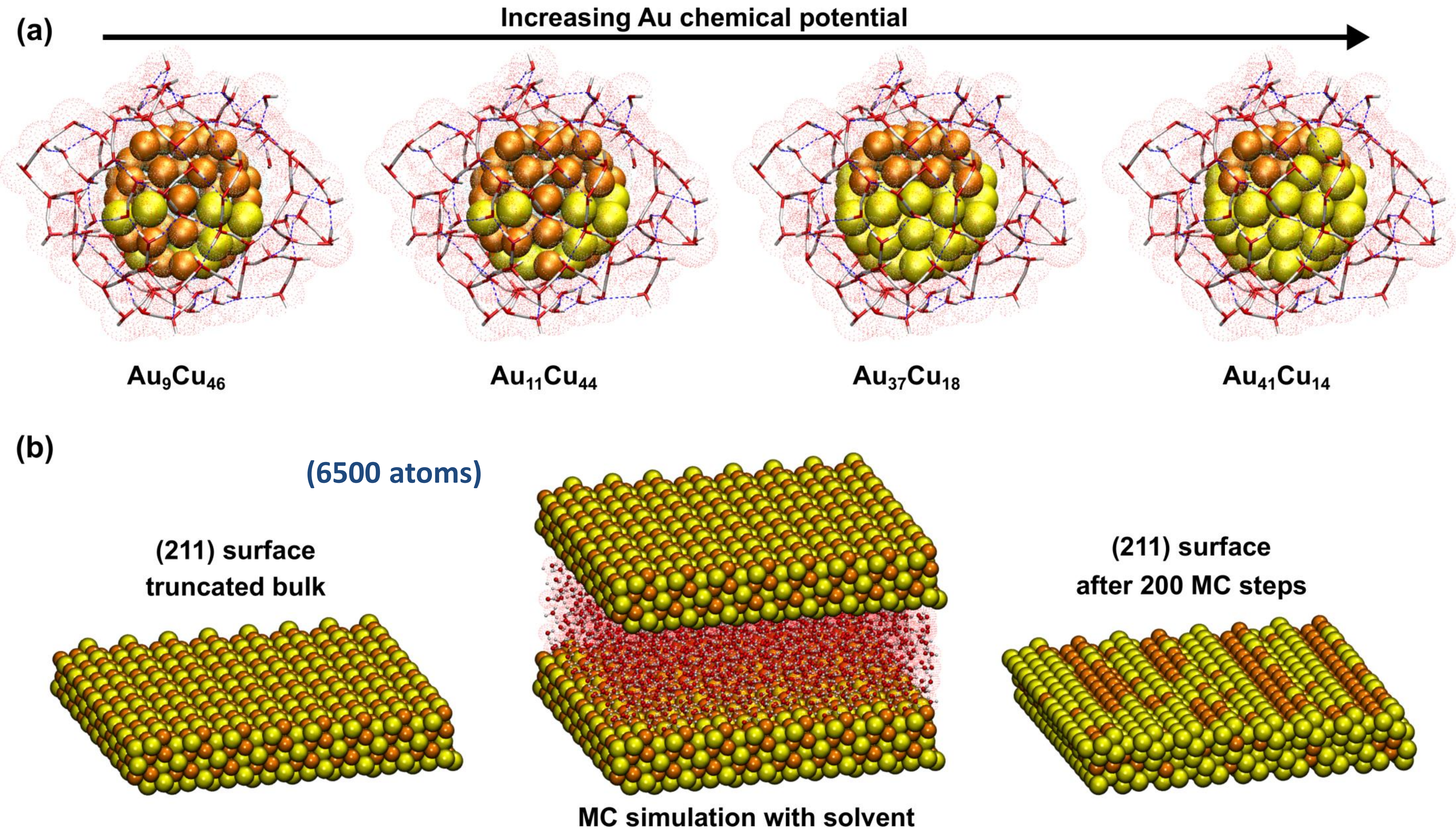




CPU time/structure: 147 atoms
DFT : 3.0 hours (16 cores)
NN : < 1 second (1 core)

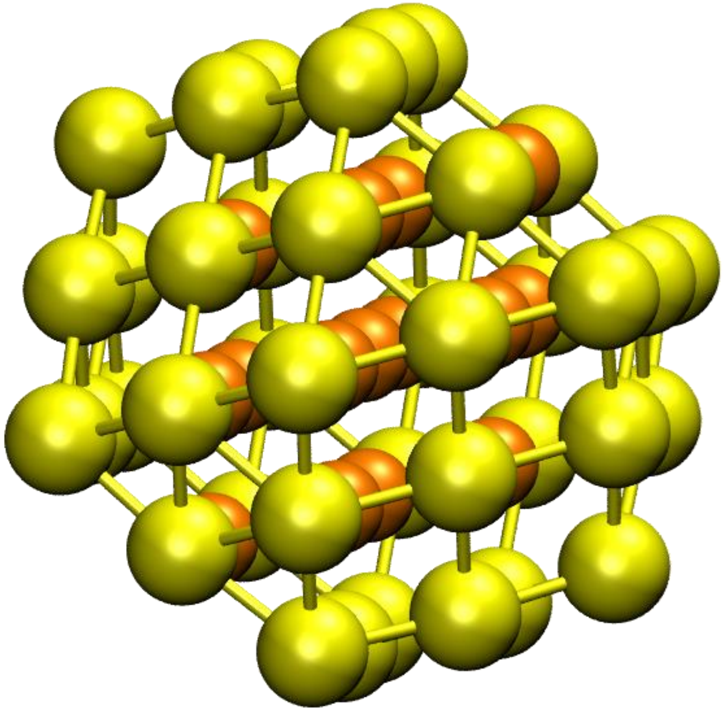
CPU time/structure: 3,915 atoms
DFT (scf only): ~3 years (512 cores)
NN : 59 seconds (1 core)

Inclusion of explicit H_2O molecules

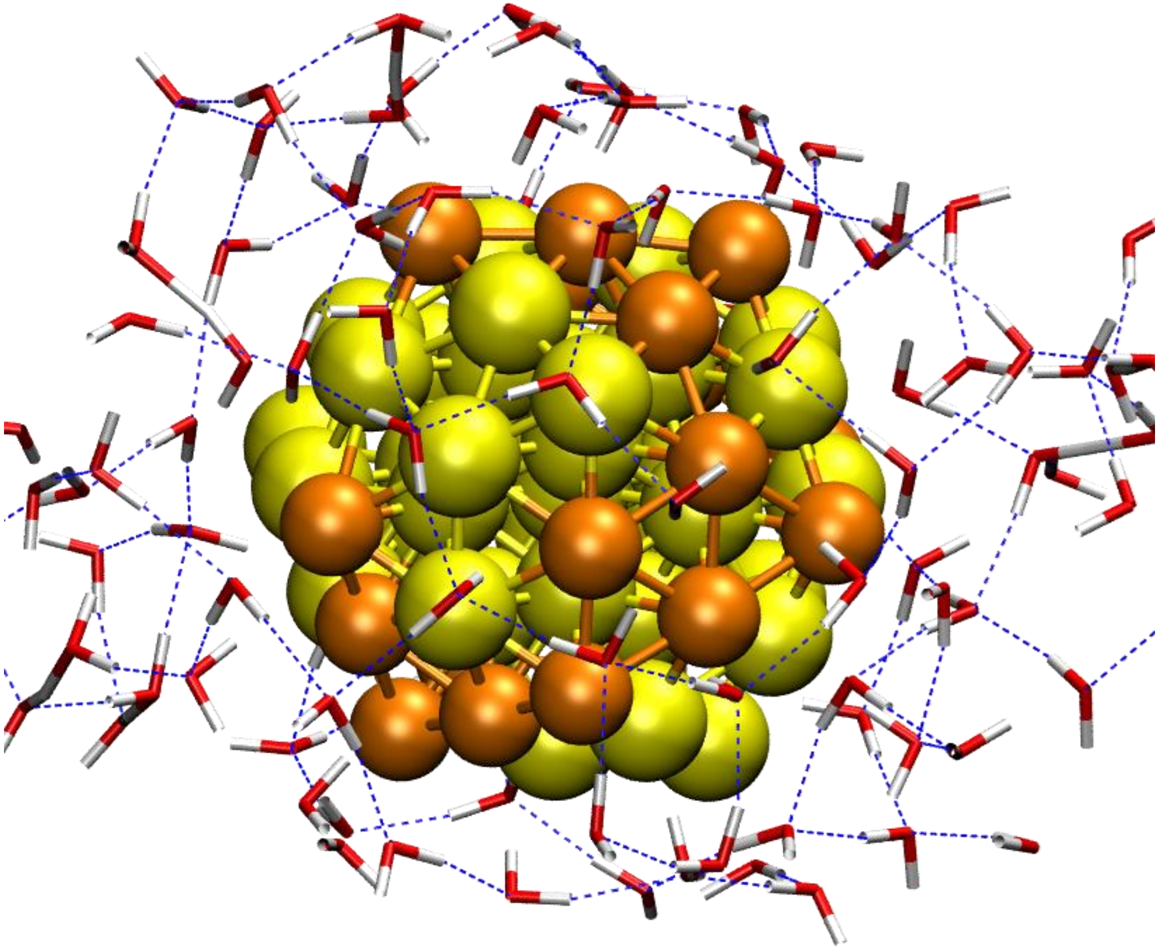


(6500 atoms)

Inclusion of explicit H_2O molecules



Core-shell nanoparticles stable in vacuum

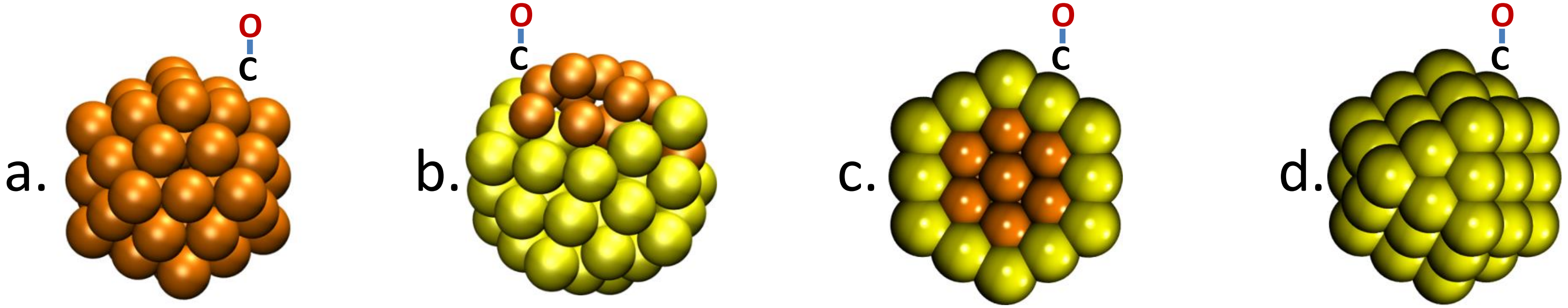


Copper atoms move to nanoparticle surface in H_2O

Surface composition effects on activity

Shape & ordering in liquid H_2O

Shape & ordering in vacuum



Clusters	CO_2 Energy(eV)	H_2 Energy(eV)	O_2 Energy(eV)	CO Energy(eV)
a. Cu_{55}	-0.194	-4.61	-1.49	-1.21
b. Au_{41} Cu_{14}	-0.191	-4.83	-0.44	-1.22
c. Au_{42} Cu_{13}	-0.187	-4.62	-0.11	-0.96
d. Au_{55}	-0.179	-4.60	-0.10	-0.90

⇒ Mixed $Au_{41}Cu_{14}$ and Cu-core/Au-shell $Au_{42}Cu_{13}$ NPs behave very differently

CAREER Award

Skoltech

Skolkovo Institute of Science and Technology

CNGMD

Incorporating Metastability


Dr. Brian Kolb


Dr. Nong Artrith

Schlumberger Foundation Faculty for the Future

NERSC

XSEDE

Extreme Science and Engineering Discovery Environment