Rethinking Computational Catalyst Searches with Alchemical Perturbation Density Functional Theory (APDFT)

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NSF GRFP NSF Graduate Research Fellowship Program
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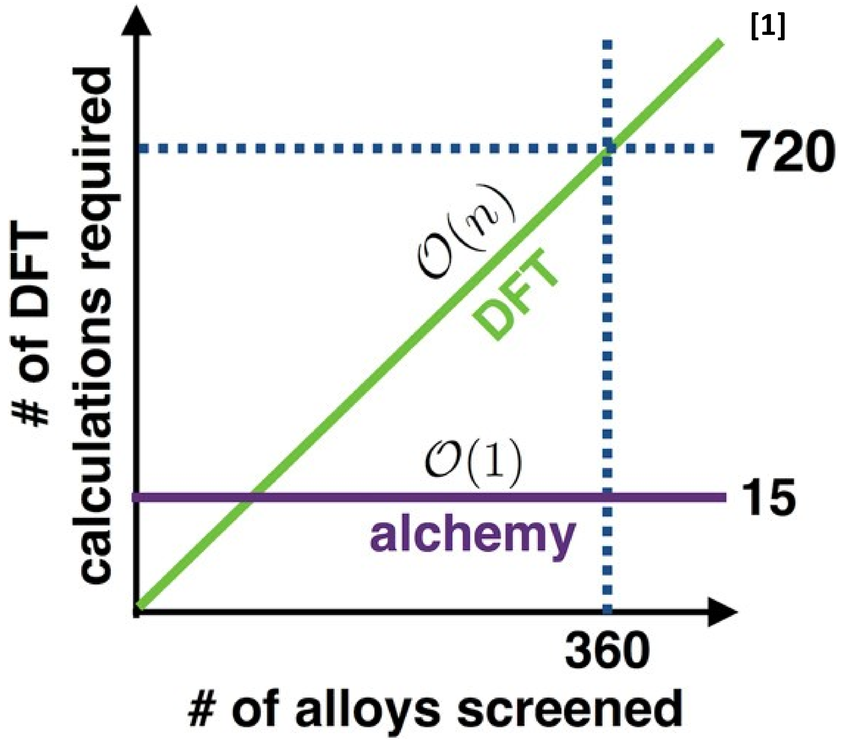
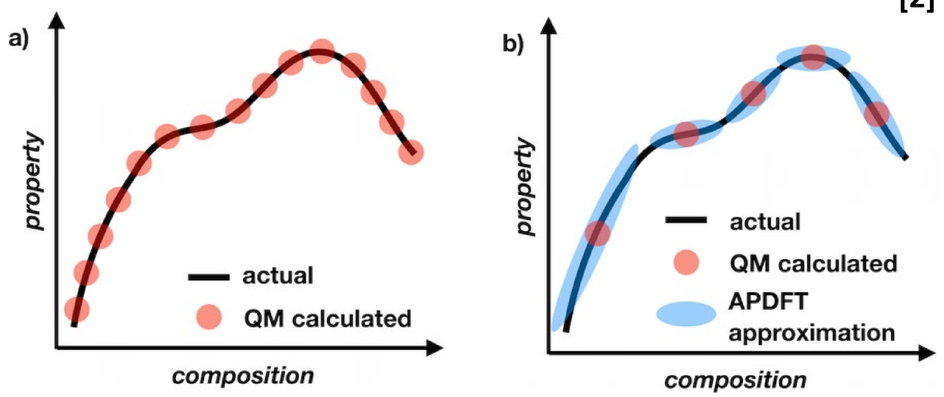
Background

- **Traditional Kohn-Sham density functional theory (KS-DFT) calculations increase the demand of computational resources.**



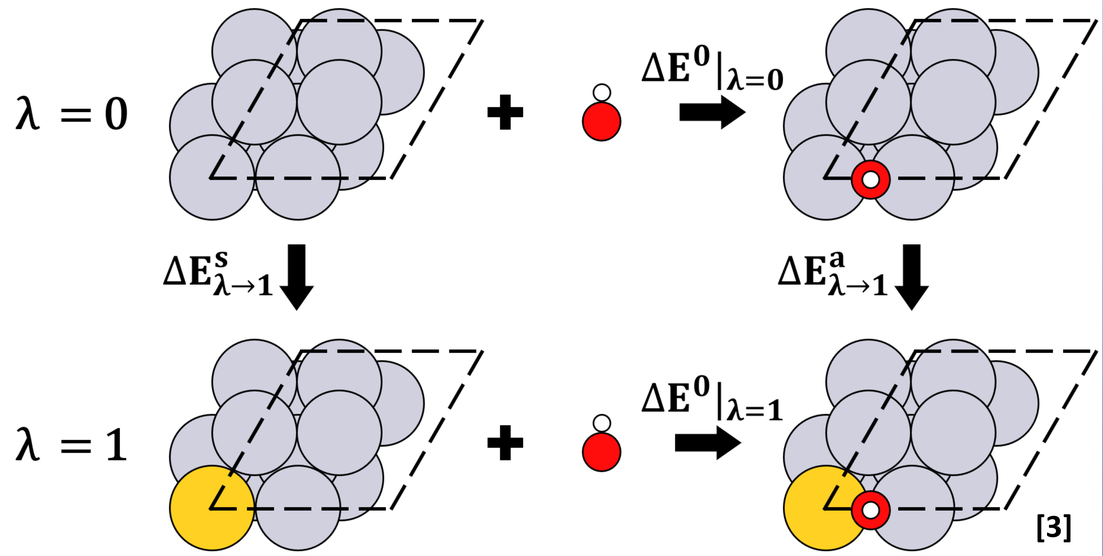
- **<u>Alchemical Perturbation Density Functional Theory (APDFT)</u> estimates catalyst descriptors with minimal computational cost.**

[2]



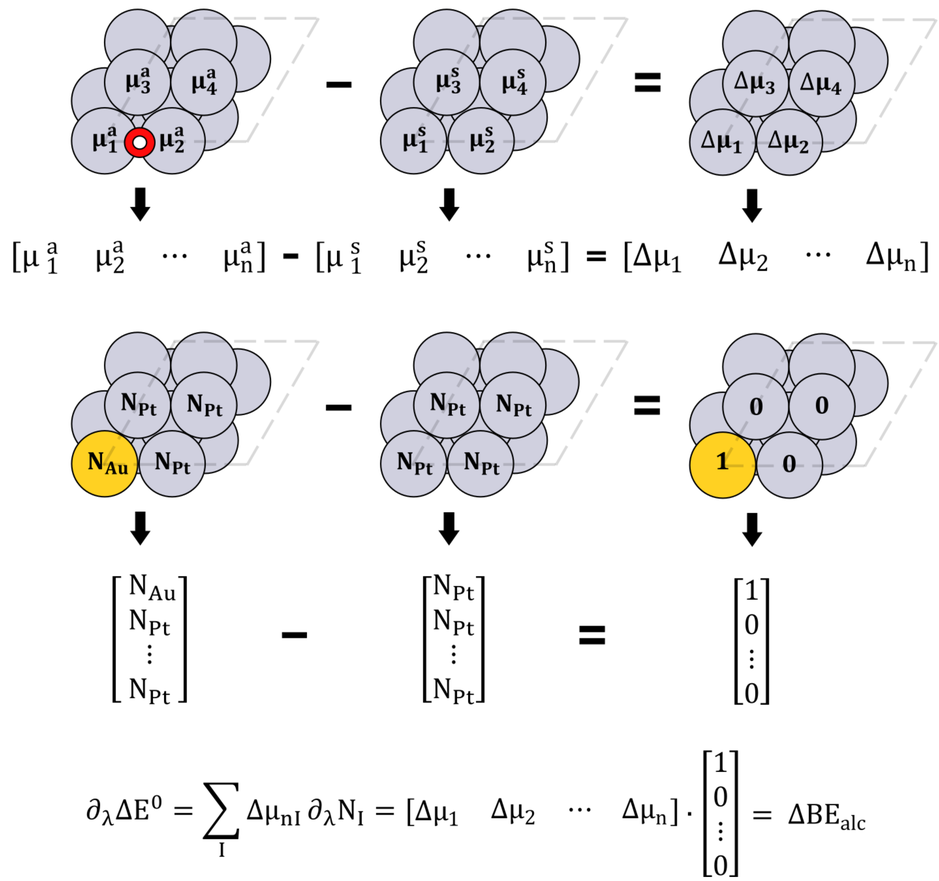
1. Karthikeyan Saravanan; John R. Kitchin; O. Anatole von Lilienfeld; John A. Keith; *J. Phys. Chem. Lett.* **2017,** 8, 5002-5007.
2. John A. Keith; *Electrochem. Soc. Interface,* **2020,** 29, 63

Scheme for calculating BE with APDFT



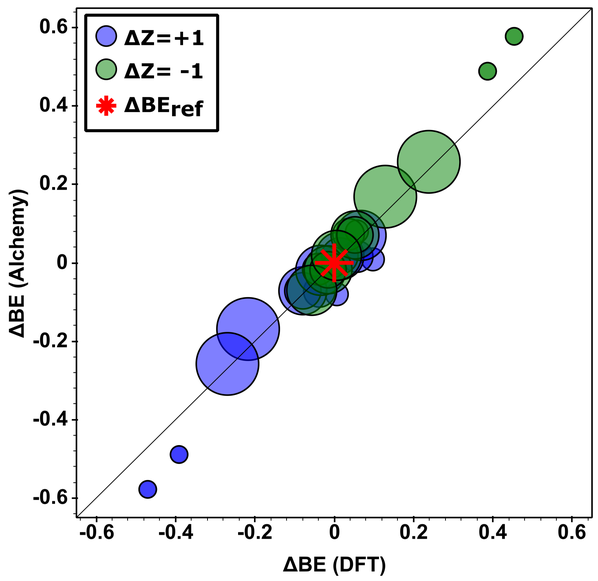
Scheme for calculating BE with APDFT

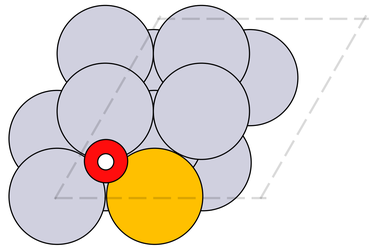
[3]



3. Charles D. Griego; John R. Kitchin; John A. Keith; *Int. J. Quantum. Chem.* **2020,** 121:e26389

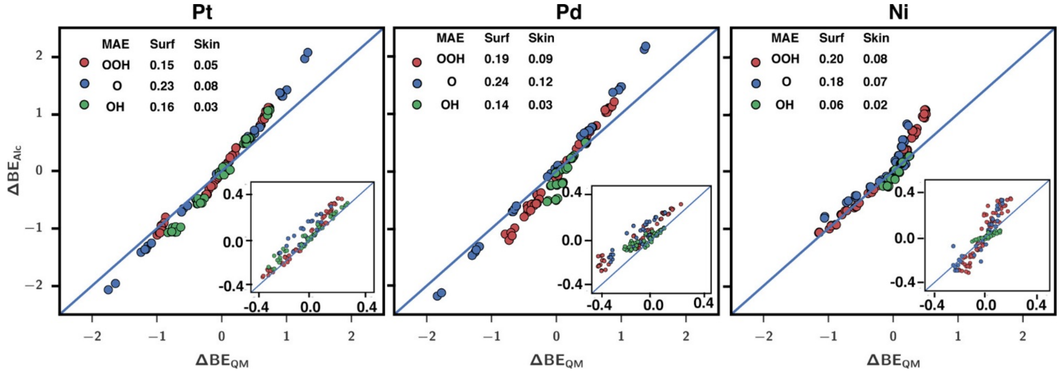
Binding Energy Predictions: Example Case [1]

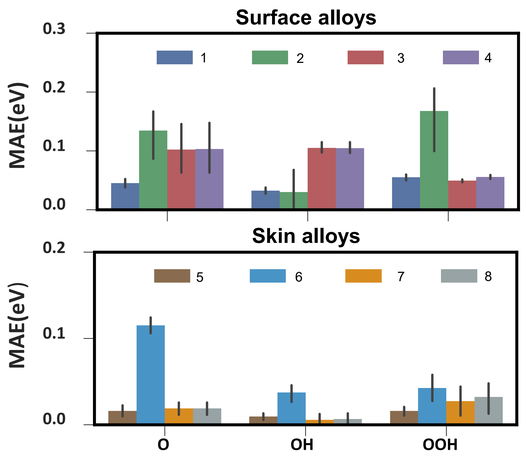




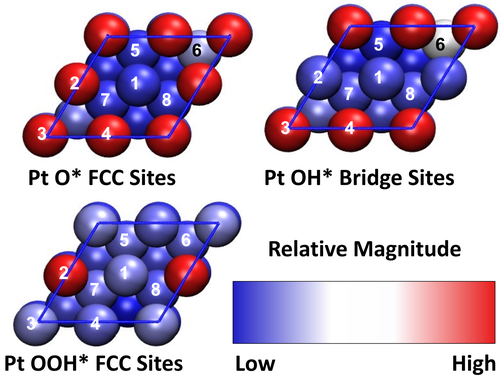
- OH* BE on 32 alloys of Pt
  - Pt → Au ($\Delta Z = +1$)
  - Pt → Ir ($\Delta Z = -1$)
- Data point size corresponds to distance of altered site from OH
- 0.05 eV mean unsigned error [1]

BE Predictions: Pt, Pd, and Ni Alloys [2]





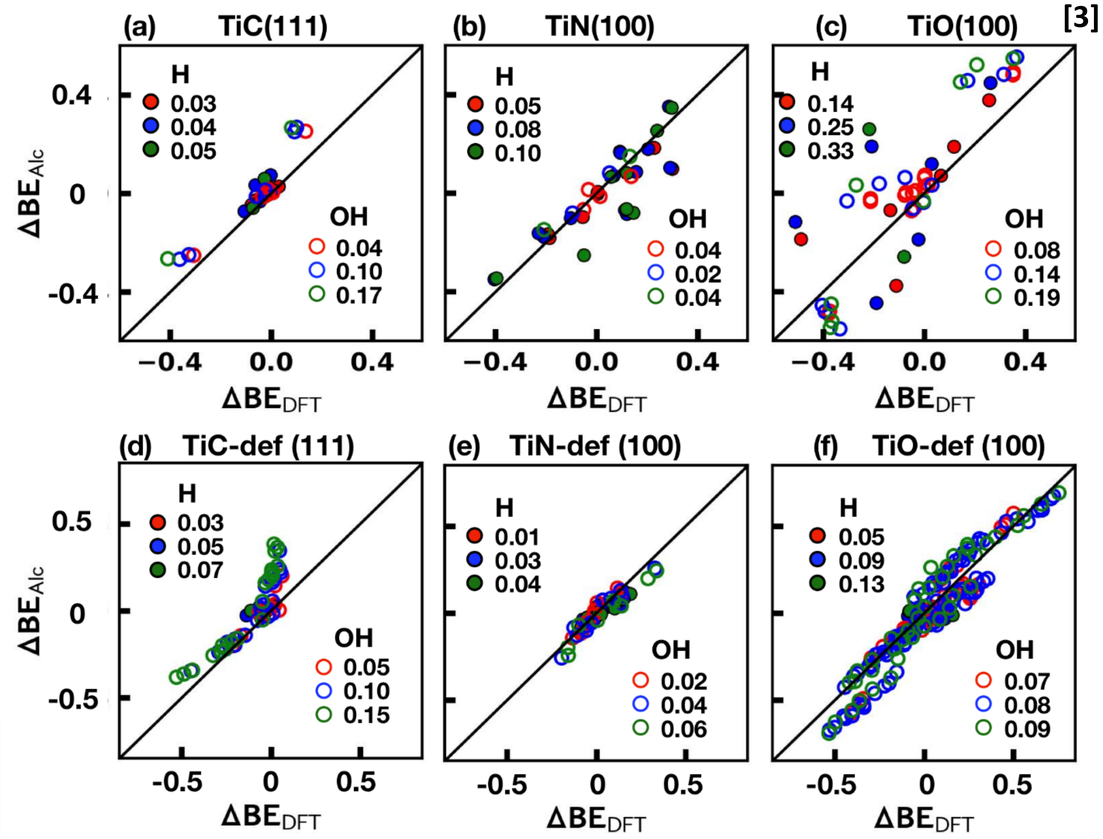
Alchemical Gradients Heat Map [2]



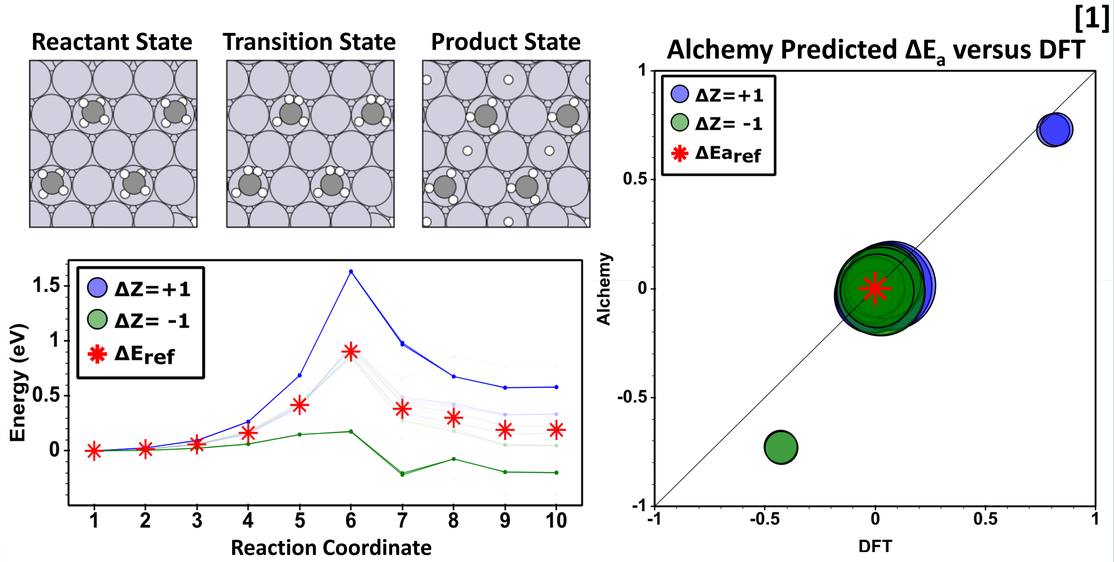
- Alchemical gradients are highest near the adsorbate sites.
- Largest errors occur when atoms are transmuted at these sites.[2]

1. Charles D. Griego; John R. Kitchin; John A. Keith; *Int. J. Quantum. Chem.* **2020,** 121:e26389
2. Karthikeyan Saravanan; John R. Kitchin; O. Anatole von Lilienfeld; John A. Keith; *J. Phys. Chem. Lett.* **2017,** 8, 5002-5007.

BE Predictions: TiC, TiN, and TiO Materials [3]



Reaction Pathways and Activation Energy [1]

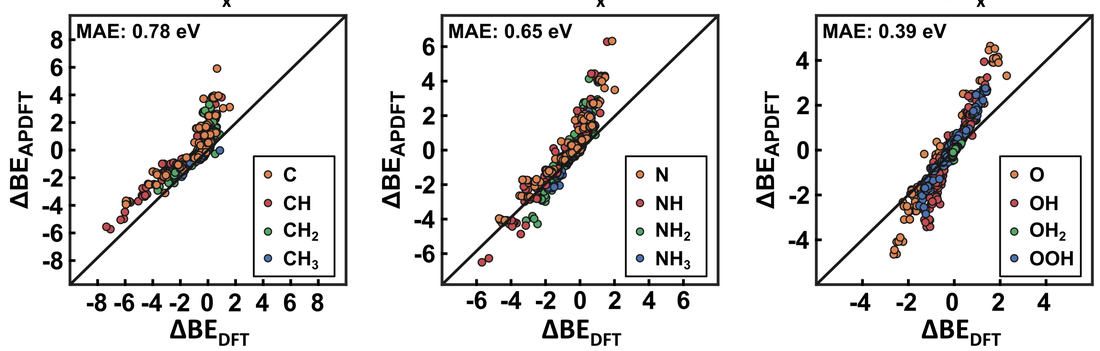


- Predicted 32 reaction pathways from one NEB calculation.
- Activation energies agree within 0.3 eV versus DFT.

3. Charles D. Griego; Karthikeyan Saravanan; John A. Keith; *Adv. Theory Sim.* ***2019,*** *2: 1800142*

Identifying Shortcomings with APDFT [1]

[1]



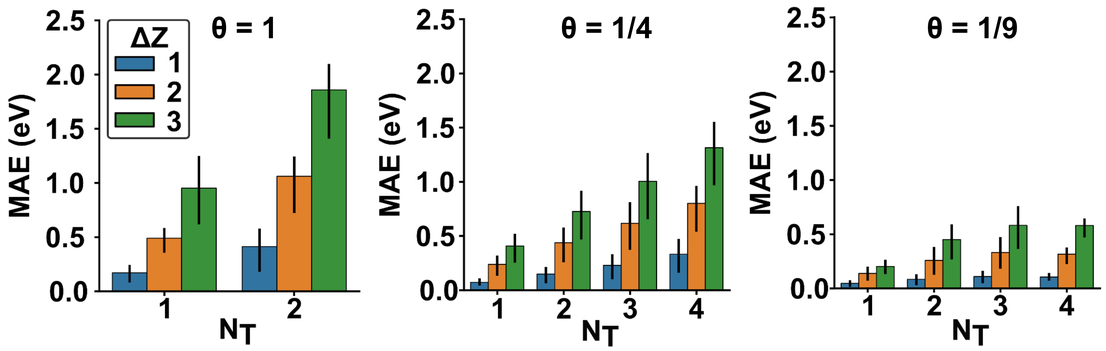
Adsorbates on Pt alloys:
- CH_x, NH_x, OH_x (x = 0-3)
- Coverage θ = 1, 1/4, 1/9

Alloy variations:
- # of transmutations N_T = 1, 2, 3, or 4
- Nuclear charge change ΔZ = 1, 2, or 3

Breaking Down Sources of Error [1]

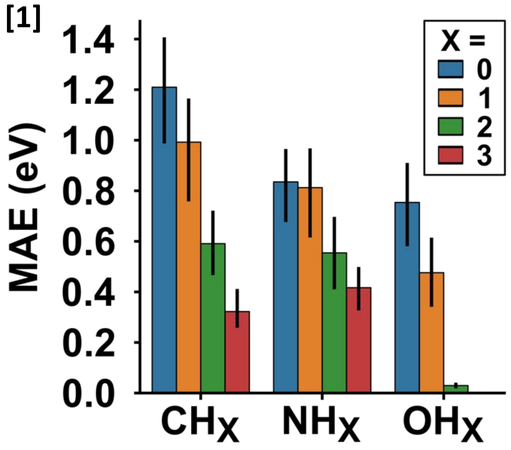
[1]

APDFT errors sorted by N_T, ΔZ, and θ



APDFT errors by adsorbate type

[1]



Overall Observations: [1]
- Errors increase with N_T and ΔZ
- Errors increase with θ
- Errors decrease with hydrogenation of the central atom in the adsorbate

1. Charles D. Griego; Lingyan Zhao; Karthikeyan Saravanan; John A. Keith; *AIChE J.* **2020,** 66:e17041

Correcting APDFT with Machine Learning [1]

ML Workflow

[1]

Input: Define a hypothetical alloy by making transmutations to a reference catalyst surface

↓

Fingerprinting: Label transmuted sites as 1 and remaining sites 0

↓

Feature Vector Construction: Record dopant fingerprints, ΔZ, N_T adsorbate type, θ, and dopant in an array

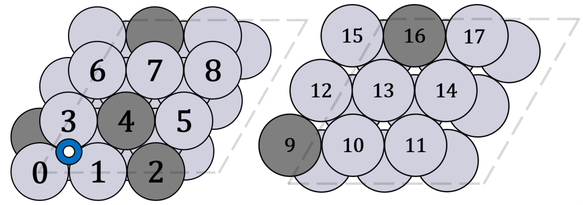
↓

ML Model: Predict error between APDFT and DFT ($Error_{ML}$)

↓

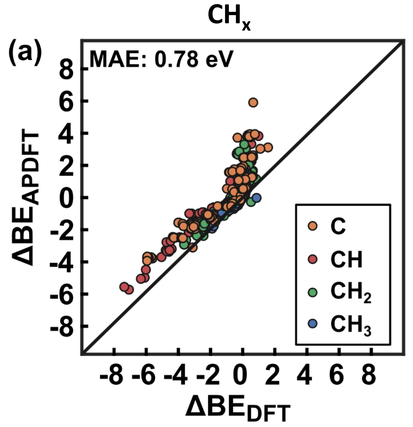
ML-corrected APDFT BE prediction:
$BE_{APDFT+ML} = BE_{APDFT} + Error_{ML}$

Fingerprinting Example:
3x3 Unit Cell (θ = 1/9)
NH Adsorbate



[0 0 1 0 1 0 0 0 0
1 0 0 0 0 0 0 1 0]

[1]



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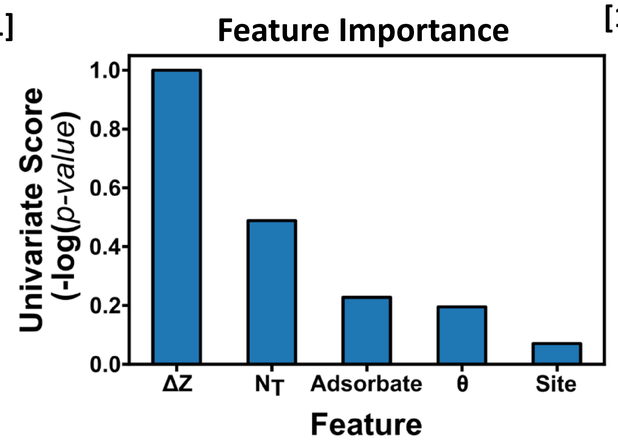

- APDFT errors are predicted with support vector regression models
- MAE reduced by an order of magnitude (dataset of CH_x adsorbates)
- ΔZ and N_T have the greatest influence on the model predictions

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