Barrier heights in heterogeneous catalysis

The good the bad and the evil

Katharina Doblhoff-Dier| TREX-CECAM meeting

Universiteit Leiden
The Netherlands

Heterogeneous catalysis

- ~80% of industrial chemical processes require catalysts[1]
- e.g., Haber-Bosch: ~1% of world's energy consumption[2]


Adapted from https://commons.wikimedia.org/wiki/File:Ammonia_production_installations_-_panoramio.jpg

[1] Ma and Zaera; Encyclopedia of Inorganic Chemistry, John Wiley & Sons (2006), doi: 10.1002/0470862106.ia084

[2] Capdevila-Crtada, Nature Catalysis (2019), doi: 10.1016/j.joule.2019.10.006

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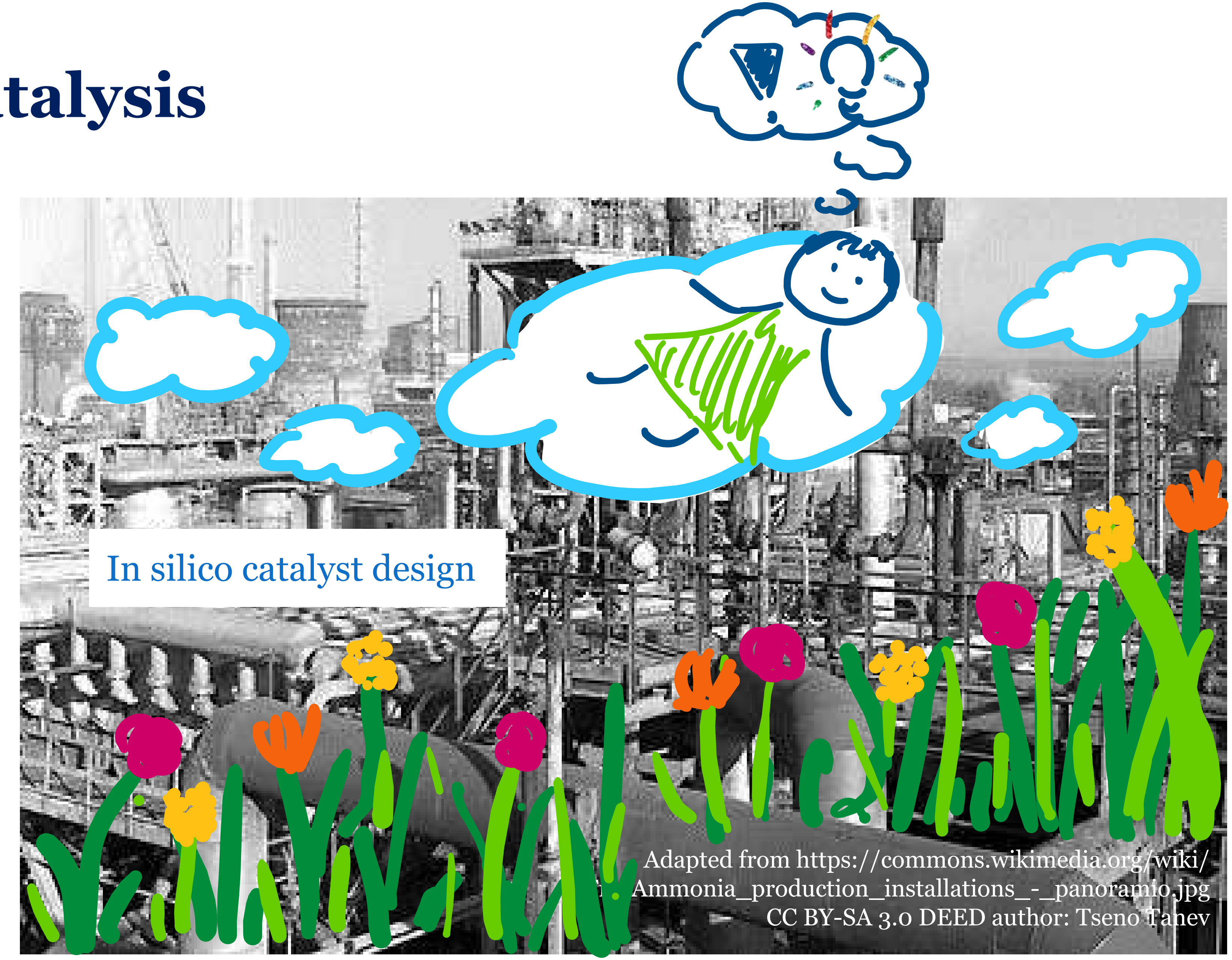

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What can quantum Monte Carlo do for heterogeneous catalysis?

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Computational heterogeneous catalysis

- Why *in silico* catalyst design is difficult…

Multiple reactants, intermediates, and products

Multiple configurations

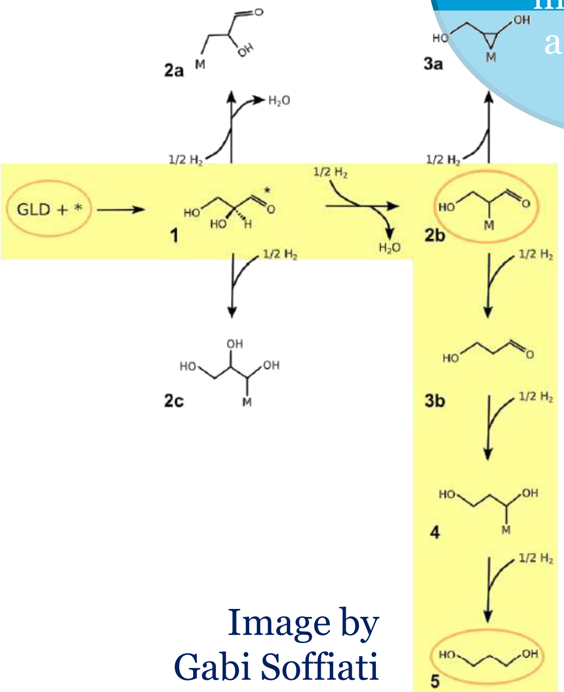
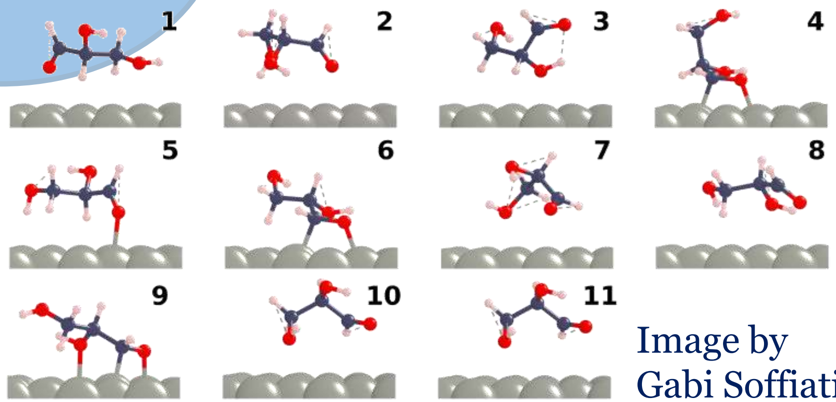


Image by Gabi Soffiati



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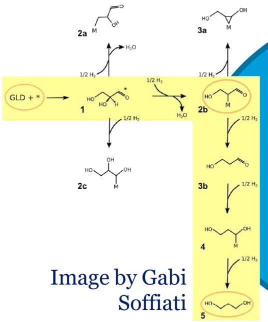

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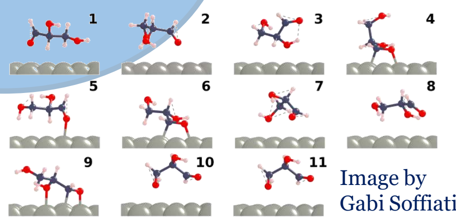

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Reaction kinetics

Reaction dynamics

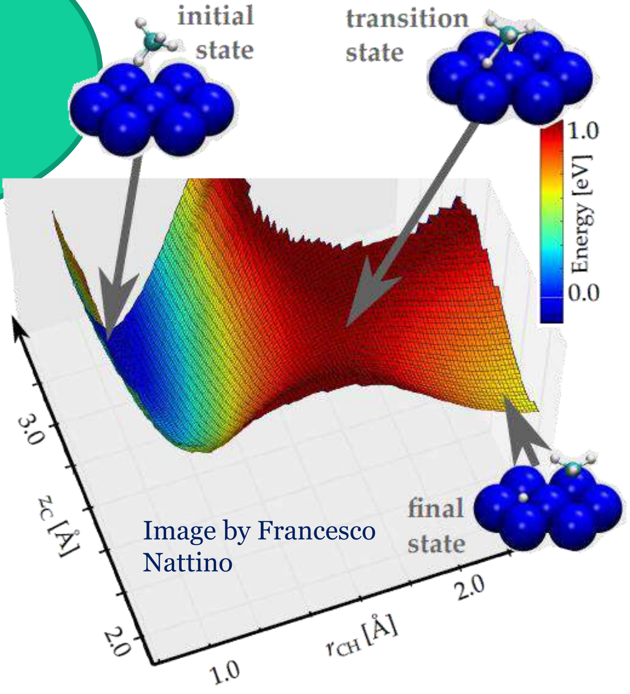

Image by Francesco Nattino

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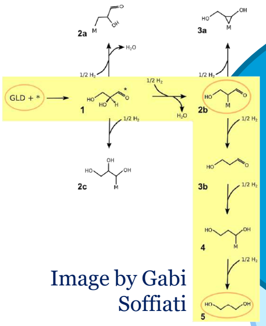

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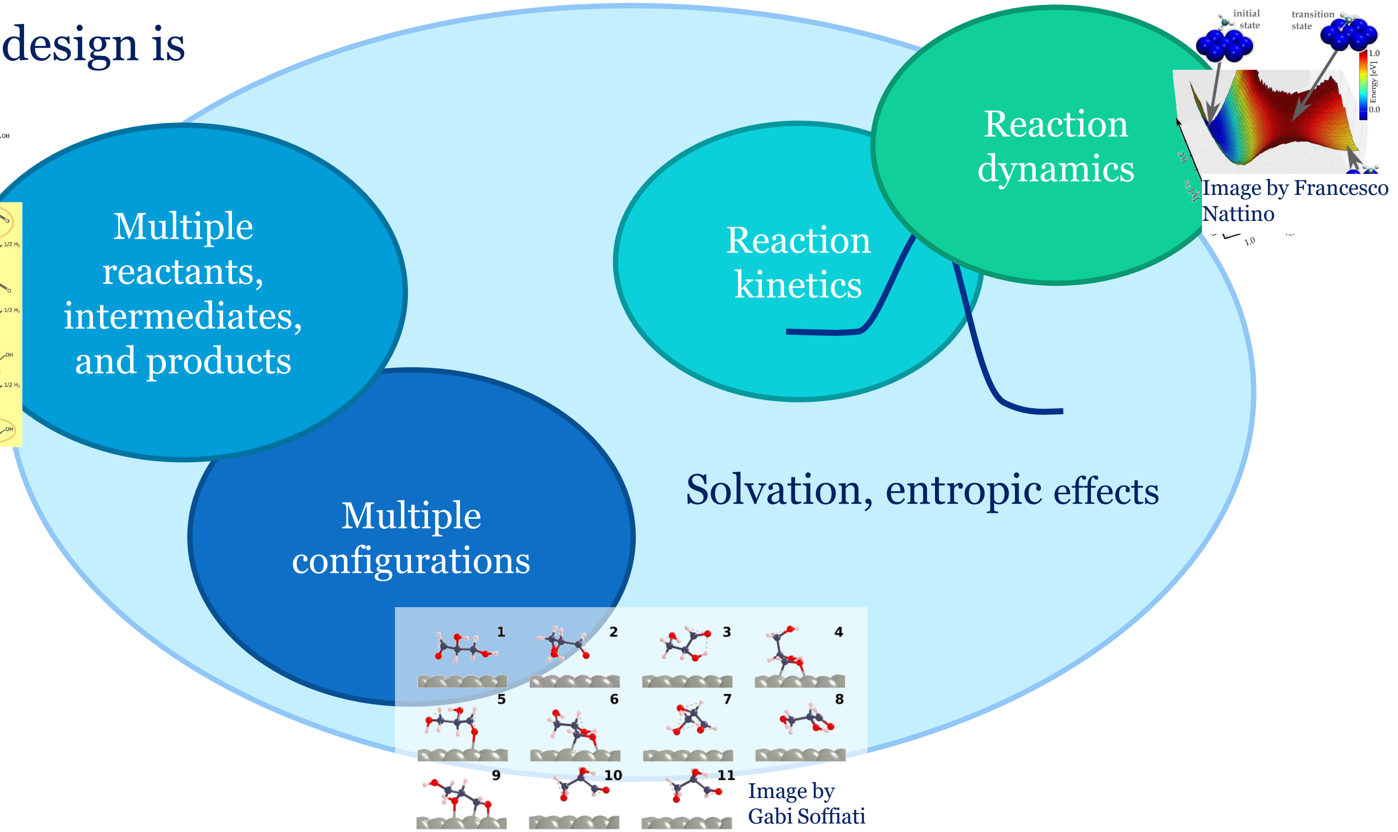

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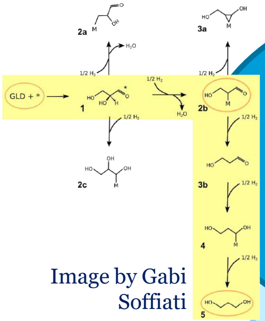

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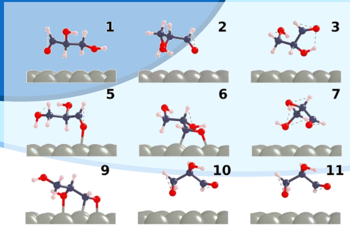

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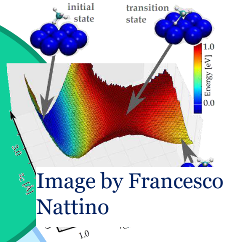

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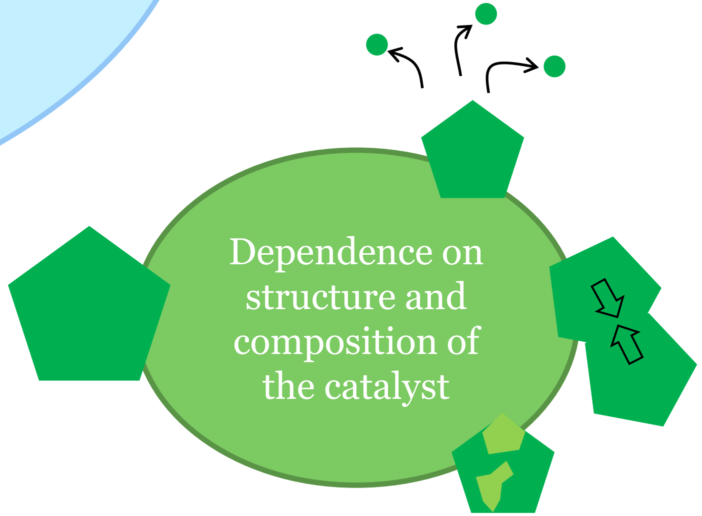
Solvation, entropic effects



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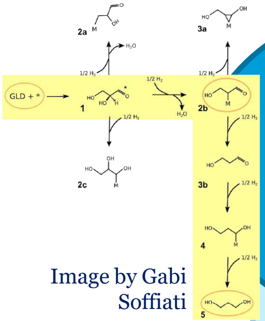

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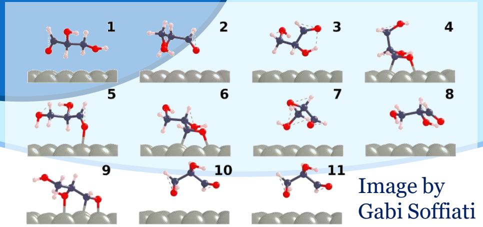

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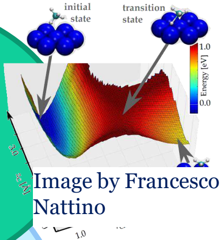

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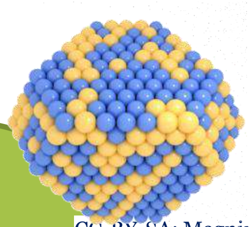
Solvation, entropic effects

nanostructures, flow profiles, …



Dependence on structure and composition of the catalyst

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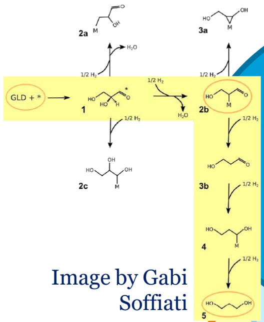

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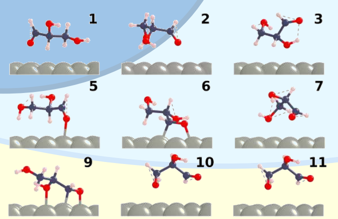

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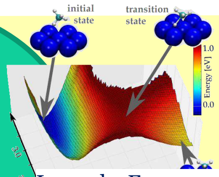

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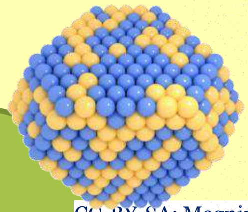

Dependence on structure and composition of the catalyst

Accuracy of the computational method

Dissociative chemisorption barriers

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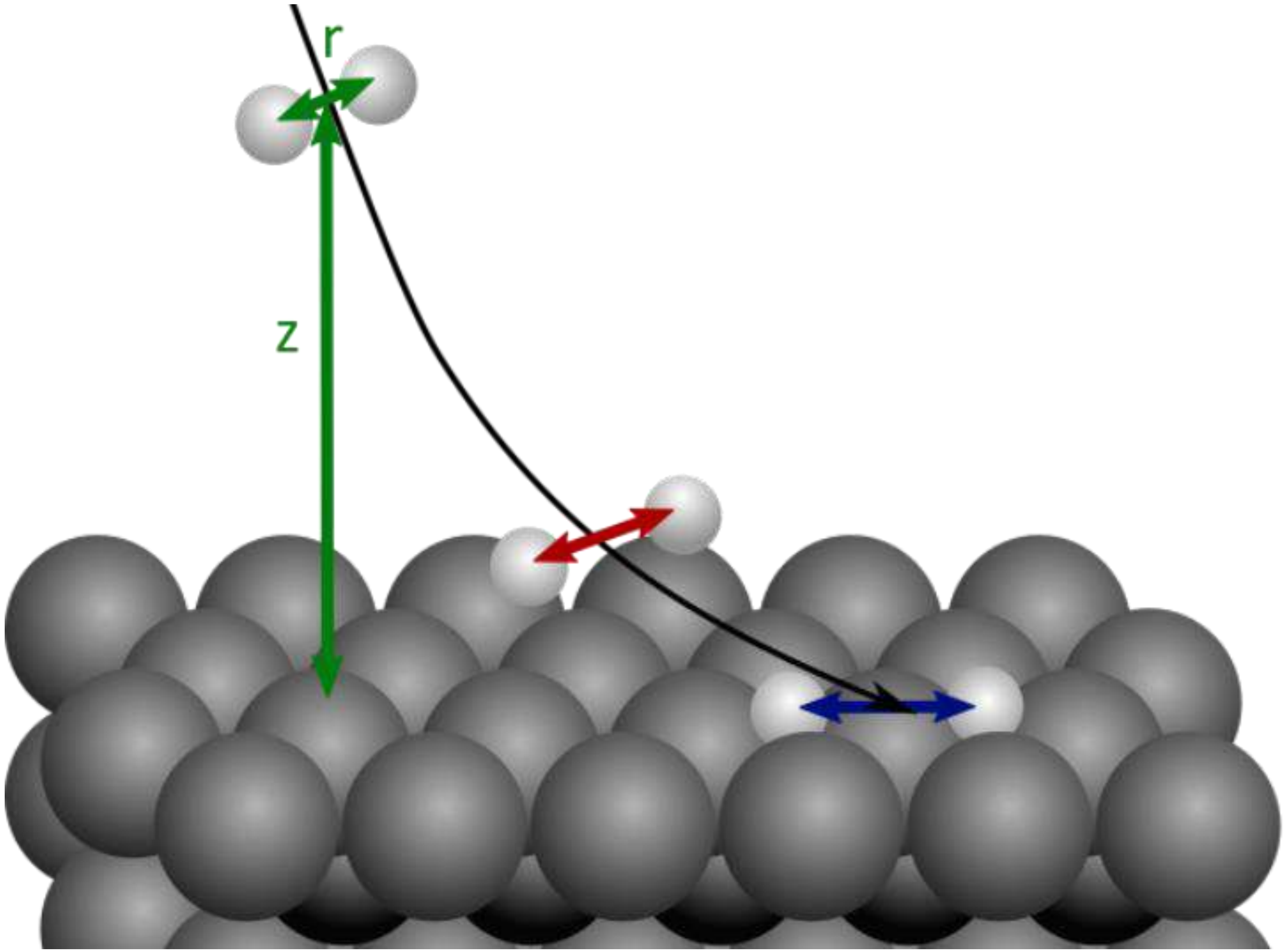
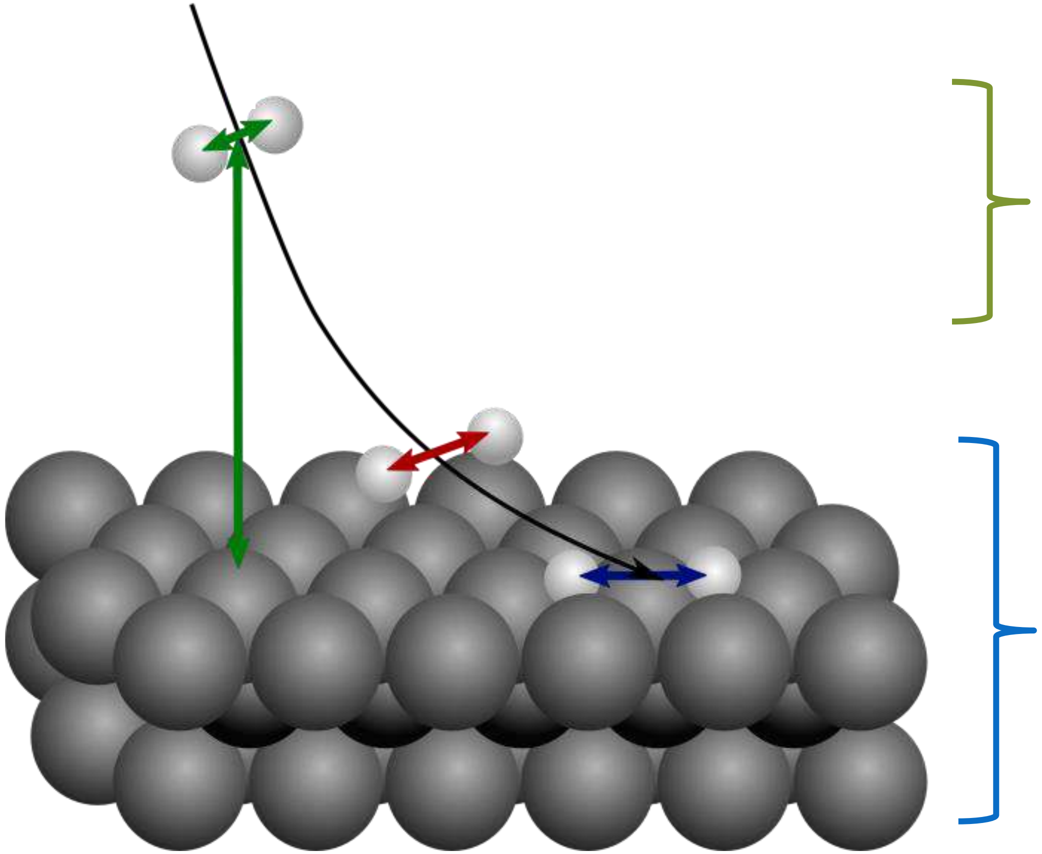
Dissociative chemisorption

- “Real” catalytic systems too complicated
- Dissociative chemisorption of small molecules often rate limiting



DFT for molecule – metal reaction barriers



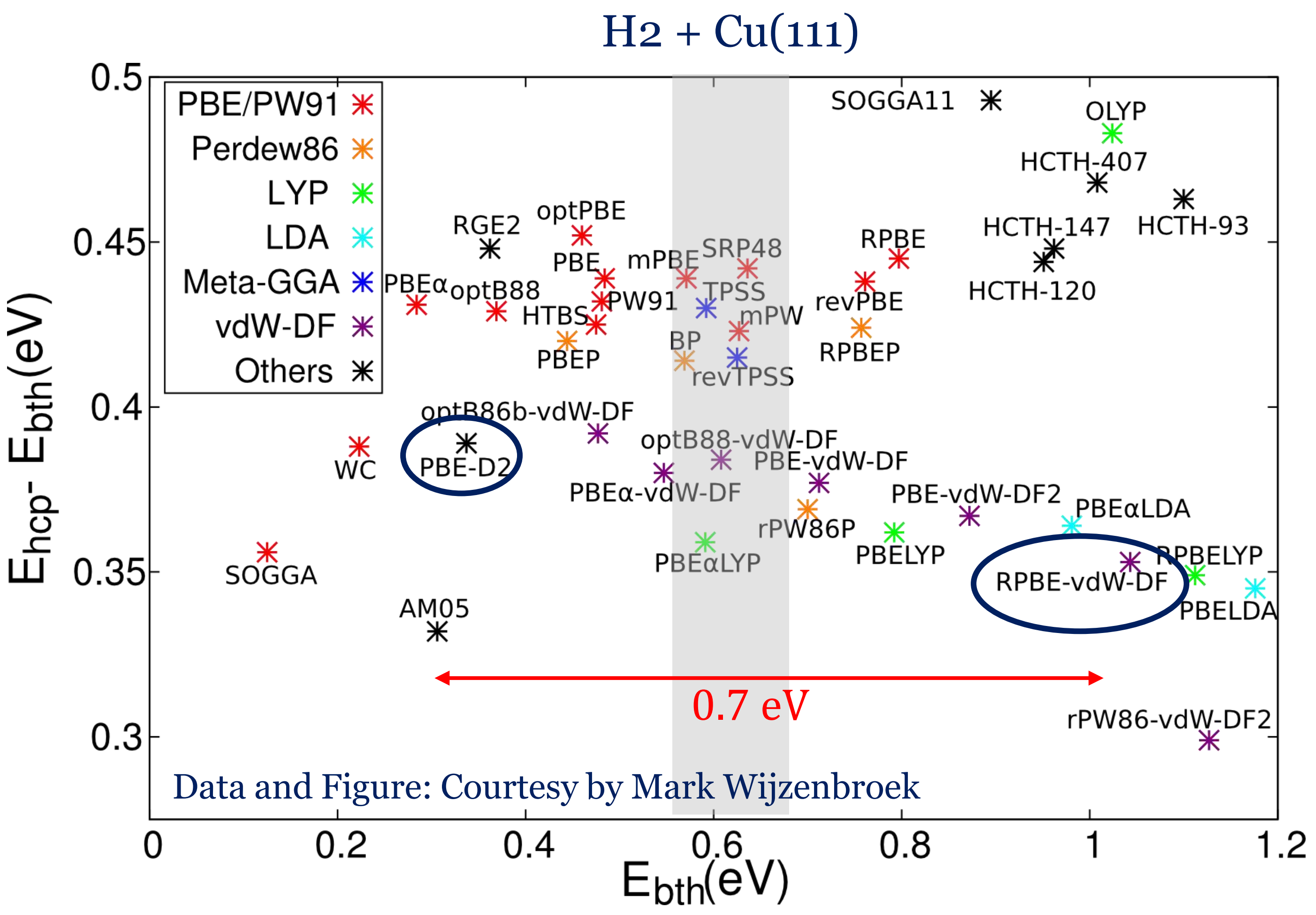
molecule
- Electrons localized
- Profit from strong long-range exchange

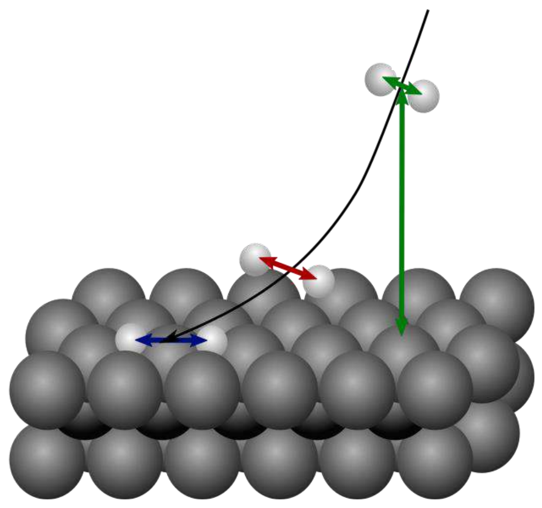
metal
- Electrons delocalized
- Profit from excluding long-range exchange

DFT

No training data

DFT for molecule – metal reaction barriers





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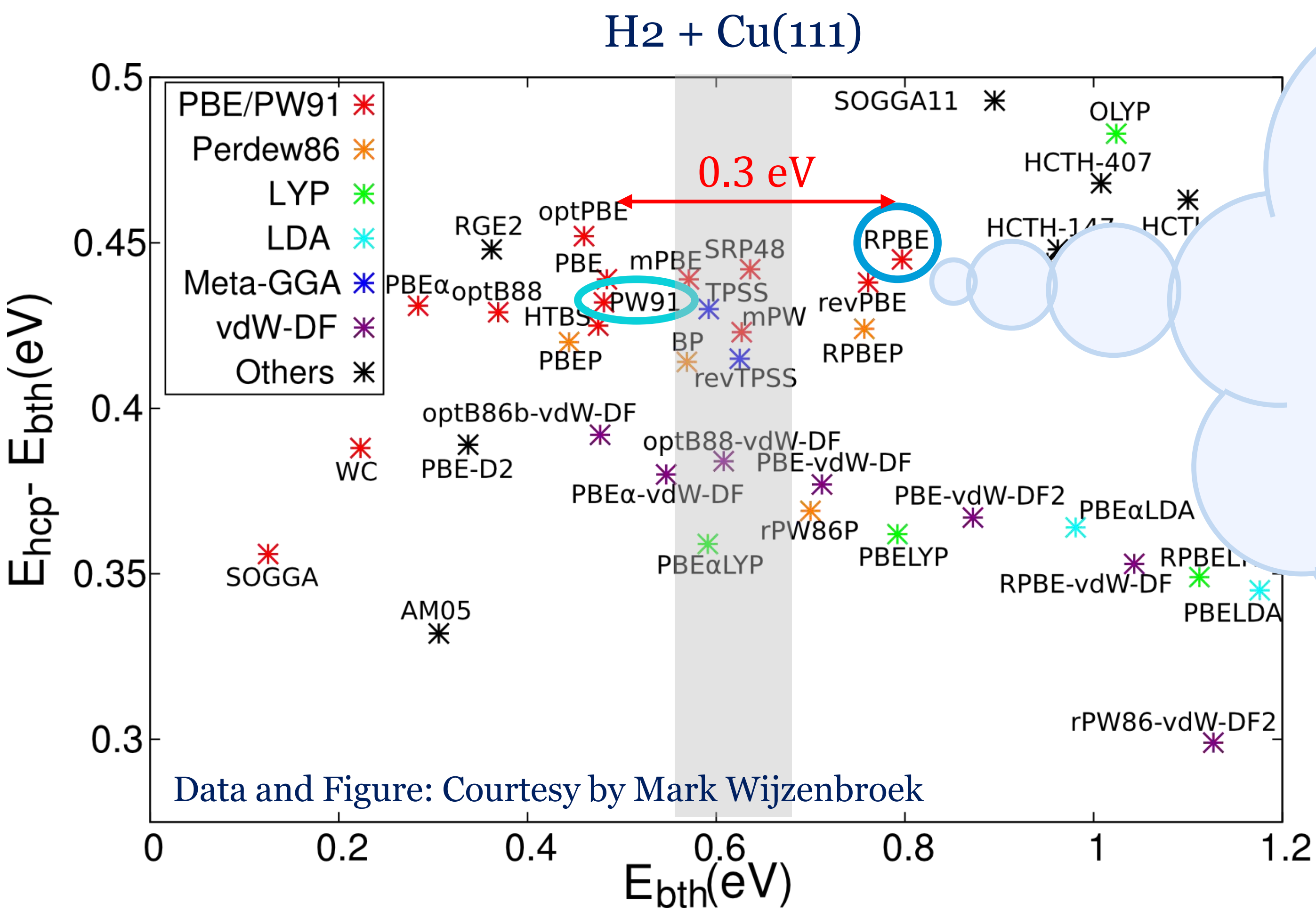
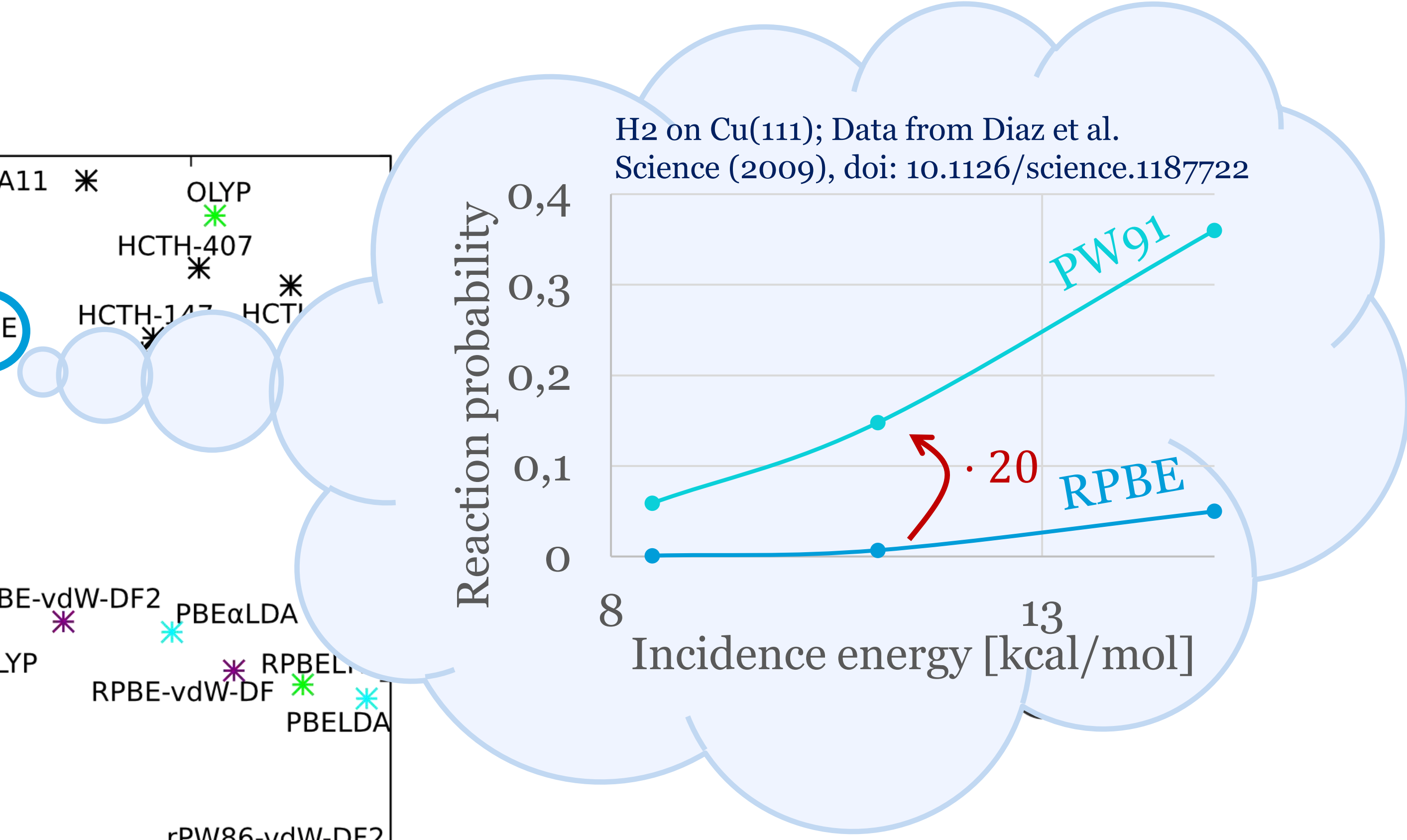
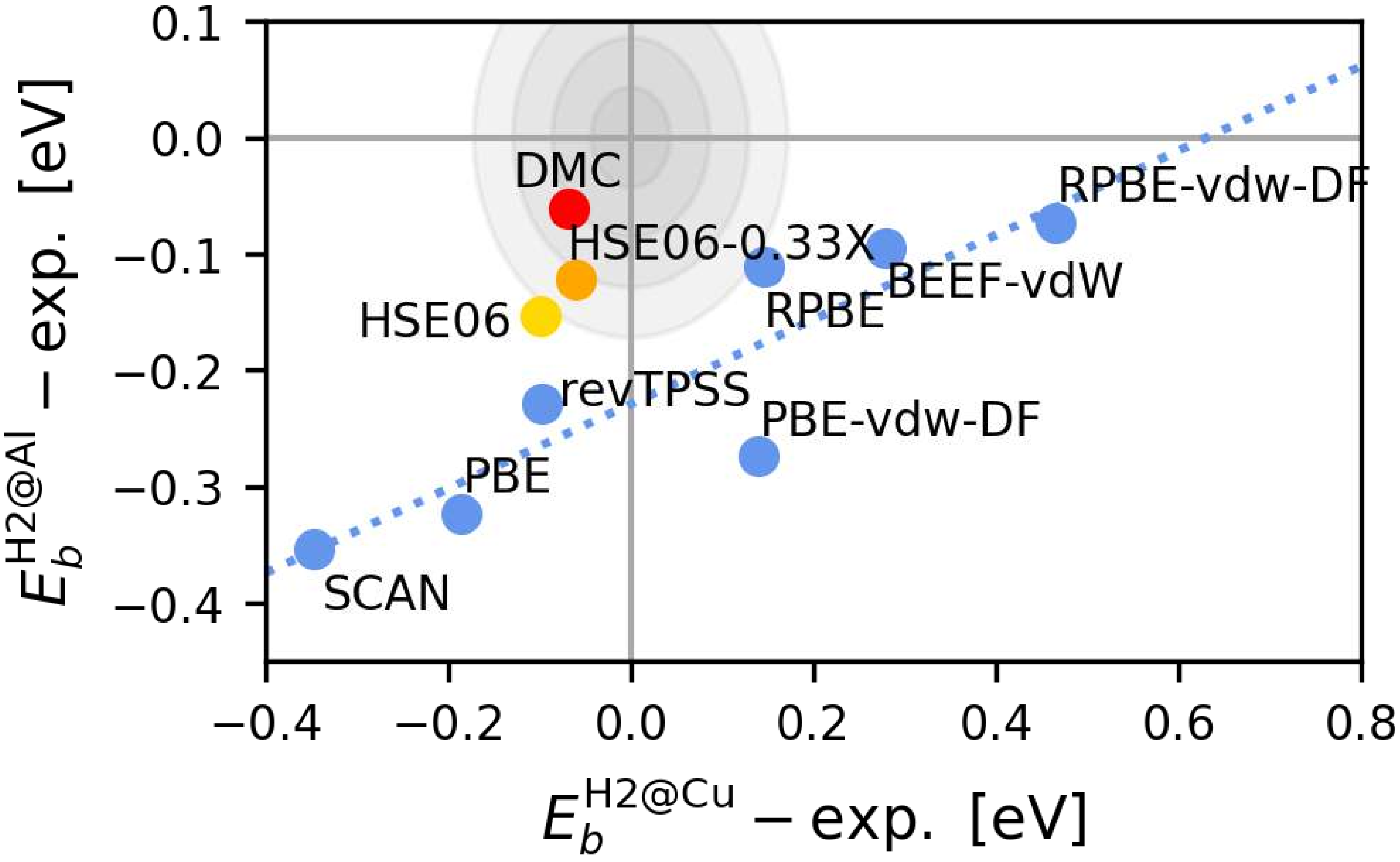




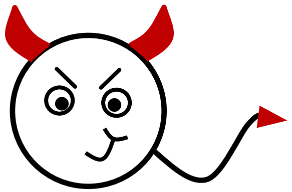
Can diffusion Monte Carlo do better?

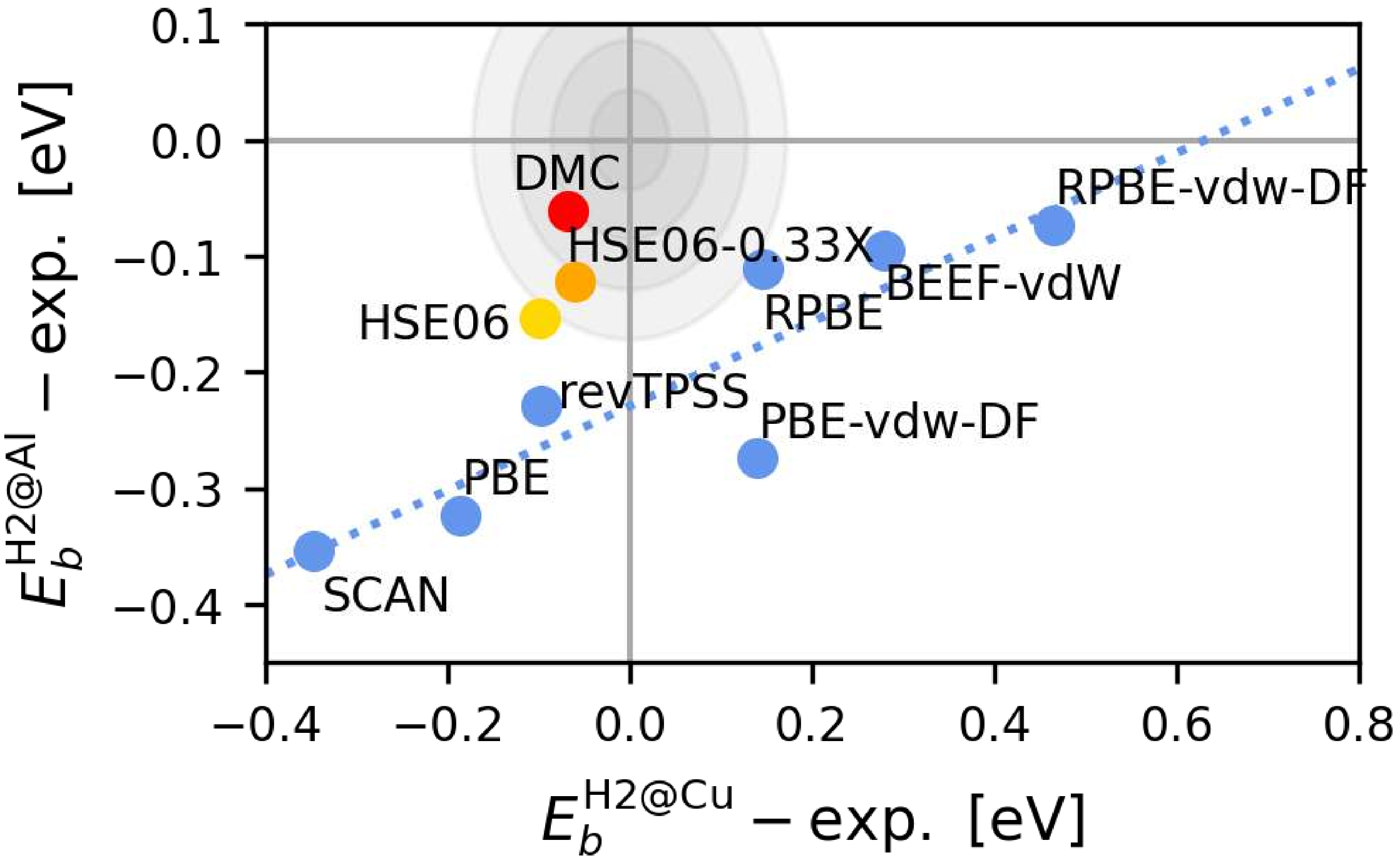


B. Oudot and K. Doblhoff-Dier, to be published

Can diffusion Monte Carlo do better?

- That is nice, but it costs 100 thousands of cpuh…





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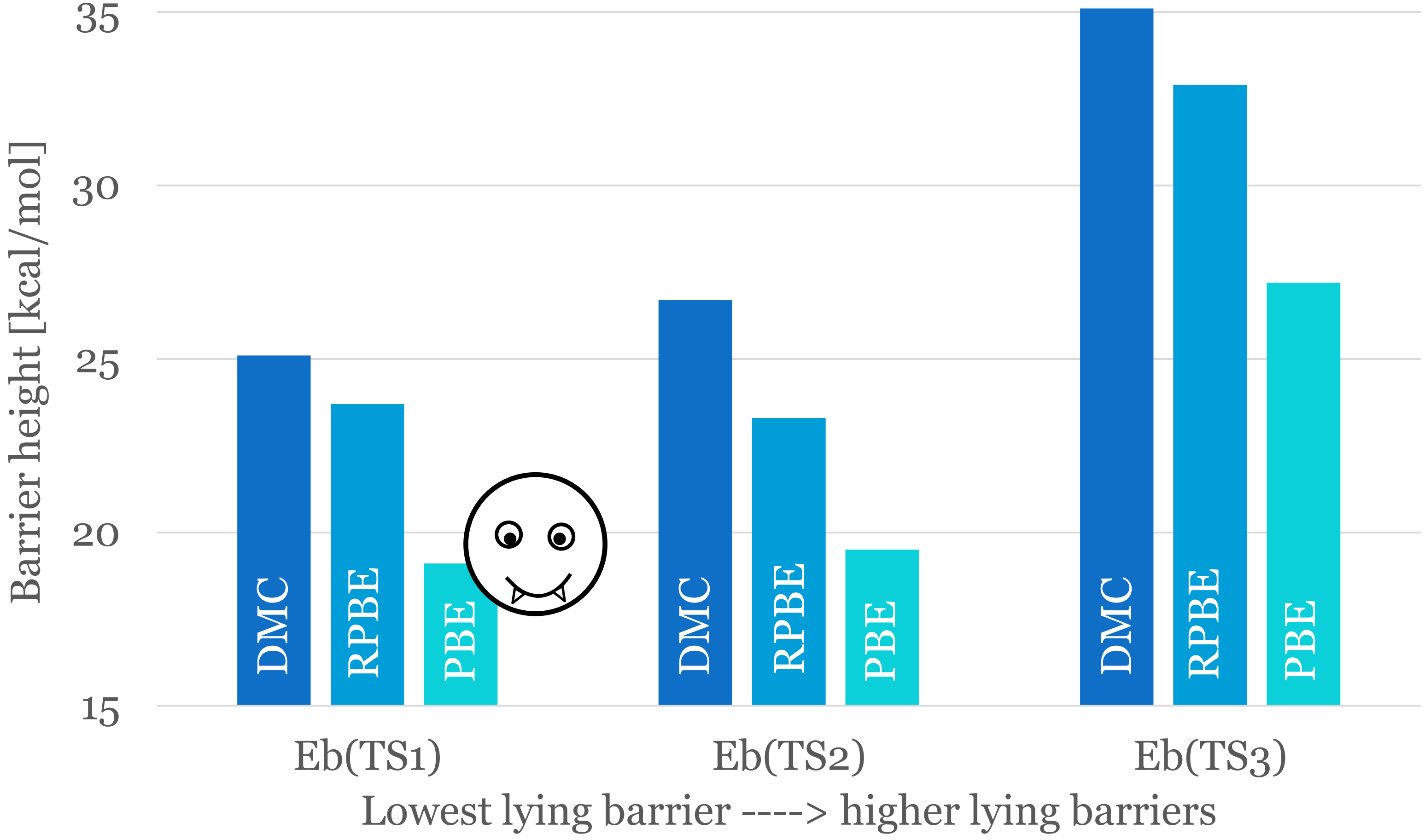
A case study: H2 on Al(110)

- Trends seem to be described correctly by most functionals



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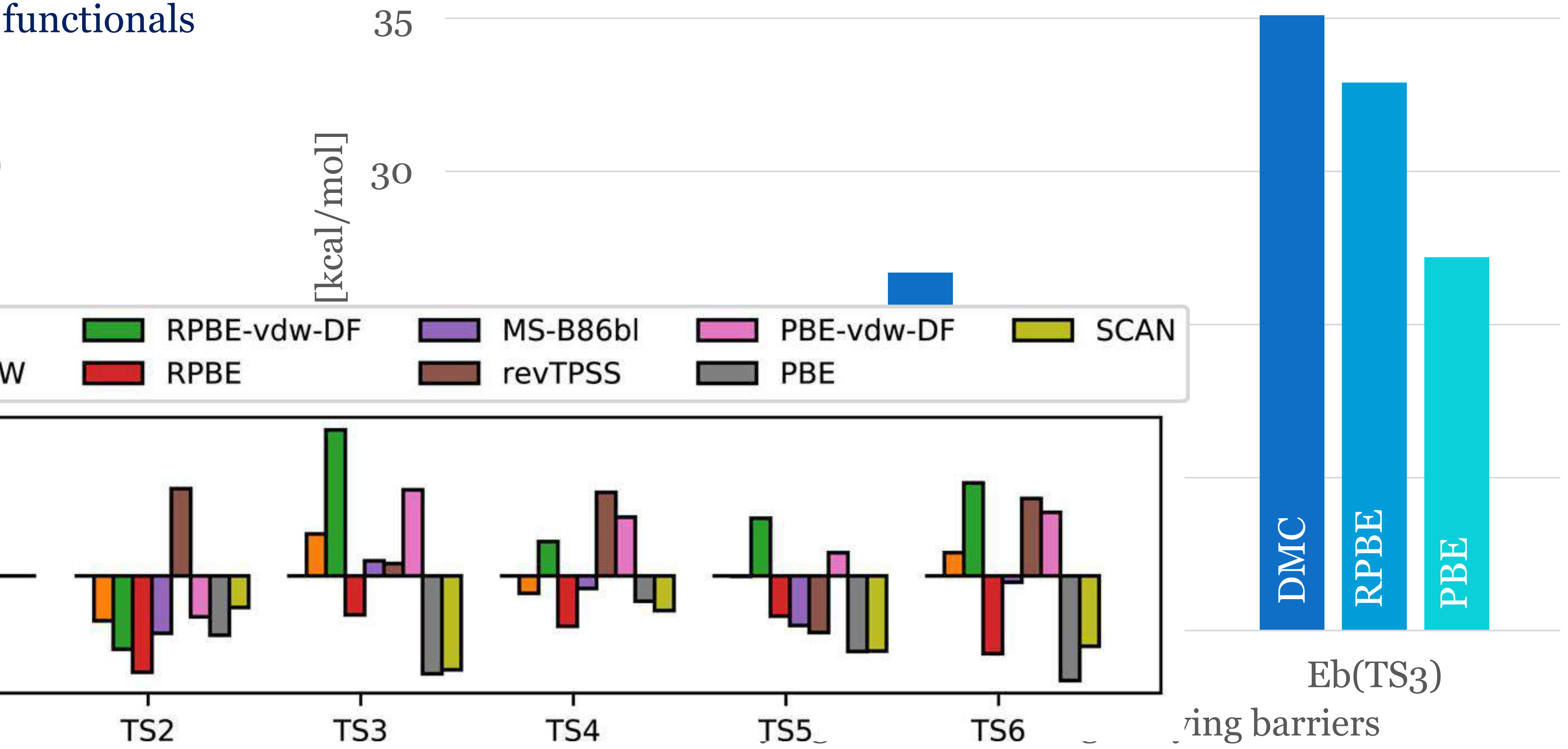

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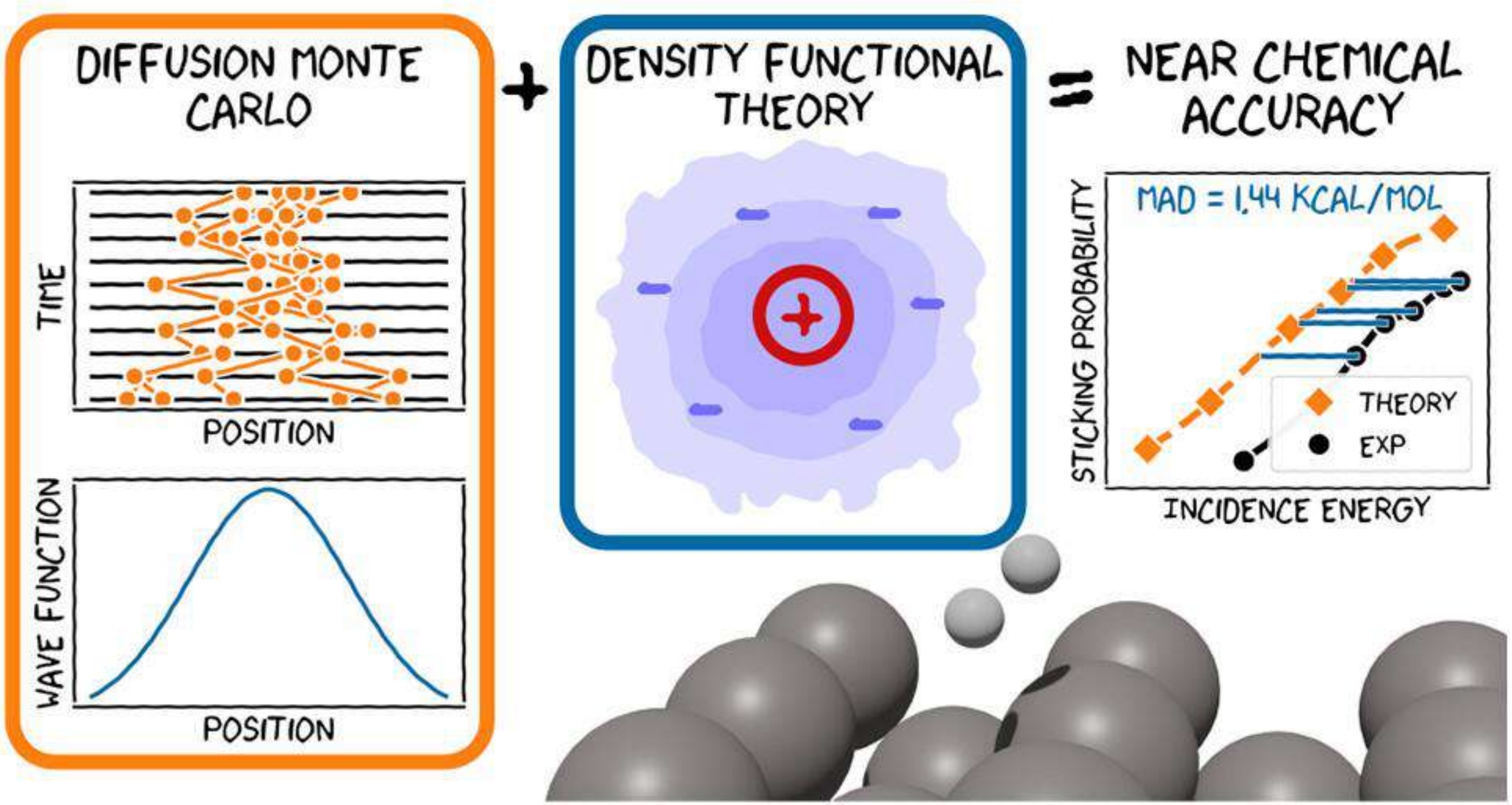

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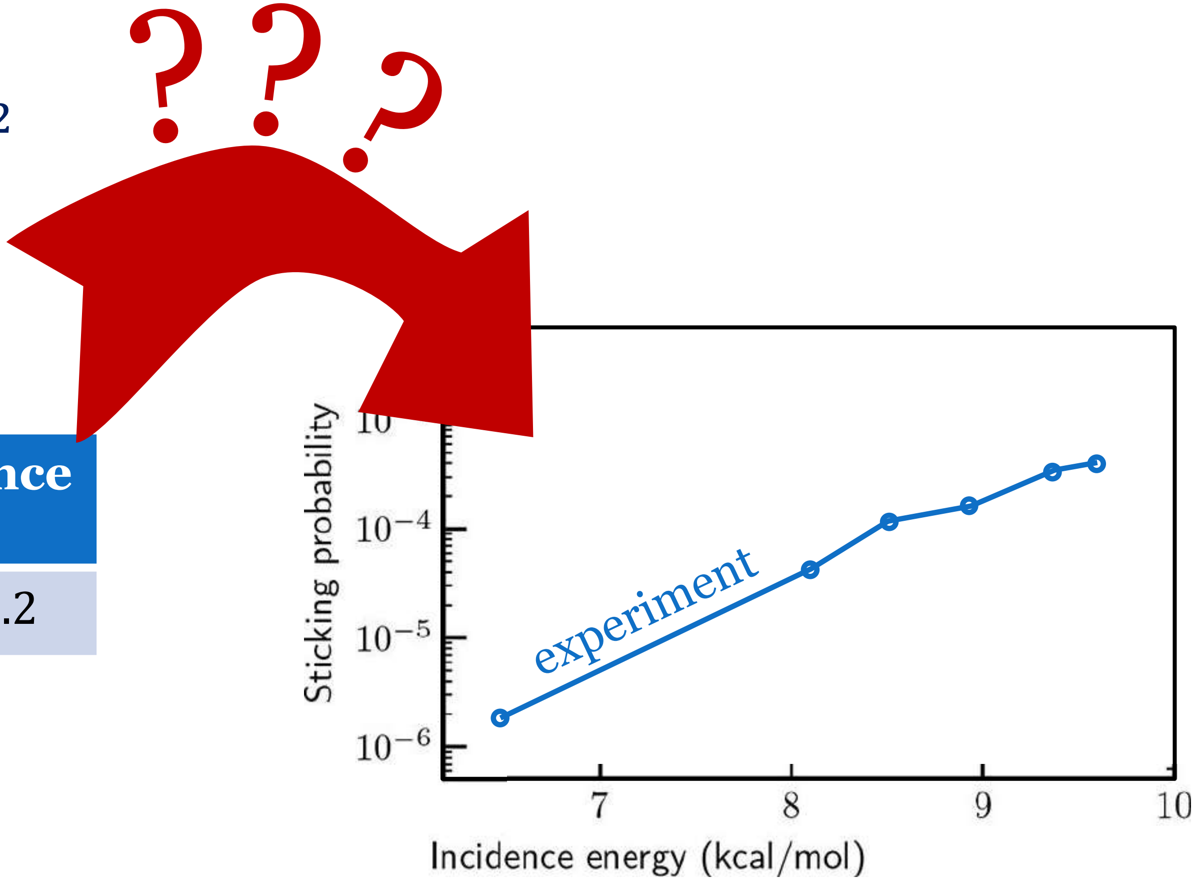
$$E_{xc} = aE_x^{RPBE} + (1-a)E_x^{PBE} + E_c^{vdW2}$$

scales gradient enhancement factor
$a = 0.71$

barrier [kcal/mol]	DMC	QMC-DF	difference
TS1	25.1 ± 0.2	25.4	0.3 ± 0.2



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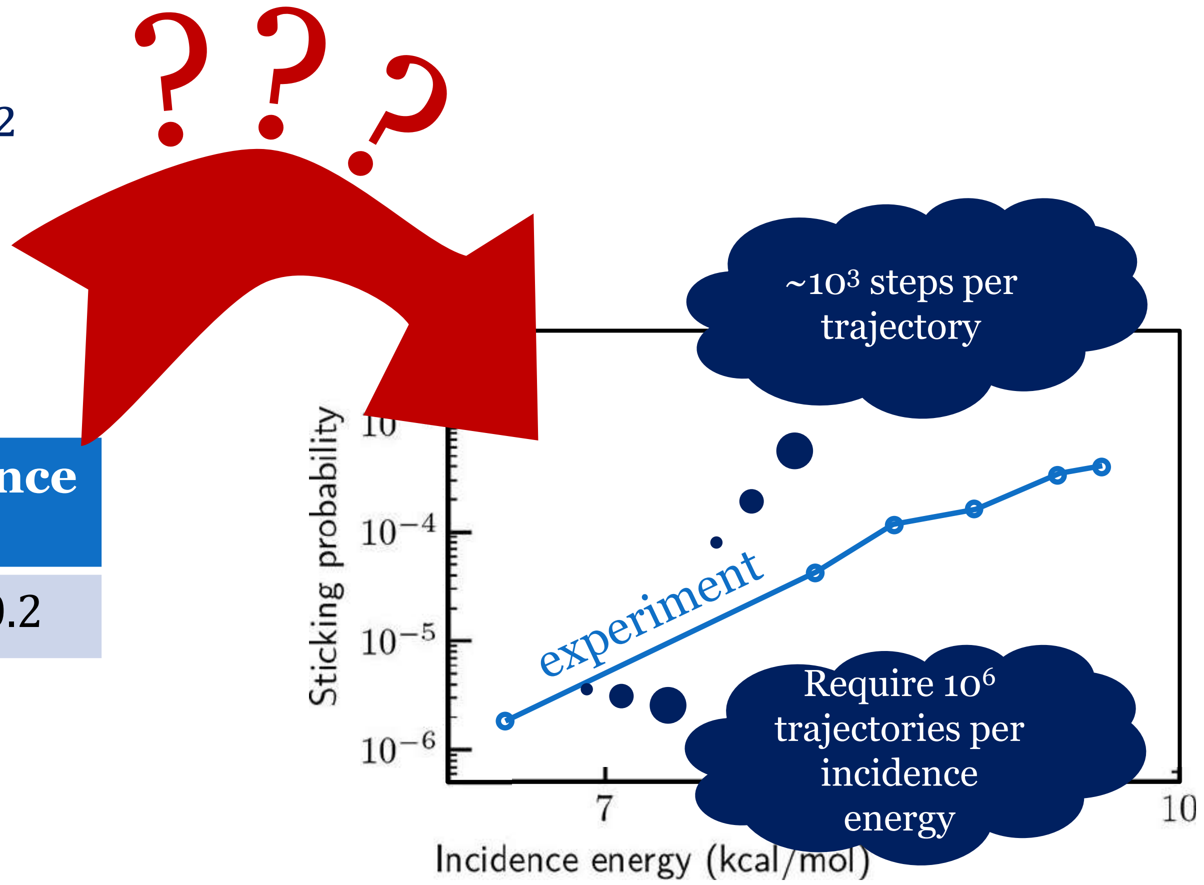

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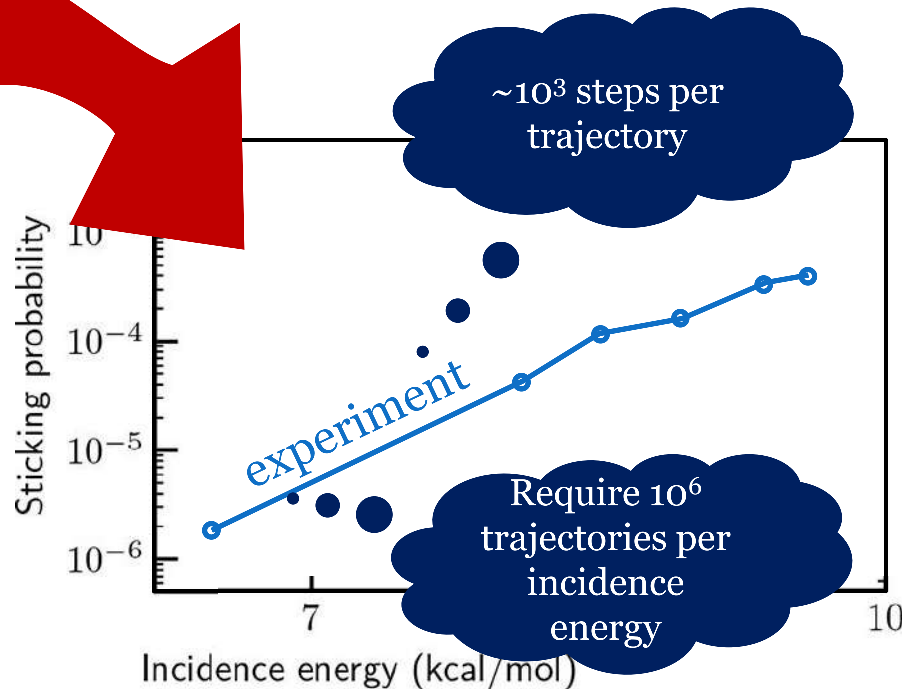

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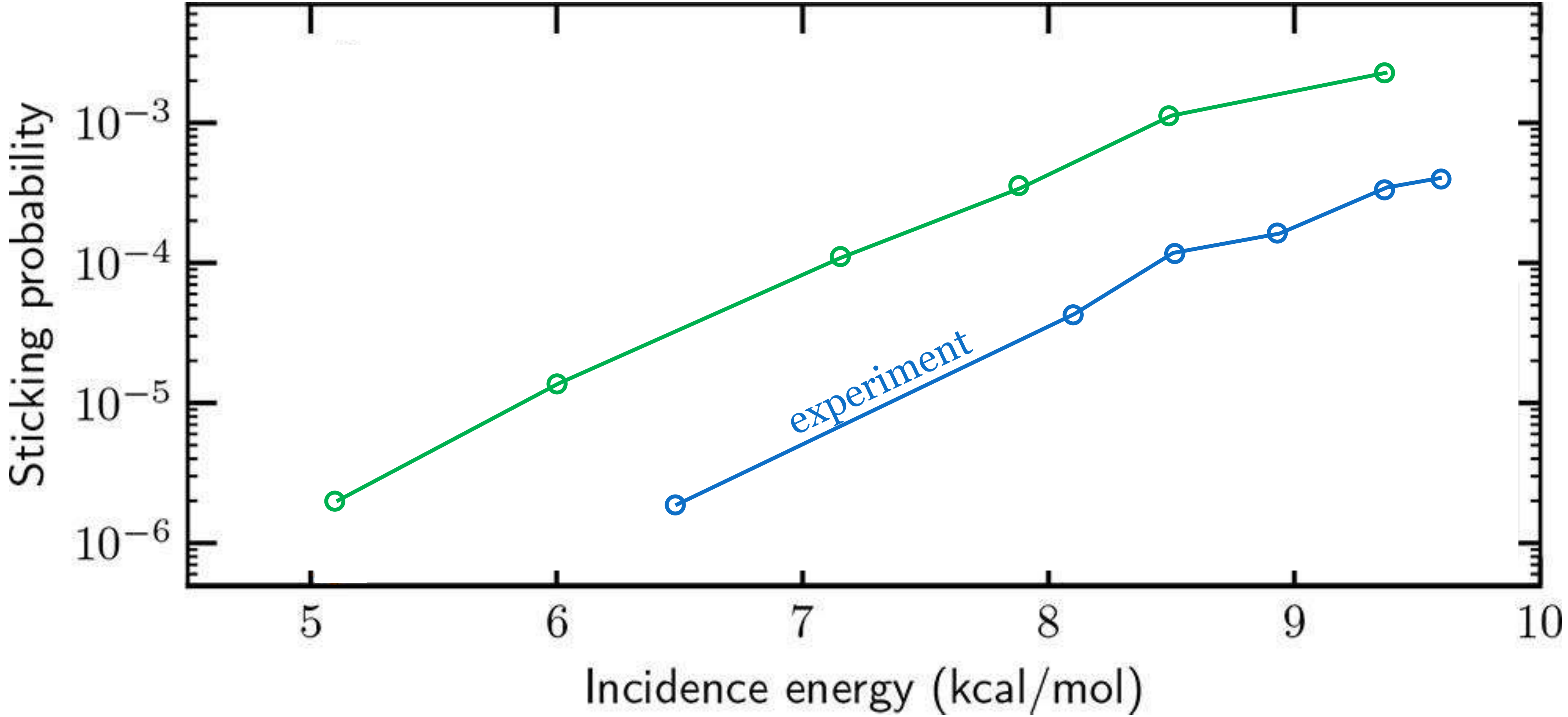

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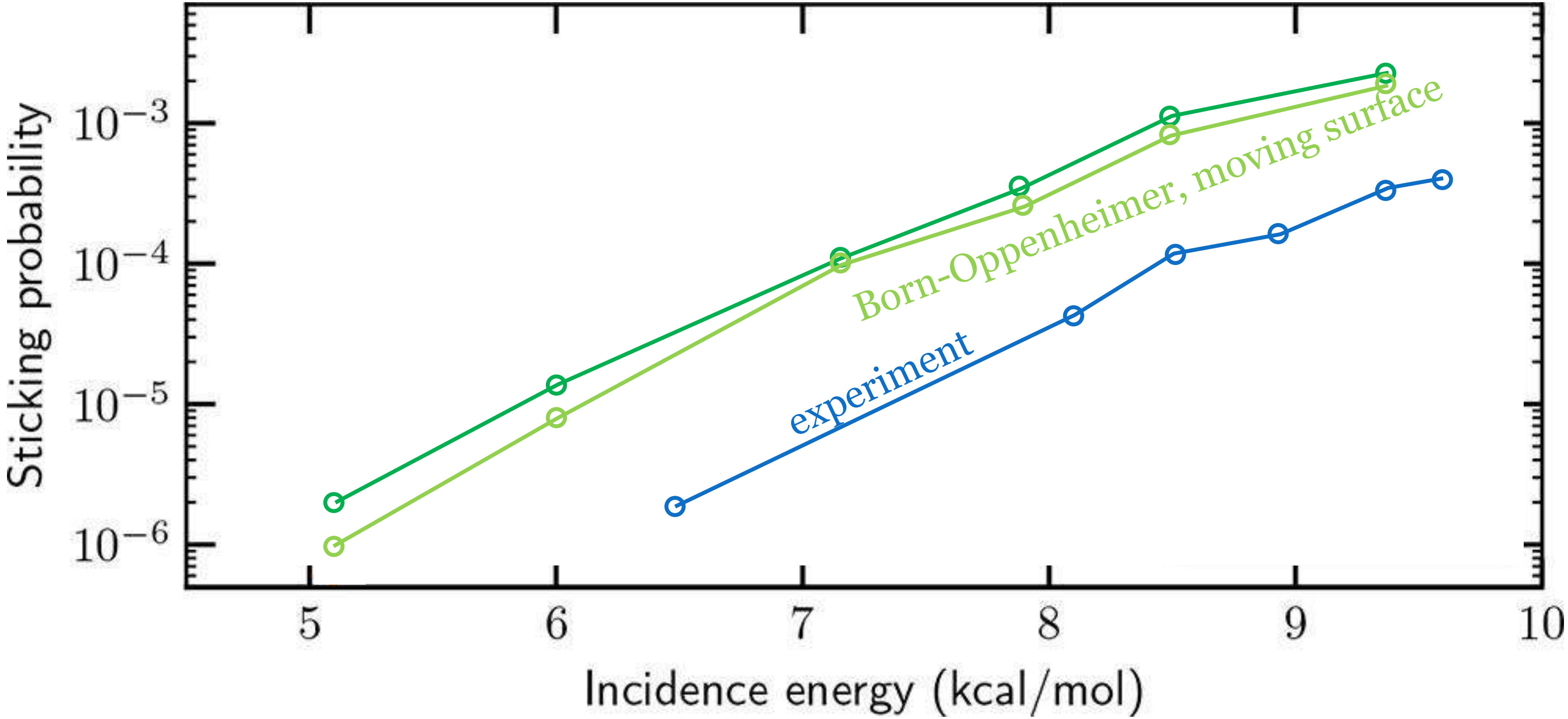

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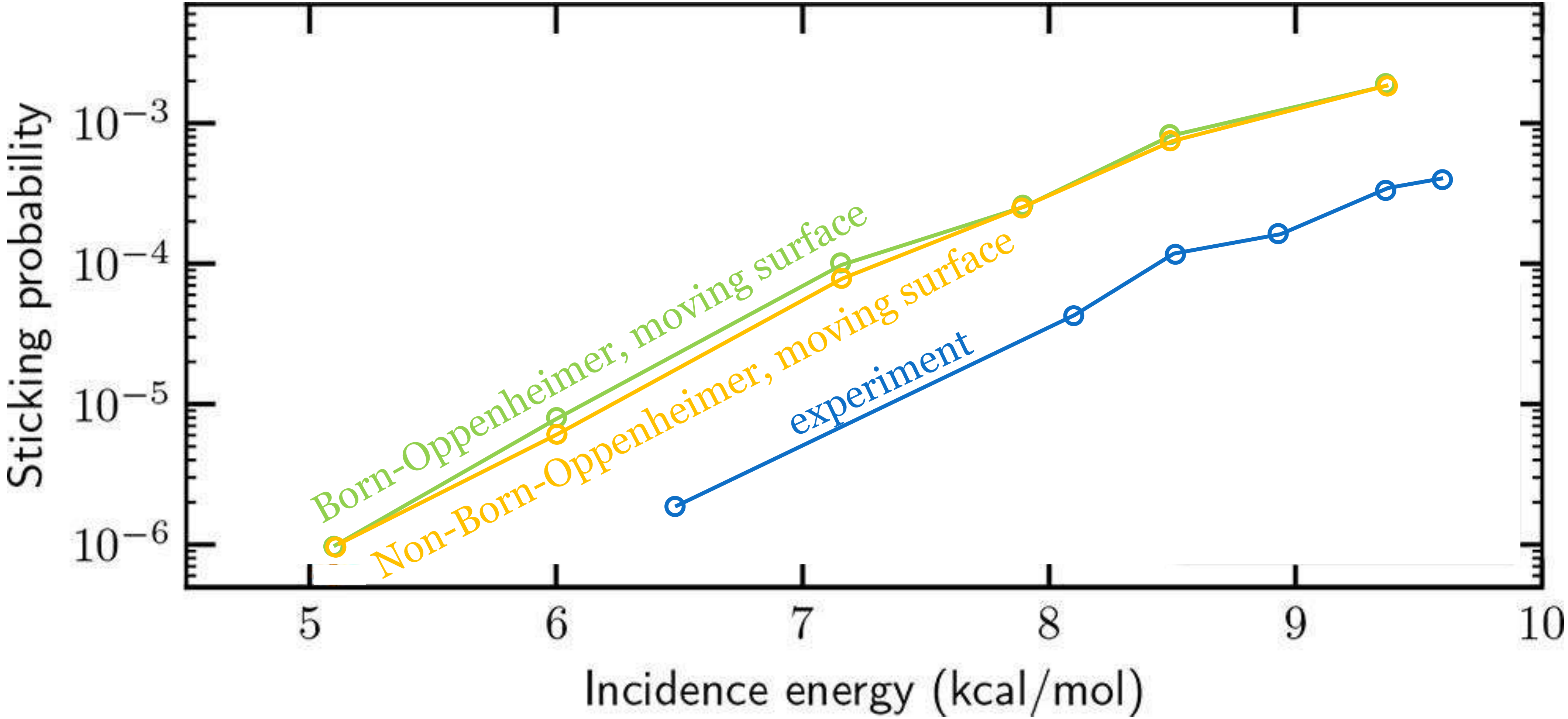

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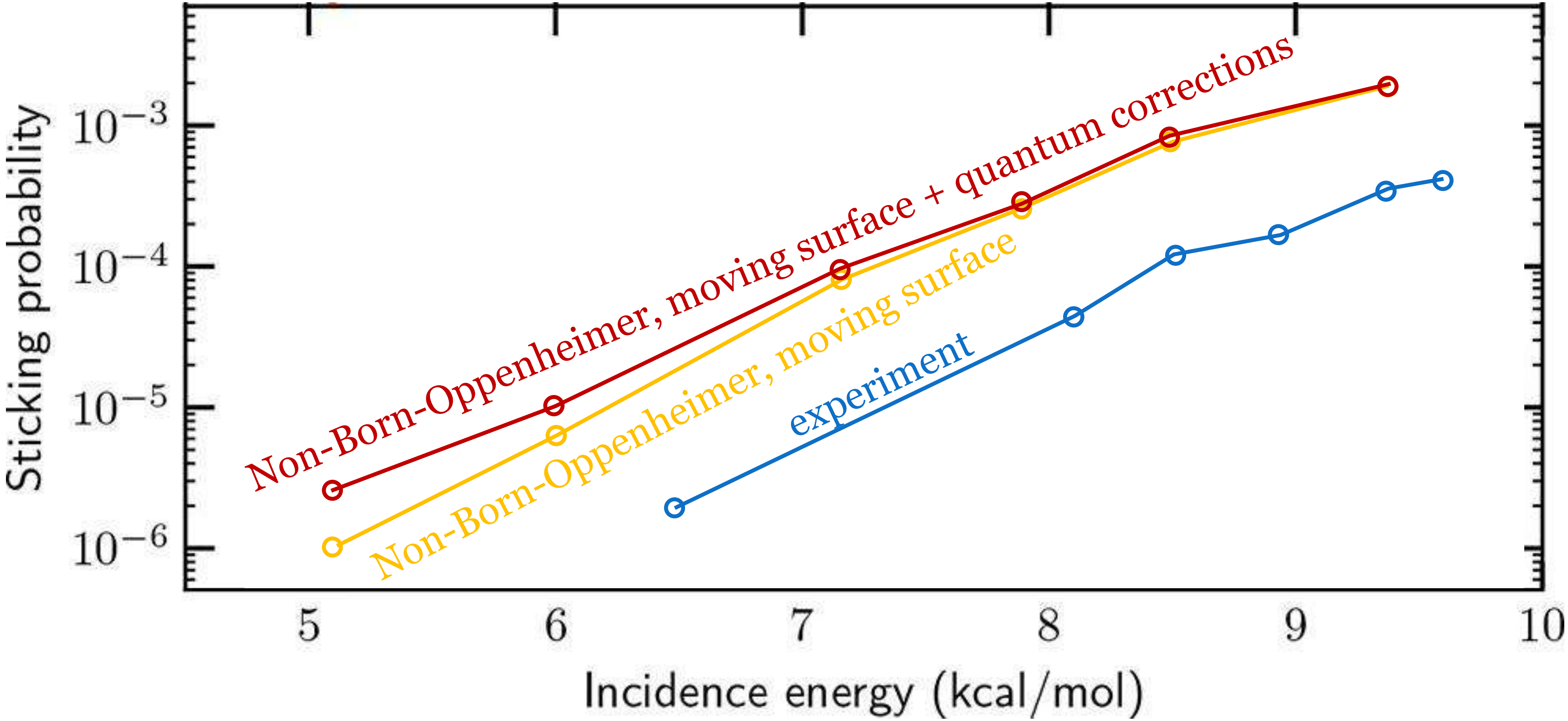

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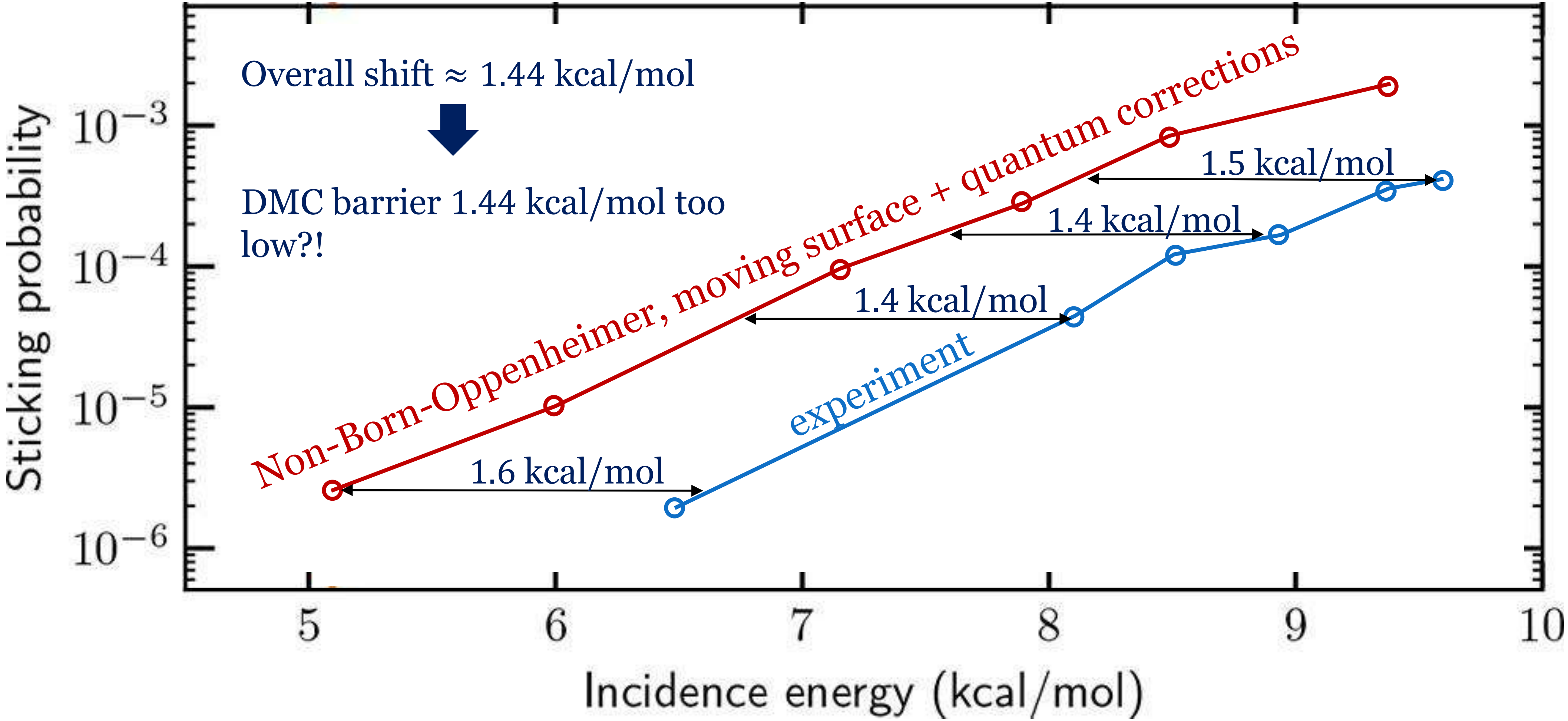

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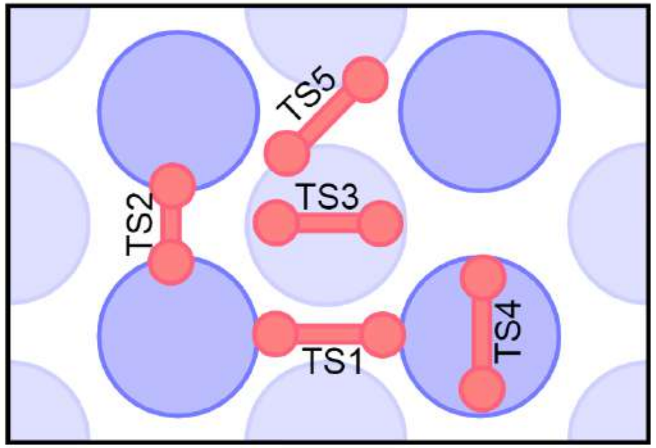

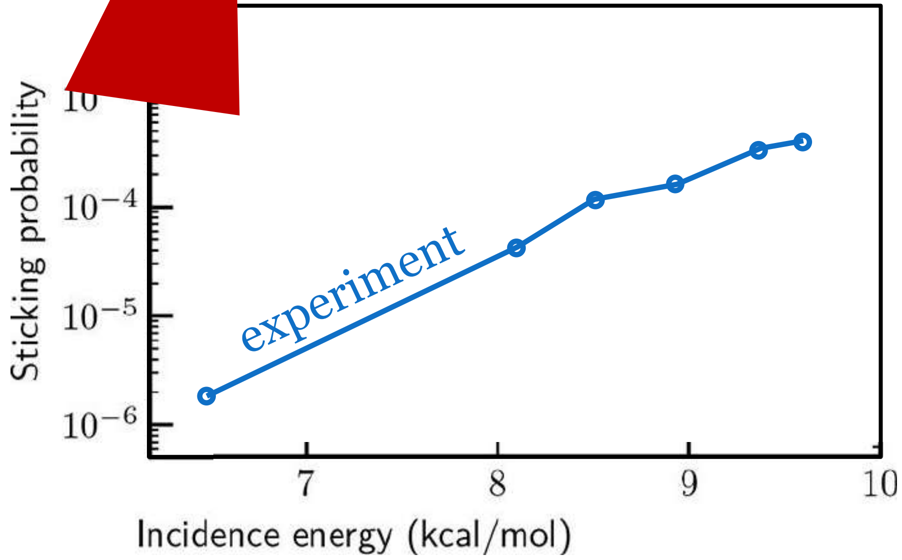

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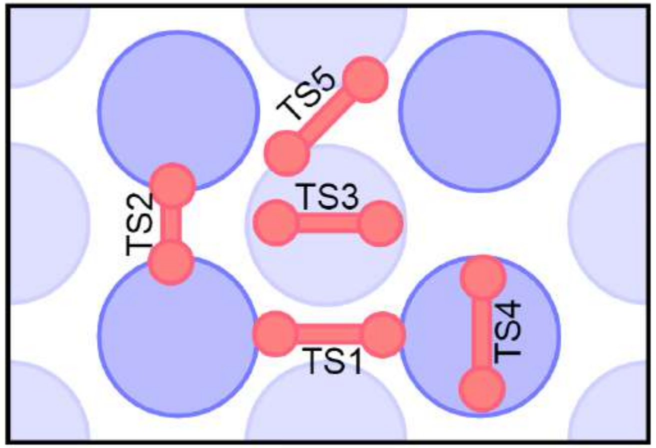

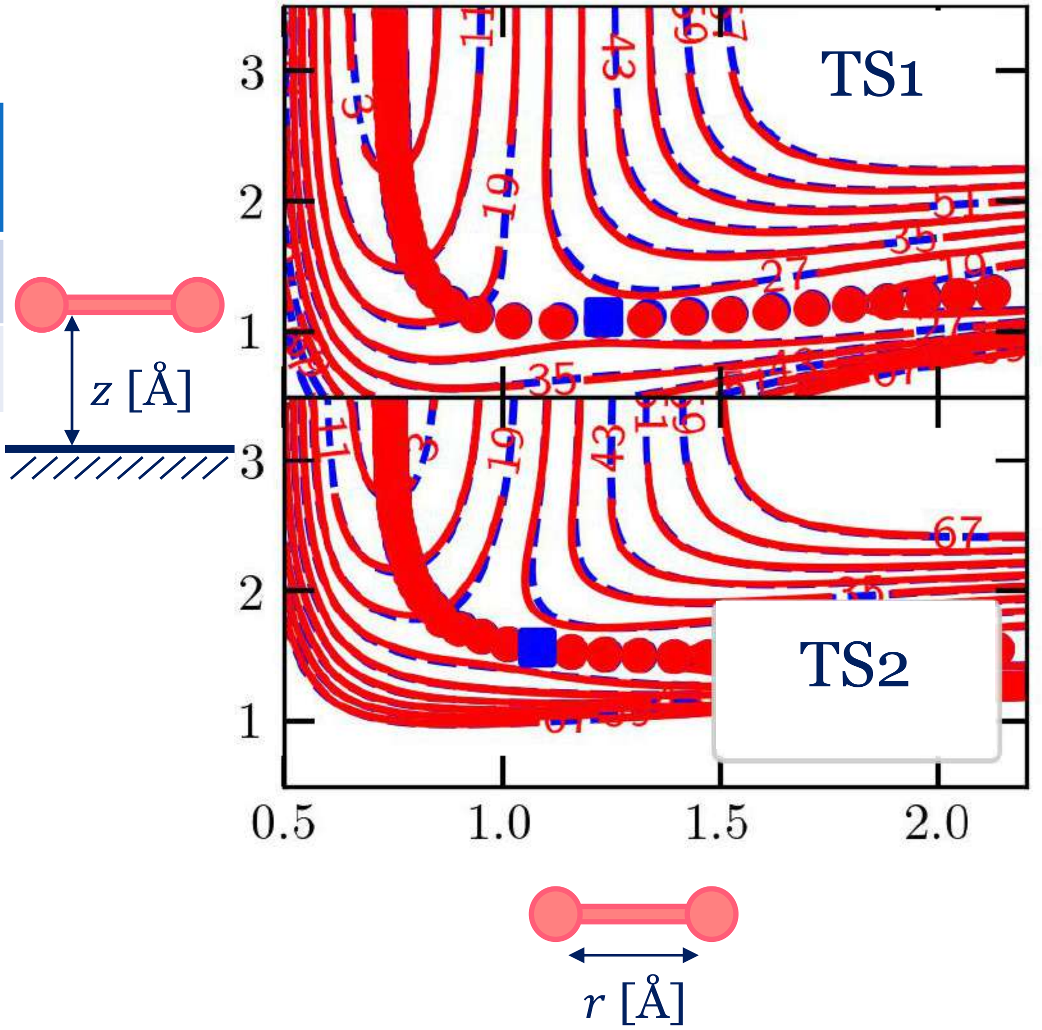

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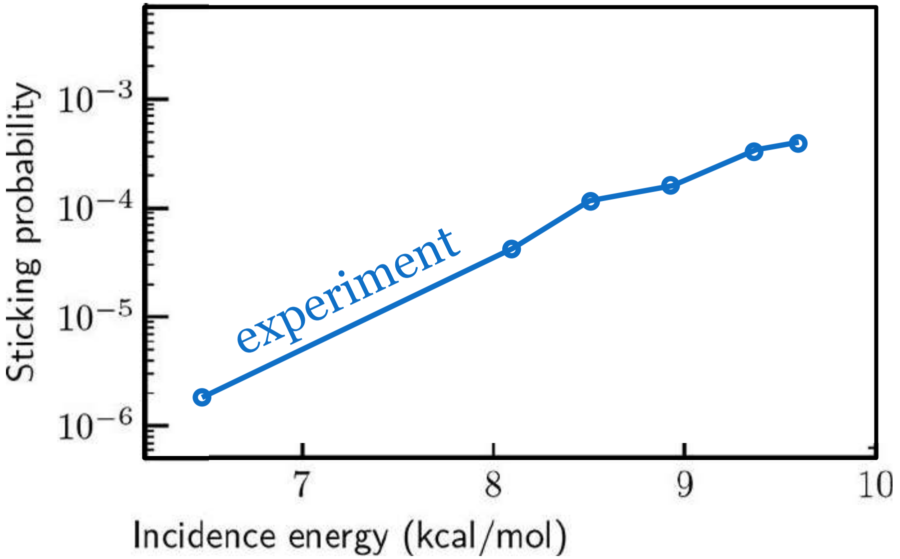

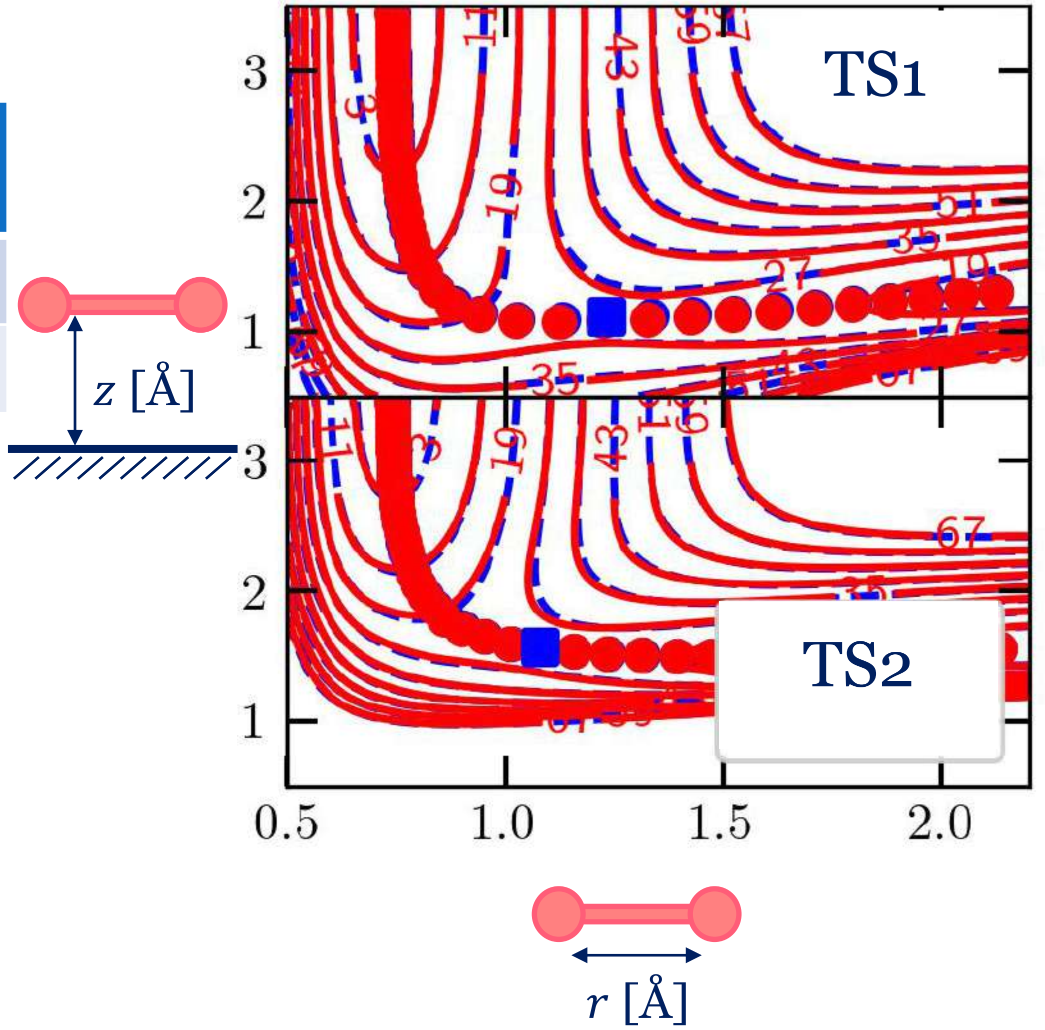

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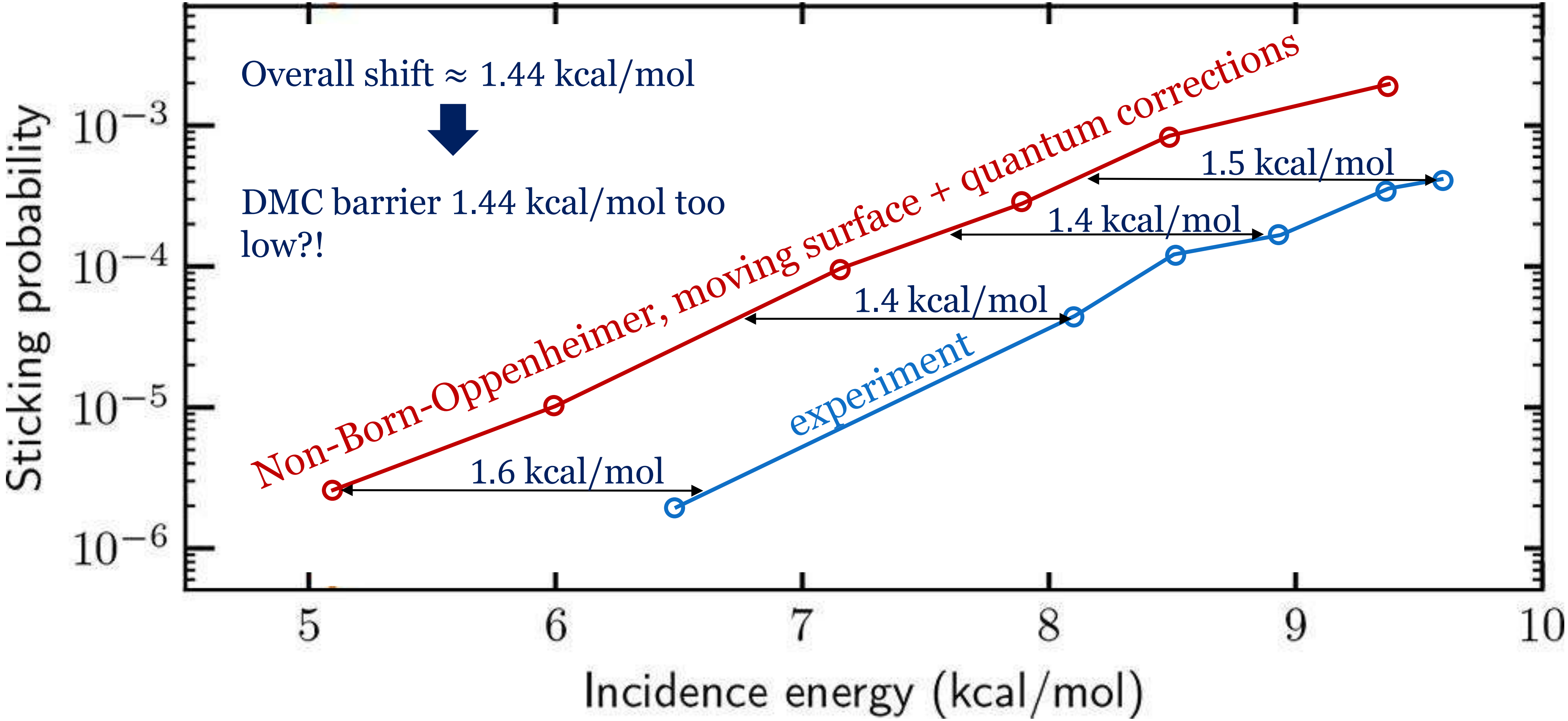

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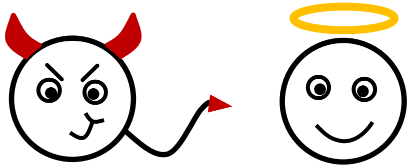
A case study: H2 on Al(110) – Take home message



1. Fit/choose a DFT functional to match (scarce) DMC data for barriers

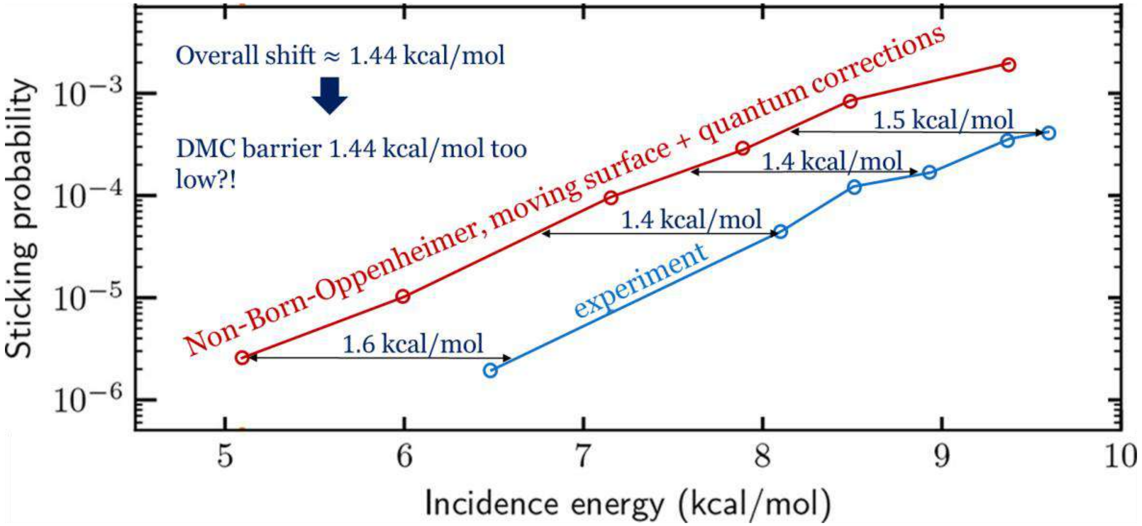
   predictive results for dissociative chemisorption

$$E_{xc} = aE_x^{RPBE} + (1-a)E_x^{PBE} + E_c^{vdW2}$$

2. Comparison to experimental reaction probabilities

   information on accuracy of DMC

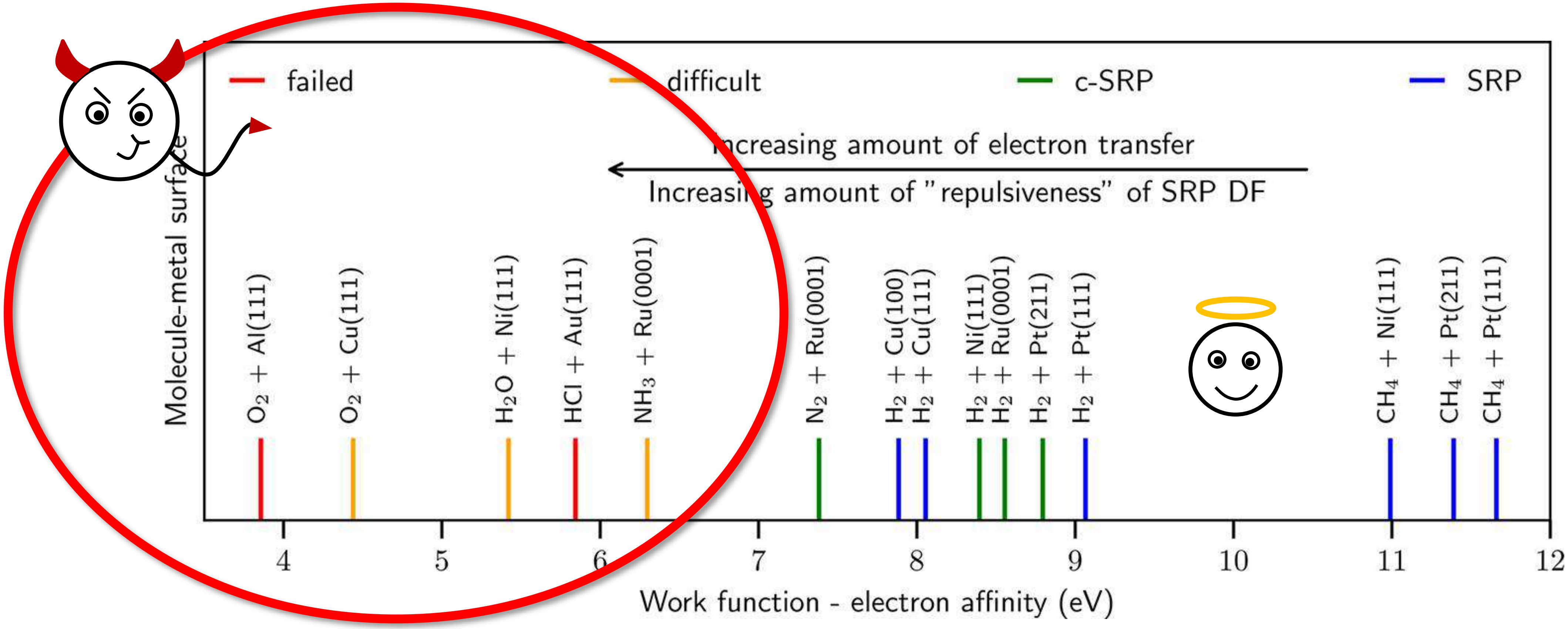
   Check though influence of all relevant barriers though!



3. Improved predictions from Δ machine learning?!

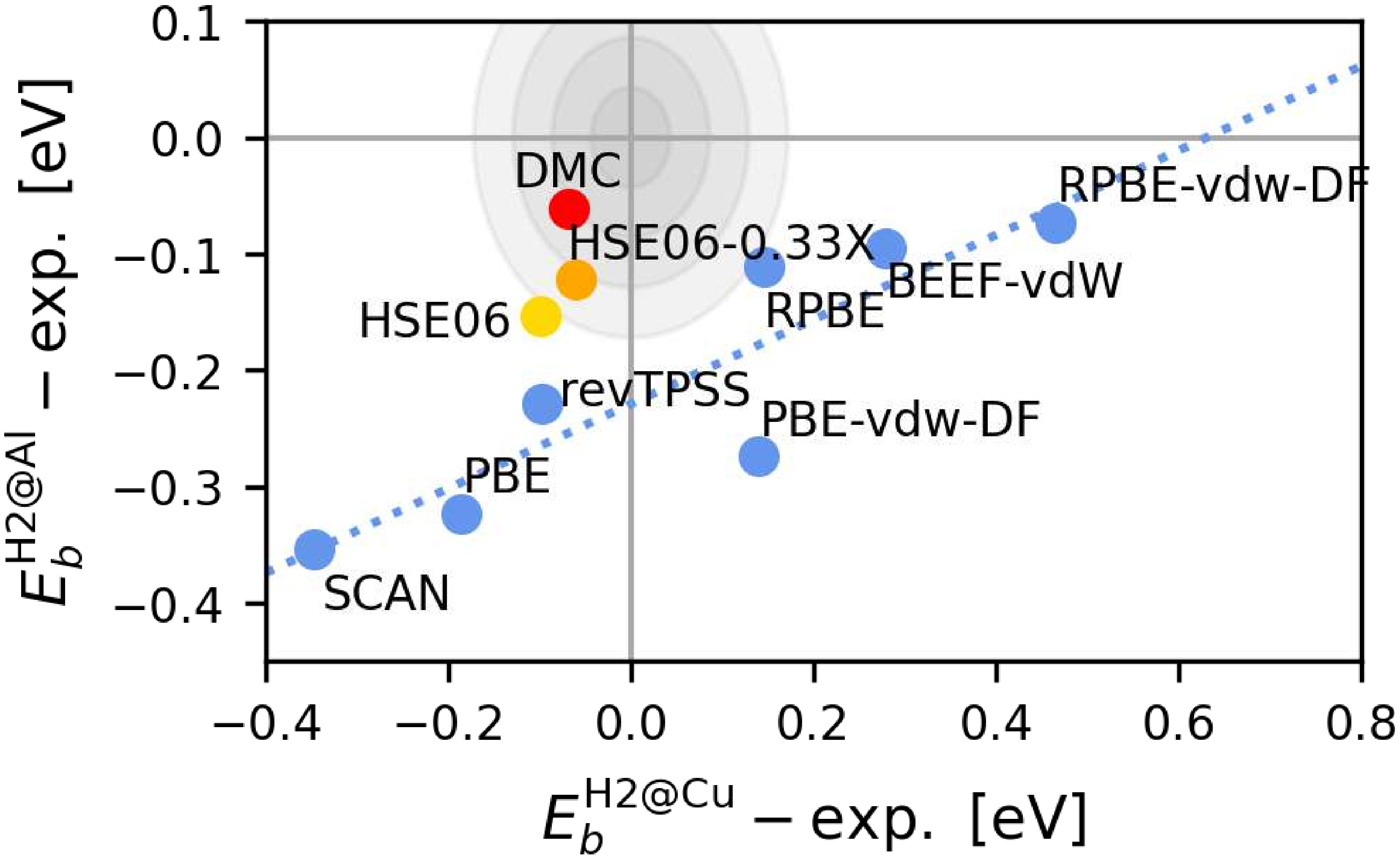
A problem remains though

- There are reactions for which no GGA functional can predict the correct barrier height



Gerrits, Smeets, Vuckovic, Powell, Doblhoff-Dier, Kroes, JPCL, 10552 (2020)

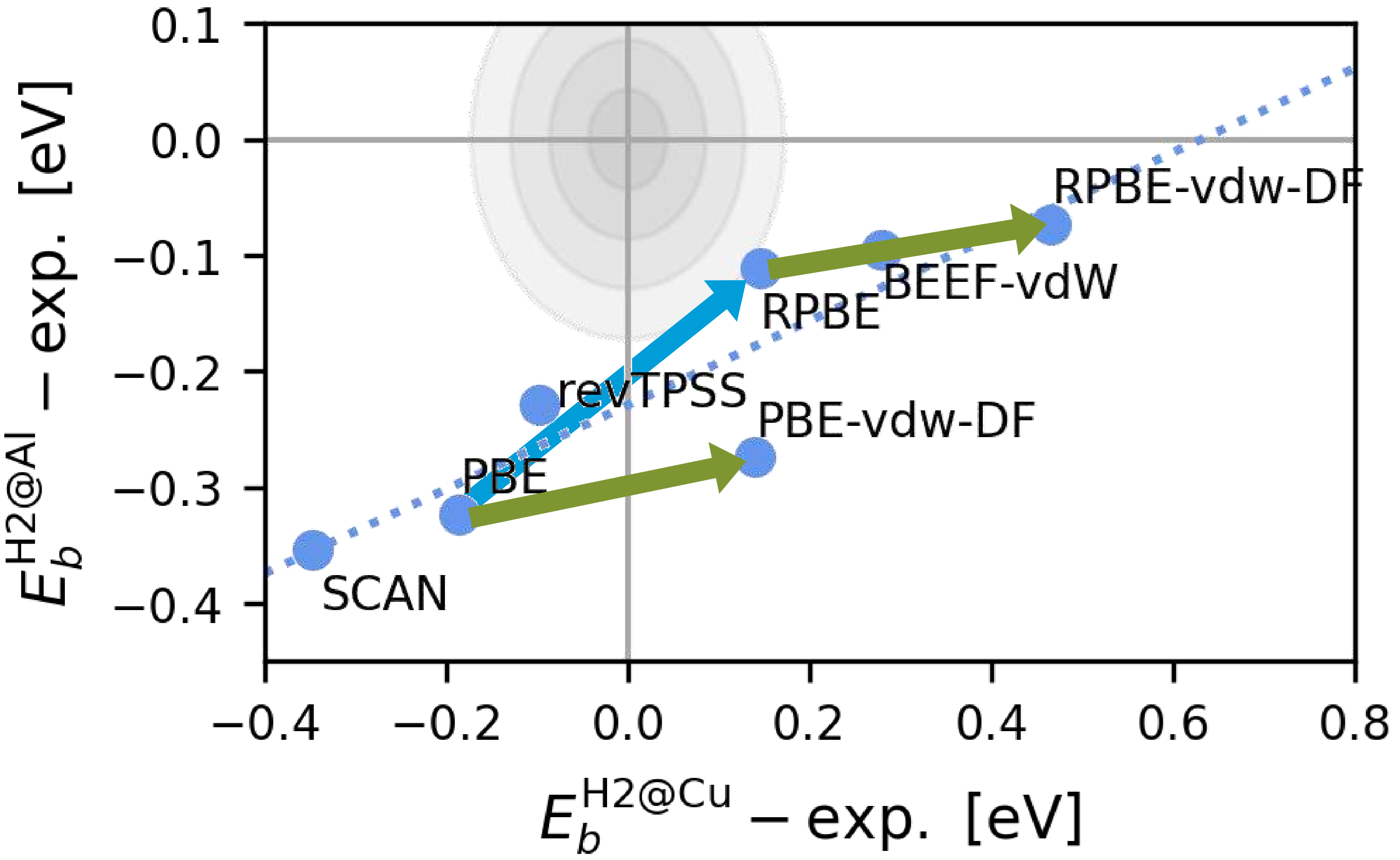
When GGA-type functional fail…



B. Oudot and K. Doblhoff-Dier, to be published

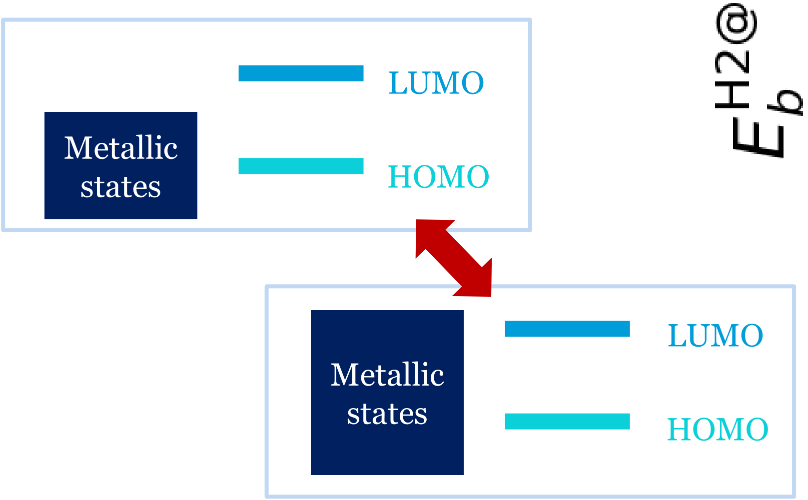
When theory learns from experiment

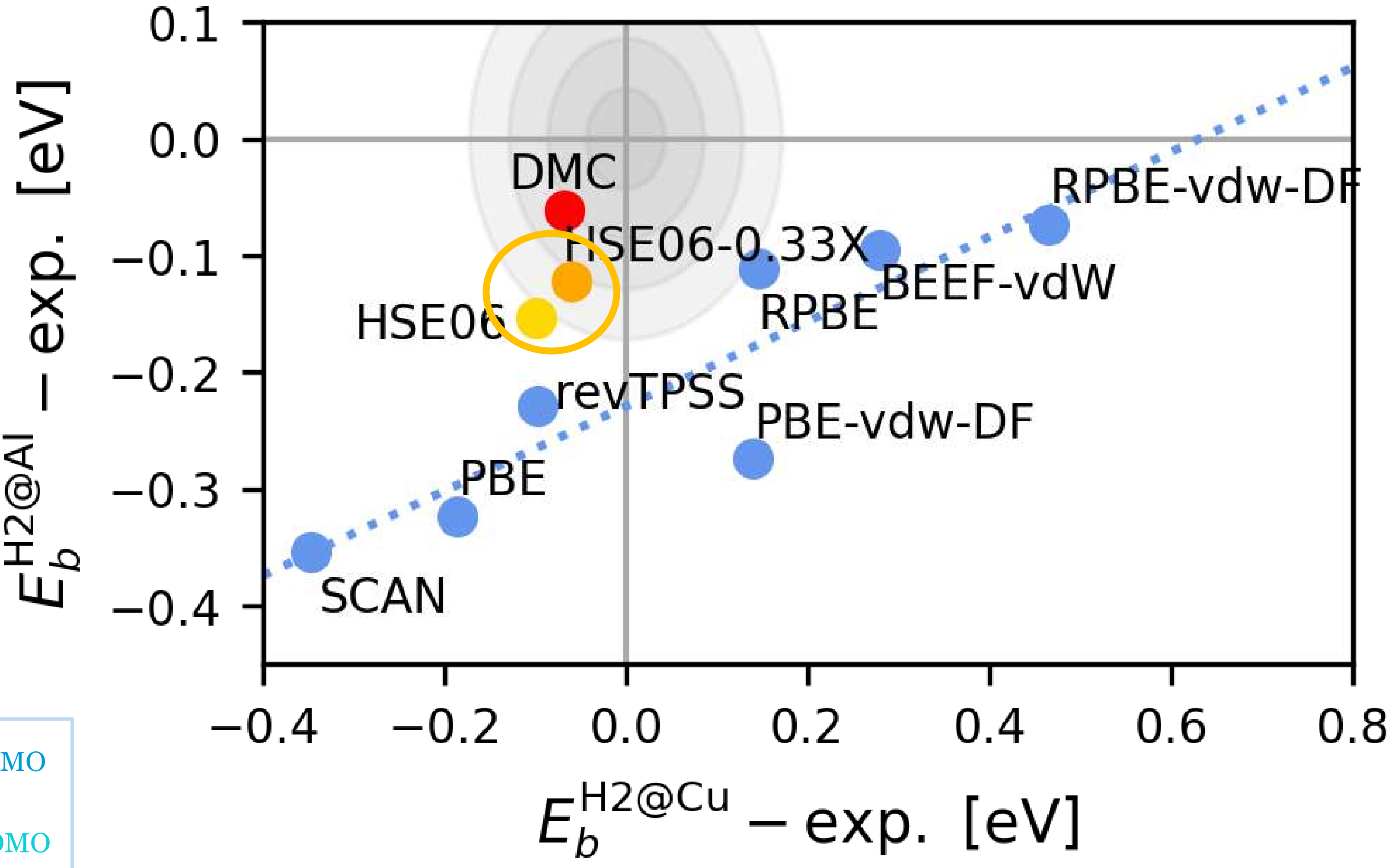
- When error cancellation fails…
- Not due to
  - Gradient enhancement factor
  - Dispersion correction



When theory learns from experiment

- When error cancellation fails…
- Not due to
  - Gradient enhancement factor
  - Dispersion correction
- Something to do with exact-exchange?!
  - Band alignment?





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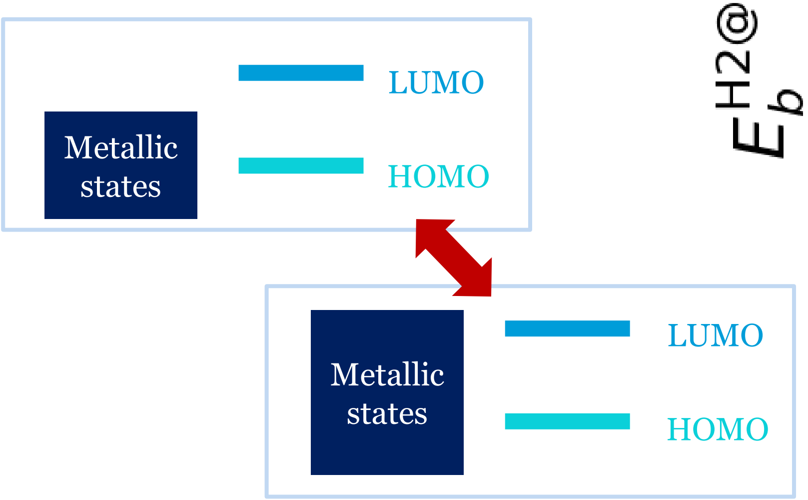

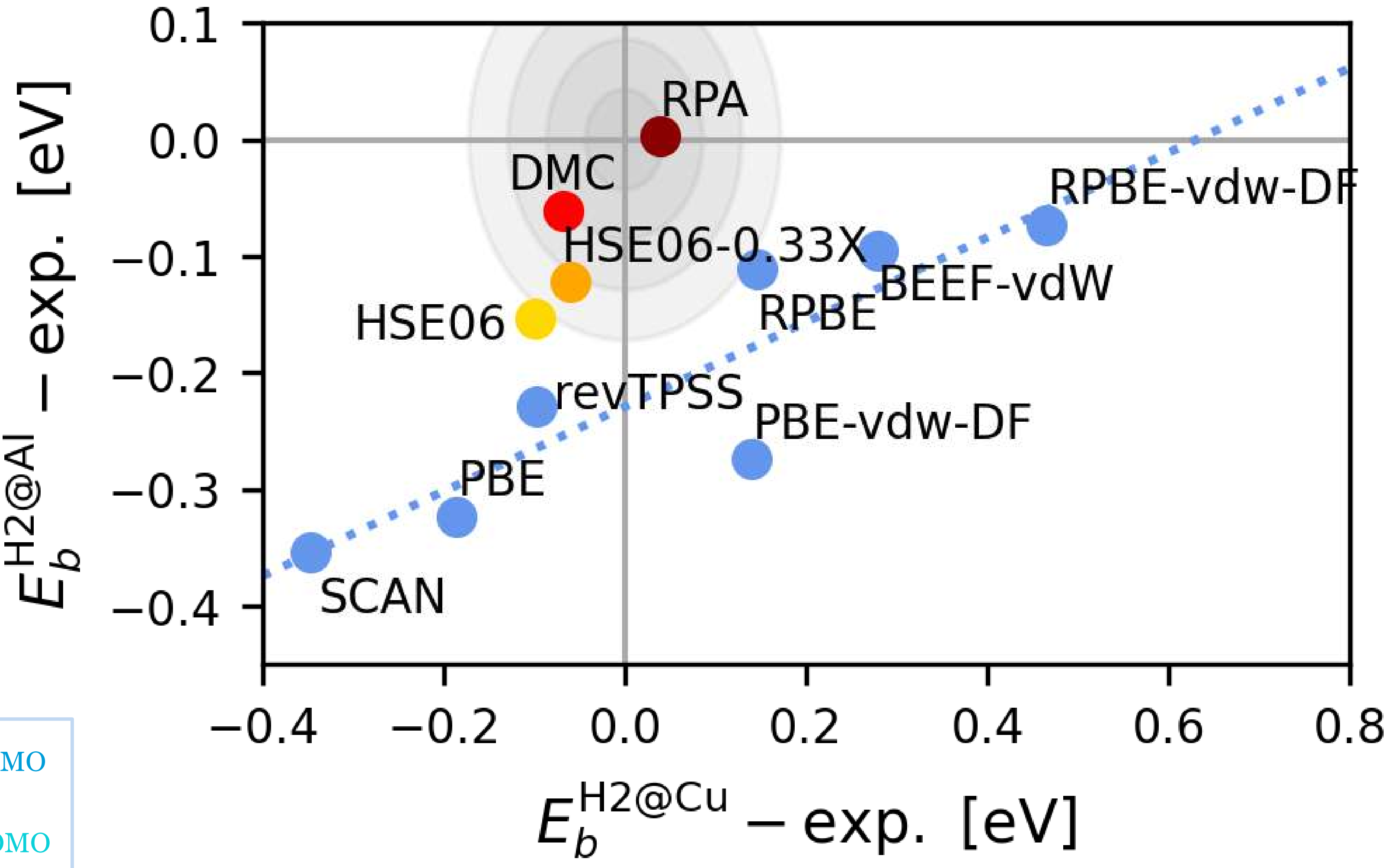

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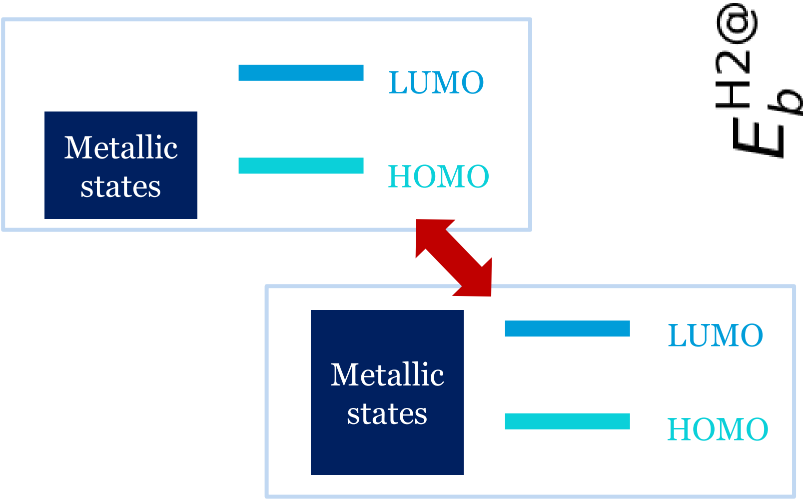

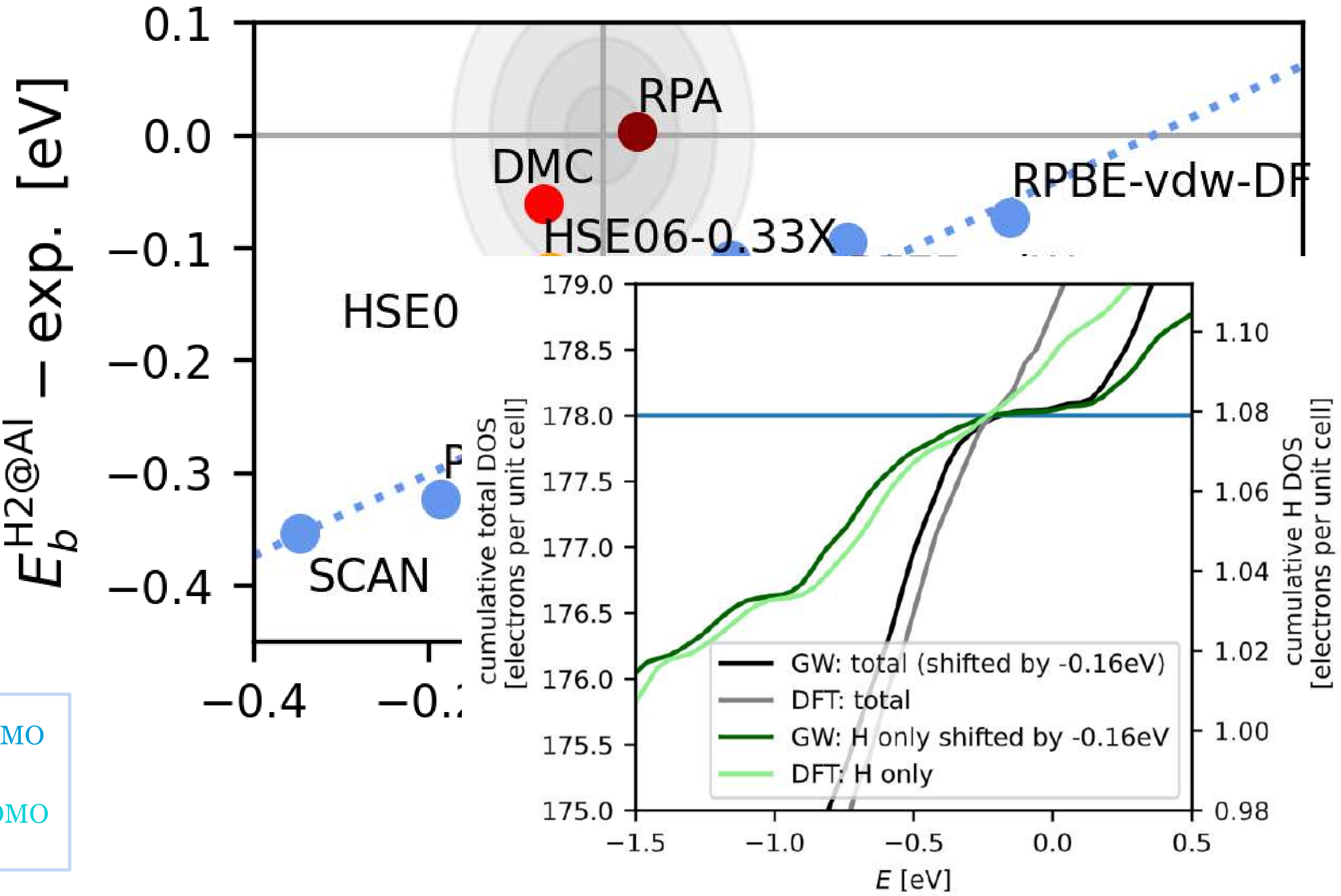

When theory learns from experiment

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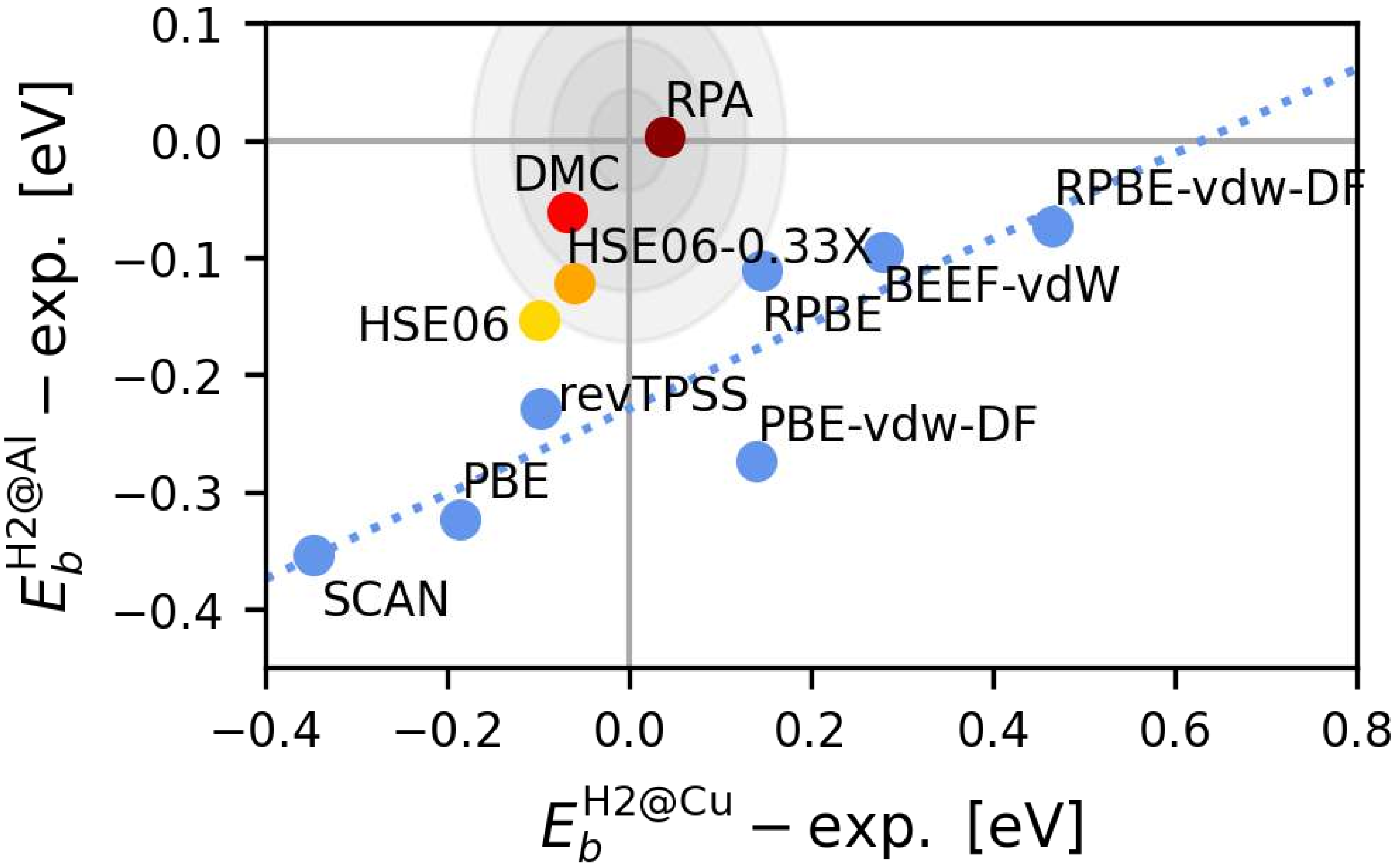
  - Band alignment
- Something to do with exact-exchange?!
  - Density driven self-interaction errors?!
  - Energy driven self-interaction errors?!



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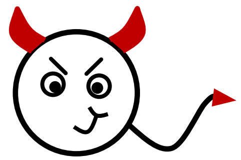
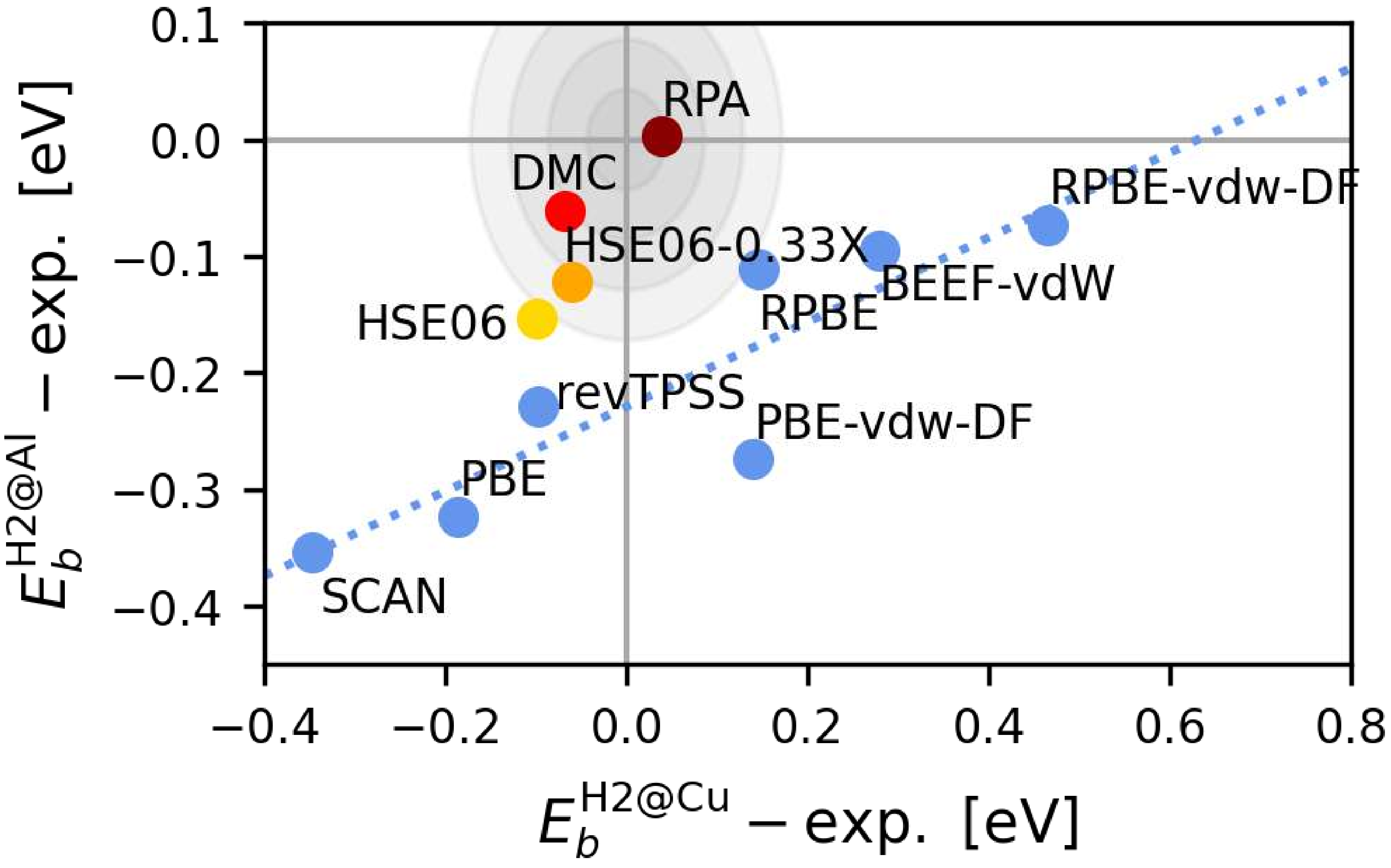
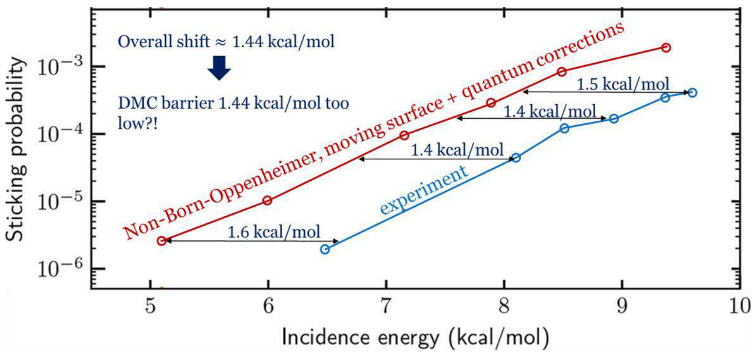


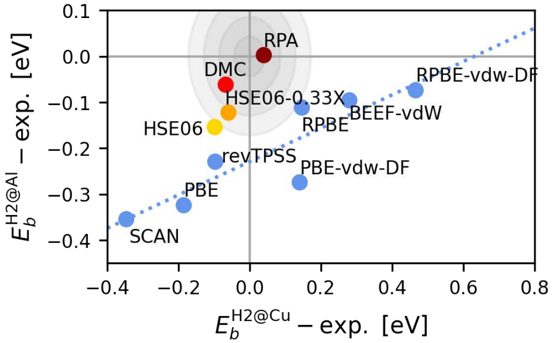


What DMC can do for heterogeneous catalysis

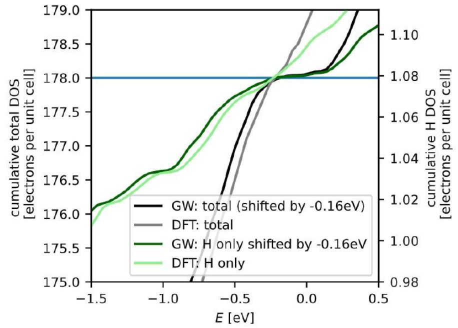
1. Allow for predictive results
   - Matching a single value
   - Aided by Δ machine learning



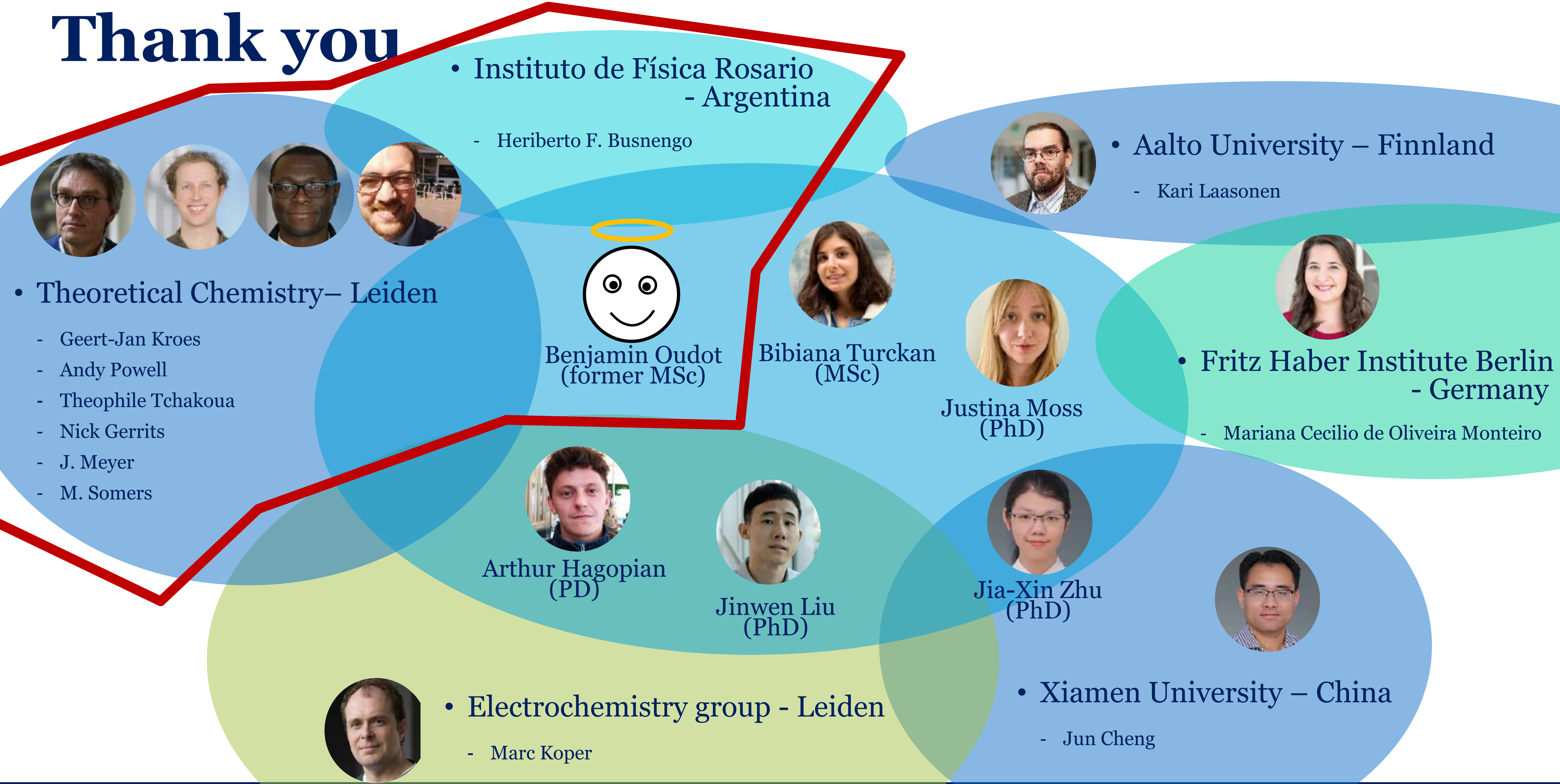
2. Provide benchmark data in absence of experimental data
   - Train DFT functionals
   - Compare to RPA → learn about accuracy of both methods



3. Combined with RPA: identify shortcomings of GGA functionals
   - Energy driven self-interaction errors??!



Thank you



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• Aalto University – Finnland
- Kari Laasonen
• Theoretical Chemistry– Leiden
- Geert-Jan Kroes
- Andy Powell
- Theophile Tchakoua
- Nick Gerrits
- J. Meyer
- M. Somers
Benjamin Oudot (former MSc)
Bibiana Turckan (MSc)
Justina Moss (PhD)
• Fritz Haber Institute Berlin - Germany
- Mariana Cecilio de Oliveira Monteiro
Arthur Hagopian (PD)
Jinwen Liu (PhD)
Jia-Xin Zhu (PhD)
• Electrochemistry group - Leiden
- Marc Koper
• Xiamen University – China
- Jun Cheng

What DMC can do for heterogeneous catalysis

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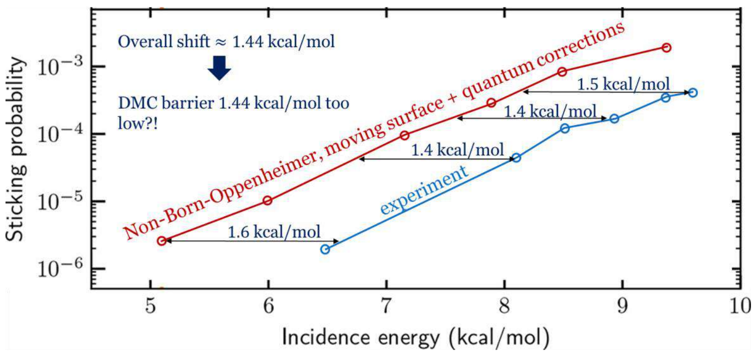

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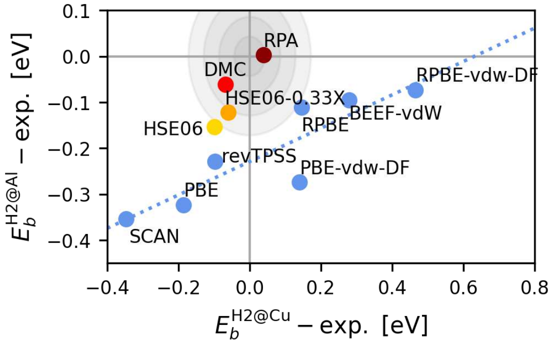

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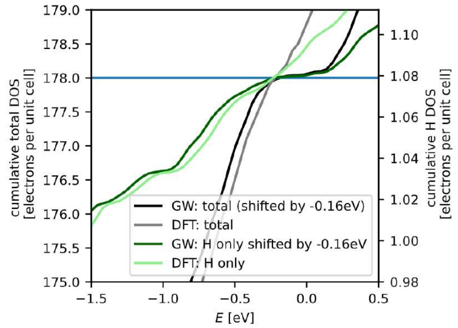
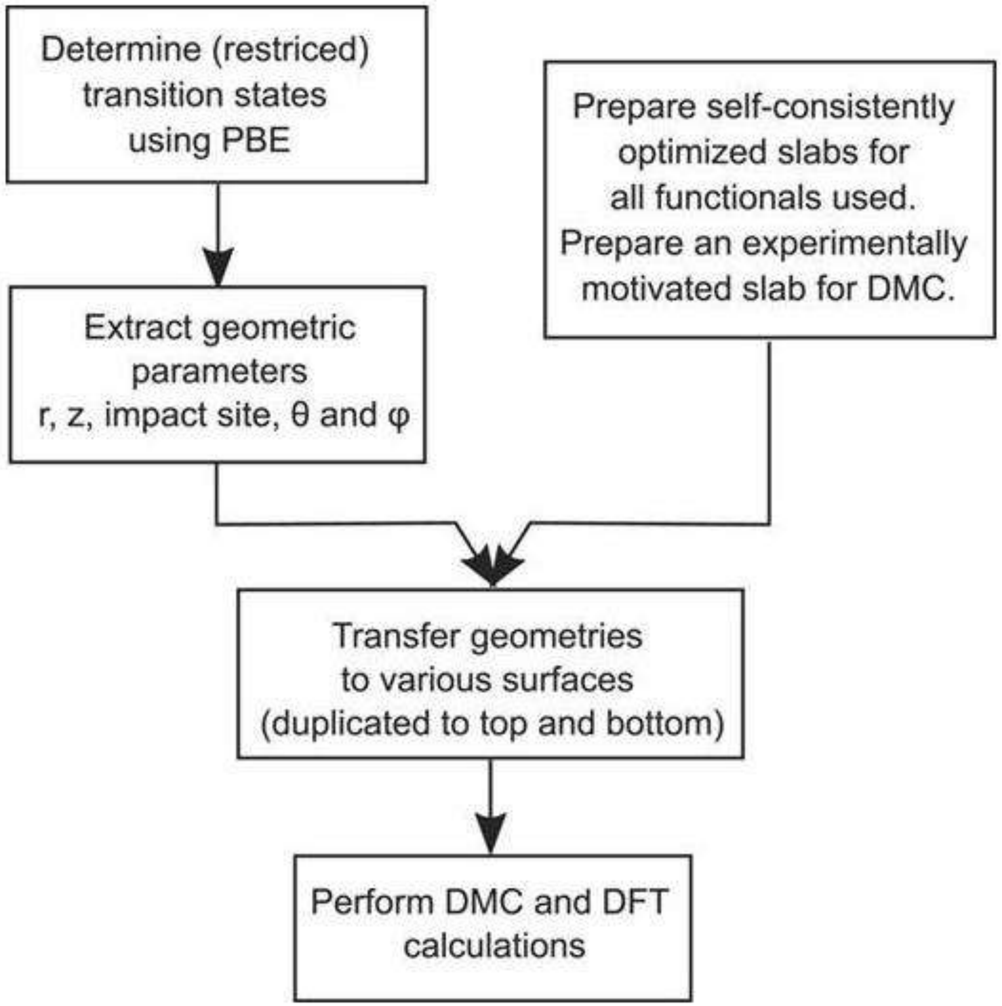
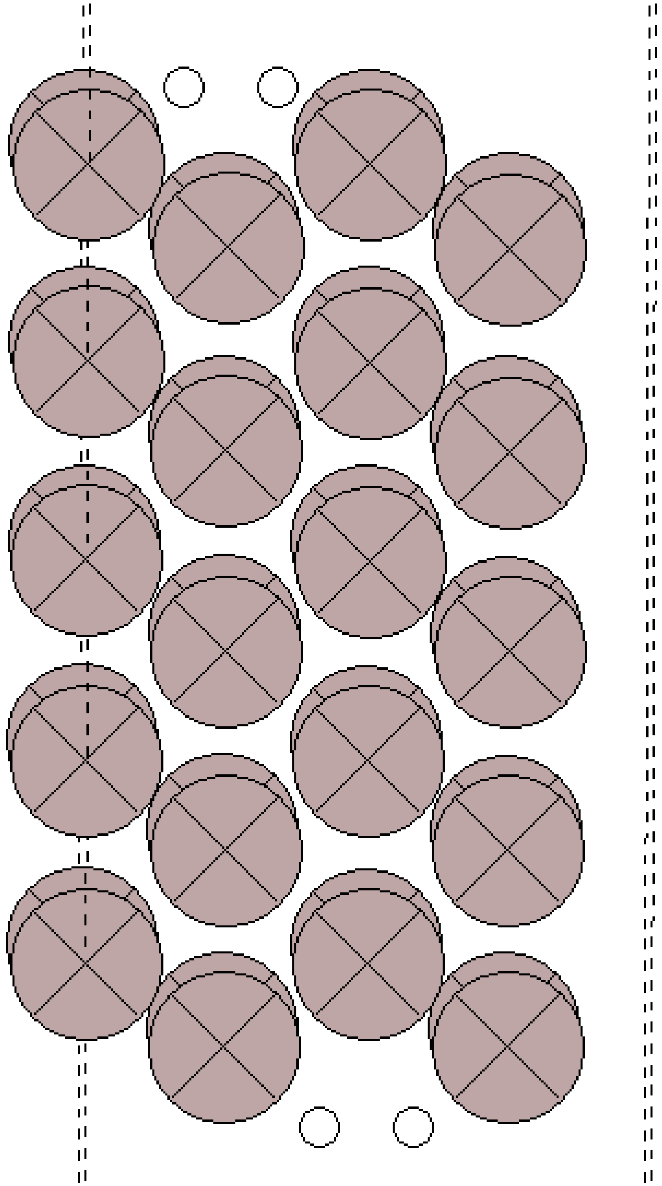


Backup

Universiteit Leiden
The Netherlands

Determining the geometry





A. Powell, G.-J. Kroes and K. Doblhoff-Dier, JCP (2020), doi: 10.1061/5.002919

Computational setup

- DFT
  - VASP
  - PAW *_GW
  - Self-consistent lattice constant and interlayer spacing
  - 14x14x1 k-points
  - Plane-wave cutoff: 500eV
  - Adsorption on top and bottom, 24 Å of vacuum between metal slabs
  - Methfesses-Paxond semaring, order 2, 0.2884eV

- DMC
  - CASINO
  - Slater part of trail wf. From QUANTUM ESPRESSO (plane wave cutoff 280Ry, 16x16x1 k-points)
  - 2+ 3 body Jastrow, optimized by minimizing the energy
  - Trail-Needs PP
    (good results for bulk lattice constant, bulk modulus, barrier for TS1 and TS2 and Al-H bining energy)
  - Experimentally motivated lattice constant and interlayer spacing
  - Twist averaging using linear extrapolation
    (based on symmetry inequivalent twists of 8x8x1 k-point grid in 2x2, and of 4x4x1 k-point grid in 4x4 cell)
  - Extrapolation to infinite system size from 2x2 to 4x4 surface unit cell

Finite size extrapolation

- Twist averaging

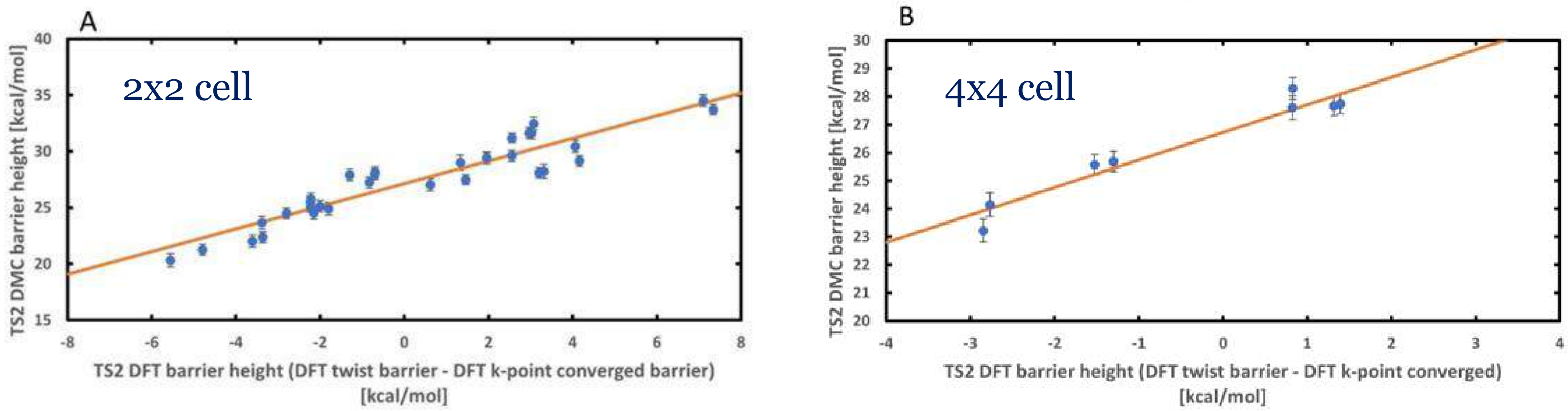


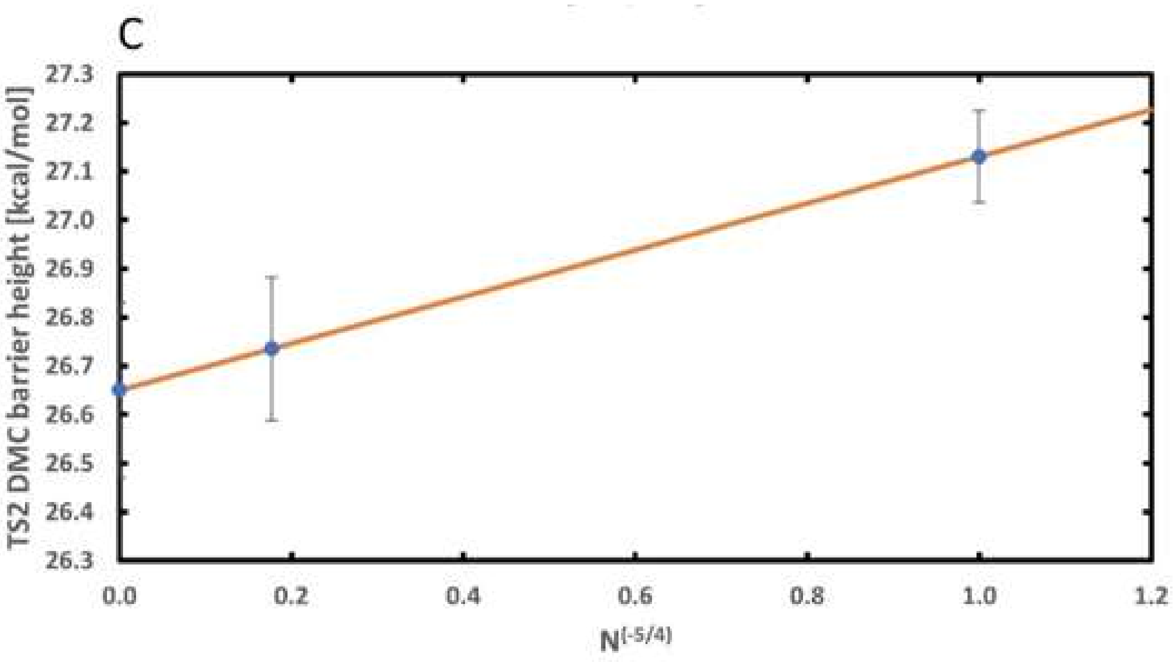
Table S25: TS2, a summary of values from the 2x2 supercell and the 4x4 supercell, leading to the DMC barrier height corrected for the single-particle finite-size errors. All energies in kcal/mol.

	TS2 2x2 supercell	TS2 4x4 supercell
$\Delta\bar{E}^{DMC}$	27.5(1)	26.2(1)
m	1.0(1)	1.0(1)
$\Delta E^{DFT}_{k-point\ conv.} - \Delta\bar{E}^{DFT}_{twists}$	-0.3	0.5
$m(\Delta E^{DFT}_{k-point\ conv.} - \Delta\bar{E}^{DFT}_{twists})$	-0.3(0)	0.5(1)
ΔE^{DMC}_{sp-fs}	27.1(1)	26.7(1)

A. Powell, G.-J. Kroes and K. Doblhoff-Dier, JCP (2020), doi: 10.1061/5.002919

Finite size extrapolation

- Finite size extrapolation



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