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

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Background

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

Alchemical Perturbation Density Functional Theory (APDFT) estimates catalyst descriptors with minimal computational cost.

Scheme for calculating BE with APDFT

\[ \Delta E^0_{\lambda=0} + \Delta E^S_{\lambda=1} \]

\[ \Delta E^0_{\lambda=1} \]

\[ \Delta E_{\lambda=1} \]

\[ \lambda = 0 \]

\[ \lambda = 1 \]


**Binding Energy Predictions: Example Case**

- 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

**BE Predictions: Pt, Pd, and Ni Alloys**

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

**BE Predictions: TiC, TiN, and TiO Materials**

- Predicted 32 reaction pathways from one NEB calculation.
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**Identifying Shortcomings with APDFT**

- Adsorbates on Pt alloys: \( \text{CH}_x, \text{NH}_x, \text{OH}_x \) (\( x = 0-3 \))
- Coverage \( \theta = 1, 1/4, 1/9 \)
- Alloy variations:
  - \( \# \) of transmutations \( N_T = 1, 2, 3, 4 \)
  - Nuclear charge change \( \Delta Z = 1, 2, 3 \)

**APDFT errors sorted by \( N_T, \Delta Z, \) and \( \theta \)**

- APDFT errors by adsorbate type
  - Overall Observations:
    - Errors increase with \( N_T \) and \( \Delta Z \)
    - Errors increase with \( \theta \)
    - Errors decrease with hydrogenation of the central atom in the adsorbate

**Correcting APDFT with Machine Learning**

- ML Workflow
  1. Input: Define a hypothetical alloy by making transmutations to a reference catalyst surface
  2. Fingerprinting: Label transmuted sites as 1 and remaining sites 0
  3. Feature Vector Construction: Record dopant fingerprints, \( \Delta Z, N_T, \) adsorbate type, \( \theta \), and dopant in an array
  4. ML Model: Predict error between APDFT and DFT (\( \text{Error}_{\text{ML}} \))

- ML-corrected APDFT BE prediction:
  \[ \text{BE}_{\text{APDFT}} + \text{Error}_{\text{ML}} \]

**Fingerprinting Example:**

- 3x3 Unit Cell (\( \theta = 1/9 \))
- NH Adsorbate