Benchmark First Principles Calculations of Adsorbate Free Energies

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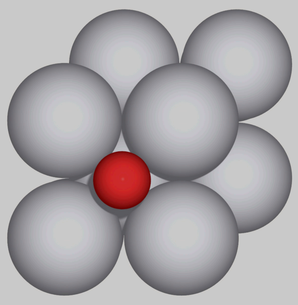
How reliable are calculated rates of catalytic reactions?

Free energies of adsorption / reaction determine rate and equilibrium constants



✔ **0 K contributions:**

accessible by density functional theory based methods

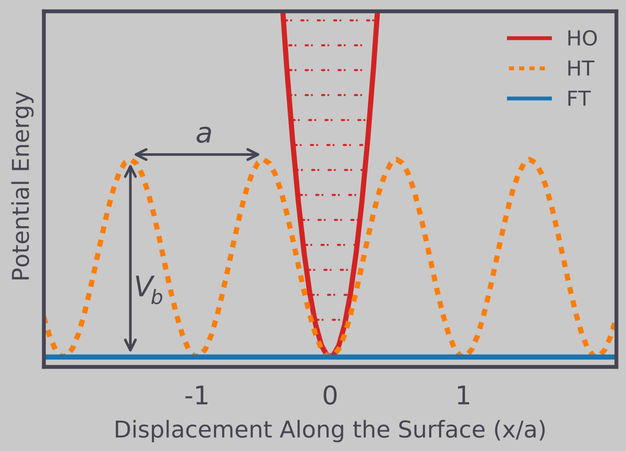
can be benchmarked to higher order calculations or using error estimation functionals

? **Contributions from motion of individual adsorbates:**

computed using partition functions extracted from assumed analytical form for the adsorbate potential energy surface (PES)

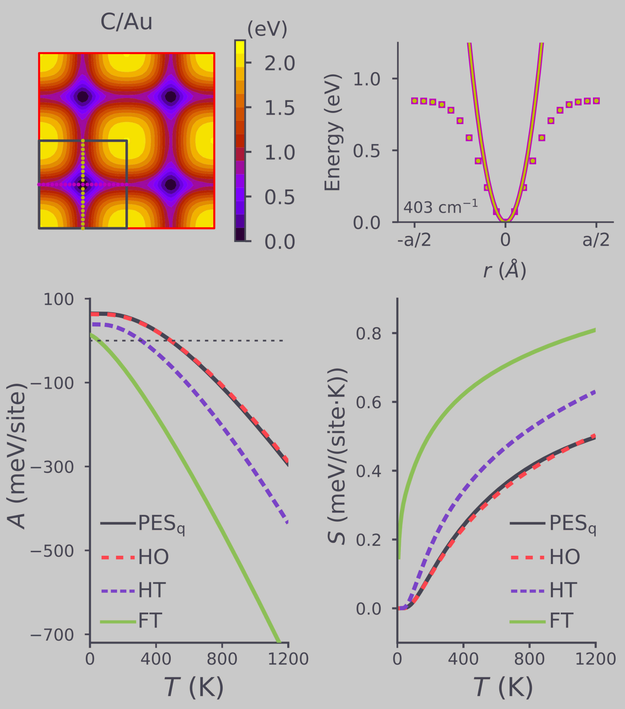
e.g. Harmonic Oscillator, Free Translator, Hindered Translator

performance is system dependent; models often combined arbitrarily

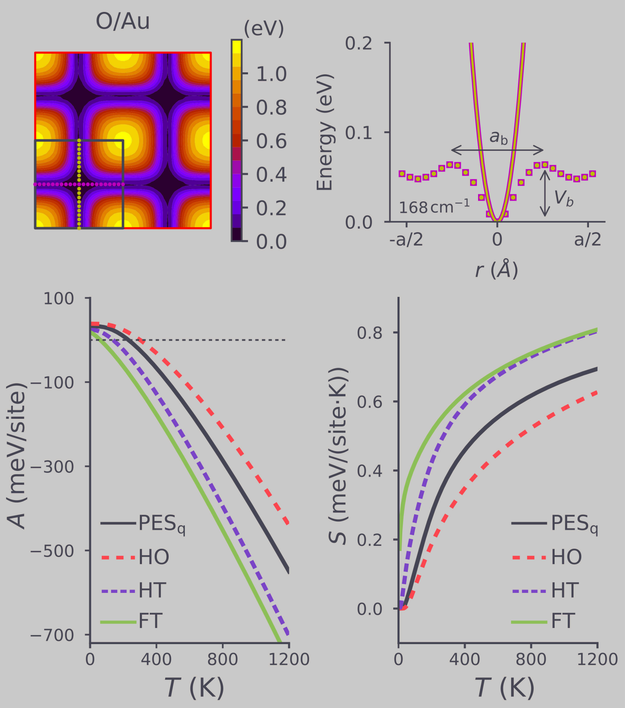


Popular models appropriate only under certain temperature ranges and PES corrugation

Deep Well Potential



Shallow Double Well Potential

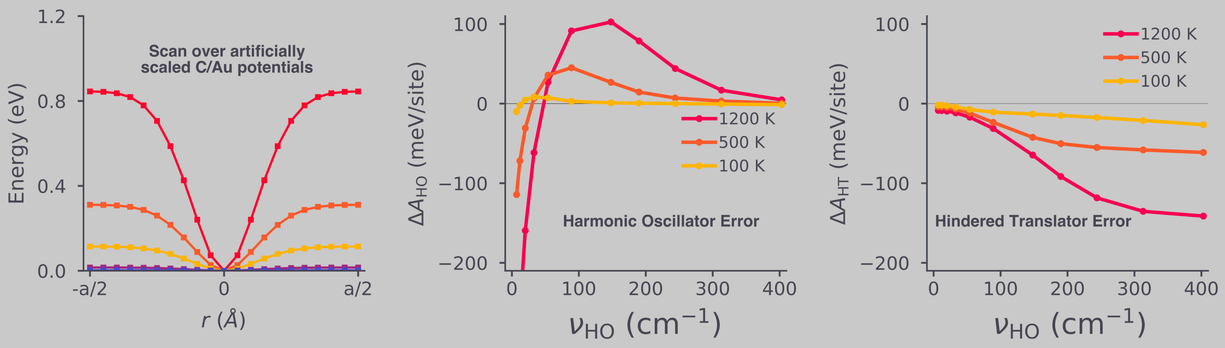


HO and PES$_q$ free energies / entropies identical for systems with high vibrational frequencies

Hindered Translator model underestimates steepness of potential

Parabolic fit follows true PES only very close to the minima; HO only appropriate at low T

Cosine HT potential fails to capture double welled PES, over-flattening the landscape



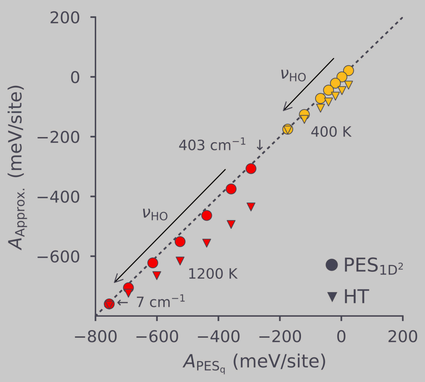
HO fails completely at freq < 50 cm^{-1} ($q \longrightarrow \infty$); HT performs poorly at high freq

The practice of using cutoff vibrational frequencies in the intermediate regime (e.g. 150 cm^{-1}) to switch between free energy approximations may compound error

HO and HT have errors similar in magnitude but of opposite sign

Using one approximation to treat the reactants and another to treat products would lead to over an order of magnitude error in the equilibrium constant

Errors in standard free energy approximations expected to quantitatively impact kinetic models



If in-plane potential is separable, 2-dimensional eigenvalue problem can be accurately replaced by two 1-dimensional problems

Advantages of quantum mechanical PES sampling:

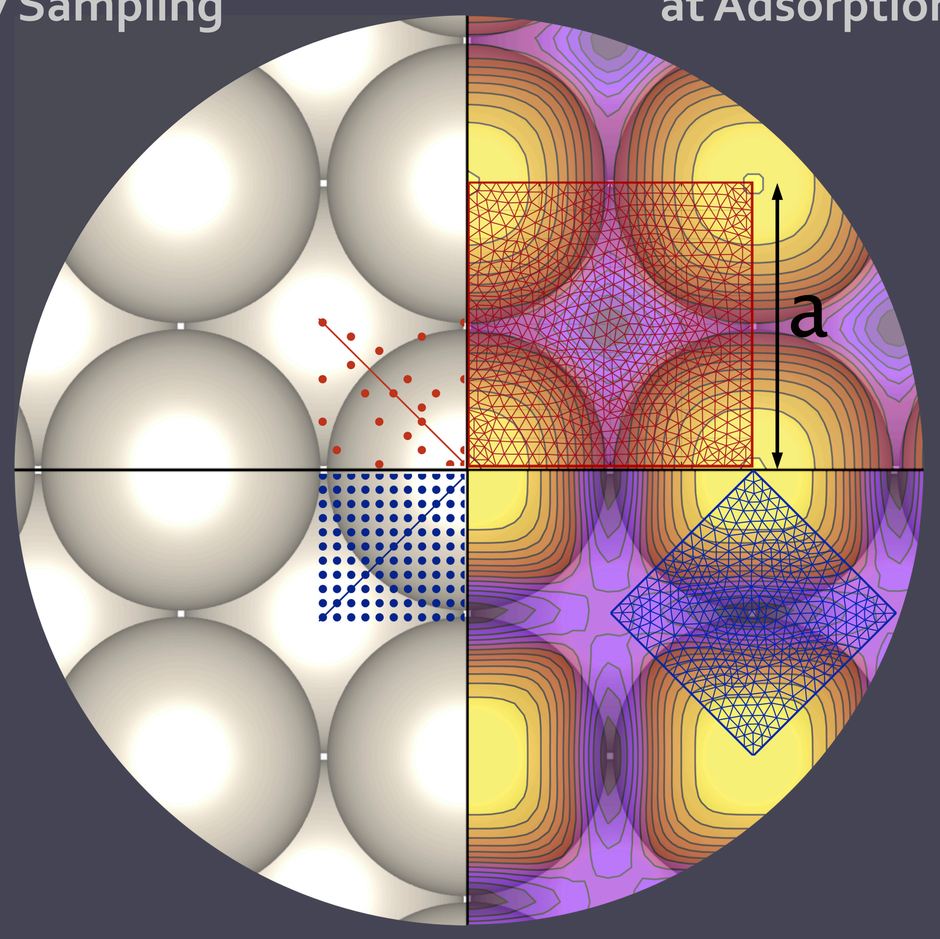
approach is general; accurate for arbitrary potentials

identical computational cost to HT method

Accurate adsorbate free energies from exact translational energy states

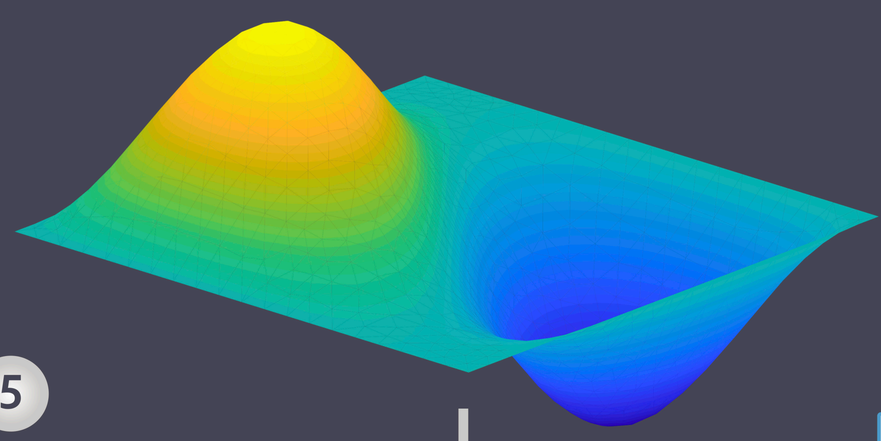
1 Coarse DFT Potential Energy Sampling

3 Finite Element Mesh at Adsorption Site



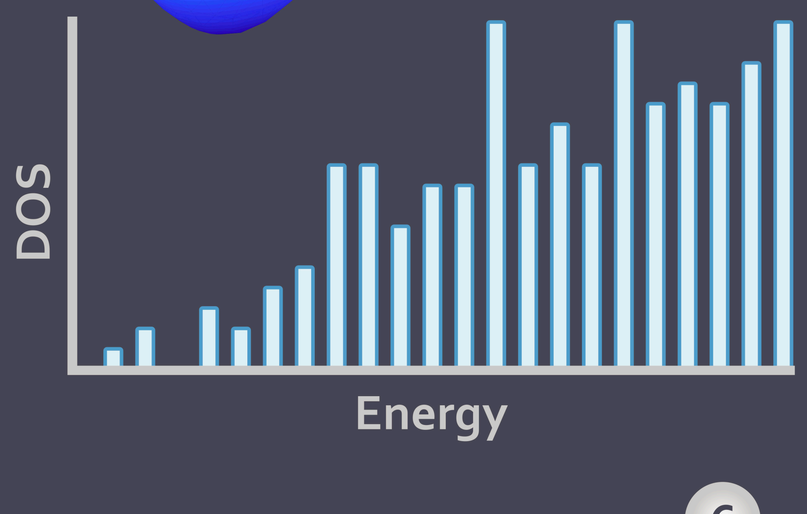
2 Fine Neural Network Potential Energy Sampling

4 Schrödinger Equation Solved Numerically



5 Partition Function from Eigenstates

$$q = \sum \exp\left(-\frac{E_i}{k_B T}\right)$$



6 Accurate Adsorbate Free Energies

$$A = -k_B T \ln(q)$$

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Eilers Fellowship

Khorshidi et al, *Comput Phys Commun*, 2016, 207, 310