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Machine Learning Meets Quantum Chemistry: Using Theory, Data, and Experiments to Design Catalysts

Siwen Wang

Materials Design

February 2021

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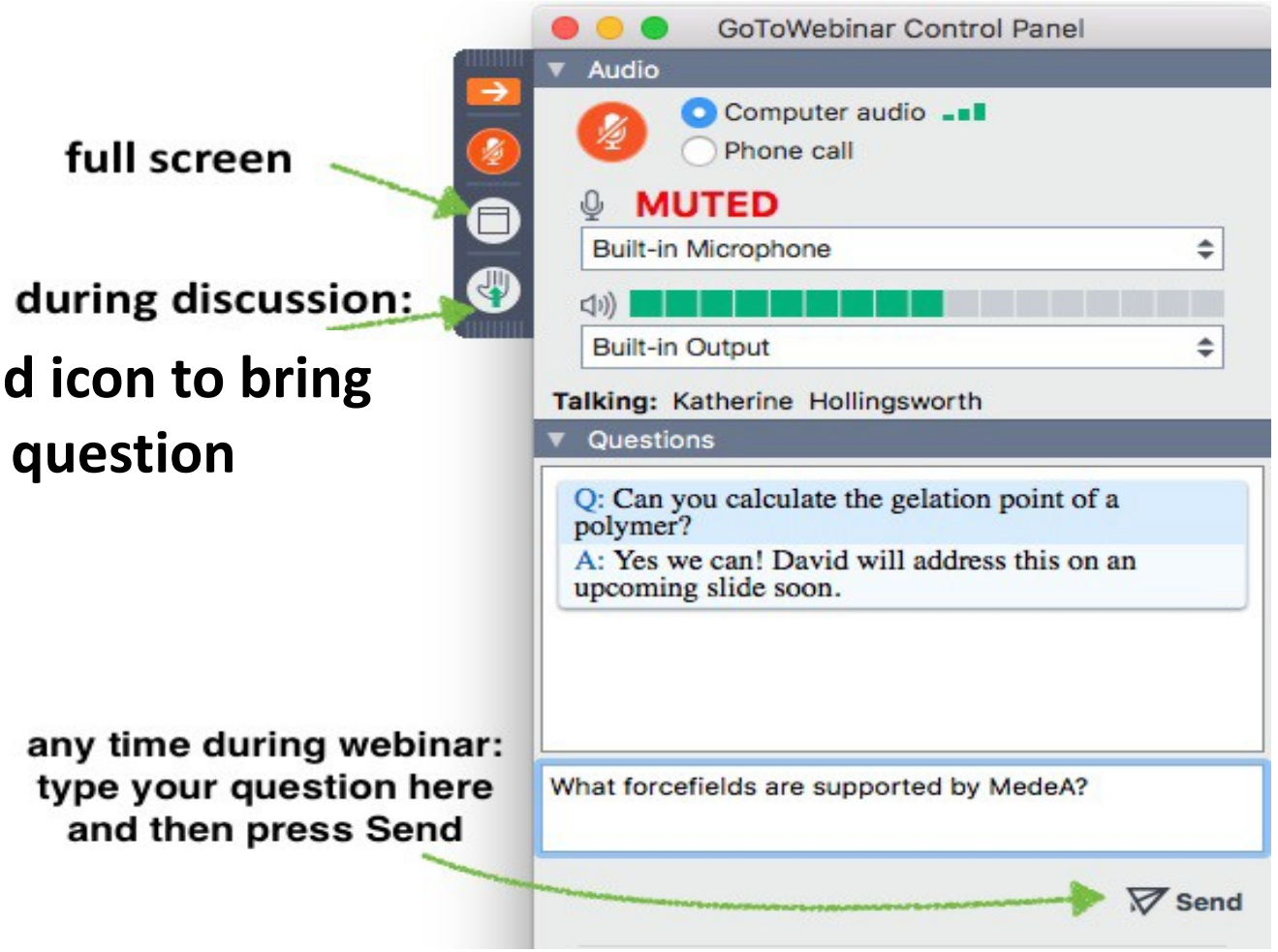

Use the raise hand icon to bring attention to your question

Webinar Speakers

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Siwen Wang
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Taylor Juran
tjuran@materialsdesign.com

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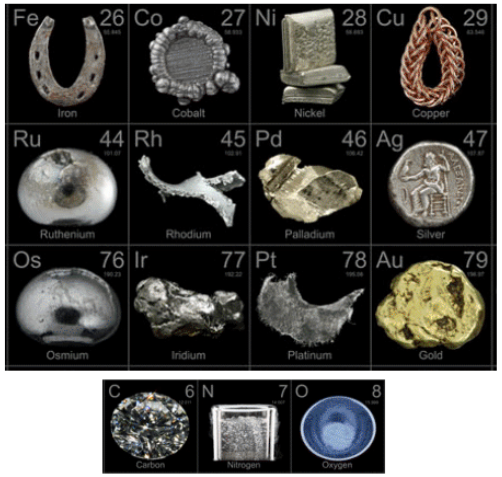
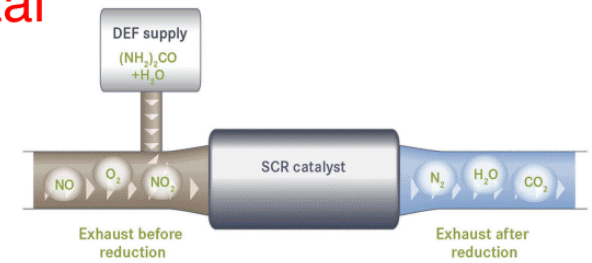
Why Catalysis?



chemical/
energy
transformation

environmental
remediation

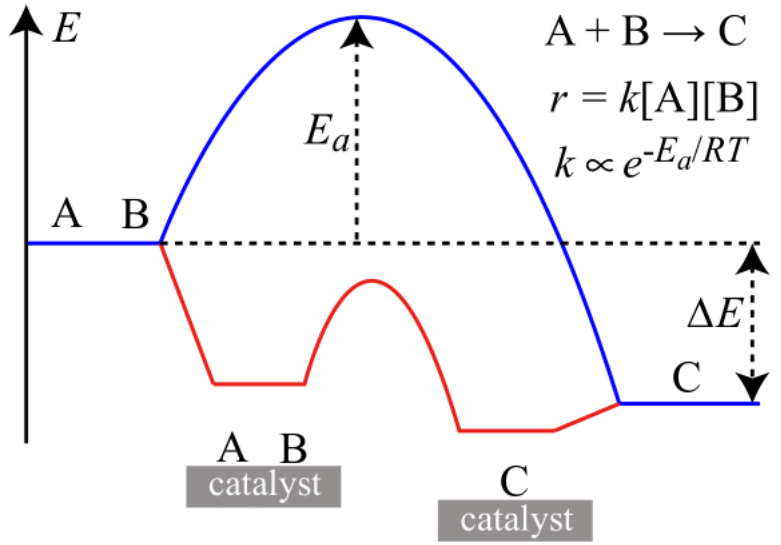


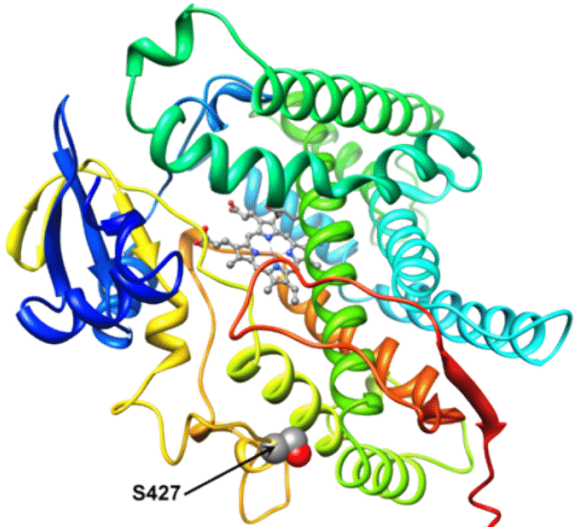
What is Catalysis?

Modern definition of catalysis

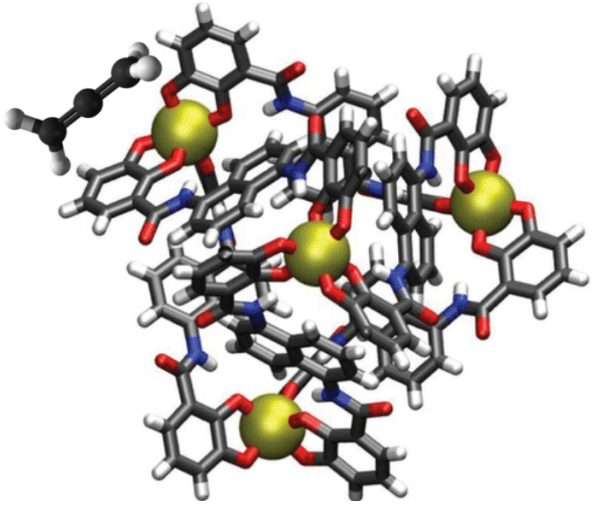
Catalysis is the acceleration of a slowly proceeding chemical reaction through the presence of a foreign substance.

Wilhelm Ostwald 1894

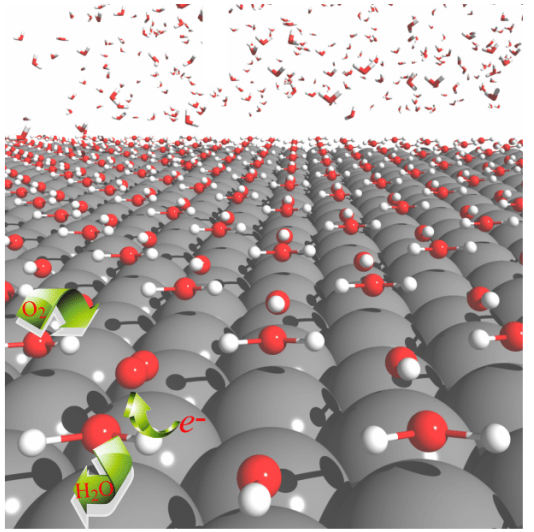




Enzyme Catalysis

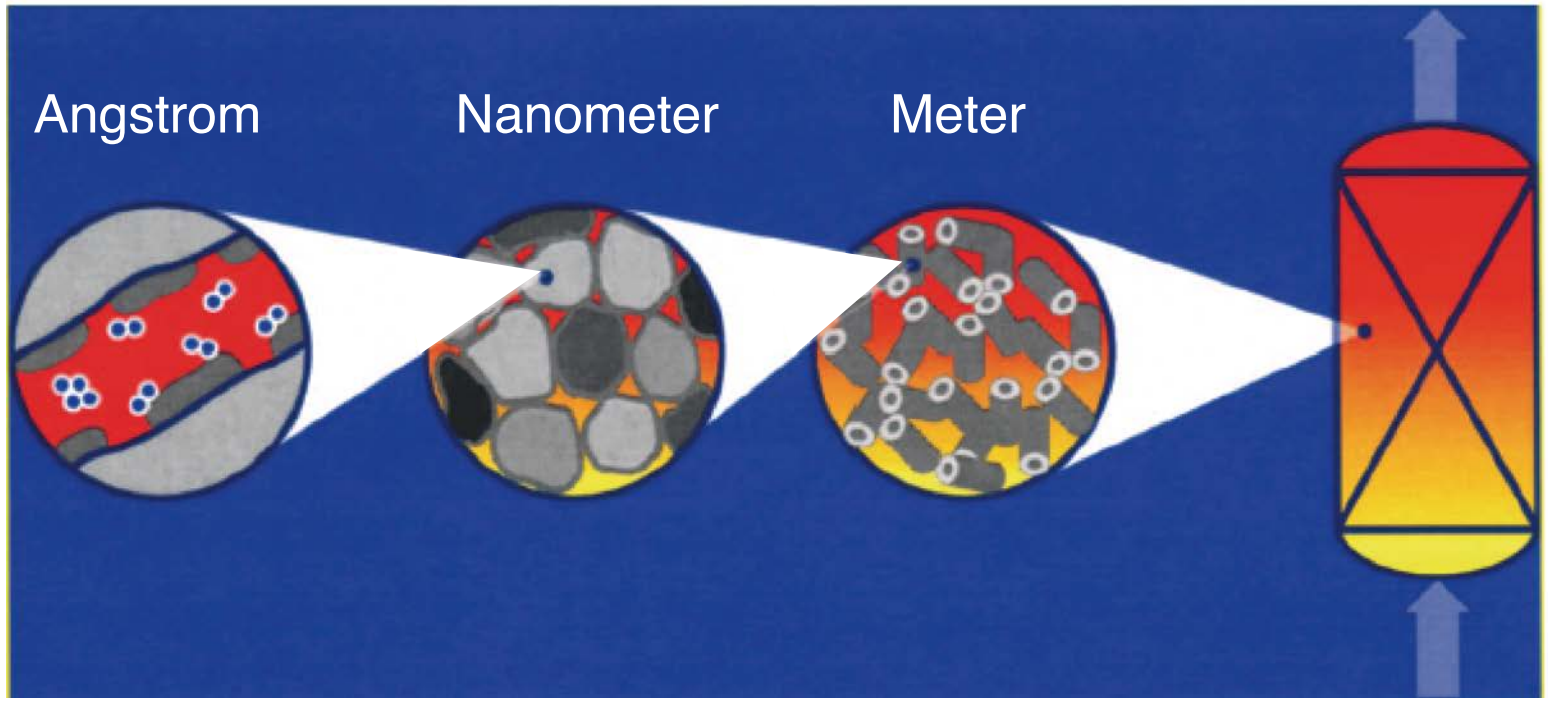


Homogeneous Catalysis

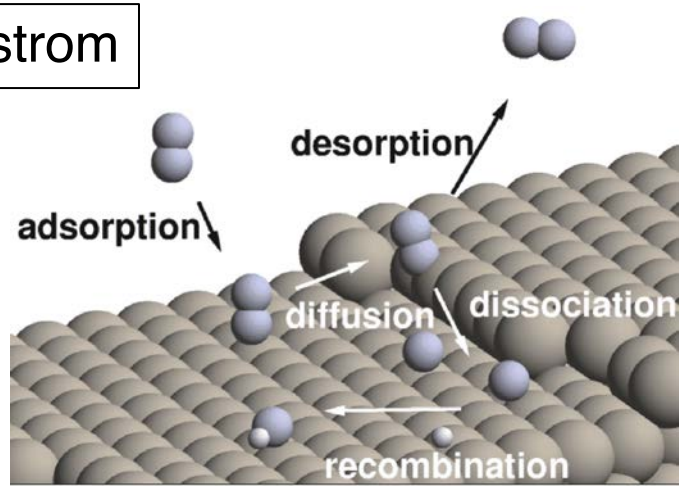


Heterogeneous Catalysis

Time and Length Scales in Heterogeneous Catalysis

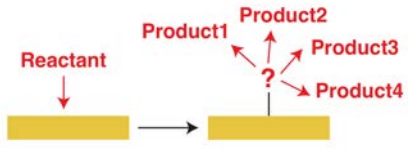


Angstrom



- Elementary events at molecular level control the catalytic performance.
- Understanding the surface chemical bonding is the key to catalyst design.
- Challenge: Rational design of catalytic sites with desired electronic properties.

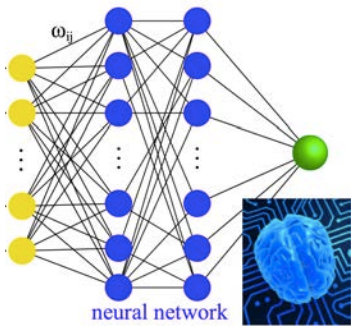
Outline



01 Understand Reaction Mechanisms

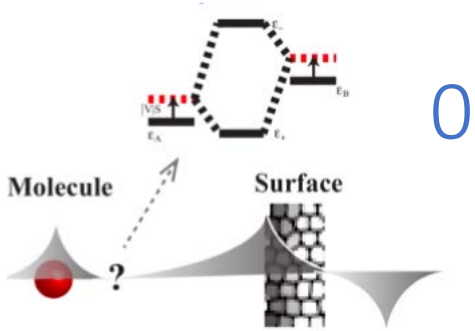
Biopolymer interaction effect in C_2H_2 hydrogenation reaction on Pd catalysts

Surface strain effect in CO_2 reduction reaction on $AgSn/SnO_x$ core-shell catalysts



02 Accelerate Materials Discovery

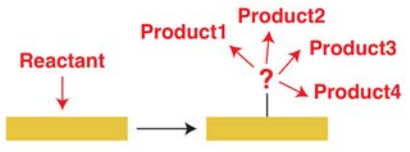
High-throughput screening of bimetallic catalysts enabled by machine learning



03 Advance Catalysis Theory

What determines reactivity of catalyst

Outline



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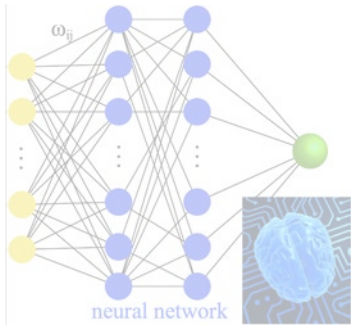

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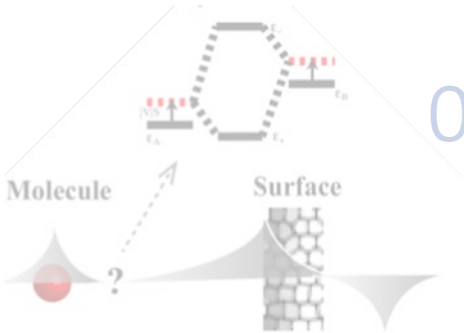
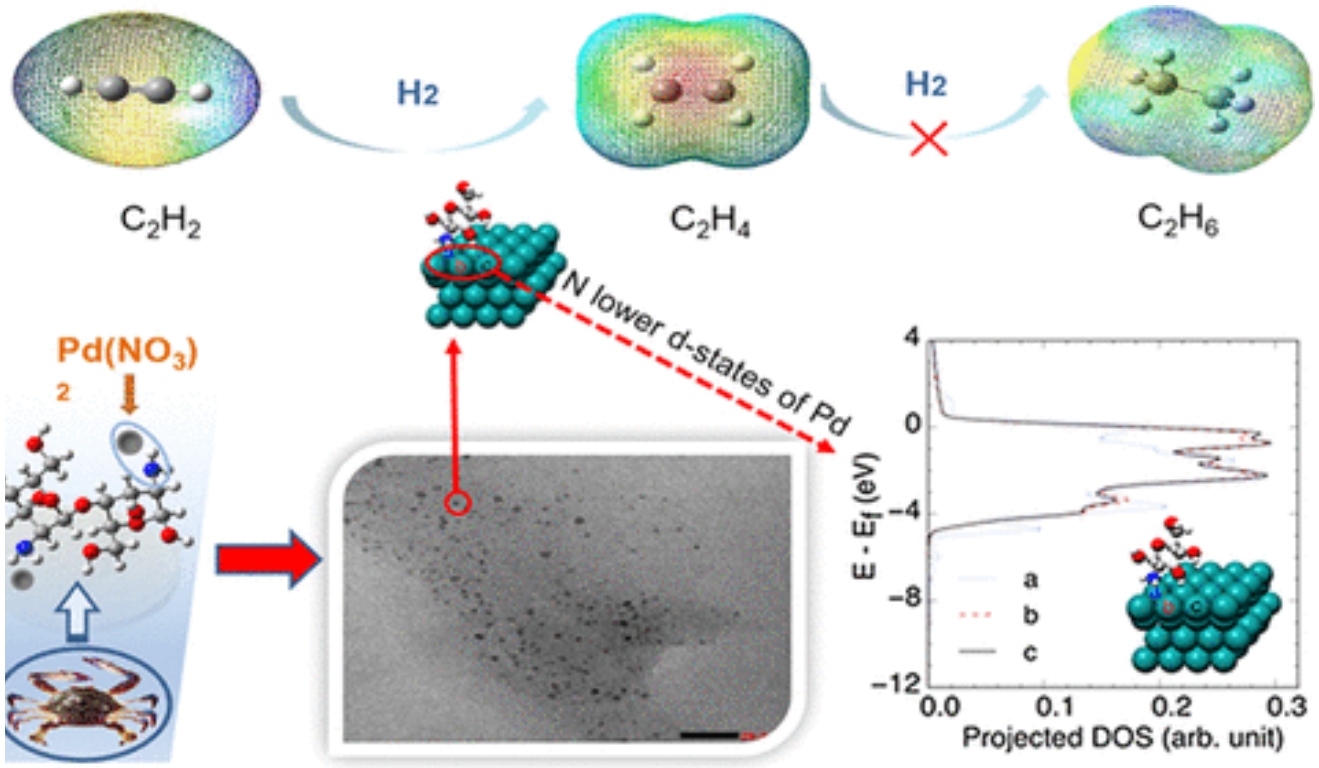


03 Advance Catalysis Theory

What determines reactivity of catalyst

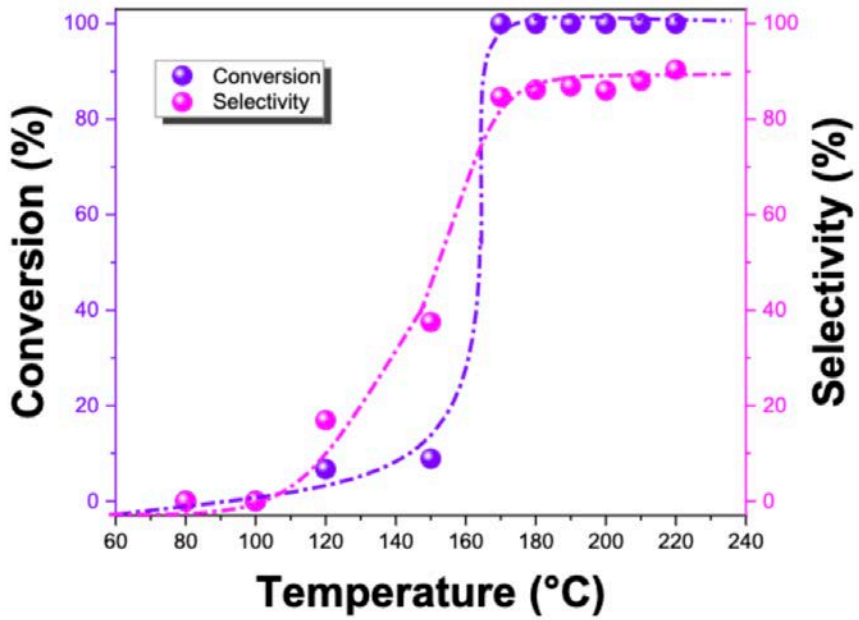
Biopolymer Interaction Effect in C_2H_2 Hydrogenation Reaction on Pd Catalysts



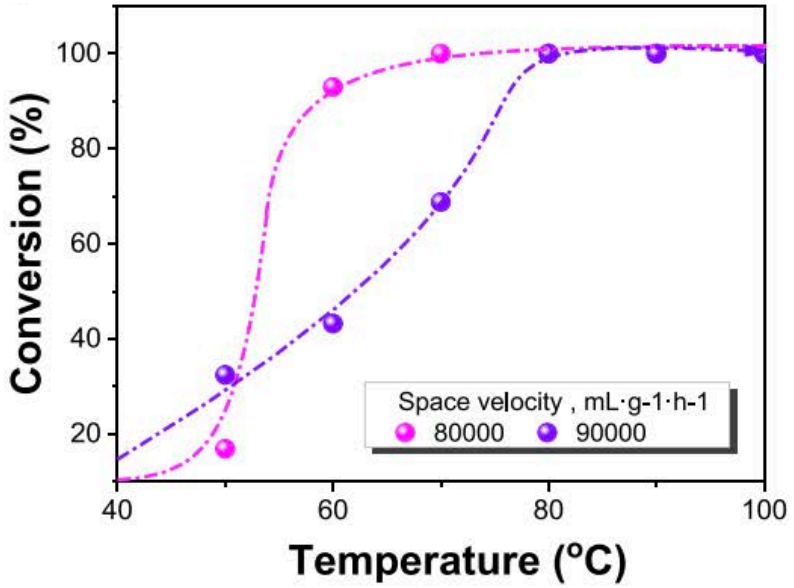
- *Q. Guan, C. Yang, **S. Wang**, et al., ACS Catal., 2019, 9 (12).*

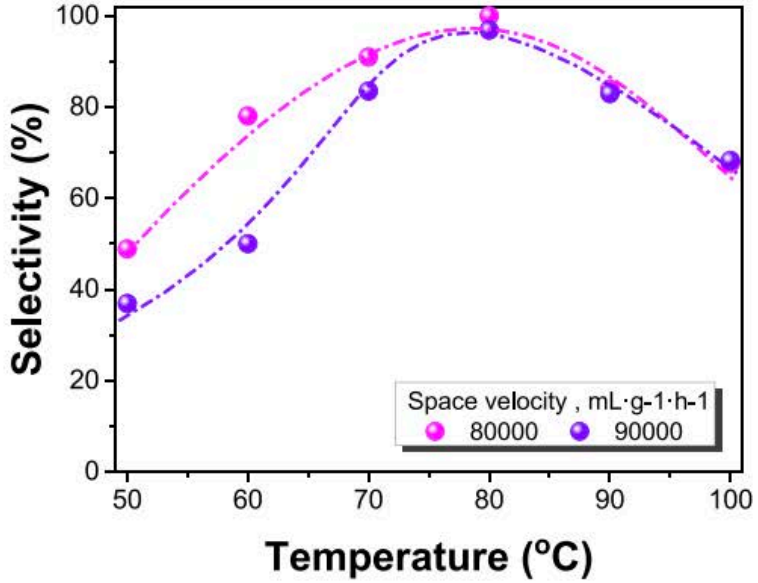
Catalytic Acetylene Conversion and Ethene Selectivity

Pd

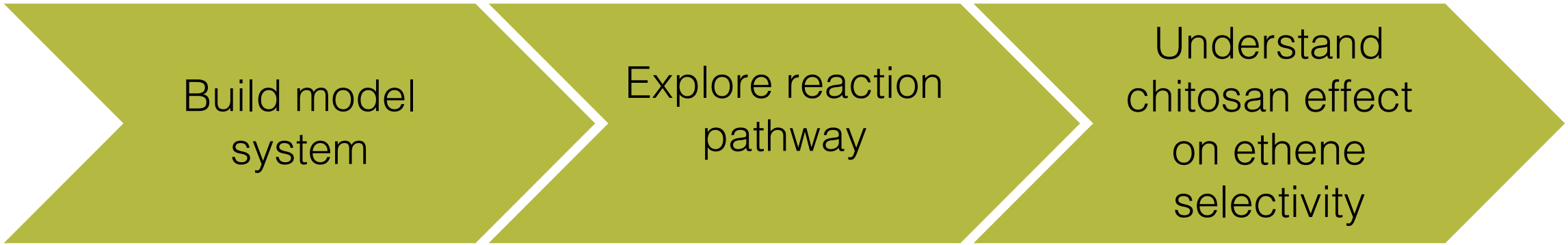


Pd + chitosan





Workflow

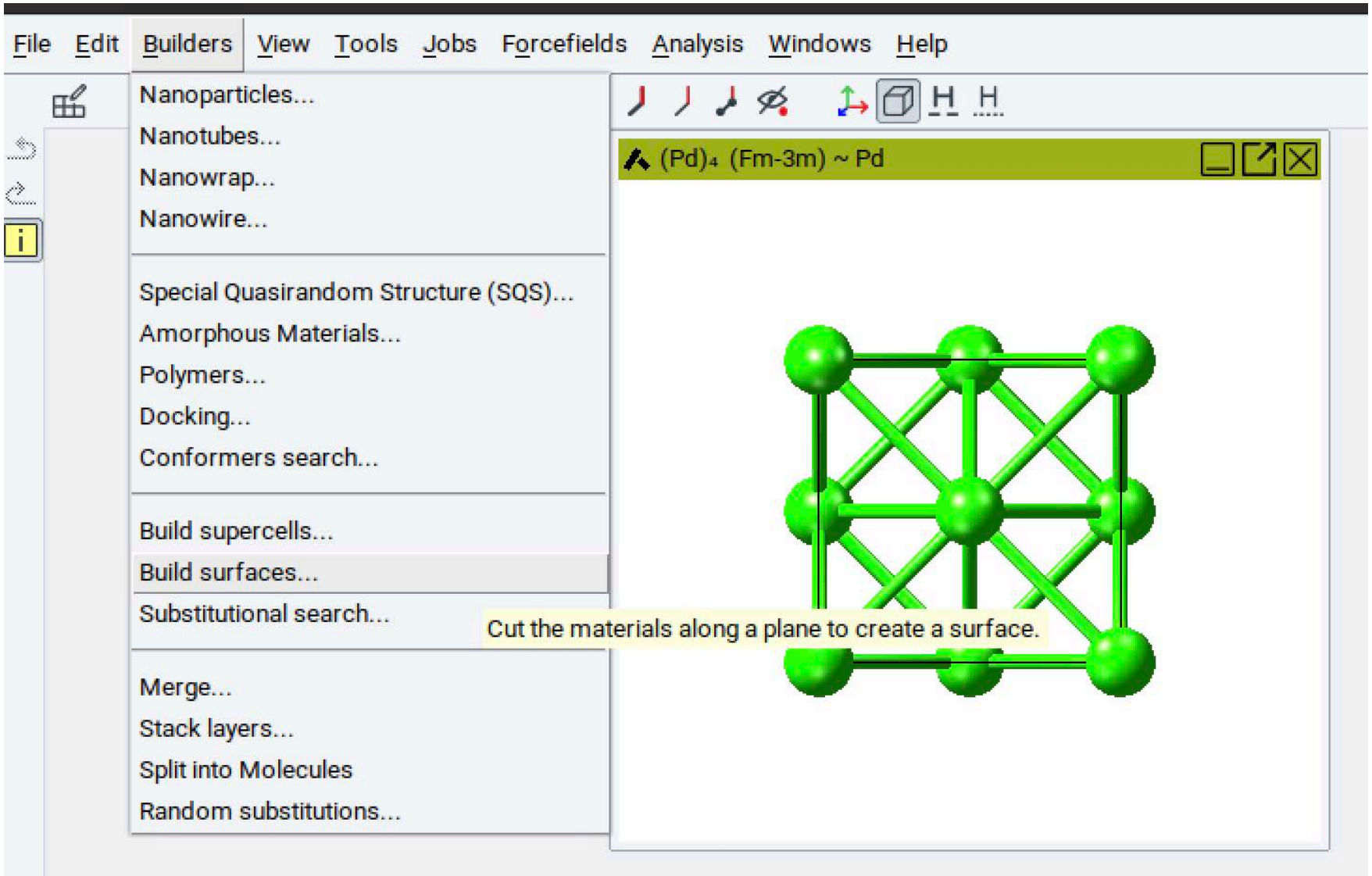


1. Retrieve Pd bulk and chitosan monomer from *MedeA* database
2. Create Pd surface with *surface builder* and *supercell builder*

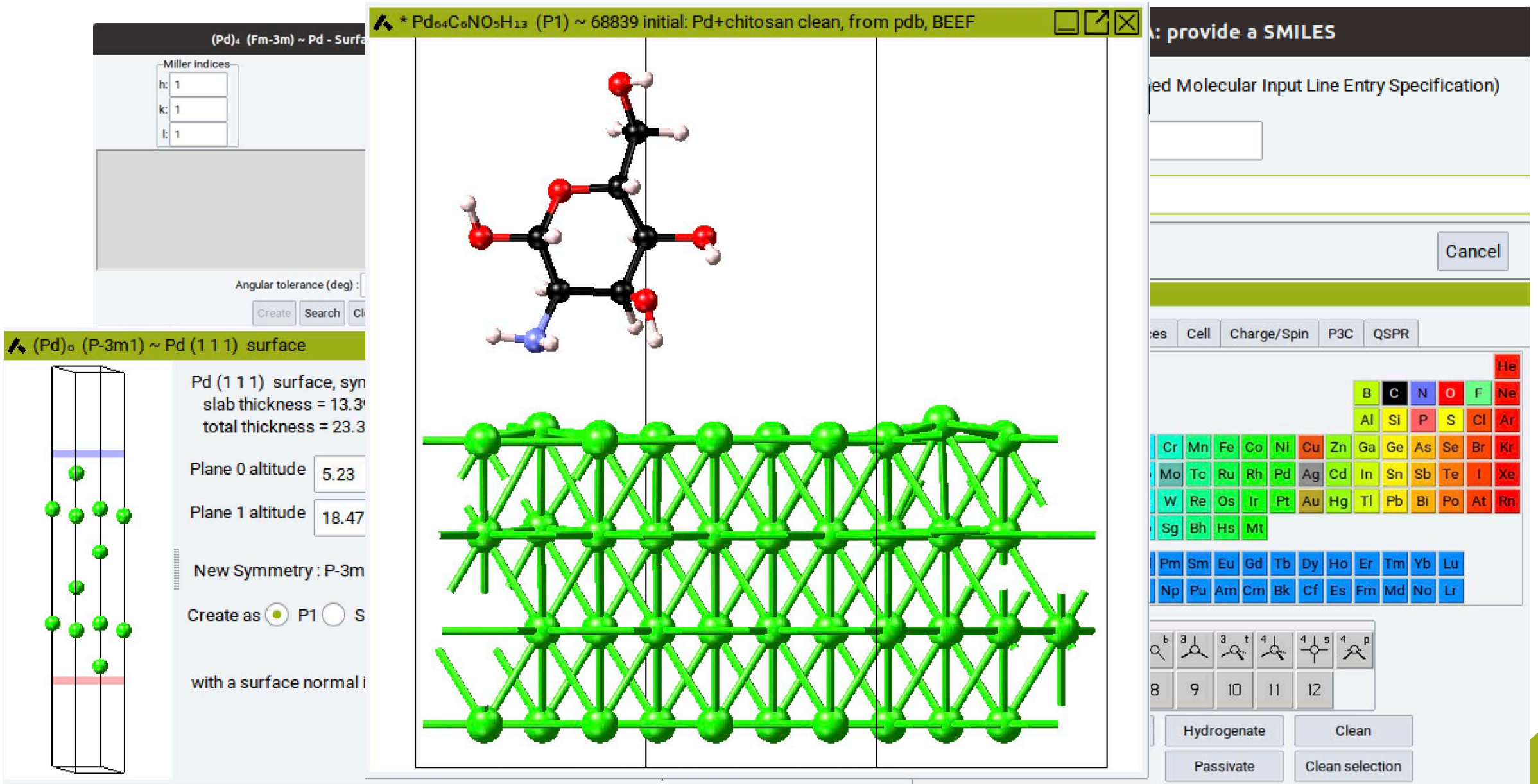
1. Find stable adsorption site/configuration with *MedeA Docking*
2. Calculate transition state with *MedeA Transition State Search (TSS)*

1. Plot potential energy diagram of C_2H_2 hydrogenation
2. Calculate projected density of states onto Pd 4d with/without chitosan

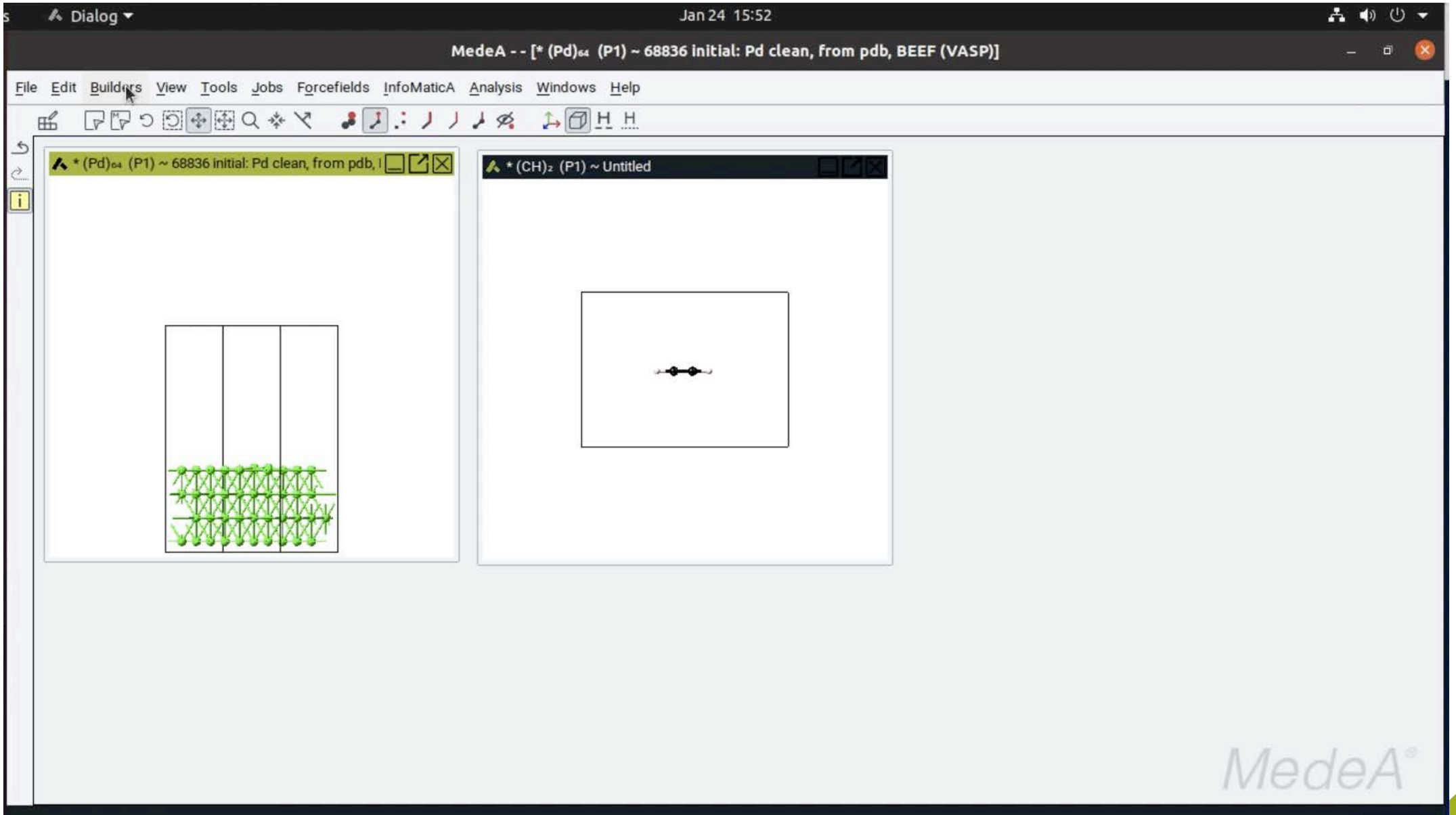
Retrieve Pd Bulk



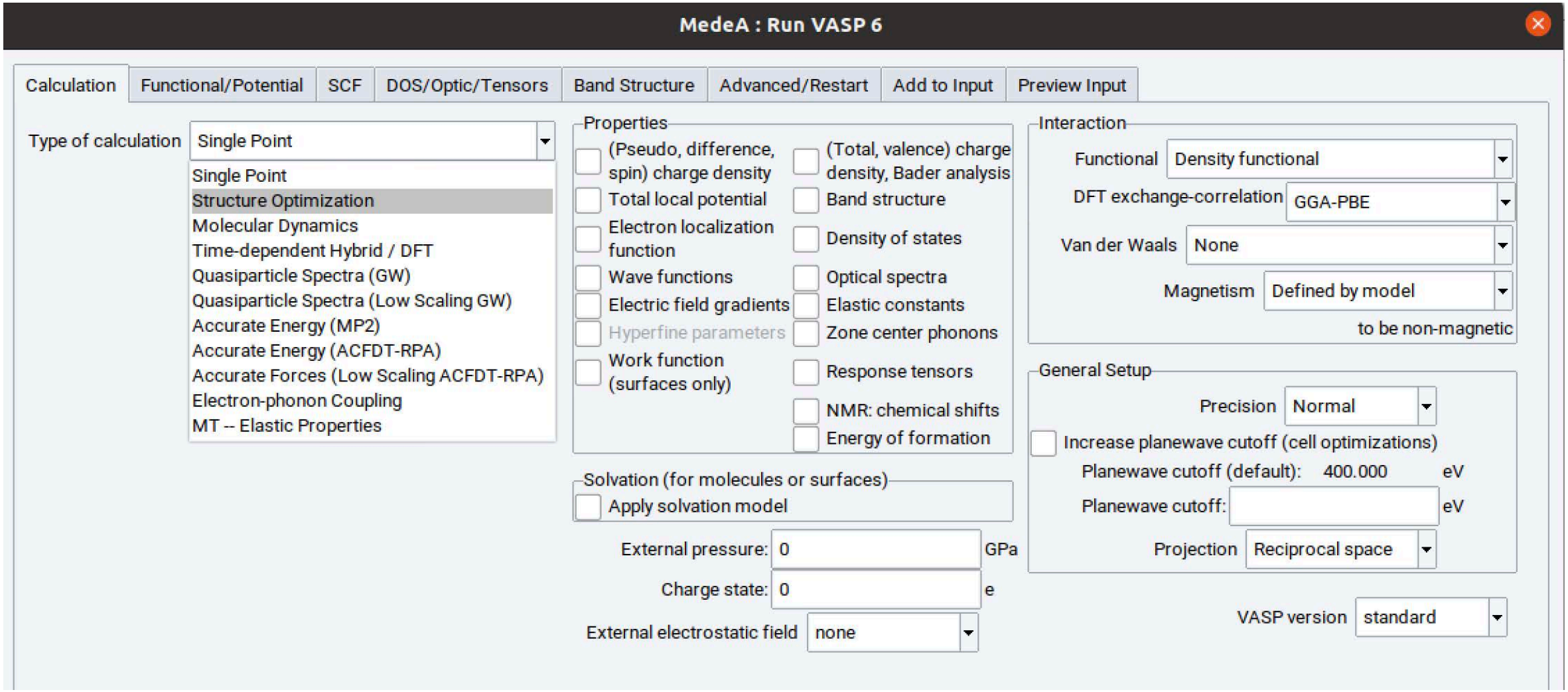
Build Pd 111 Surface With/Without Chitosan



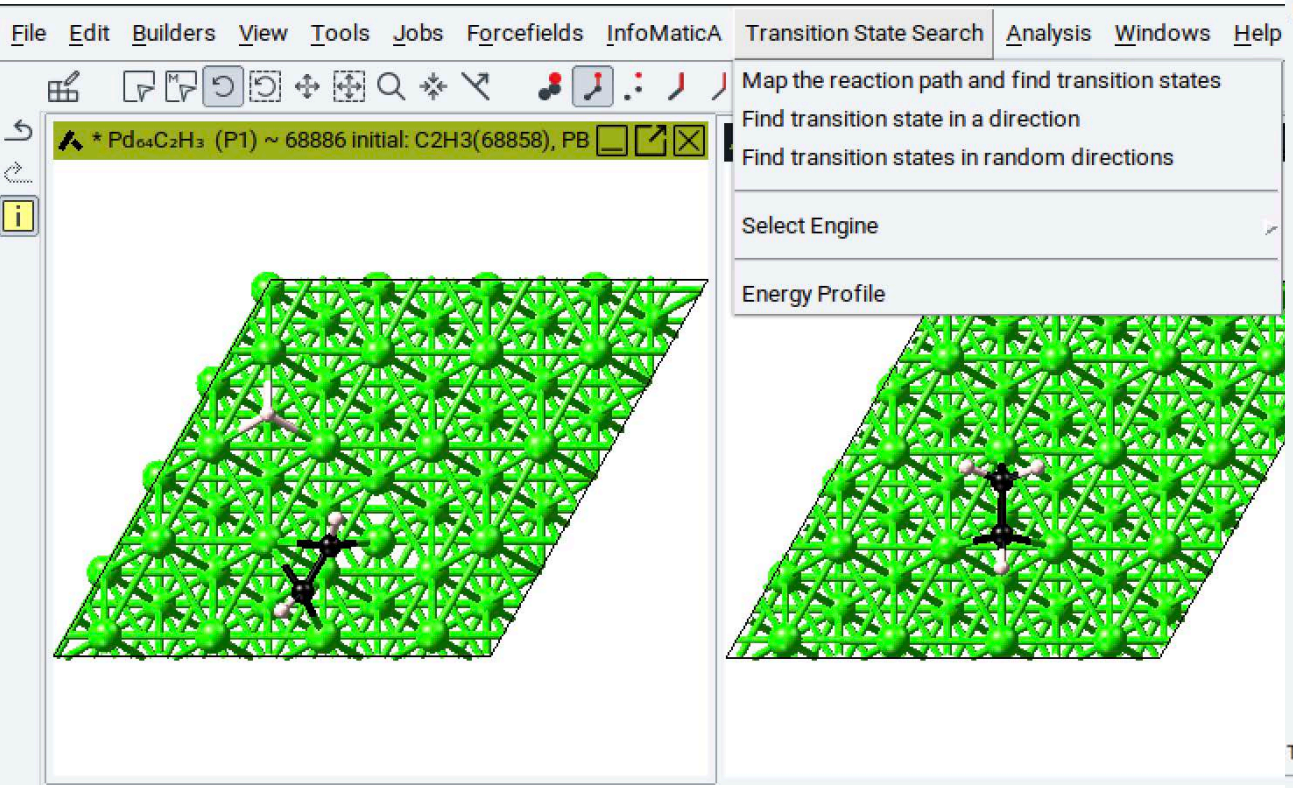
Find Stable Adsorption Site Using *Docking*

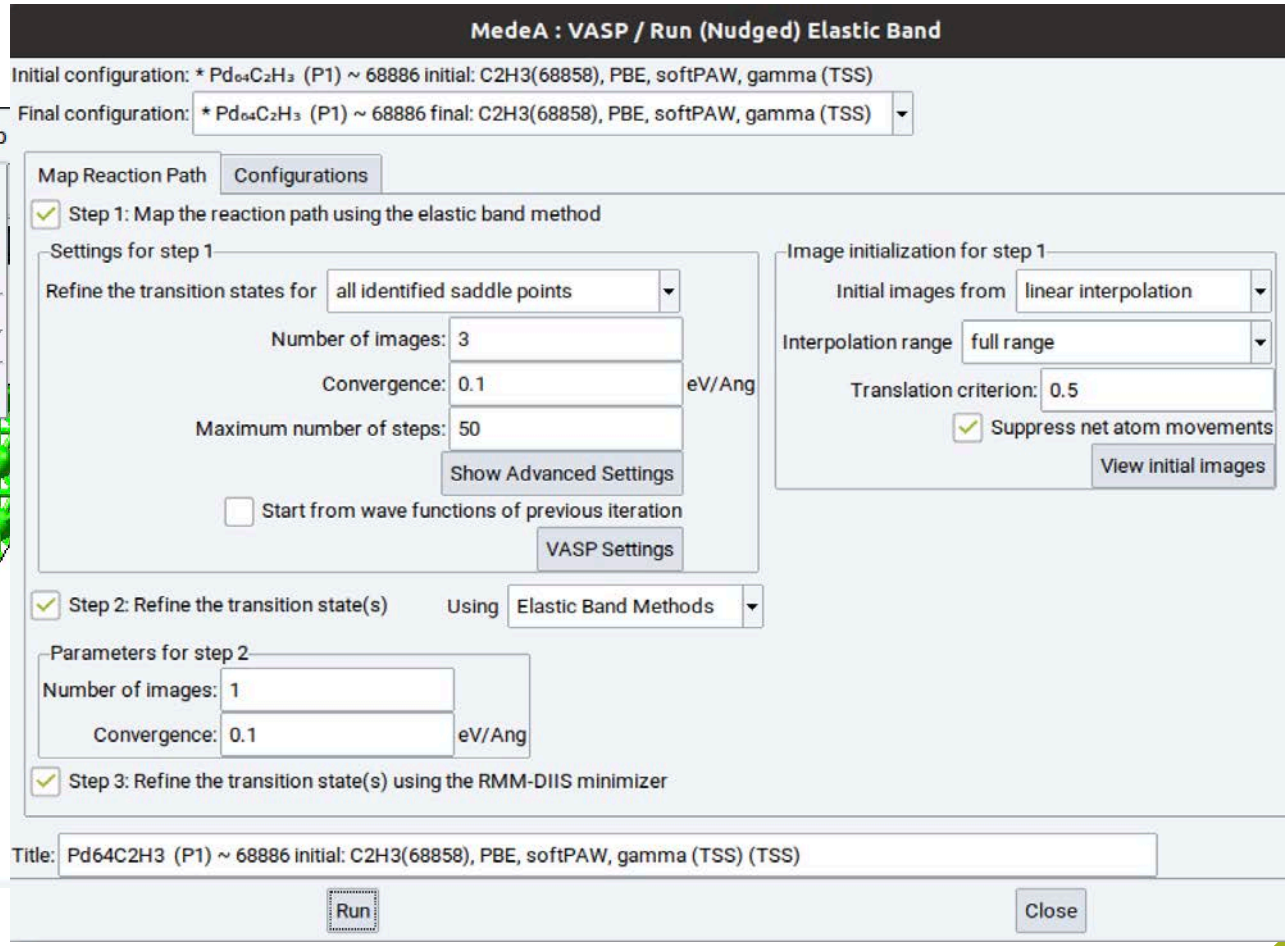


Geometry Optimization with *MedeA VASP*

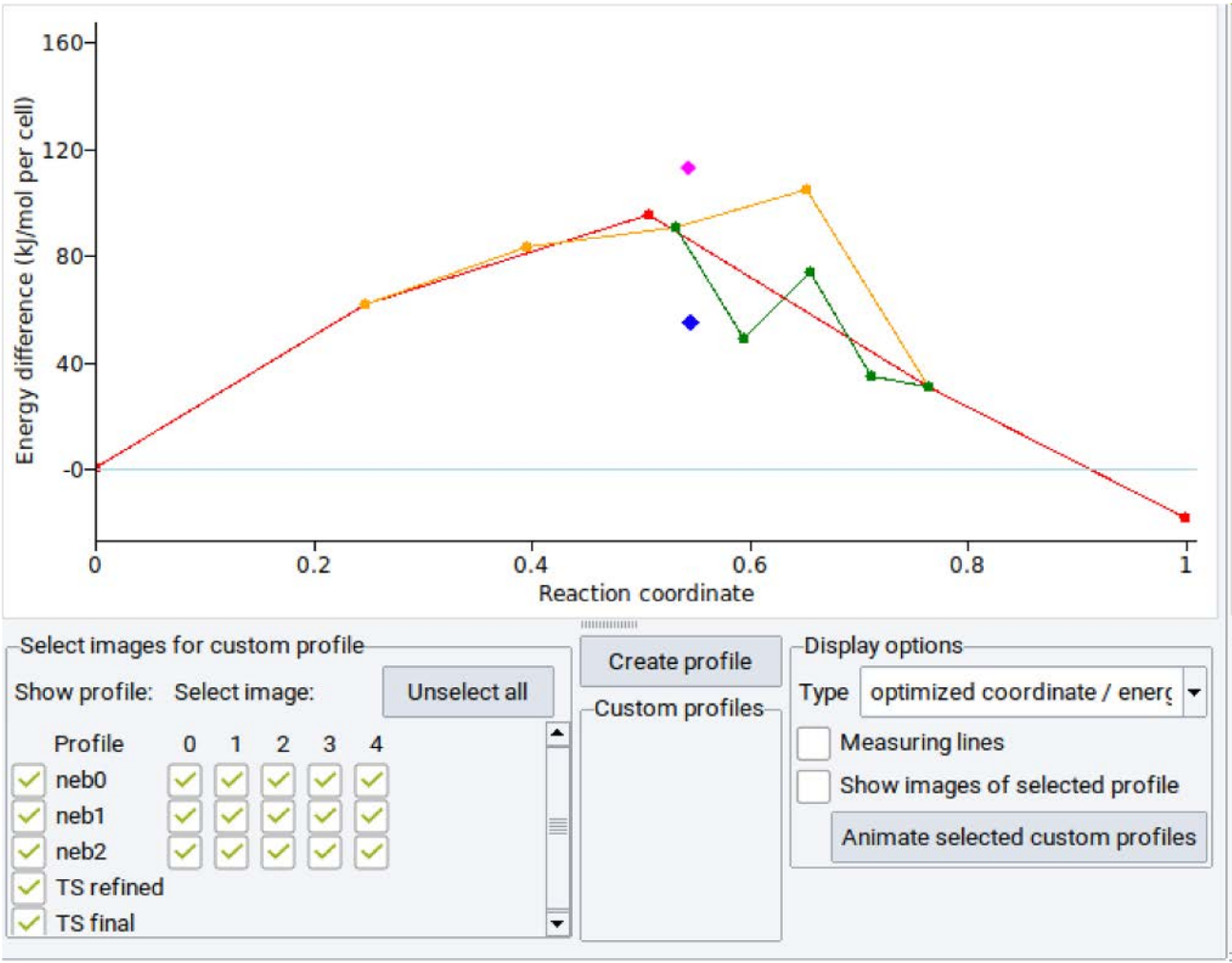


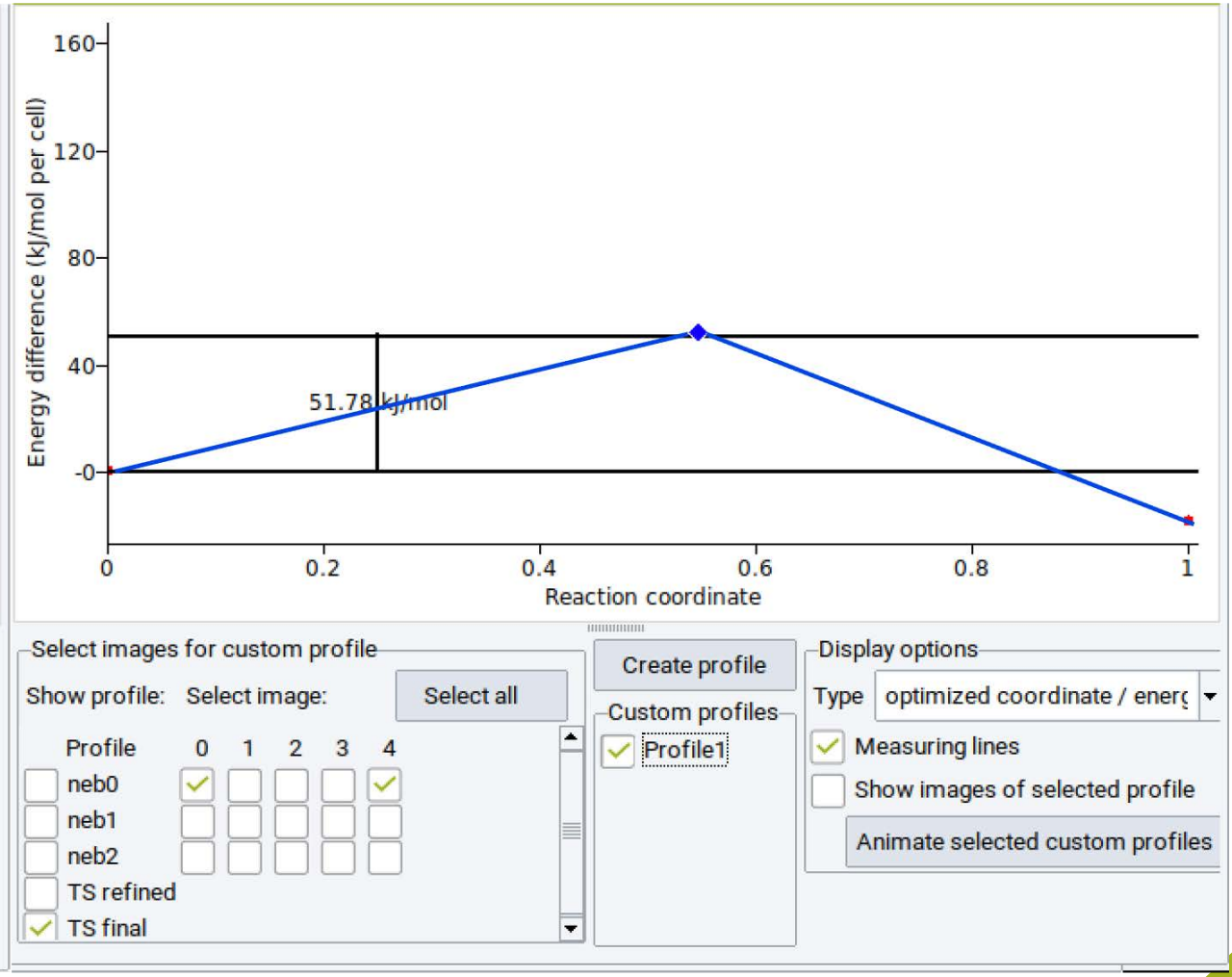
Calculate Energy Barrier with *MedeA TSS*



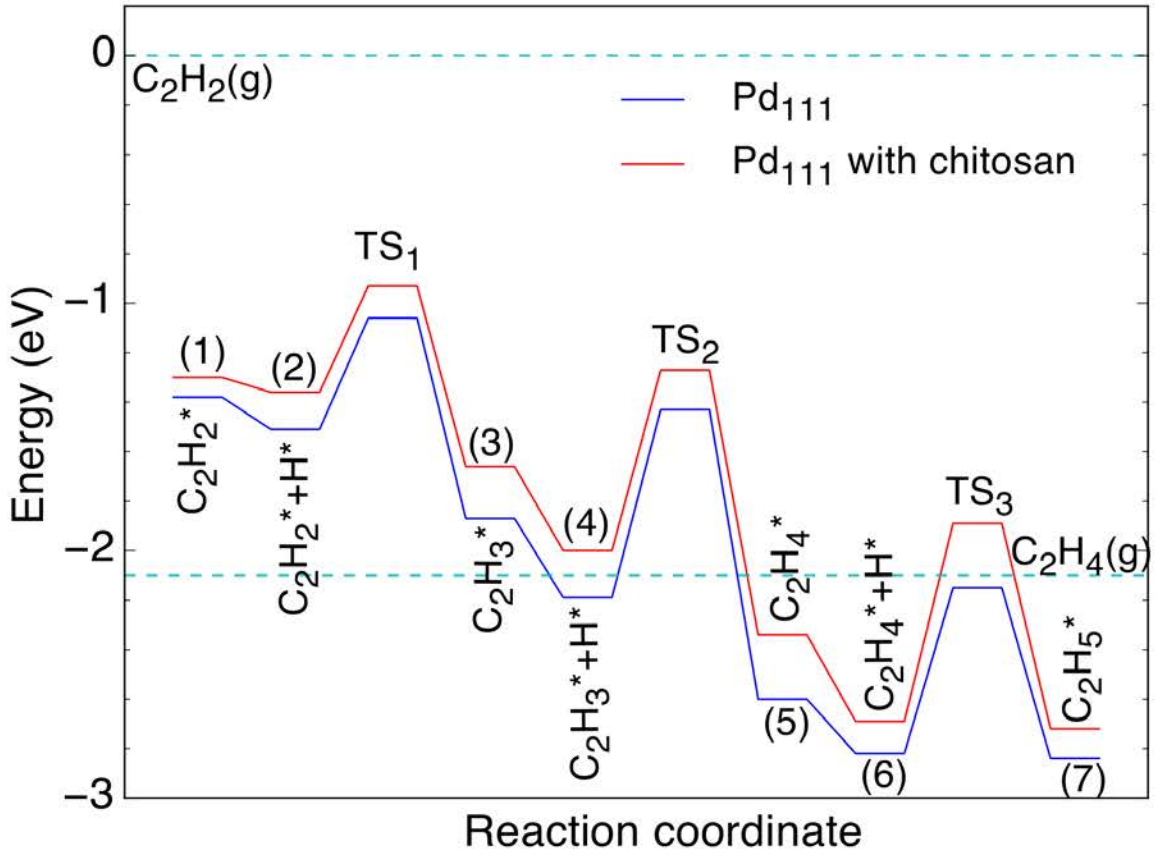


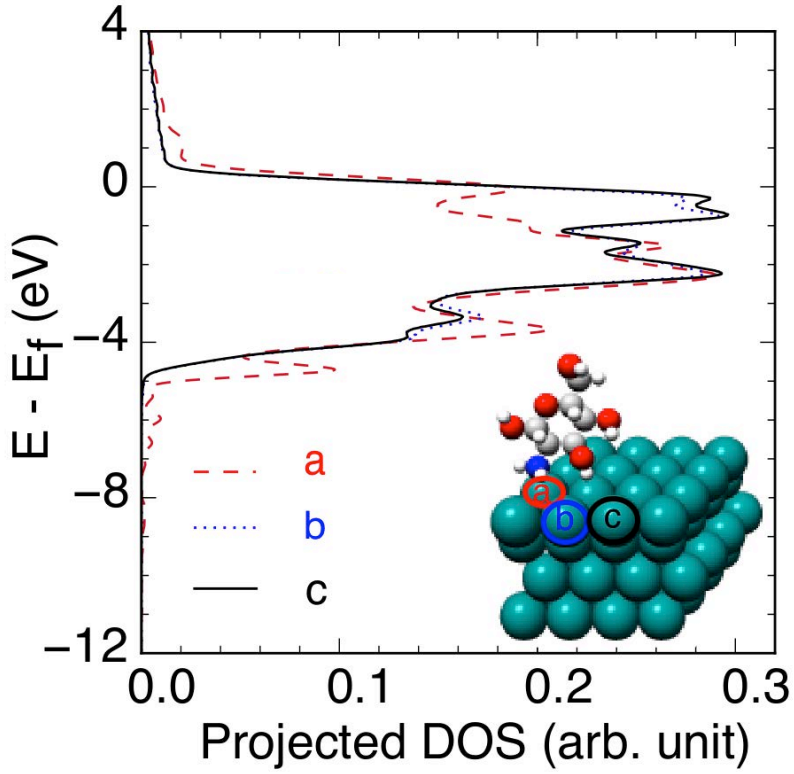
Energy Profile (Transition State Search)

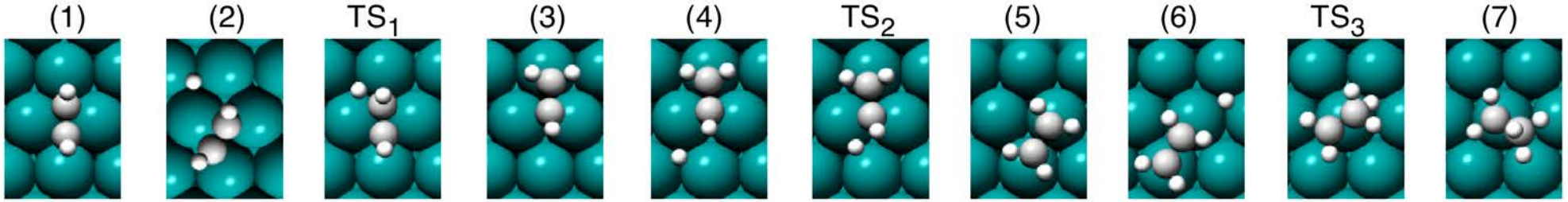




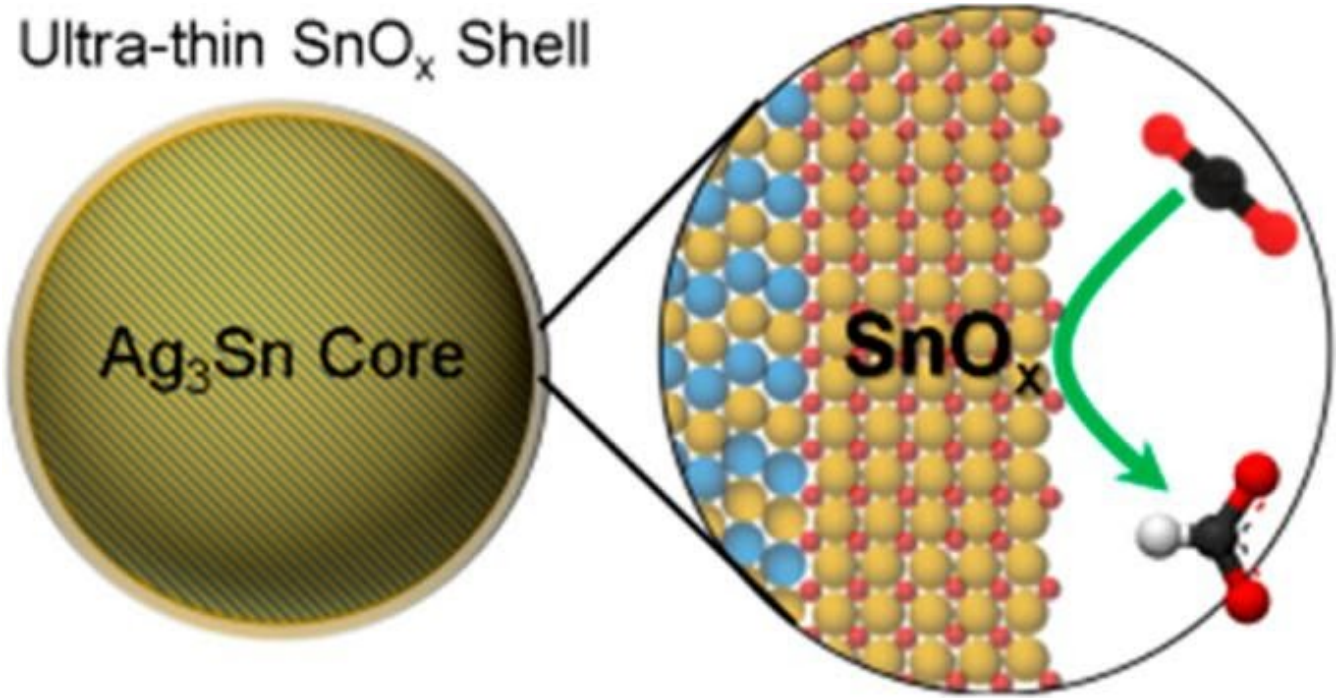
Potential Energy Diagram of C_2H_2 Hydrogenation and Projected DOS





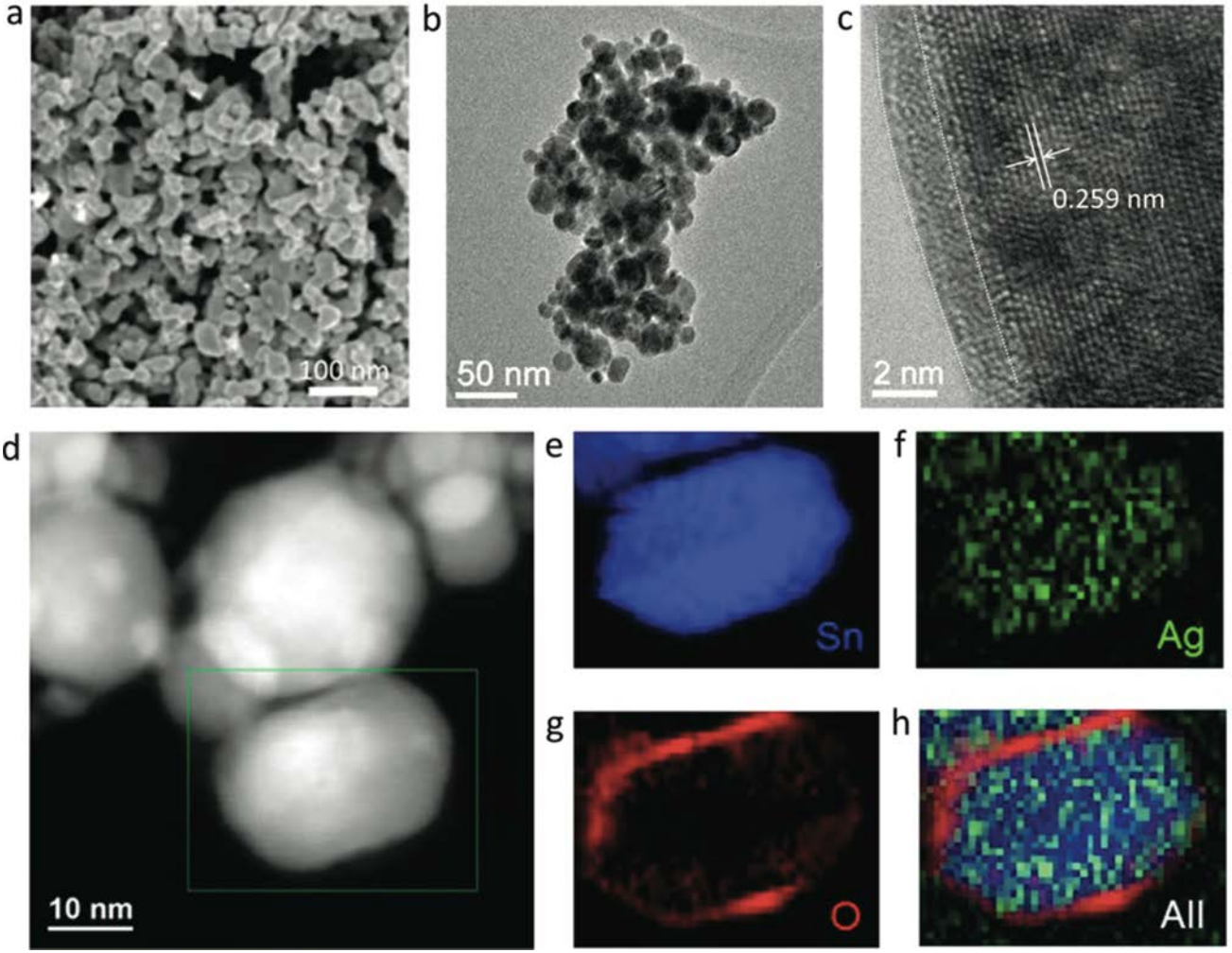


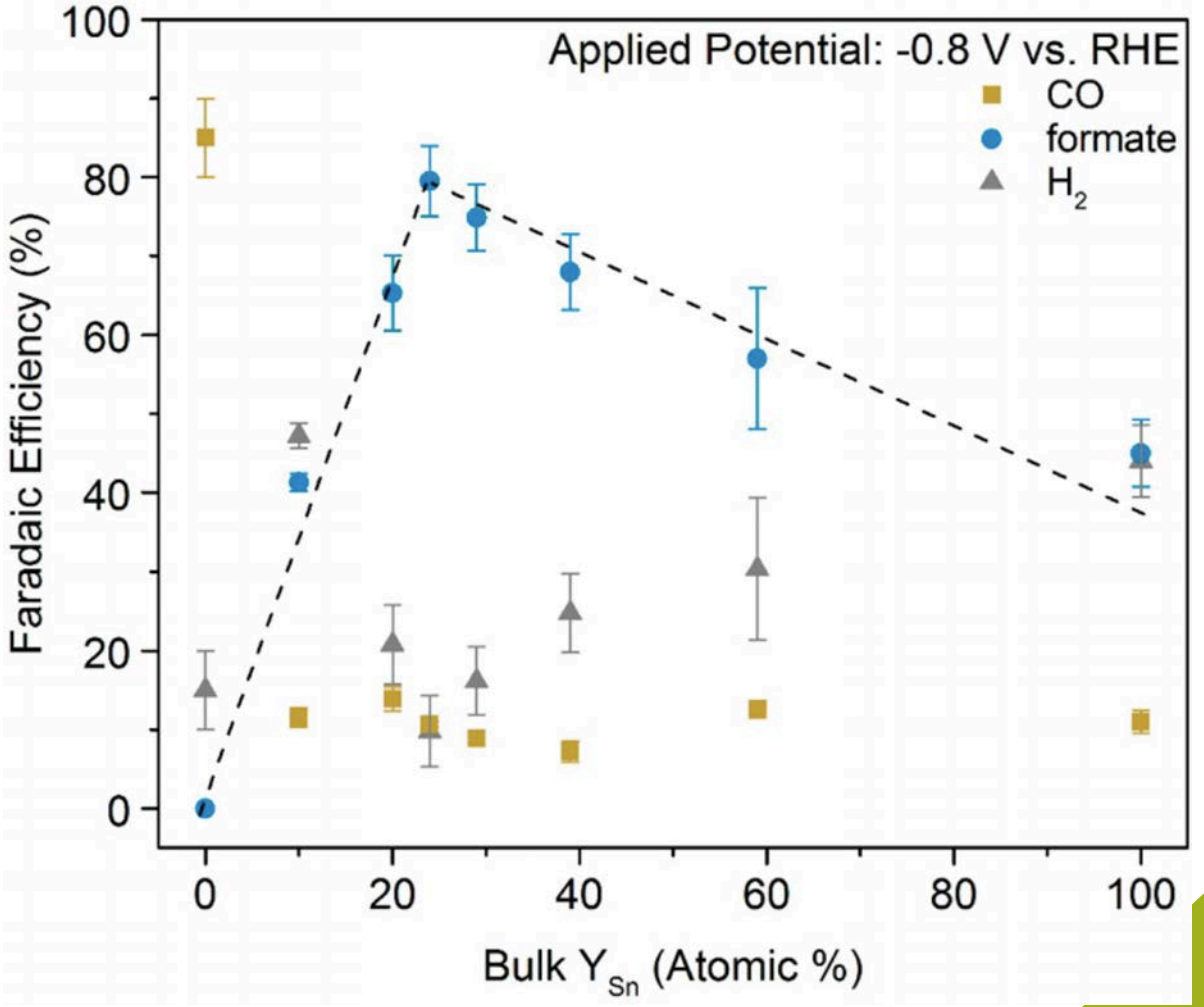
Surface Strain Effect in CO_2 Reduction Reaction on $AgSn/SnO_x$ Core-Shell Catalysts



- *W. Luc, C. Collins, **S. Wang**, et al., J. Am. Chem. Soc., 2017, 139 (5).*
- ***S. Wang**, J. Wang, and H. Xin, Green Energy & Environment, 2017, 2(2), 168.*

Direct Imaging of AgSn/SnOx Core-Shell Nanoparticles and CO_2 Reduction Efficiency





Workflow

Build model system

1. Retrieve SnO bulk from *MedeA* database *InfoMaticA*®
2. Create SnO (101) surface with surface builder and supercell builder

Probing stability of SnO_x surfaces

1. Calculate free formation energy of SnO_x surfaces as function of different operating potentials

Apply strain to SnO_x surface

1. Compress/Expand SnO_x surface with structure editing tool
2. Calculate SnO_x surface with different strains in one flowchart

Retrieve SnO Bulk from *InfoMaticA*

MedeA InfoMaticA: Search

File Edit Options

ID	completeness	space group name H-M	sum	structural	name systematic
COD.110002(	Missing Atoms	Cmc21	O Sn	Sn O	Tin (II) oxide - red modification
COD.901214(	Complete	P4/nmmO1	O Sn	O Sn	
COD.9011217	Complete	P4/nmmO1	O Sn	O Sn	
COD.900895(	Complete	P4/nmmO1	O Sn	SnO	
COD.720647(	Complete	P4/nmmO2	O Sn	O Sn	?
COD.4124667	Complete	P4/nmmO1	O Sn	O Sn	Sn O
COD.110103[	Missing Atoms	Cmc21	O Sn	Sn O	Tin (II) oxide - red modification

Search Criteria | Detailed Information | Coordinates | Geometry | Coordination | Pair Correlation | Powder pattern

Require that | is | SnO

Require that | --A

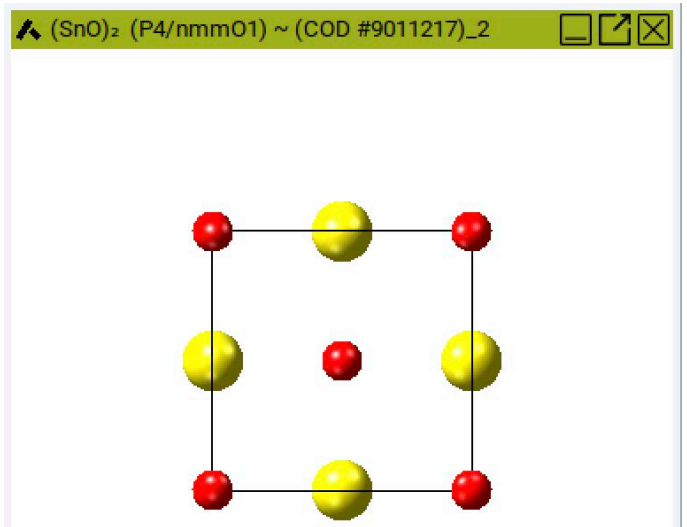
--Delete--

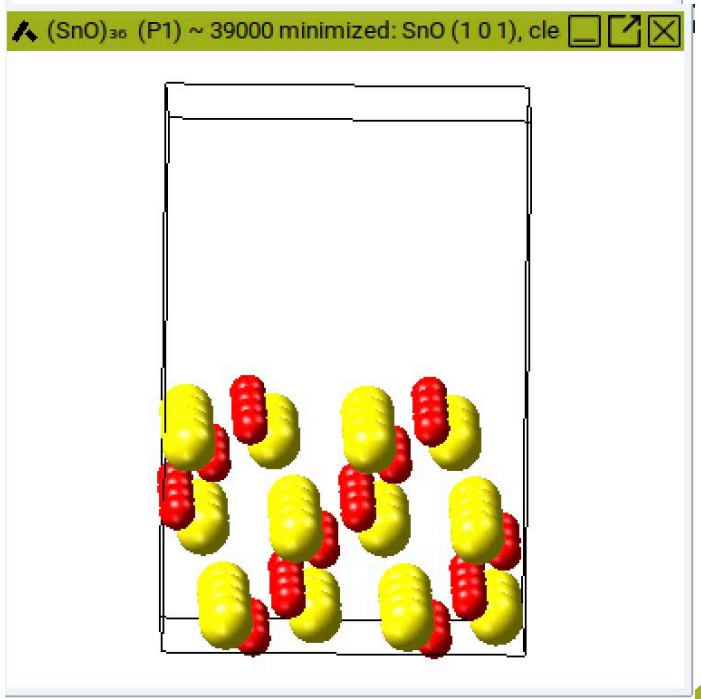
database ID
formula
number of elements
structural completeness
author
title
systematic name
mineral name
remark

Advanced

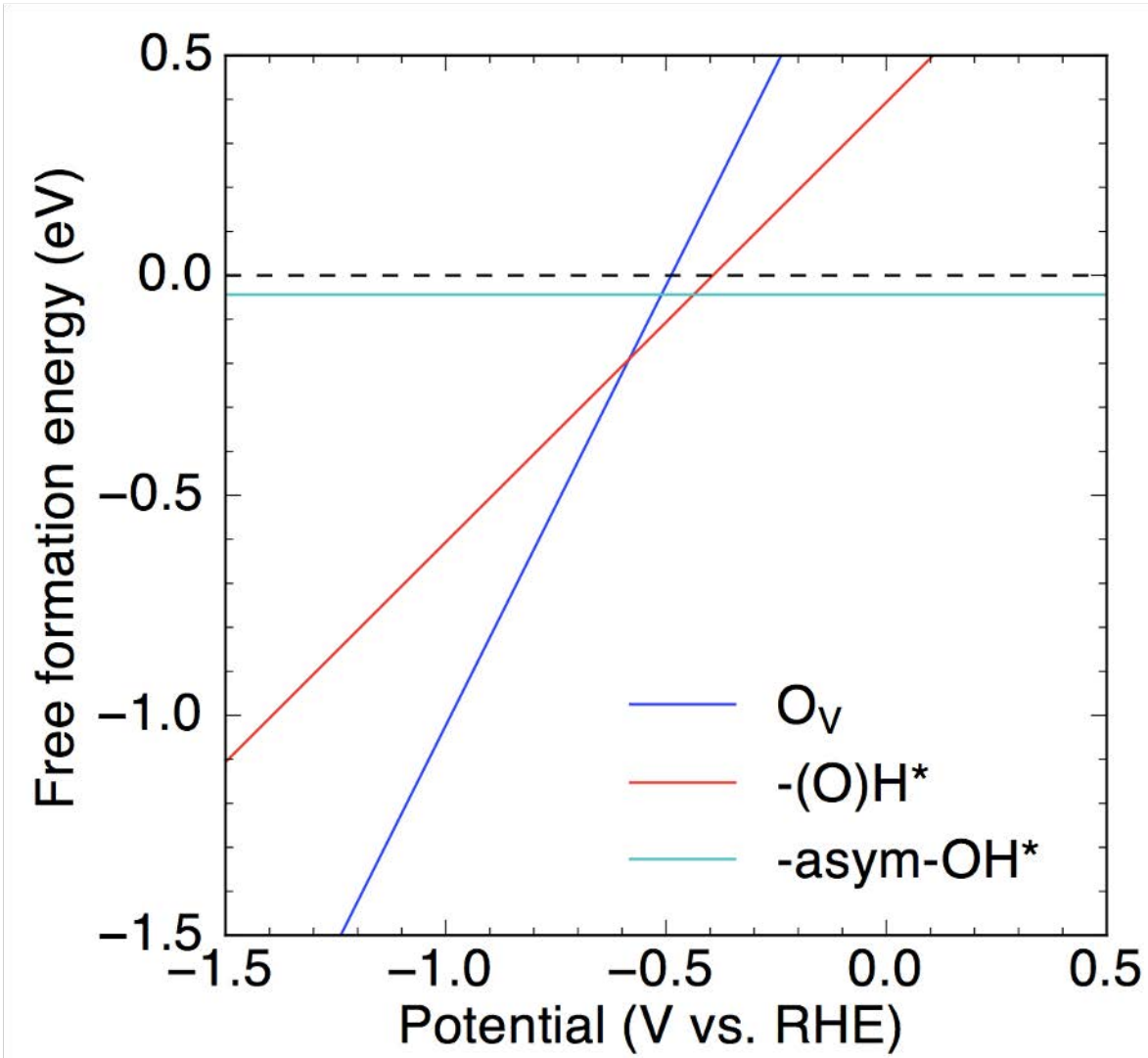
Run search | Clear

Displaying 7 of 7 hits

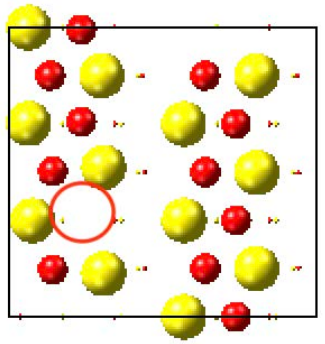




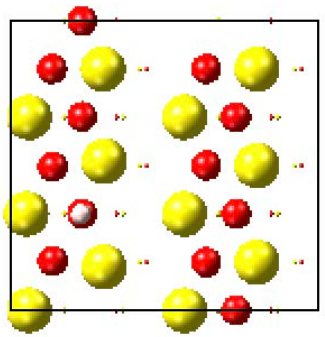
Probing Stability of SnO_x Surfaces



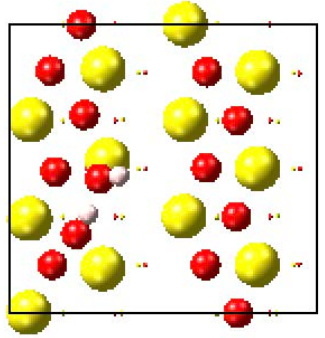
Ov



-(O)H*



-asym-OH*



Two H^+/e^- transfer:

$* + 2(H^+ + e^-) \rightarrow O_V + H_2O$

One H^+/e^- transfer:

$* + (H^+ + e^-) \rightarrow$ -(O)H*

H_2O dissociation:

$* + H_2O \rightarrow$ -(O)H* + -OH*

Gibbs Free Energy for Bulk and Surface

Thermodynamic functions:

- Cv: heat capacity
- E(T)-E(0): change in vibrational internal energy from 0 K
- S(T): vibrational entropy
- -(A(T)-E(0)): change in the vibrational Helmholtz free energy
- E(T): change in vibrational internal energy plus the ZPE
- A(T): internal energy plus vibrational Helmholtz energy
- alpha: coefficient of linear thermal expansion

```
Electronic contributions:
                         Empirical Formula            Cell
                                  SnO              (SnO)36
                         ----------------- -----------------
VASP Energy                     -11.352005      -408.672189 eV
                =               -1095.302     -39430.862 kJ/mol
```

Gibbs: G(T) = U + ZPE + PV – TS(T)

Computational hydrogen electrode

RHE: $H^+(aq) + e^- \leftrightarrow 1/2H_2(g)$

at 0V:$G[H^+ + e^-] = G[H_2]/2$

$\Delta G(V) = \Delta G_0 + eV$

```
Electronic energy =     0.00 kJ/mol (set to zero since reference energies are unavailable)
          PV term =     8.01 kJ/mol
Zero-point energy =     8.62 kJ/mol
```

T K	Cv J/K/mol	E(T)-E(0) kJ/mol	S(T) J/K/mol	-(A(T)-E(0)) kJ/mol	E(T) kJ/mol	A(T) kJ/mol
0	0.0000	0.0000	0.0000	-0.0000	8.6195	8.6195
1	0.0052	0.0000	0.0019	-0.0000	8.6195	8.6195
2	0.0160	0.0000	0.0086	0.0000	8.6196	8.6195
3	0.0325	0.0000	0.0180	0.0000	8.6196	8.6195
4	0.0545	0.0001	0.0302	0.0000	8.6196	8.6195
5	0.0830	0.0001	0.0453	0.0001	8.6197	8.6195
10	0.4135	0.0012	0.1820	0.0006	8.6208	8.6190
15	1.2417	0.0051	0.4881	0.0022	8.6247	8.6174
20	2.5196	0.0144	1.0121	0.0058	8.6339	8.6137
25	4.0375	0.0307	1.7346	0.0126	8.6503	8.6069
30	5.6428	0.0549	2.6121	0.0235	8.6745	8.5961
35	7.2533	0.0872	3.6031	0.0389	8.7067	8.5806
40	8.8284	0.1274	4.6750	0.0596	8.7469	8.5599
45	10.3501	0.1754	5.8033	0.0858	8.7949	8.5338
50	11.8126	0.2308	6.9700	0.1177	8.8503	8.5018
55	13.2169	0.2934	8.1622	0.1555	8.9129	8.4640
60	14.5667	0.3629	9.3705	0.1994	8.9824	8.4202
65	15.8671	0.4390	10.5881	0.2493	9.0585	8.3703
70	17.1224	0.5215	11.8102	0.3052	9.1410	8.3143
75	18.3367	0.6101	13.0331	0.3674	9.2297	8.2522
80	19.5124	0.7048	14.2543	0.4356	9.3243	8.1840
85	20.6516	0.8052	15.4716	0.5099	9.4247	8.1097
90	21.7552	0.9112	16.6834	0.5903	9.5308	8.0293
95	22.8239	1.0227	17.8884	0.6767	9.6422	7.9428
100	23.8577	1.1394	19.0856	0.7692	9.7589	7.8504
⋮	⋮	⋮	⋮	⋮	⋮	⋮
2800	49.6722	130.9391	164.8746	330.7067	139.5587	-322.0872
2850	49.6752	133.4228	165.7537	338.9724	142.0423	-330.3529
2900	49.6780	135.9066	166.6177	347.2818	144.5262	-338.6622
2950	49.6807	138.3906	167.4670	355.6339	147.0101	-347.0143
3000	49.6832	140.8746	168.3020	364.0281	149.4942	-355.4086

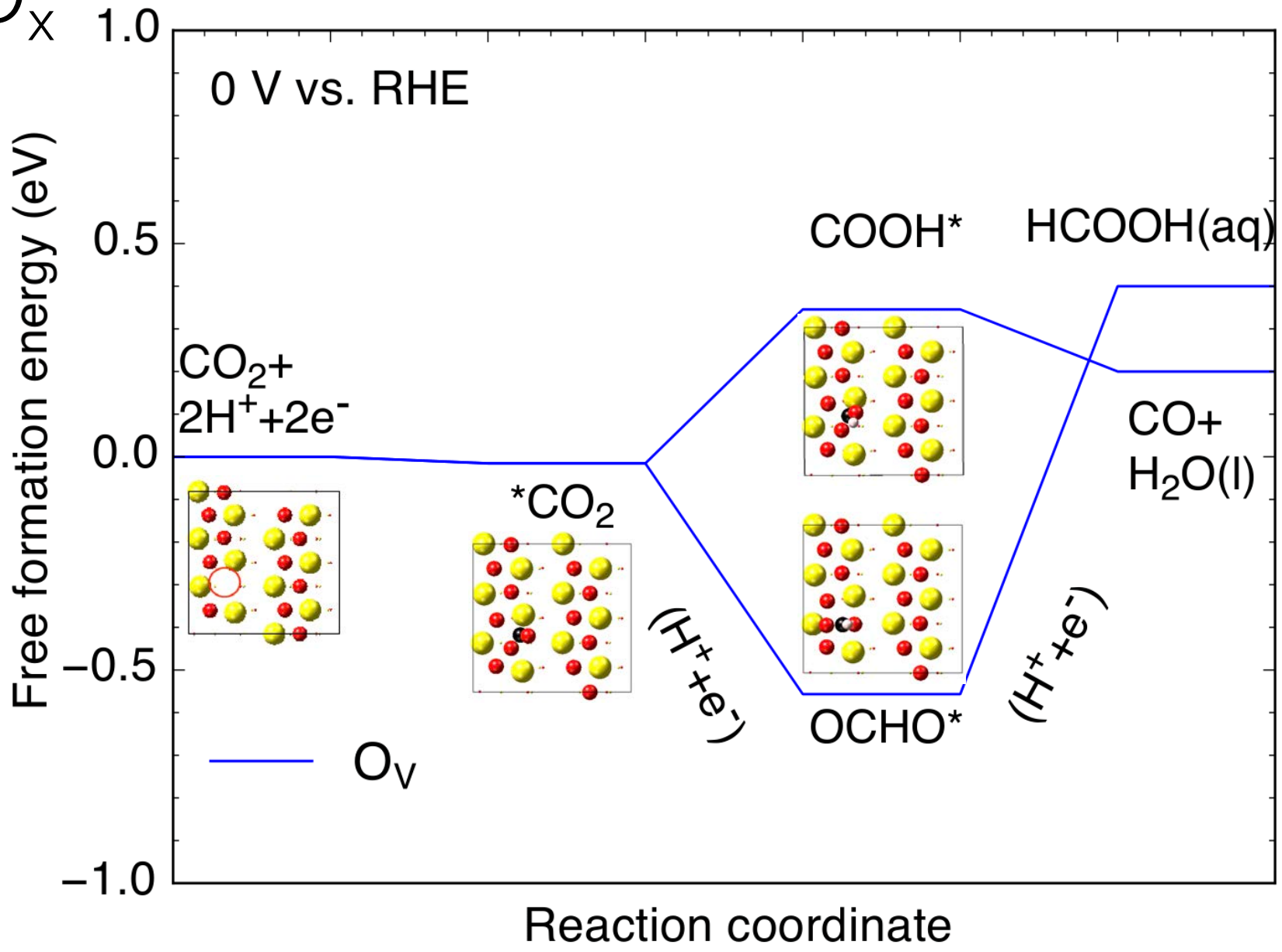
Gibbs Free Energy for Gas Phase Molecule

Mode	Symmetry	Frequency (1/cm)	IR Intensity (km/mol)	Reduced mass (u)	Force constant (mDyne/Ang)
1	PI	656.5615	67.1636	12.8774	3.2706
2	PI	656.5615	67.1636	12.8774	3.2706
3	SG	1407.4617	0.0000	15.9949	18.6683
4	SG	2374.5040	918.7885	12.8774	42.7783

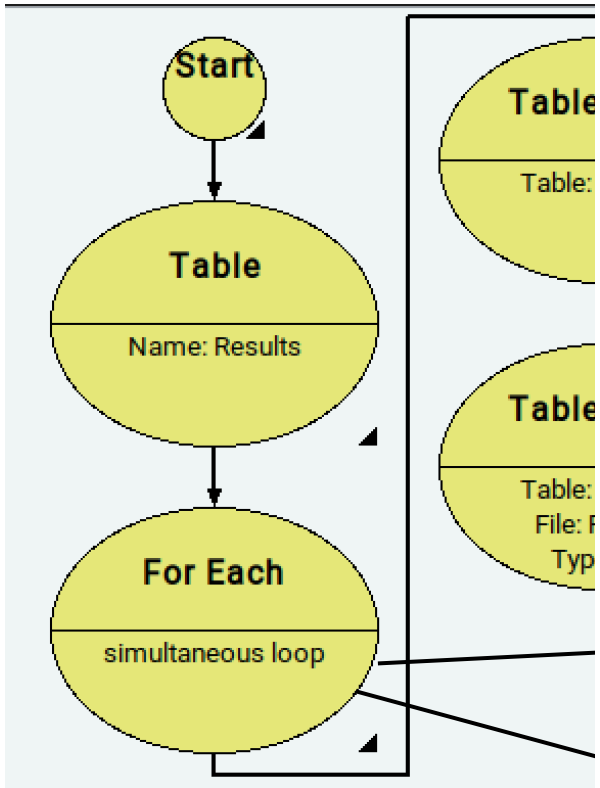
Temperature (K): 298.150
Pressure (atm): 1.00000

	Hartree	kcal/mol	kJ/Mol	
Zero-point vibrational energy:	0.011607	7.284	30.47	
Thermal correction to energy:	0.014238	8.934	37.38	
Thermal correction to enthalpy:	0.015182	9.527	39.86	
Thermal correction to Gibbs free energy:	-0.009745	-6.115	-25.59	
Sum of electronic and zero-point energy:	-187.503346	-117660.140	-492290.03	E0 = Eelec + ZPE
Sum of electronic and thermal energy:	-187.500715	-117658.489	-492283.12	E = E0 + Evib + Erot + Etrans
Sum of electronic and thermal enthalpy:	-187.499771	-117657.897	-492280.64	H = E + RT
Sum of electronic and thermal free energy:	-187.524698	-117673.539	-492346.09	G = H - TS

Free Energy Pathway of CO_2 Reduction on Ov/SnO_x

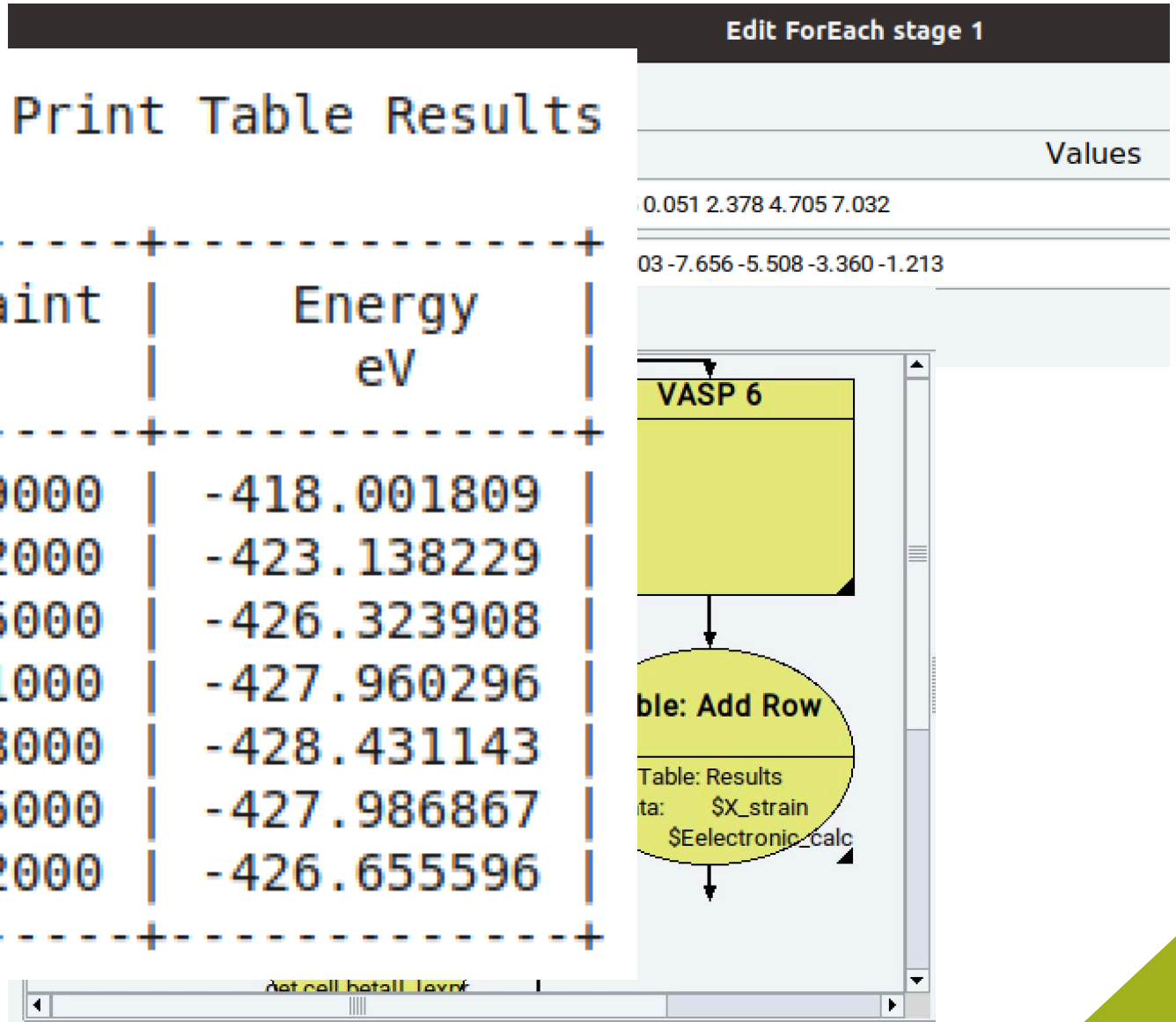


Strain Effect on Ov/SnO_x with *MedeA HT*

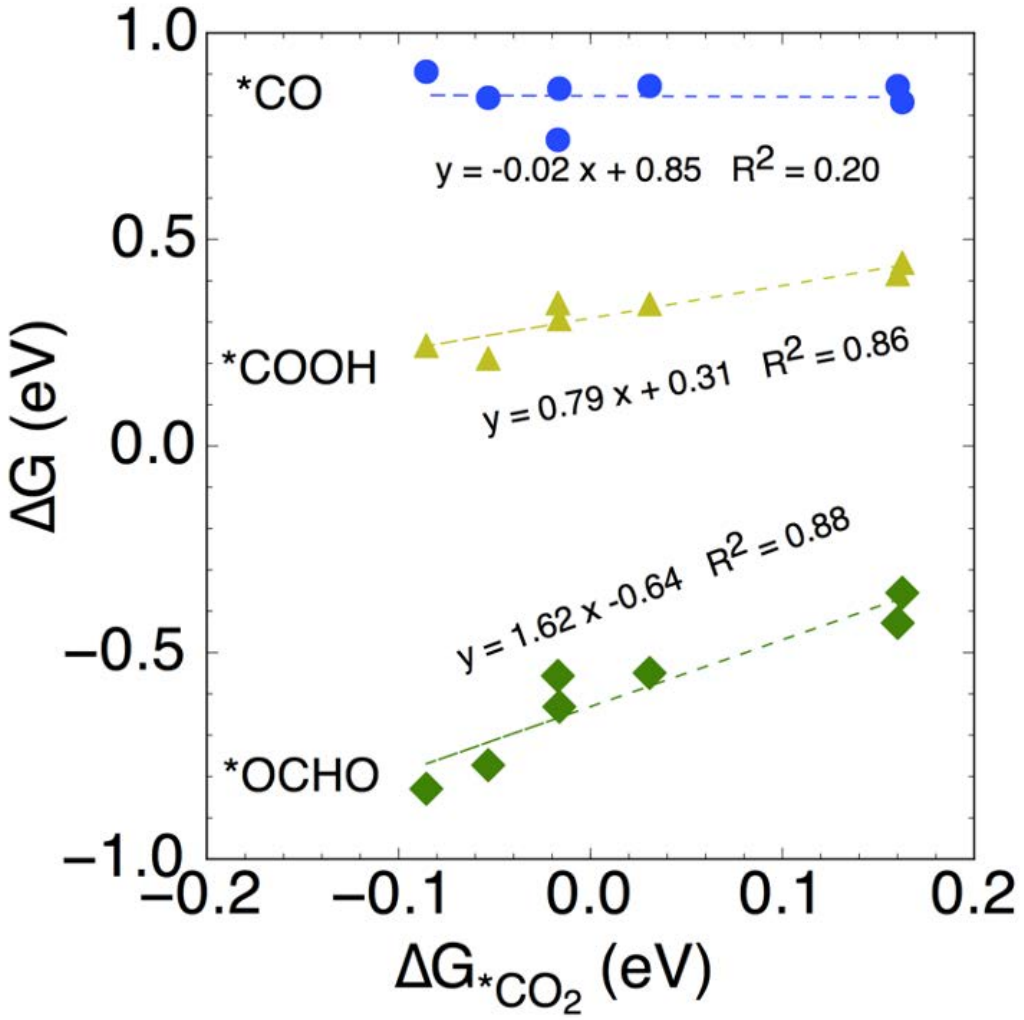


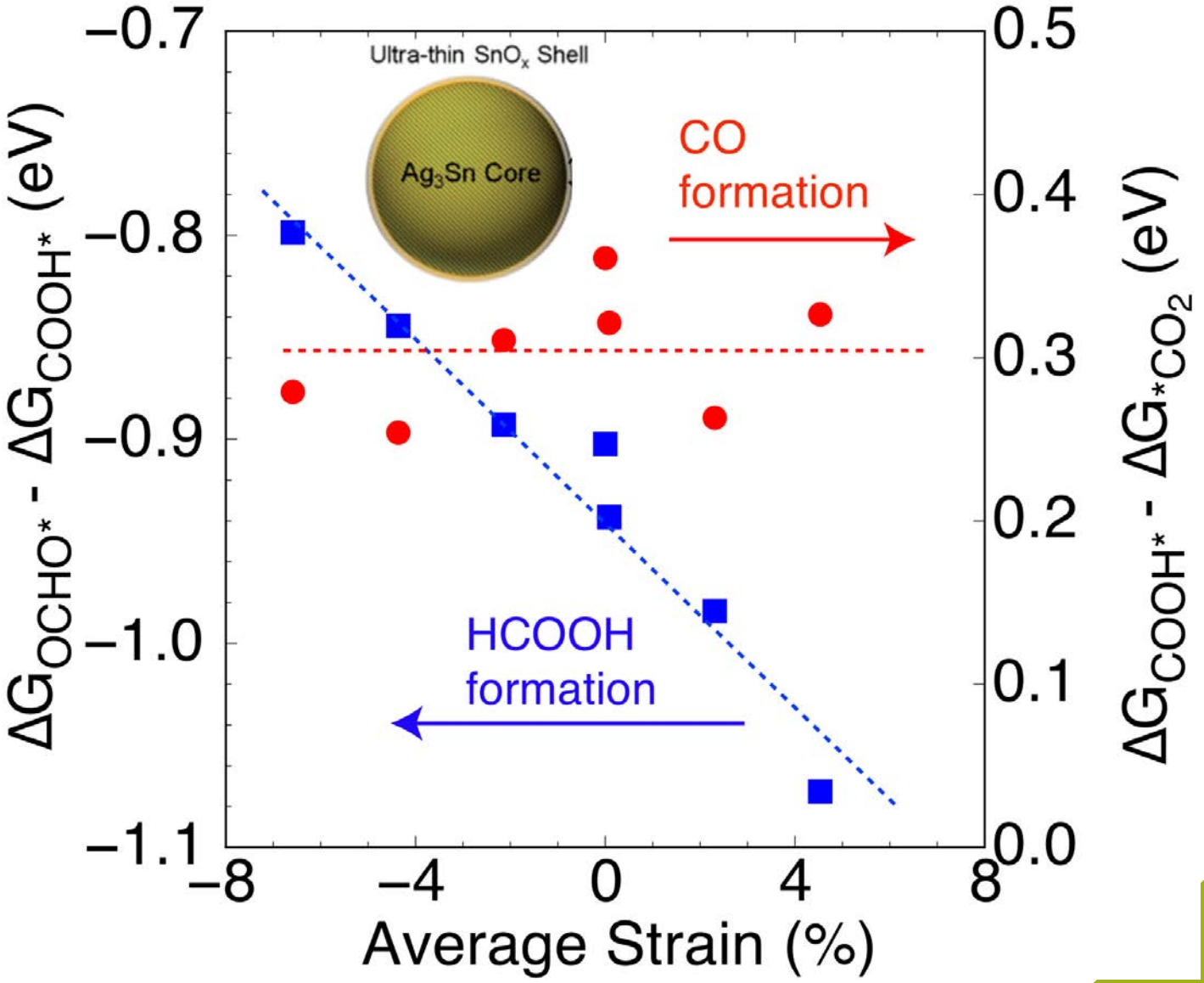
Stage 3: Print Table Results

Constraint	Energy eV
-6.929000	-418.001809
-4.602000	-423.138229
-2.275000	-426.323908
0.051000	-427.960296
2.378000	-428.431143
4.705000	-427.986867
7.032000	-426.655596



Strain as an Origin of Improved Efficiency





Outline

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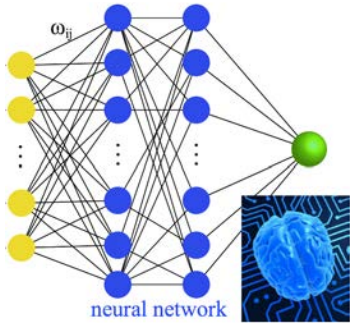
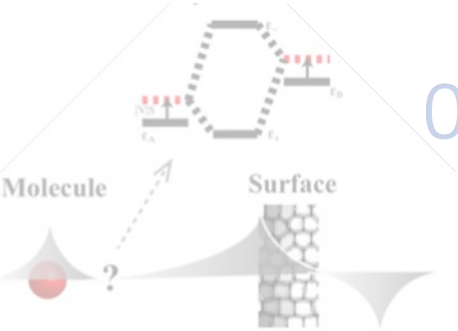
Biopolymer interaction effect in C_2H_2 hydrogenation reaction on Pd catalysts

Surface strain effect in CO_2 reduction reaction on $AgSn/SnO_x$ core-shell catalysts



02 Accelerate Materials Discovery

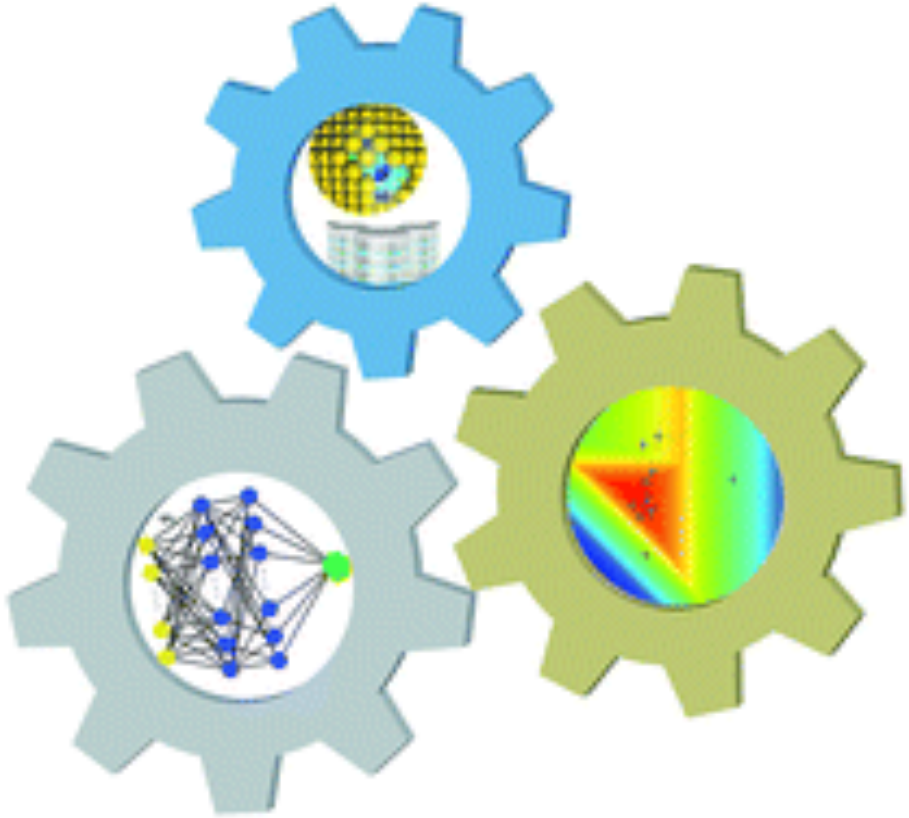
High-throughput screening of bimetallic catalysts enabled by machine learning



03 Advance Catalysis Theory

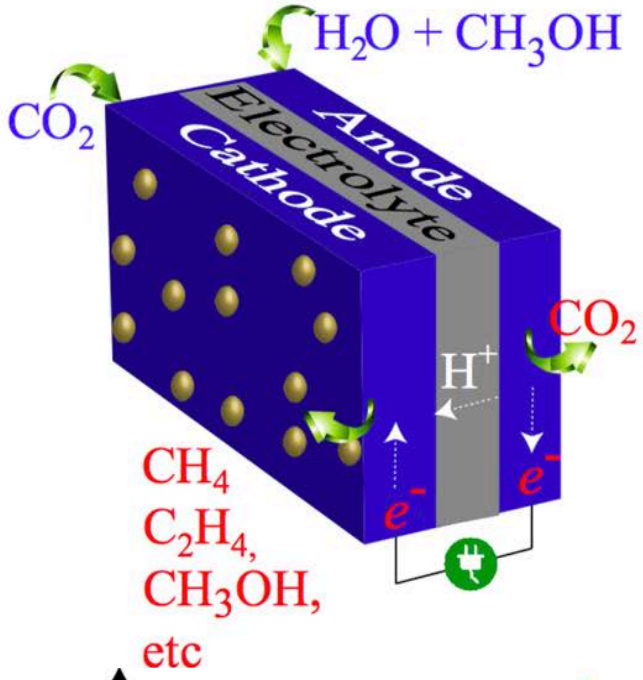
What determines reactivity of catalyst

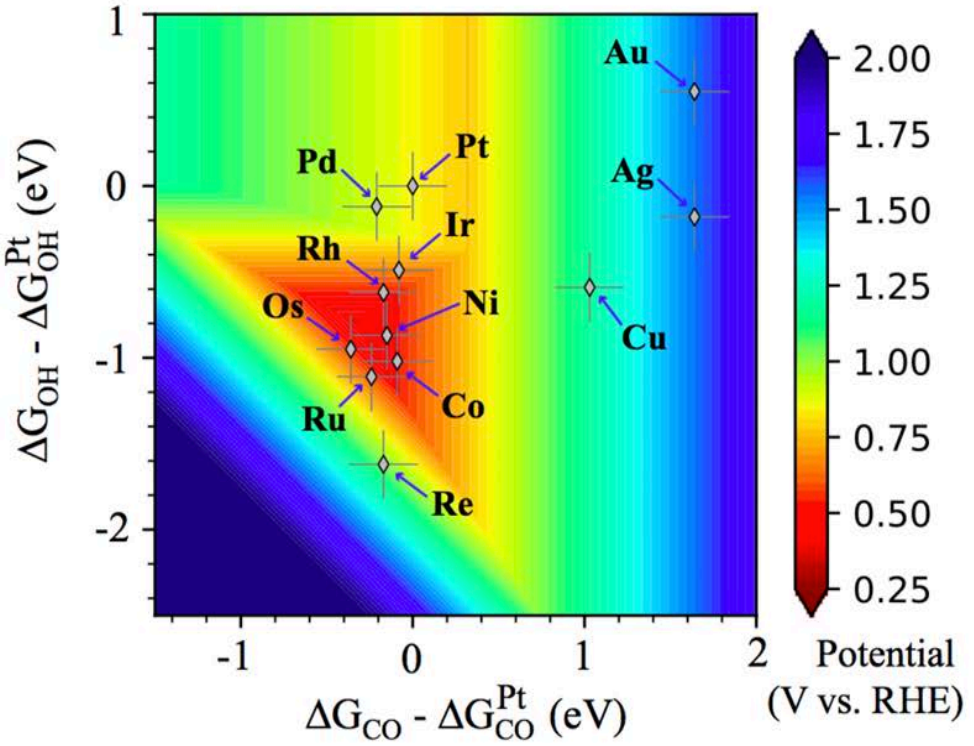
High-throughput Screening of Bimetallic Catalysts Enabled by Machine Learning

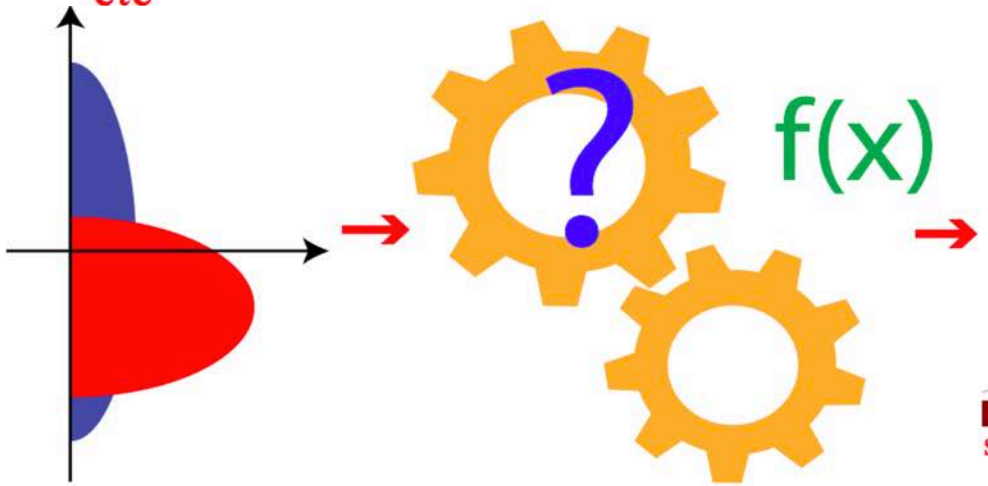


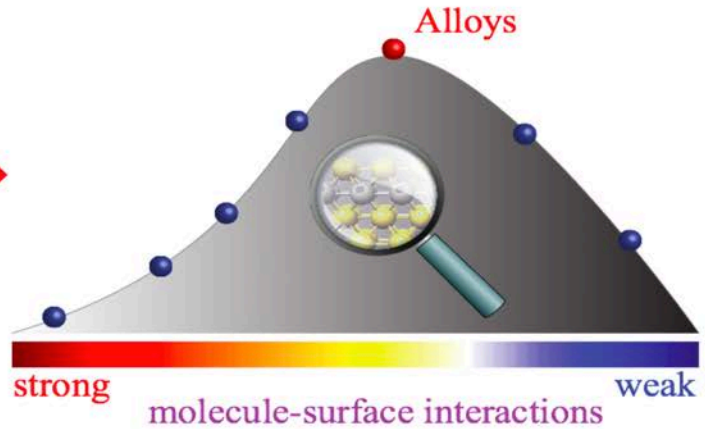
- *Z. Li, **S. Wang**, et al., J. Mater. Chem. A, 2017, 5, 24131.*

Design Bifunctional Alloy Catalysts for DMFCs

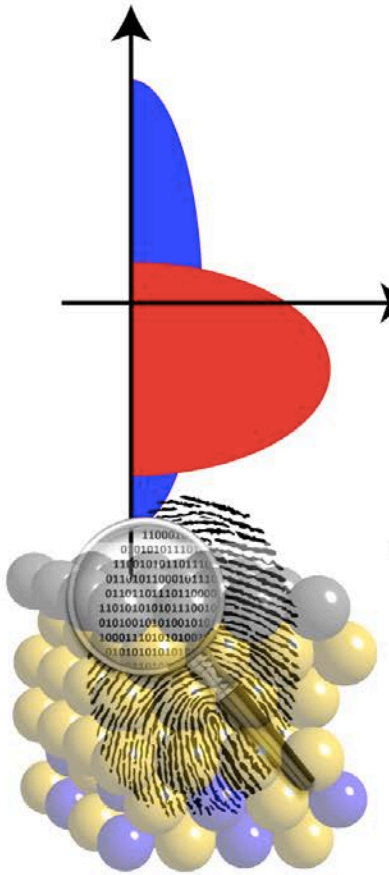








Site Representation Inspired by the *d*-band Theory

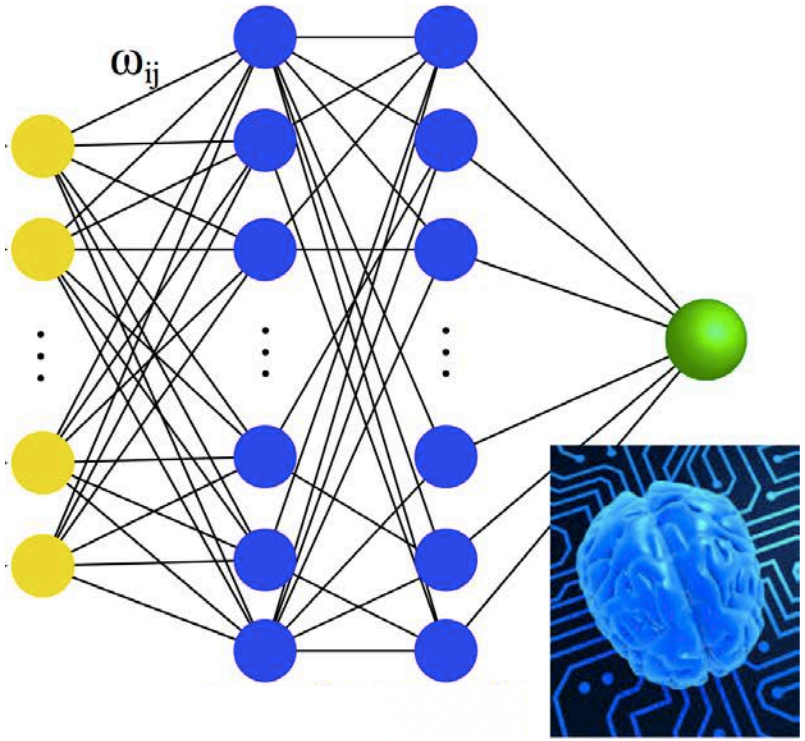


fingerprint vector

f_d filling
ε_d center
W_d width
r_d d-orbital radius
⋮
φ work function
I ionic potential
A electron affinity
r_0 atomic radius
$\Delta\chi$ averaged electronegativity

hidden layers

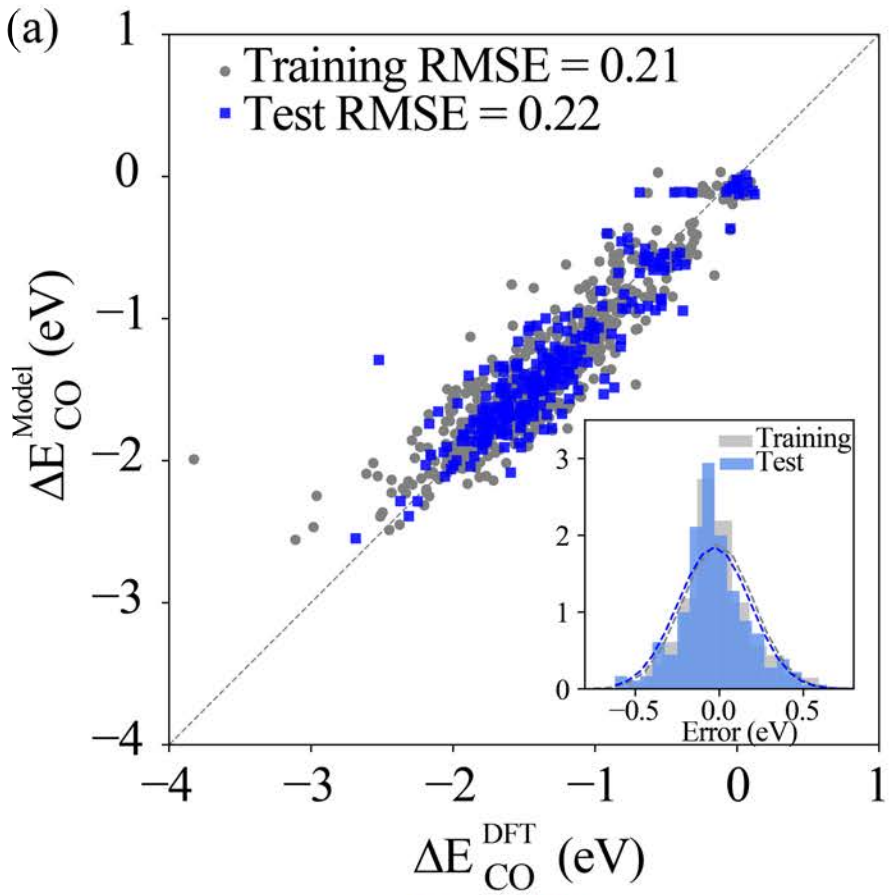
reactivity descriptor

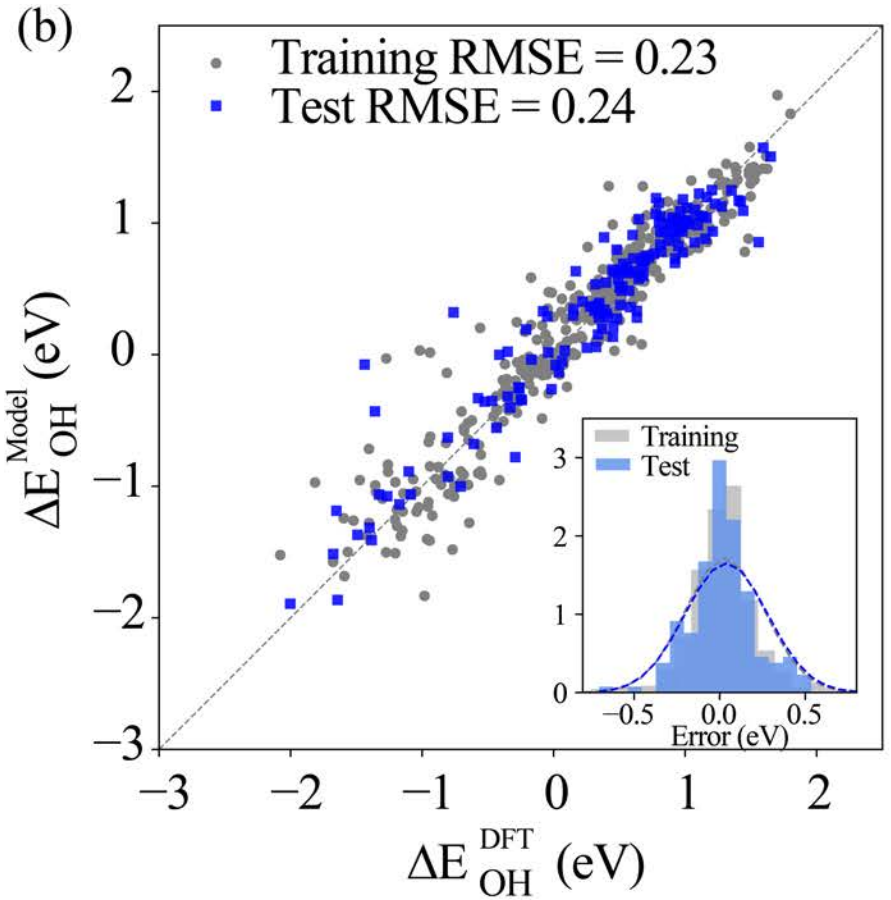


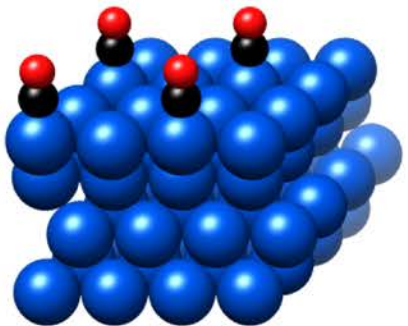
- Material properties of clean alloy surfaces are reduced to fingerprint vectors.
- Inputs are then mapped to reactivity descriptors through an artificial neural netwo

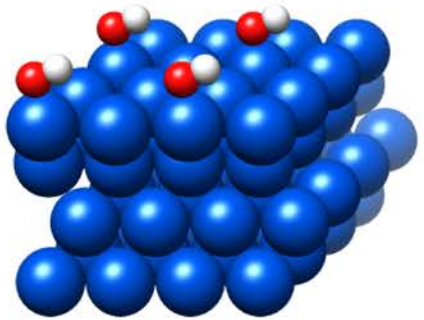
http://pybrain.org/

Neural Network Model Development

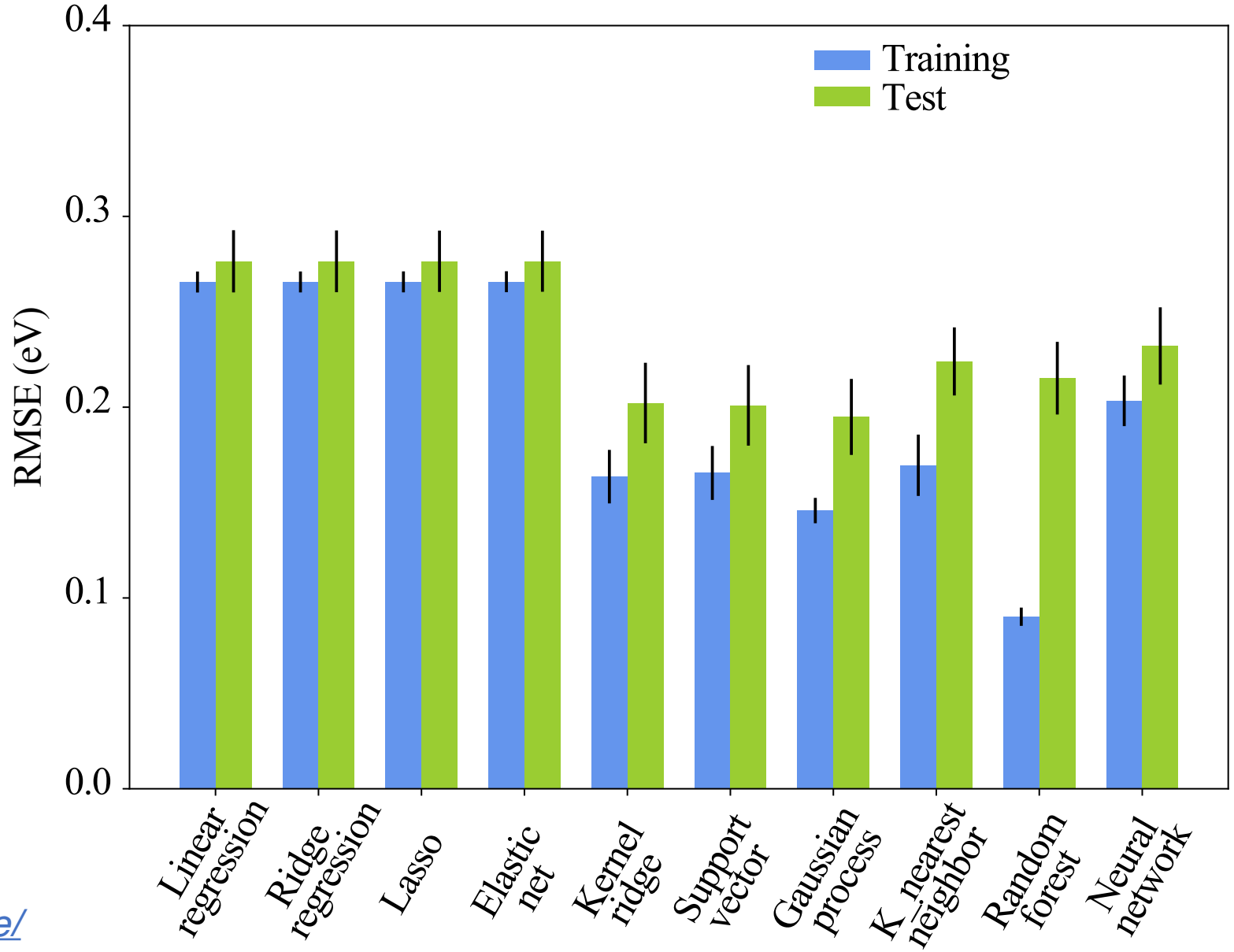






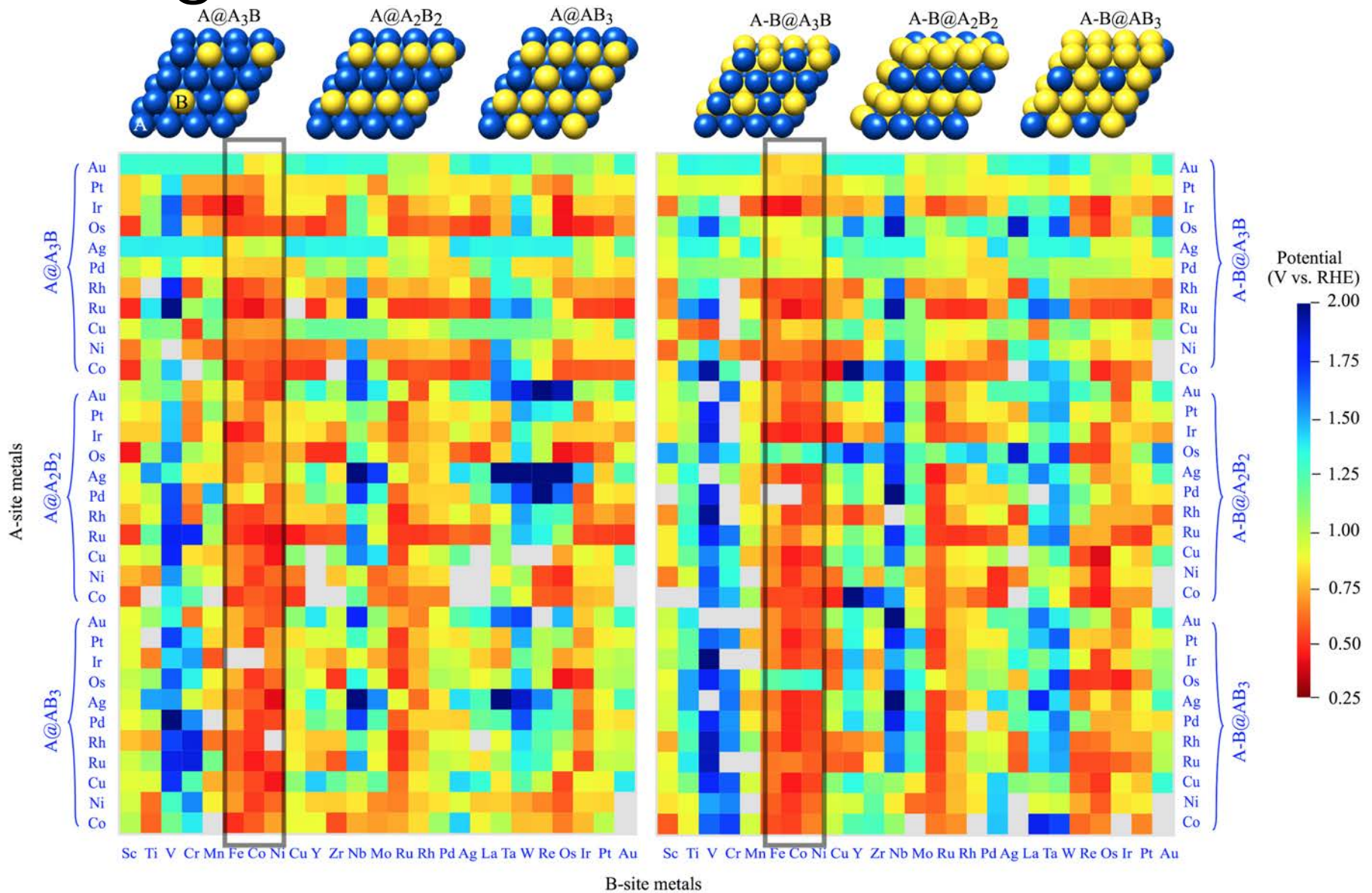


Alternative Machine Learning Models

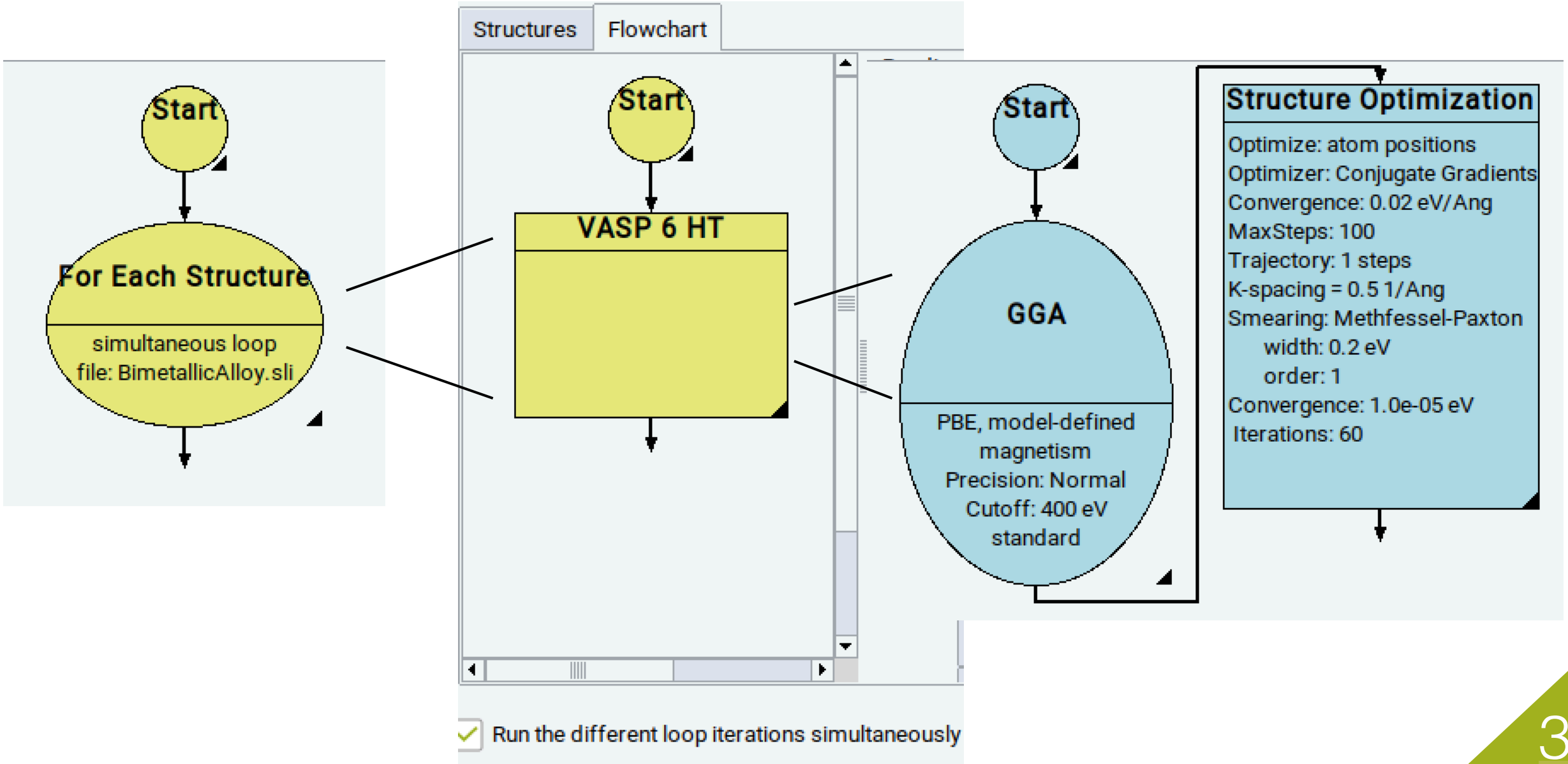


https://scikit-learn.org/stable/

Predicting New Alloys Using Machine Learning Models



Optimize Structures with *MedeA* High-throughput Module



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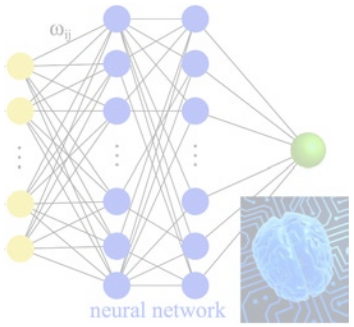
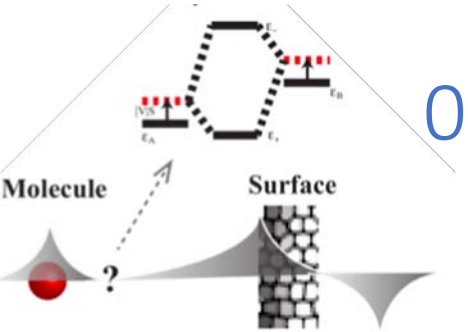


02 Accelerate Materials Discovery

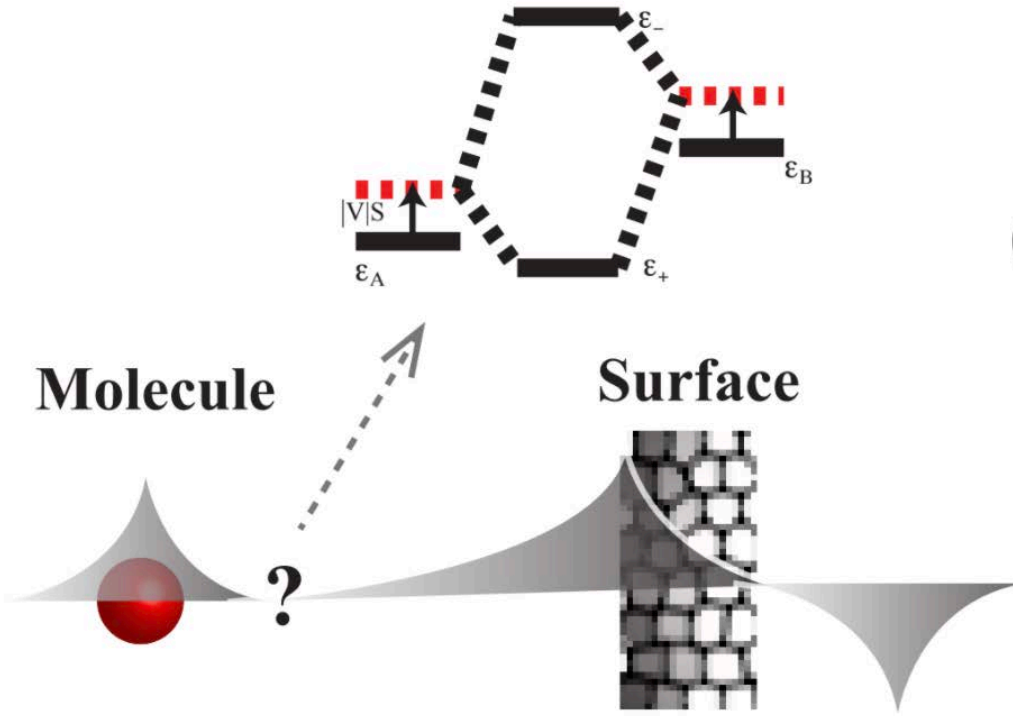
High-throughput screening of bimetallic catalysts enabled by machine learning



03 Advance Catalysis Theory

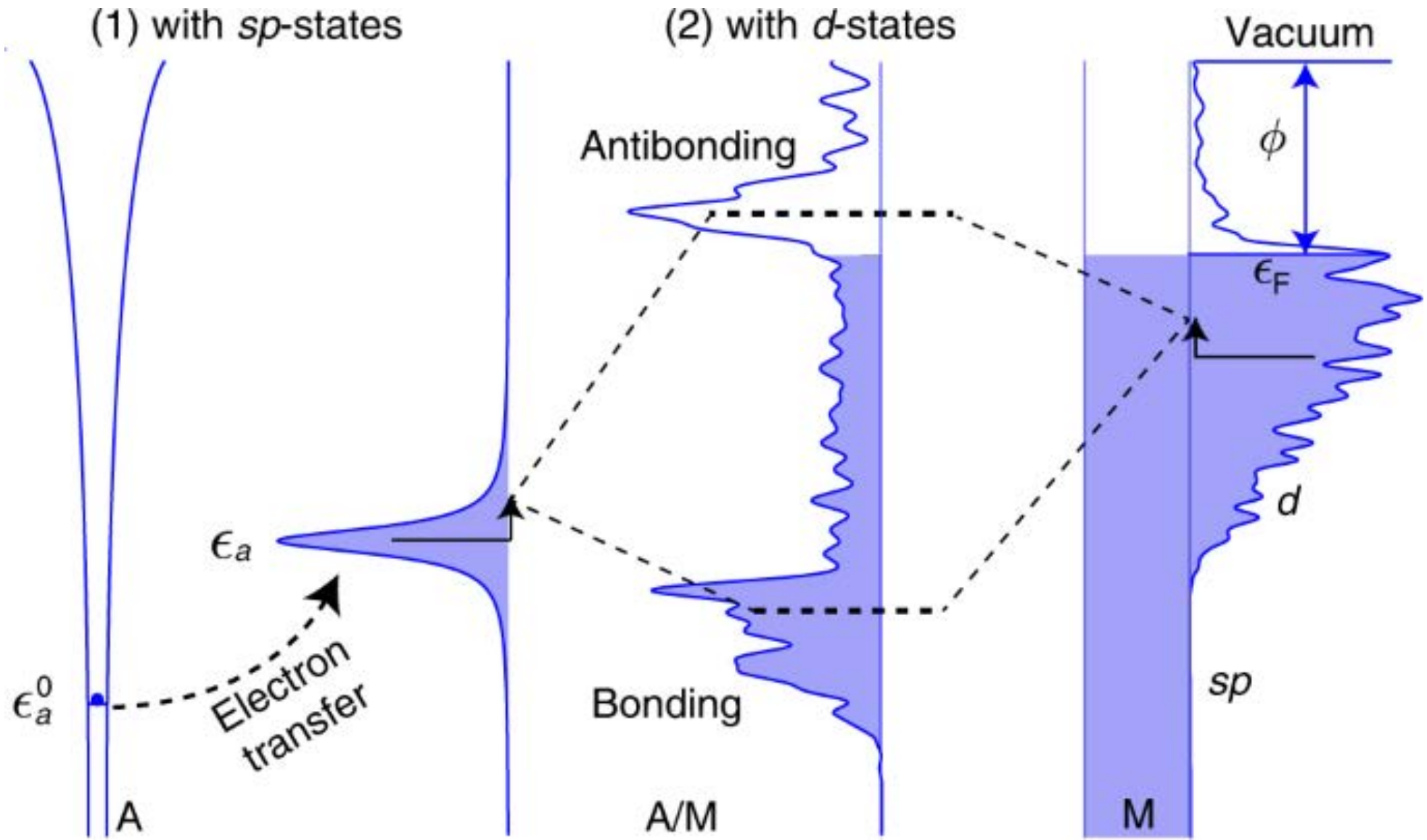
What determines reactivity of catalyst

Bayesian Learning of Chemisorption for Bridging the Complexity of Electronic Descriptors



- ***S. Wang**, et al., Nat Commun 11, 6132 (2020).*

d-band Reactivity Theory



Central Equations of *d*-band Reactivity Theory

$$\hat{\mathcal{H}} = \sum_{\sigma} \left\{ \epsilon_{a\sigma} n_{a\sigma} + \sum_{k} \epsilon_{k} n_{k\sigma} + \sum_{k} (V_{ak} c^{\dagger}_{k\sigma} c_{a\sigma} + H.c.) \right\}$$

Green's Function Approach

$$(I\varepsilon - H^{\sigma} + i\delta) G^{\sigma}(\varepsilon) = I$$

$$G^{\sigma}_{aa}(\varepsilon) = \left[\varepsilon - \varepsilon_{\sigma} - \sum_{k} \frac{|V_{ak}|^2}{\varepsilon - \varepsilon_k + i\delta} \right]^{-1} = [\varepsilon - \varepsilon_{\sigma} - \Lambda(\varepsilon) + i\Delta(\varepsilon)]^{-1}$$

$$\Delta(\varepsilon) = -Im \sum_{k} [|V_{ak}|^2 / (\varepsilon - \varepsilon_k + i\delta)] = \pi \sum_{k} |V_{ak}|^2 \delta(\varepsilon - \varepsilon_k)$$

$$\Lambda(\varepsilon) = \frac{P}{\pi} \int_{-\infty}^{\infty} \frac{\Delta(\varepsilon') d\varepsilon'}{\varepsilon - \varepsilon'}$$

$$\rho_{a}(\epsilon) = \frac{1}{\pi} \frac{\Delta(\epsilon)}{[\epsilon - (\epsilon_{a} + \Lambda(\epsilon))]^2 + \Delta(\epsilon)^2}$$

ΔE_{sp}

$$\Delta E = \Delta E_0 + \frac{2}{\pi} \int_{-\infty}^{\epsilon_F} \tan^{-1} \left[\frac{\Delta(\epsilon)}{\epsilon - \epsilon_a - \Lambda(\epsilon)} \right] d\epsilon - \frac{2}{\pi} \int_{-\infty}^{\epsilon_F} \tan^{-1} \left[\frac{\Delta_0(\epsilon)}{\epsilon - \epsilon_a} \right] d\epsilon + 2(\langle \tilde{n}_a \rangle + f) \alpha \beta V_{ad}^2$$

ΔE_d^{hyb} ΔE_d^{orth}

D. M. Newns, Phys. Rev. 178(1969)1123

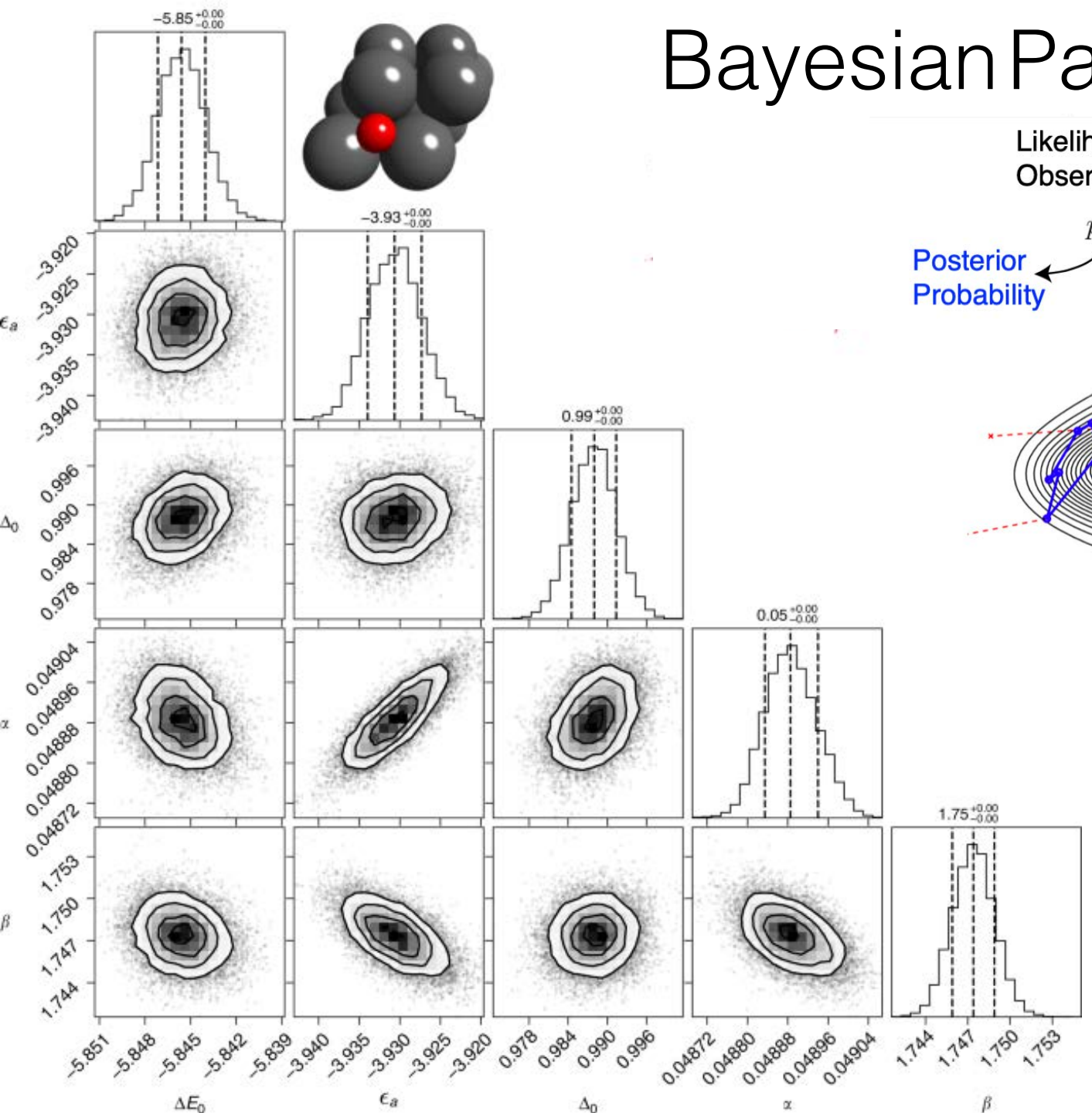
Unknown Parameters in the *d*-band Reactivity Theory

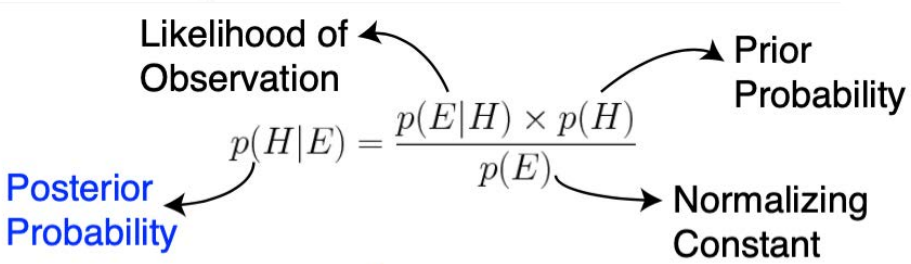
$$\rho_a(\epsilon) = \frac{1}{\pi}\frac{\Delta(\epsilon)}{[\epsilon - (\epsilon_a + \Lambda(\epsilon))]^2 + \Delta(\epsilon)^2}$$

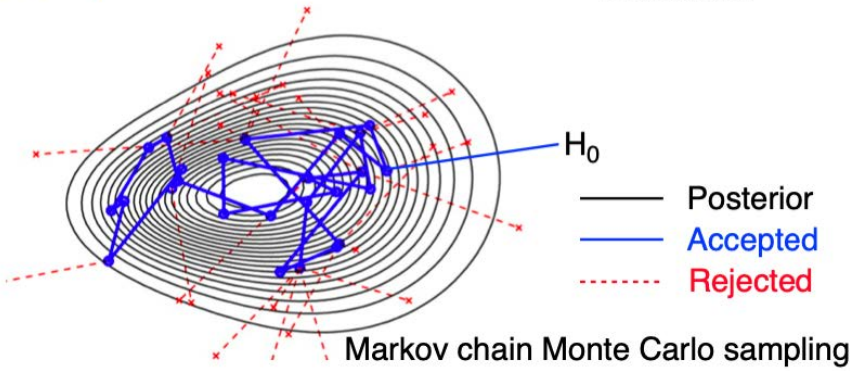
$$\Delta E = \underbrace{\Delta E_0}_{\Delta E_{sp}} + \underbrace{\frac{2}{\pi}\int_{-\infty}^{\epsilon_F} \tan^{-1}\left[\frac{\Delta(\epsilon)}{\epsilon-\epsilon_a-\Lambda(\epsilon)}\right] d\epsilon - \frac{2}{\pi}\int_{-\infty}^{\epsilon_F} \tan^{-1}\left[\frac{\Delta_0(\epsilon)}{\epsilon-\epsilon_a}\right] d\epsilon}_{\Delta E_d^{hyb}} + \underbrace{2(\langle \tilde{n}_a \rangle + f)\alpha\beta V_{ad}^2}_{\Delta E_d^{orth}}$$

- ΔE_0 : energy change due to the interaction of the unperturbed adsorbate orbital(s) with the delocalized *sp*-states
- ε_α: adsorbate resonance energy relative to the Fermi level
- Δ_0: chemisorption function contributed from delocalized *sp*-states
- α: orbital overlap coefficient
- β: denotes the orbital coupling coefficient

Bayesian Parameterization



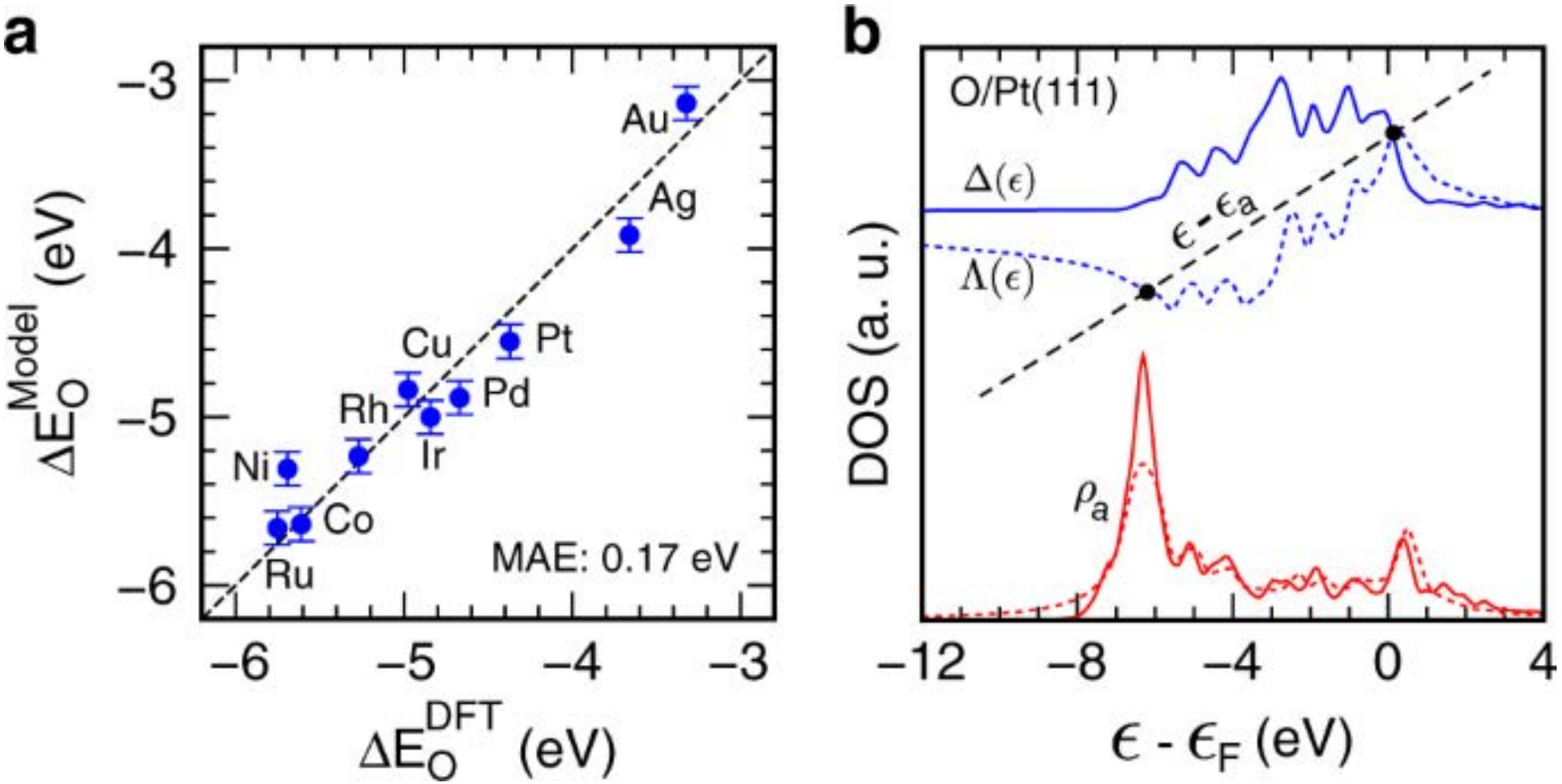




- Independent of initial guess.
- Less prone to trapping at local minima.

https://github.com/hlxin/bayeschem

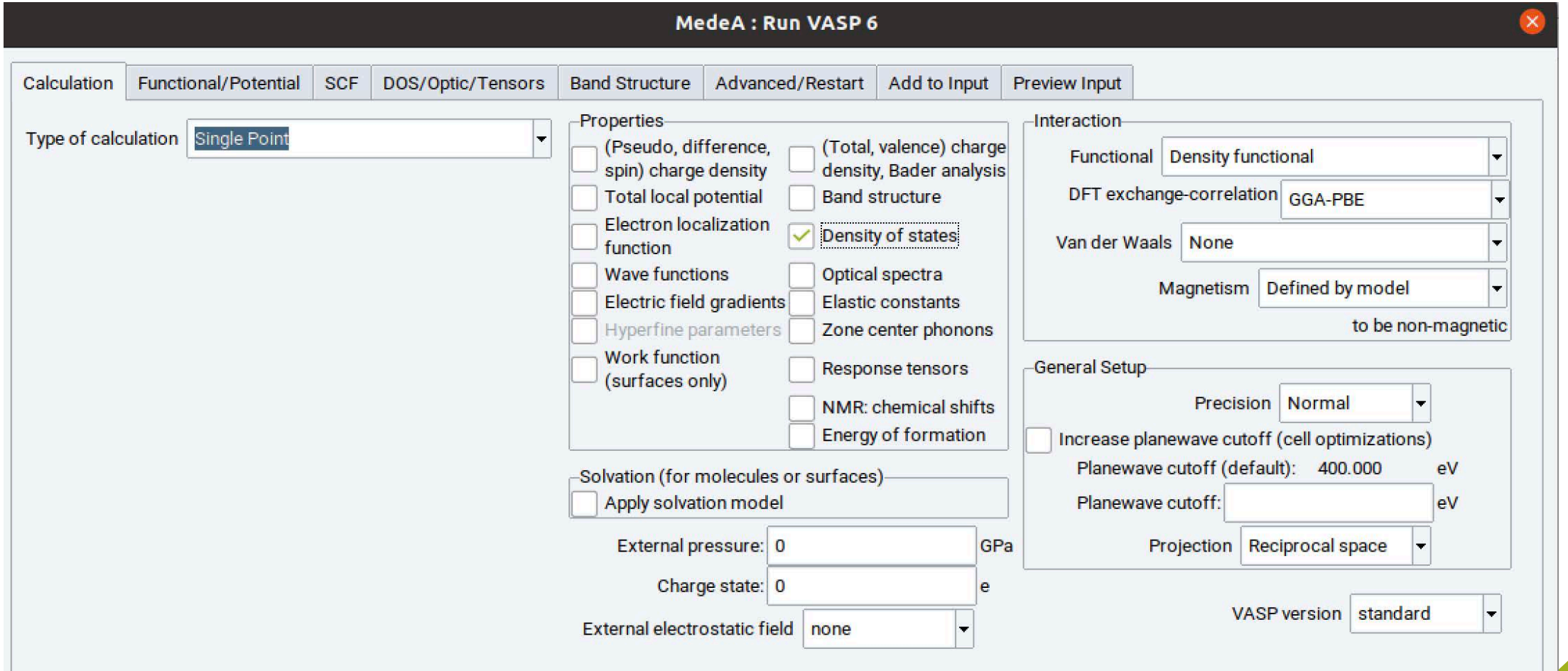
Adsorption Properties of O/M(111) Using Learned Parameters



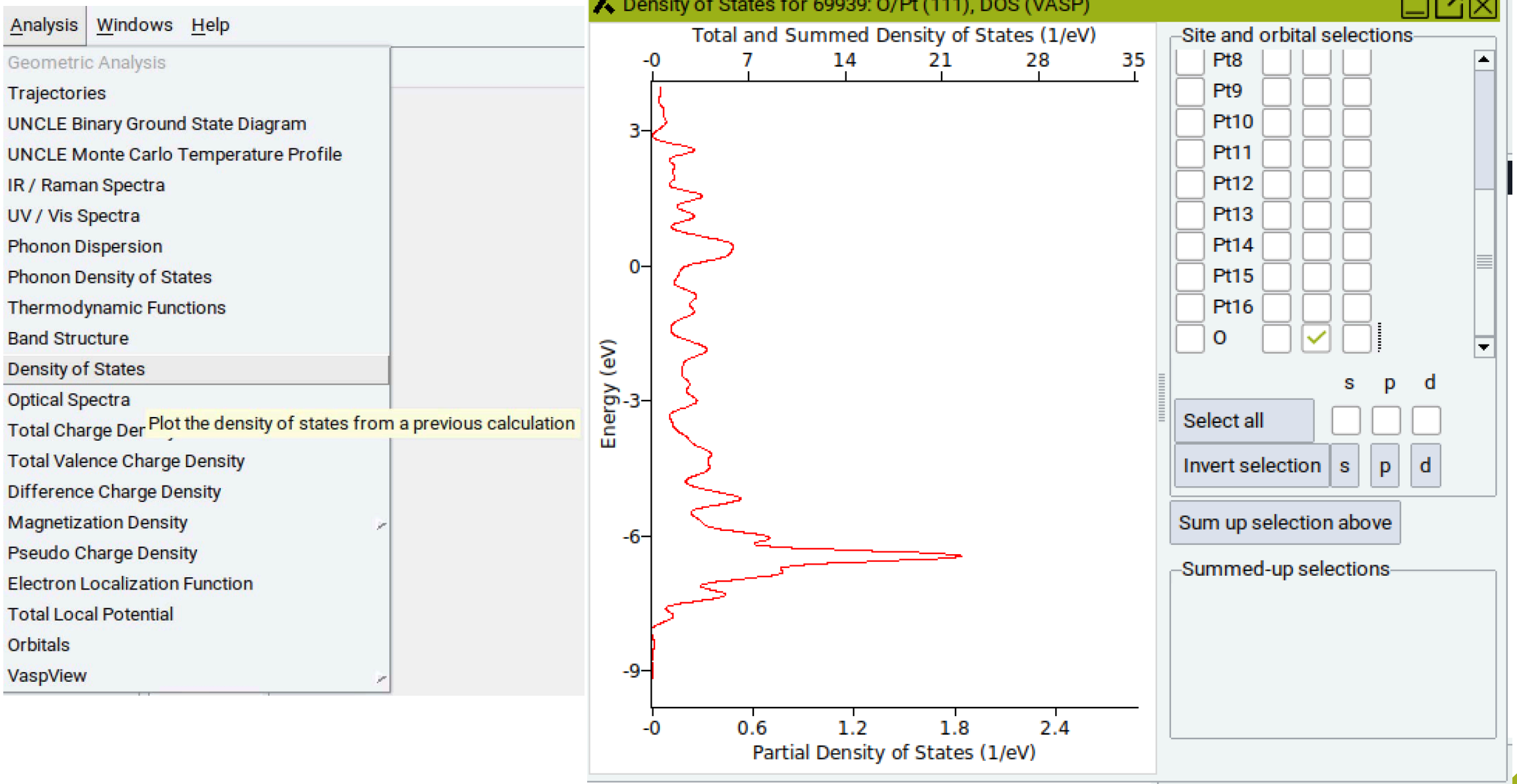
Interaction Energy and DOS Calculation within *MedeA*

$$A + * \longrightarrow A^*$$

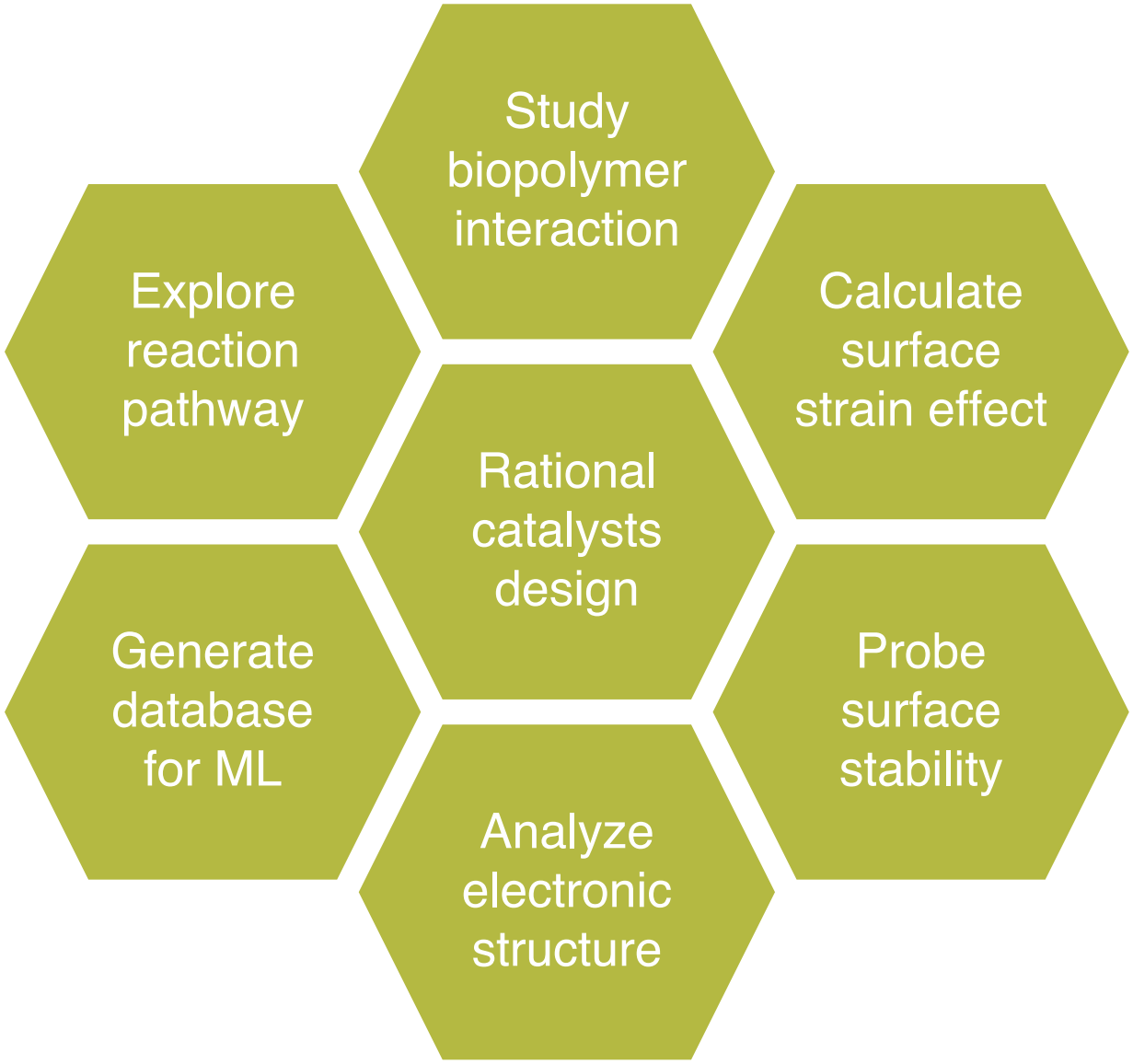
$$BE = E_{A^*} - E_* - E_A$$



Analysis Tool for Density of States



Conclusion


Study biopolymer interaction
Explore reaction pathway
Calculate surface strain effect
Rational catalysts design
Generate database for ML
Probe surface stability
Analyze electronic structure

Online Training and Demo

Orbital Level Understanding of Adsorbate-Surface Interactions in Catalysis

Next Thursday, February 11, 2021

USA/EUROPE:

10:00 am PST/1:00 pm EST

7:00 pm CEST

Register for the training:

https://register.gotowebinar.com/rt/9025371295921111054

*Training open to everyone

Design Catalysts

- MedeA modules mentioned in today's webinar

  https://www.materialsdesign.com/compute-engines
  https://www.materialsdesign.com/analysis-tools

  MedeA Environment
  MedeA VASP
  MedeA HT
  MedeA Phonon
  MedeA Gaussian
  MedeA Transition State Search (TSS)

- Webinar: Live and Recorded
  https://www.materialsdesign.com/webinars
- Publications
  https://www.materialsdesign.com/Publications
- Application Notes
  https://www.materialsdesign.com/application-notes
- For questions or comments contact:

Katherine Hollingsworth
khollingsworth@materialsdesign.com

Question and Answer Session

Dr. Siwen Wang

Materials Design

Dr. Taylor Juran

Materials Design

Questions about Materials Design Webinars

Katherine Hollingsworth

khollingsworth@materialsdesign.com

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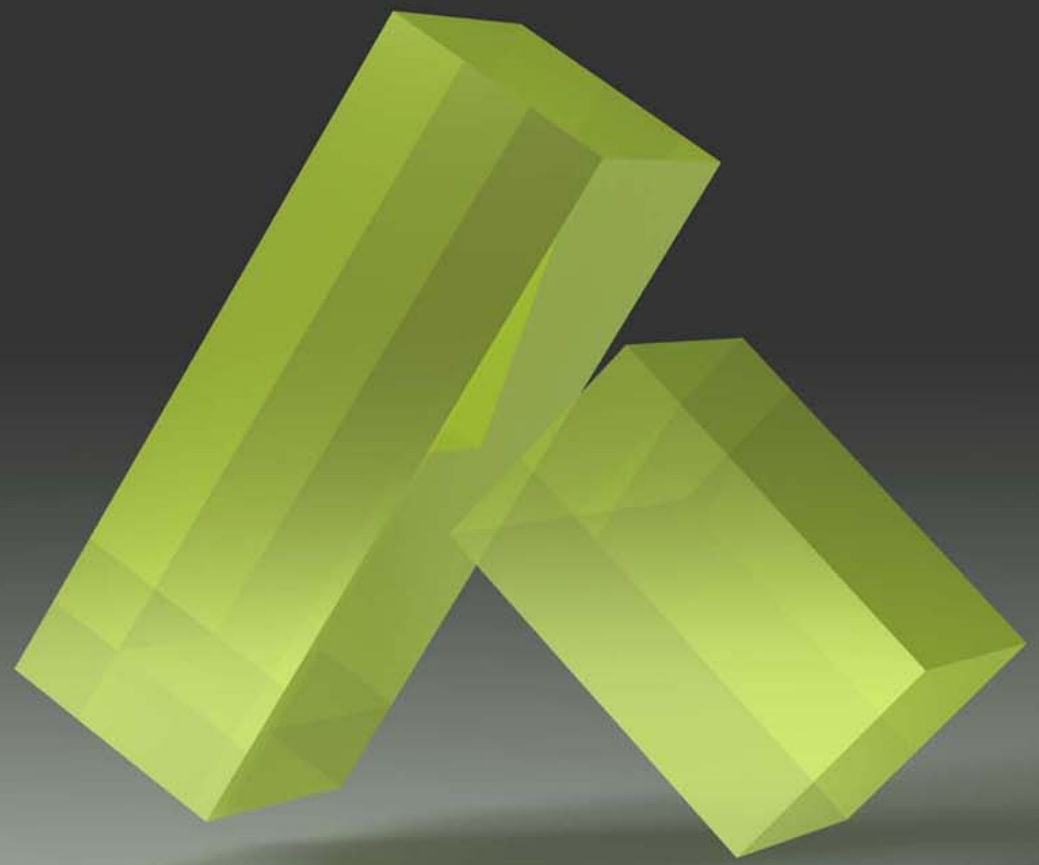
info@materialsdesign.com

www.materialsdesign.com



MedeA

Innovation by Simulation