Multi-Lattice Approach to Kinetic Monte Carlo

Max J. Hoffmann

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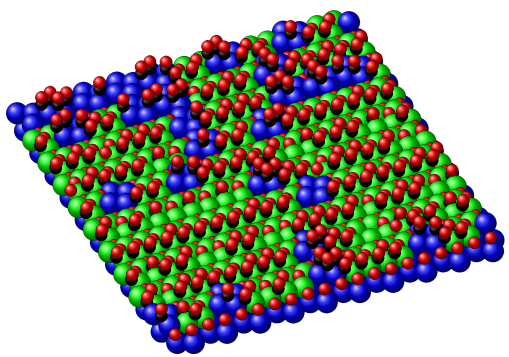
TU München

Jan 25, 2011



Outline

- introduction to DFT+kMC approach for heterogeneous catalysis
- multi-lattice kMC for CO oxidation on PdO($\sqrt{5}\times\sqrt{5}$)R27/Pd(100)[1]

[1] master thesis www.fhi-berlin.mpg.de/th/publications/Hoffmann_diploma.pdf

Motivation

- prediction of (model) catalysts performance from first principles

trial'n'error $\leftrightarrow$ rational design

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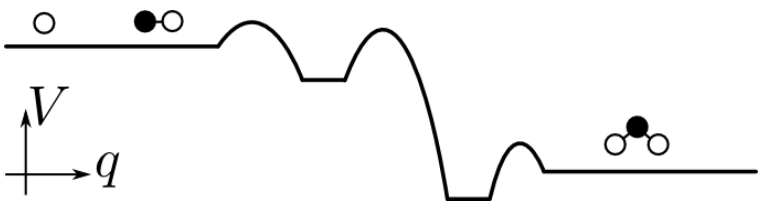
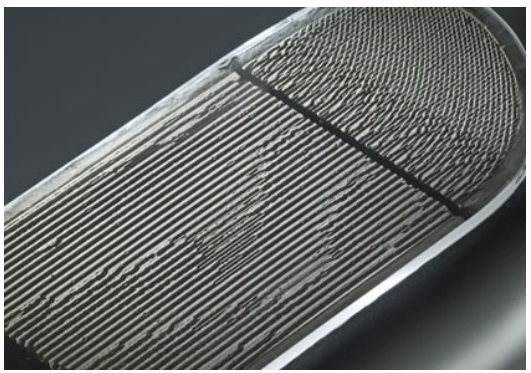
- development of multi-scale methods





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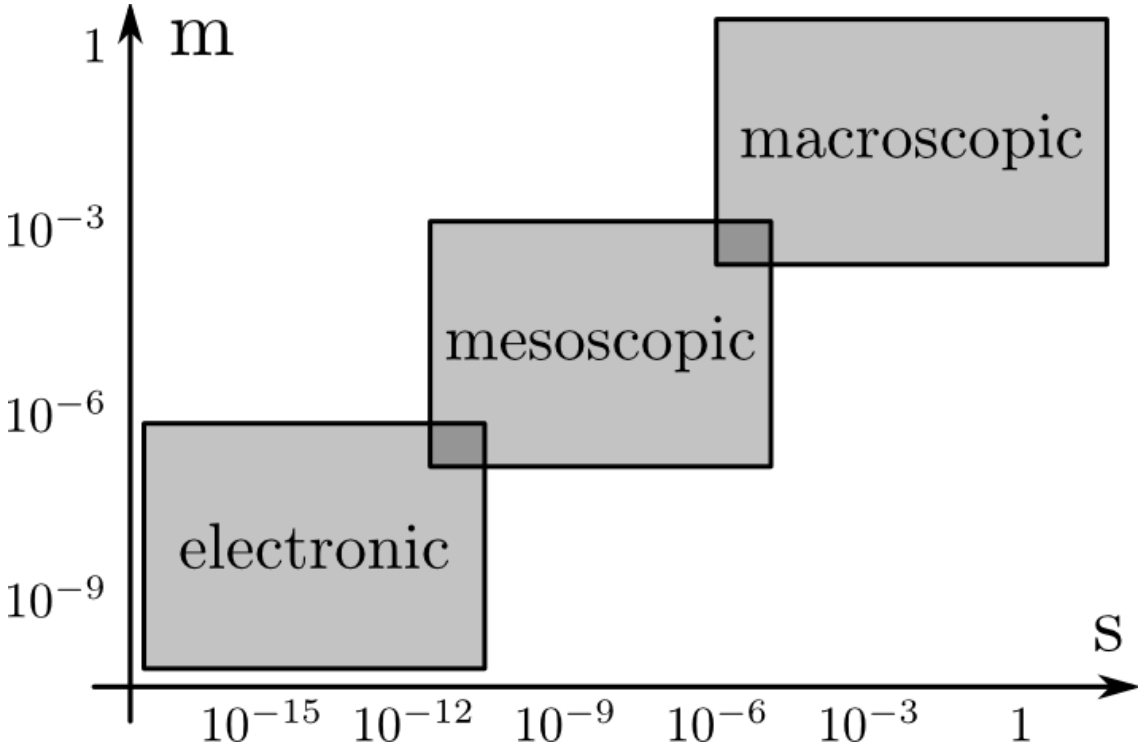
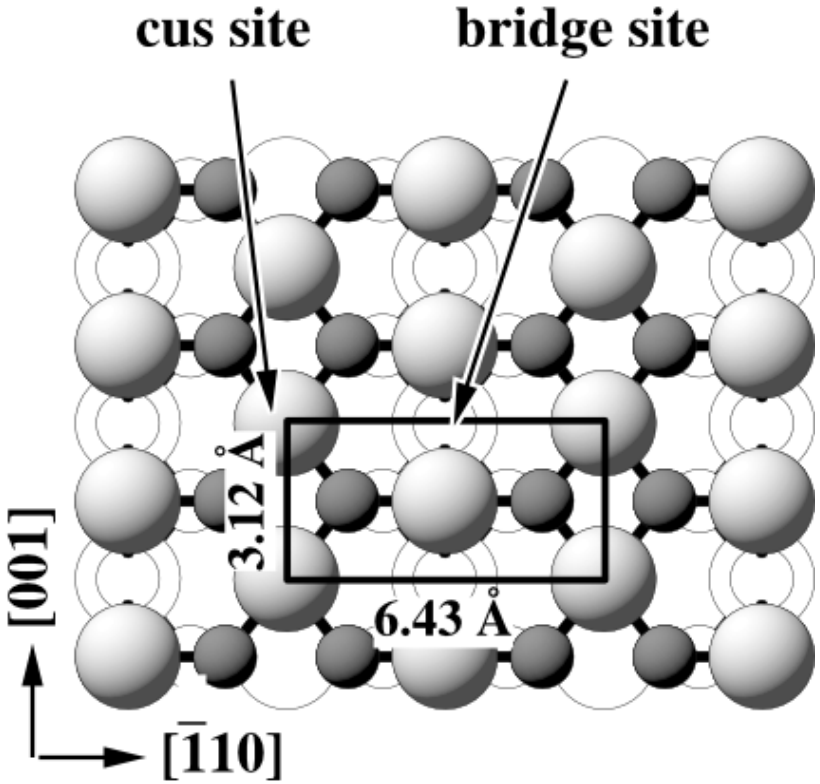


$$\mathbf{CO} + \tfrac{1}{2}\mathbf{O}_2 \rightarrow \mathbf{CO}_2\mathbf{@RuO}_2(110)^2$$



[2] Reuter *et al* (2005) in Handbook of Materials Modelling, Springer
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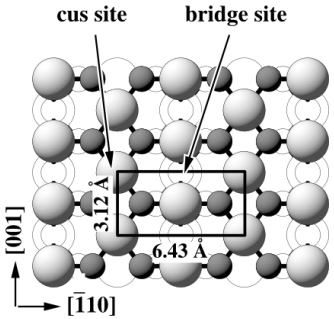

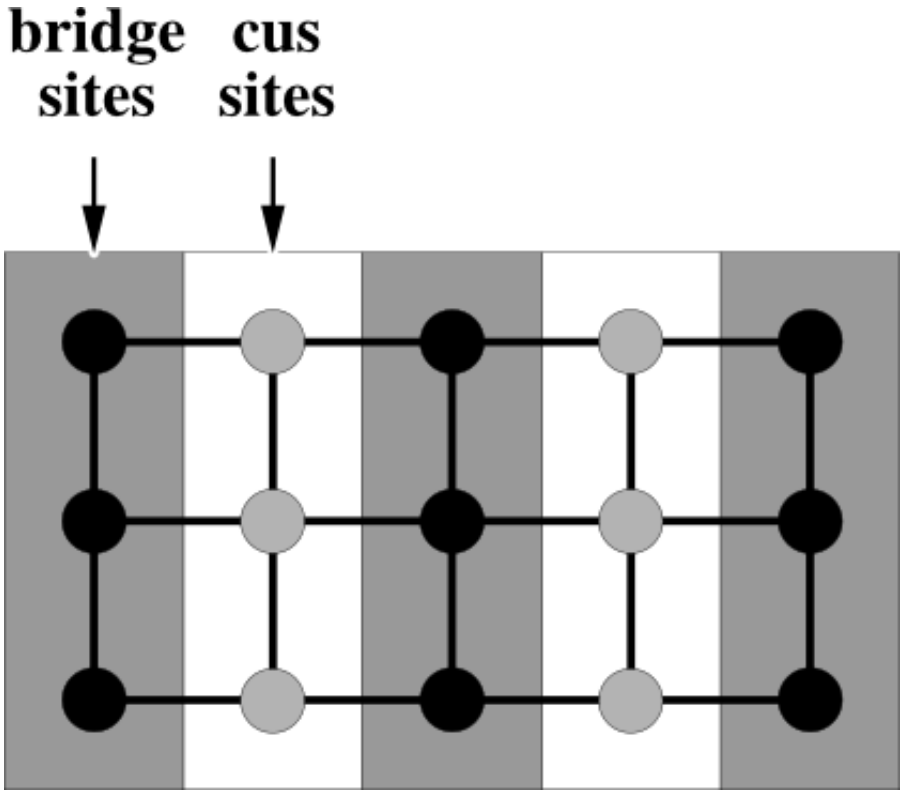

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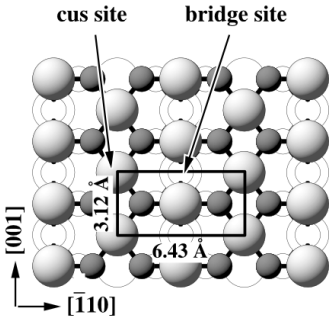

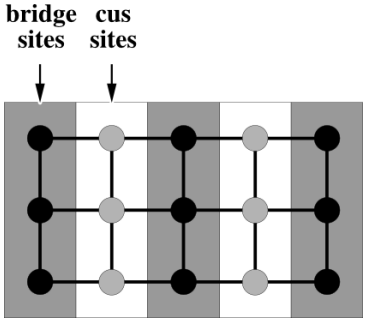

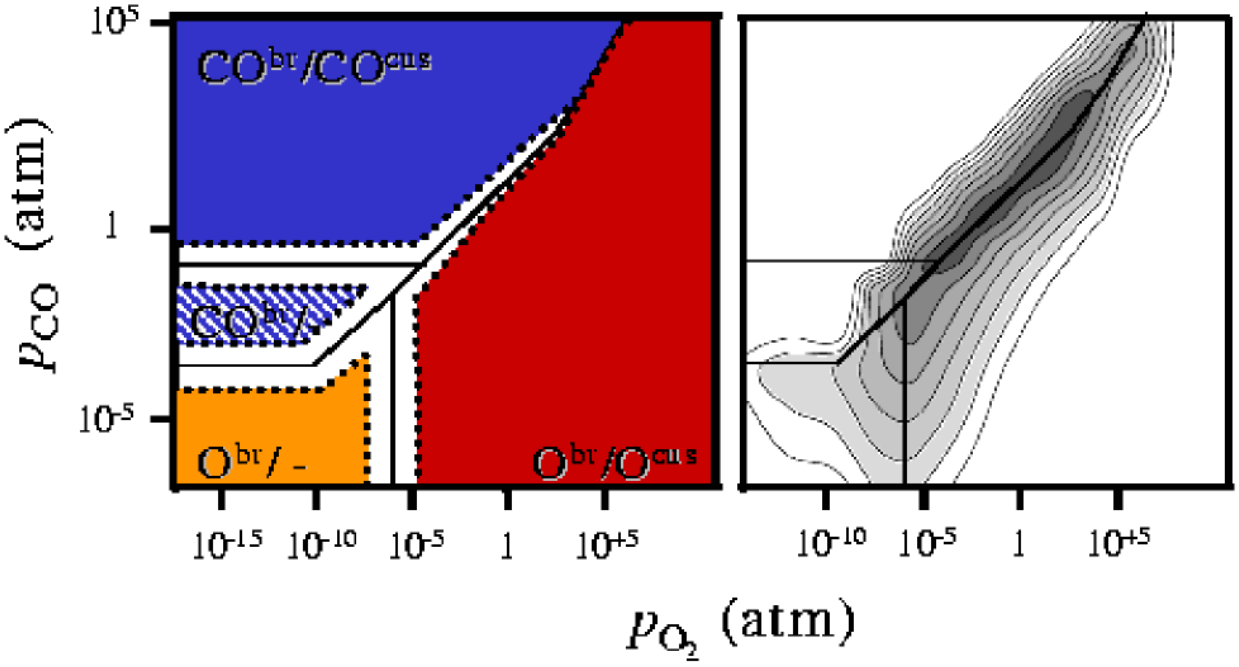

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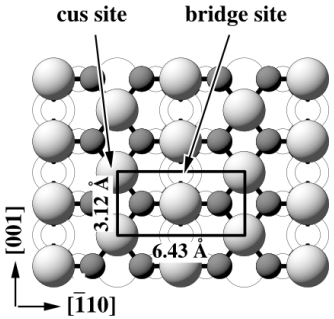

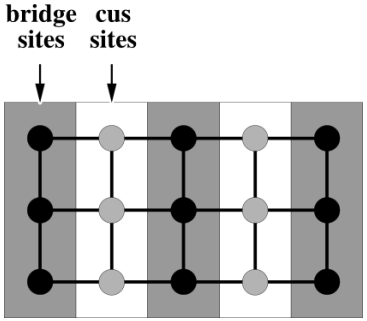

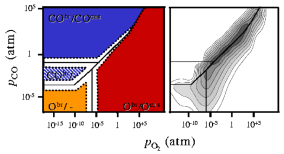

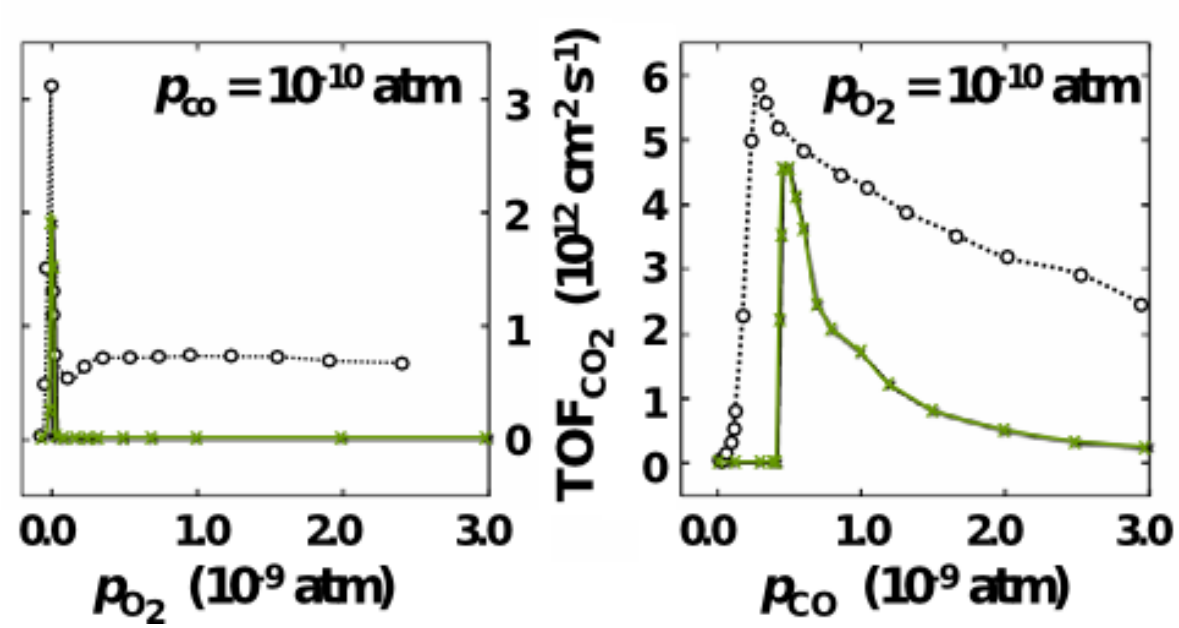

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What is kMC?

kinetic Monte Carlo (= dynamic Monte Carlo (DMC), Bortz-Kalos-Lebowitz (BKL-Method)[3], n-fold way, Gillespie[4]) all refer to the same basic idea

[3] BKL (1975), J Comput Phys **17**, 10
[4] Gillespie (1976), J Comput Phys **22**, 403

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kinetic Monte Carlo (= dynamic Monte Carlo (DMC), Bortz-Kalos-Lebowitz (BKL-Method)[3], n-fold way, Gillespie[4]) all refer to the same basic idea
generate state-to-state trajectory from initial configuration, catalog of elementary steps, and rate constants.

$$\dot{p}_i = \sum_i k_{ij} p_j - k_{ji} p_i$$

k_{ij} : transition probability $i \rightarrow j$

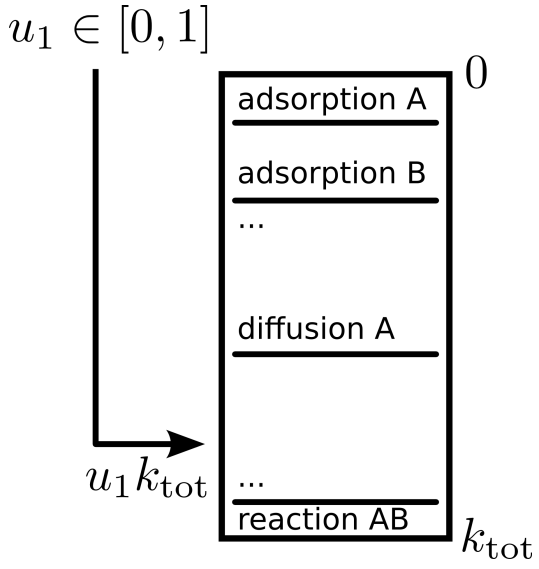
Transition State Theory

$$k_{ij} = \frac{k_B T}{h} \mathrm{e}^{-\Delta G / k_B T}$$

[3]BKL (1975), J Comput Phys **17**, 10
[4]Gillespie (1976), J Comput Phys **22**, 403

More formally[5]

- pick next process based on random number, weighted by rate constant



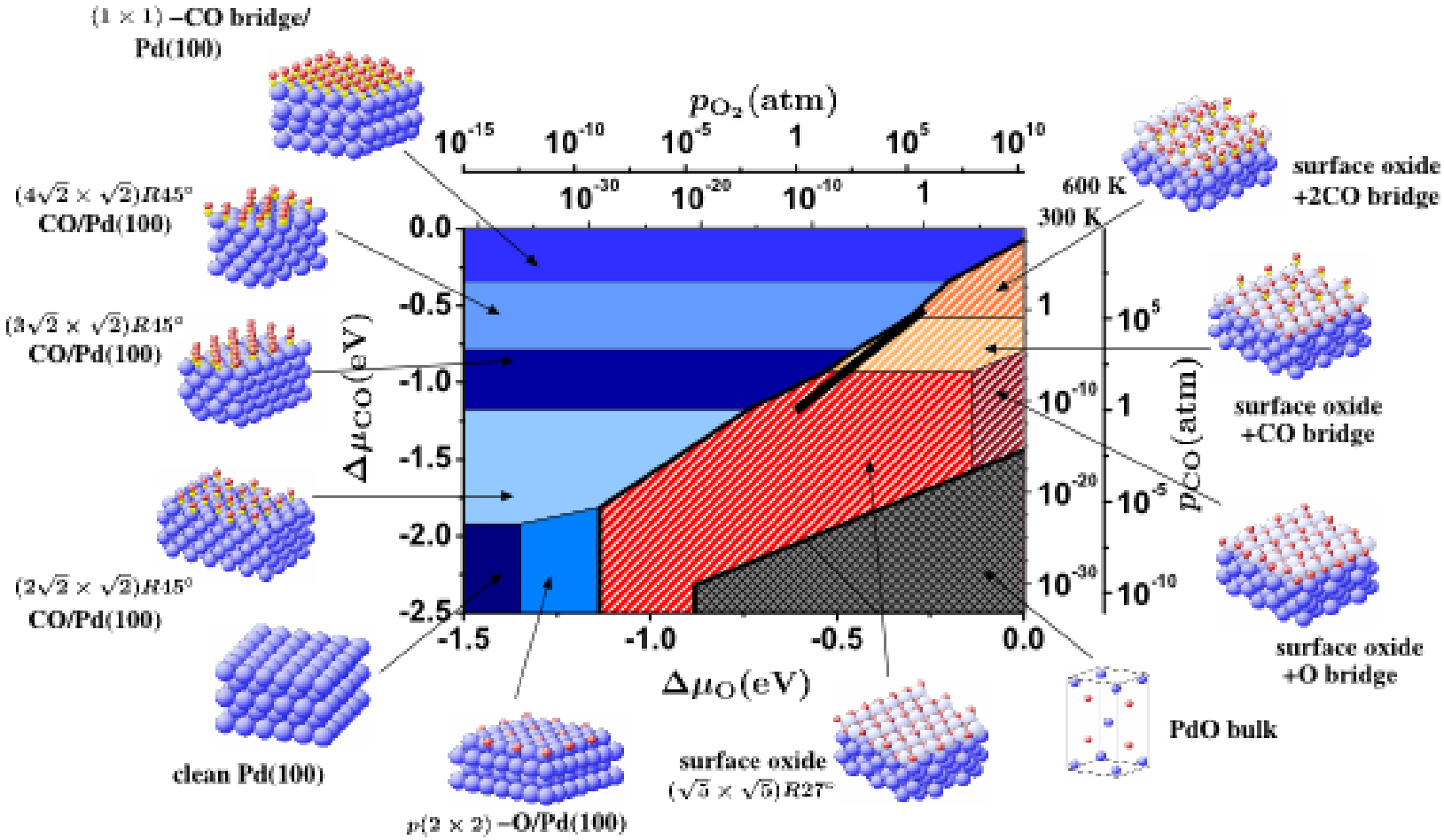
- increase time by

$$t \to t - \frac{\ln(u_2)}{k_{tot}} \qquad u_2 \in (0, 1]$$

[5] Fichthorn, Weinberg, (1991), J Chem Phys **95**, 1090

Consider PdO/Pd(100)

- non-trivial surface reconstruction under reactive conditions[6]



[6] Rogal *et al* (2007), PRL **98**, 046101

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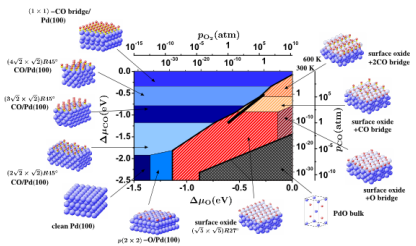
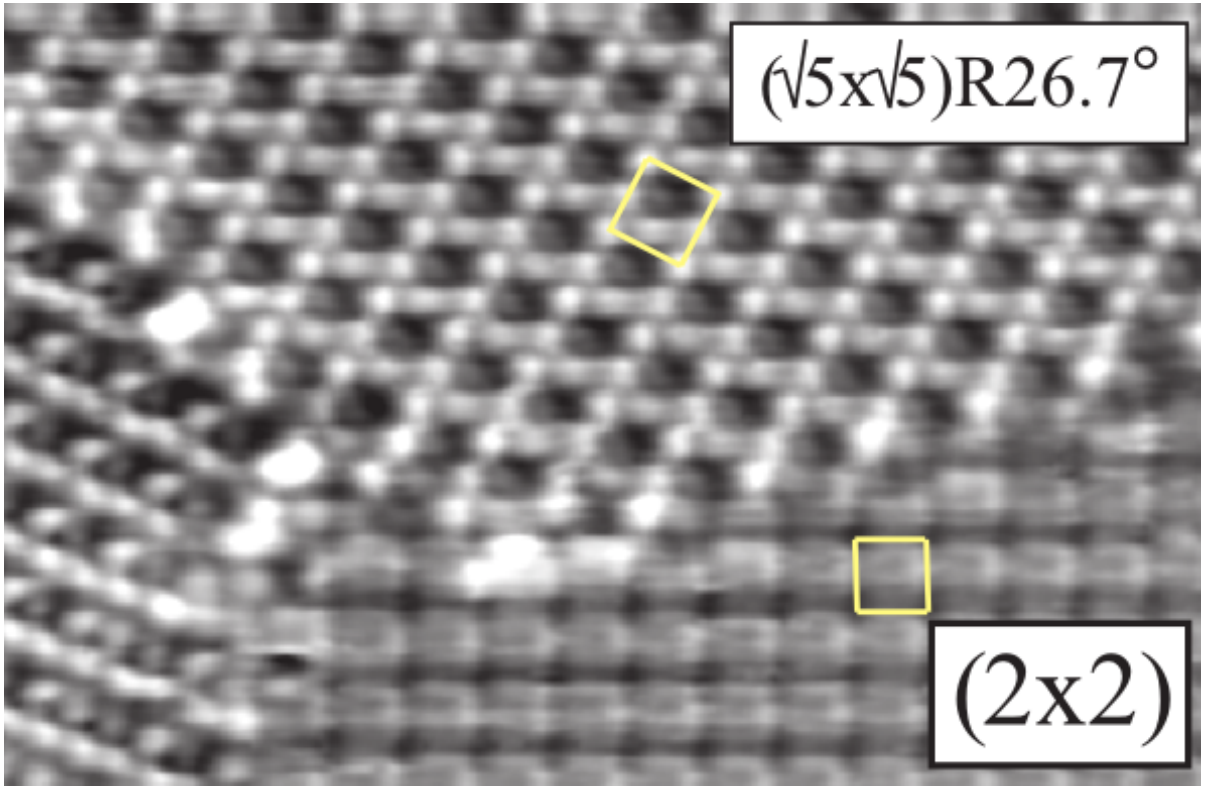
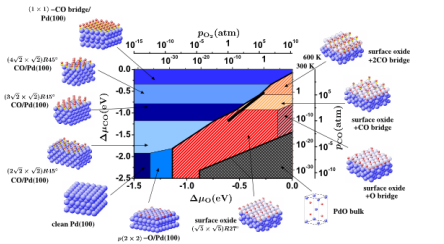


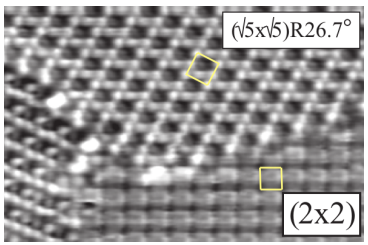


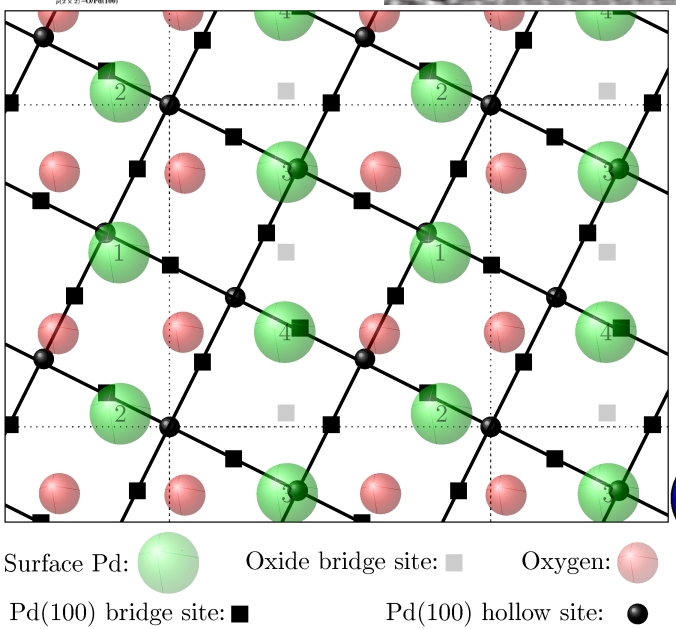
[6] Lundgren (2006), J Phys Cond Matter **30**, R481

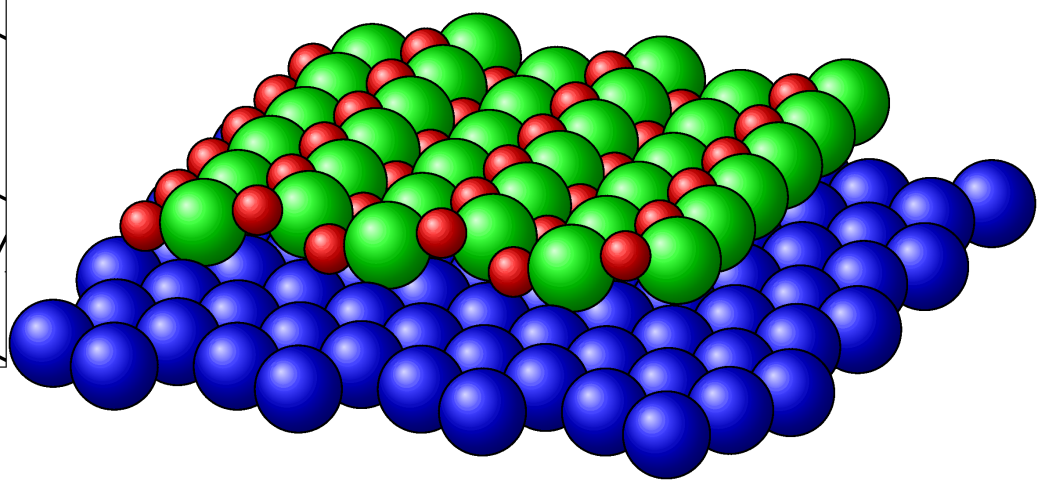
Consider PdO/Pd(100)

- non-trivial but *commensurable* [6]





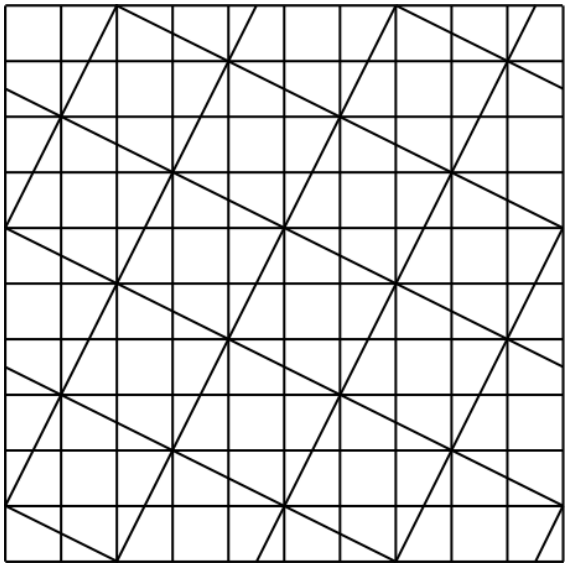




[6] Todorova *et al* (2003), Surf Sci **541**, 101

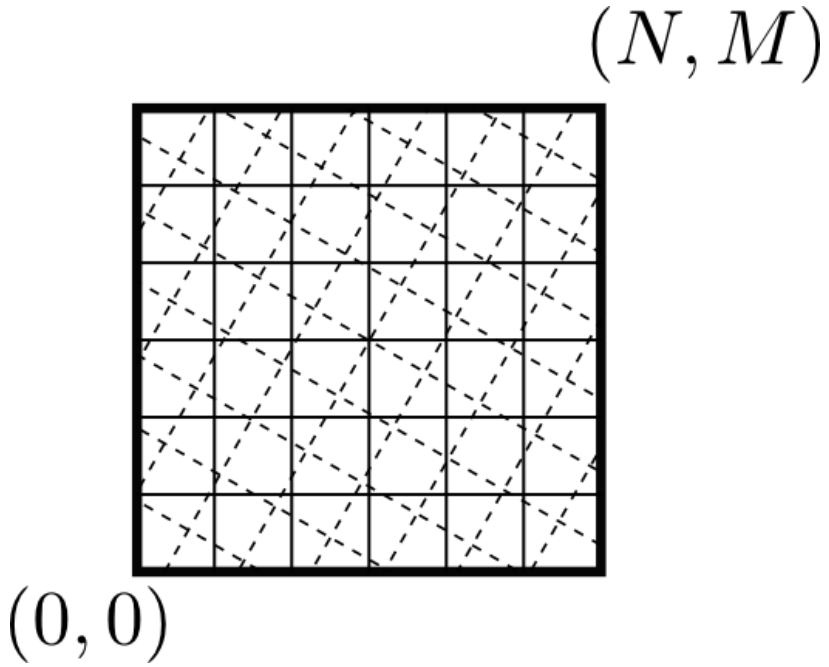
Considerations for Multi-Lattice kMC

- lattices need to be pairwise commensurable (!)



Considerations for Multi-Lattice kMC

- lattices need to be pairwise commensurable
- integer coordinates desirable



Considerations for Multi-Lattice kMC

- lattices need to be pairwise commensurable
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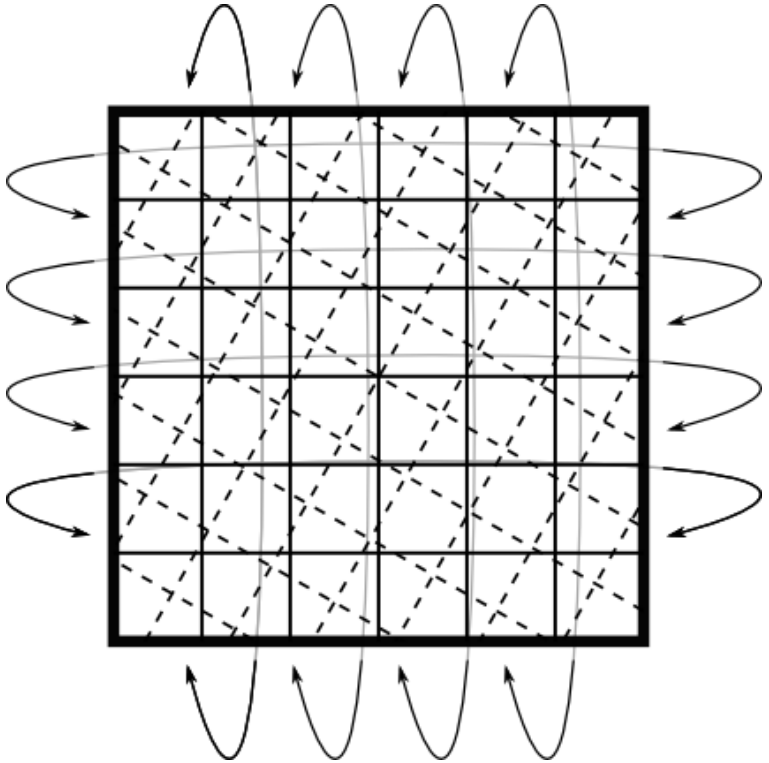
- support periodic boundary conditions



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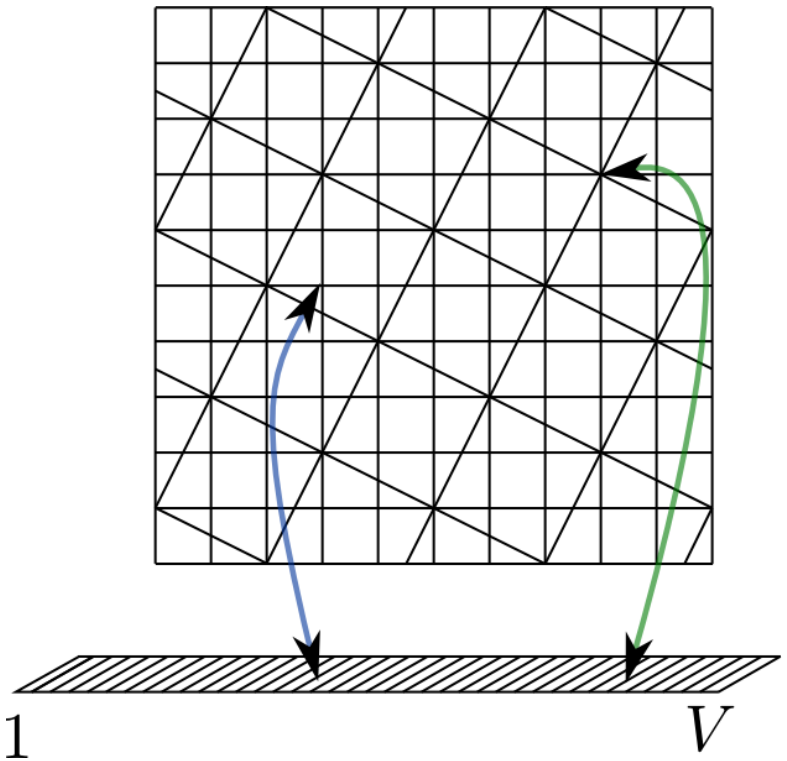
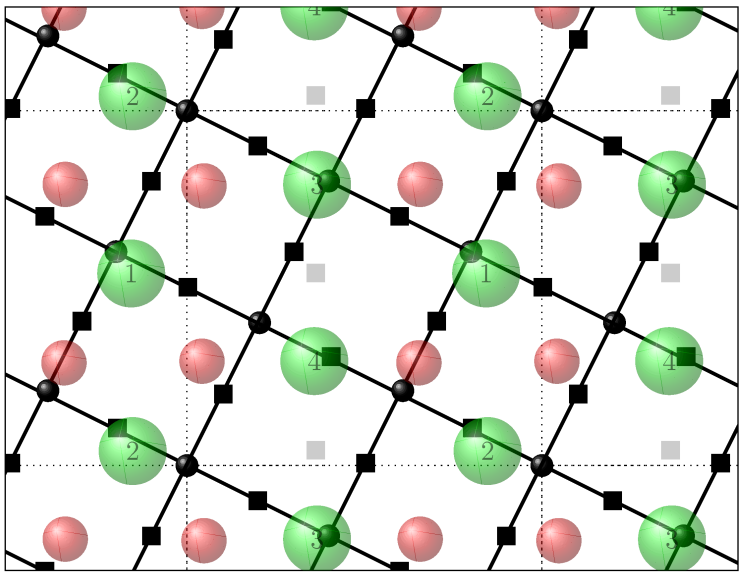
↪mapping approach



- only some sites are active
- describe processes in convenient coordinates

Reconstruction mechanism

- geometrical considerations



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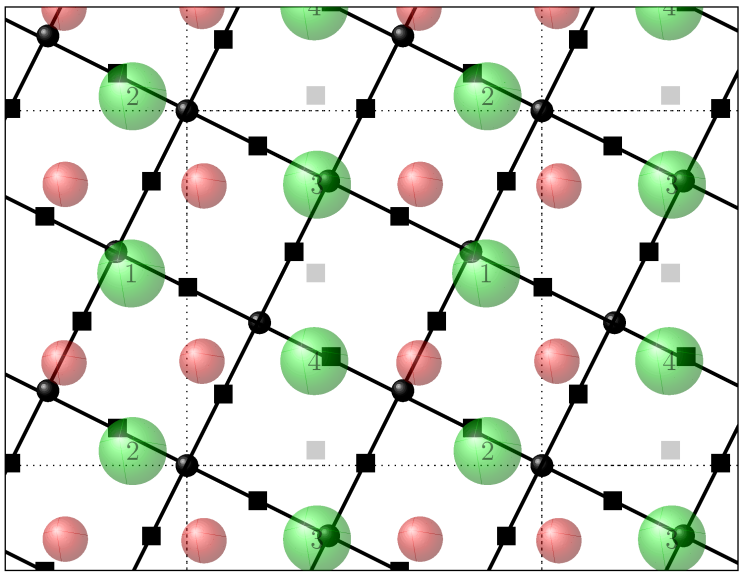
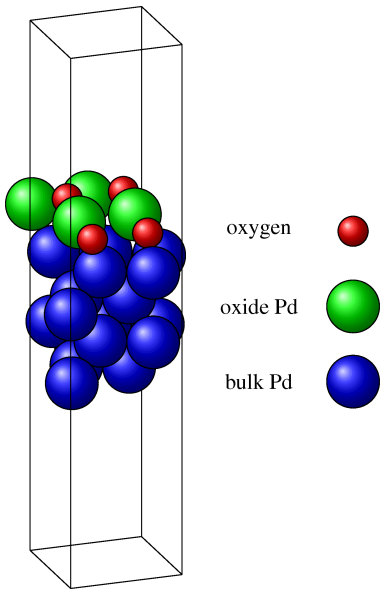
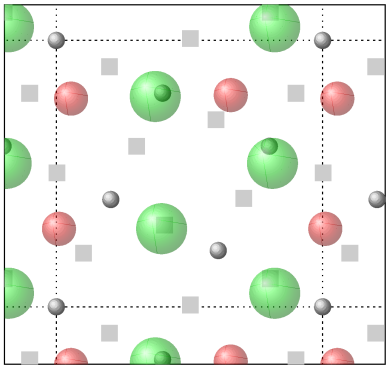


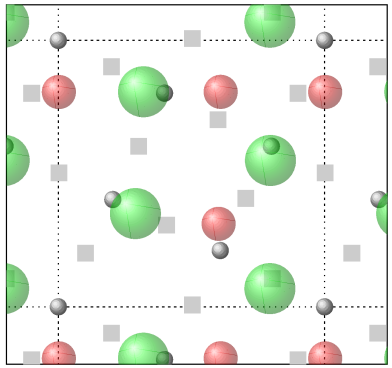
- surface slab geometry optimizations

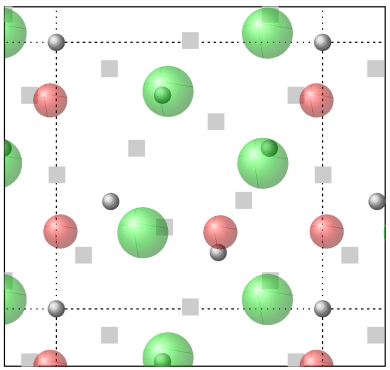


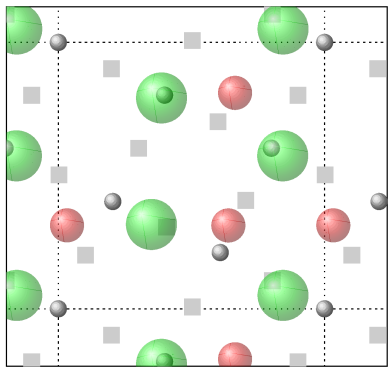
DFT, VASP, PW-91, J. Jelic

Remove one oxygen atom





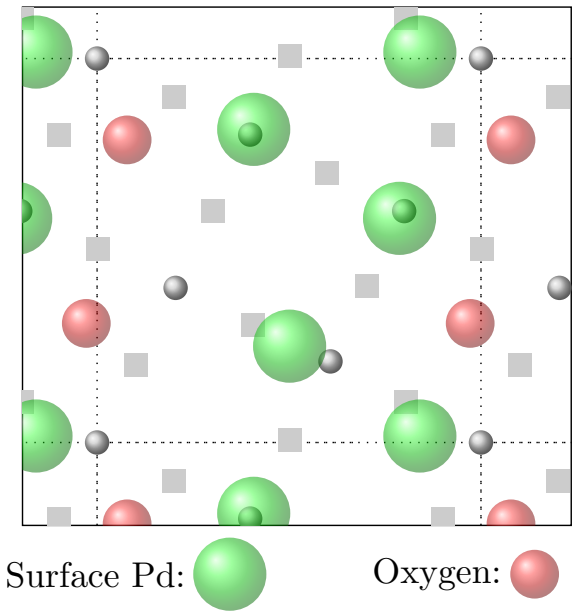


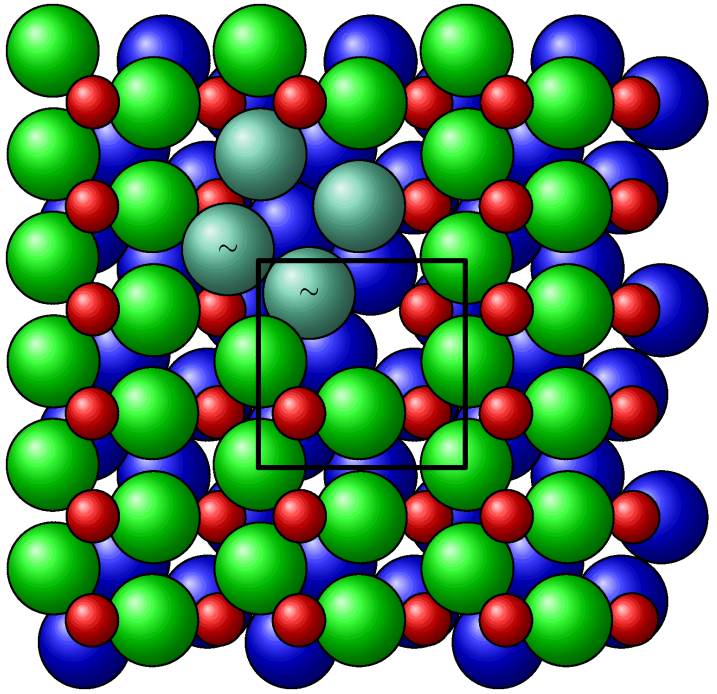


$\hookrightarrow$no significant change

Remove two oxygen atoms

- structural changes occur

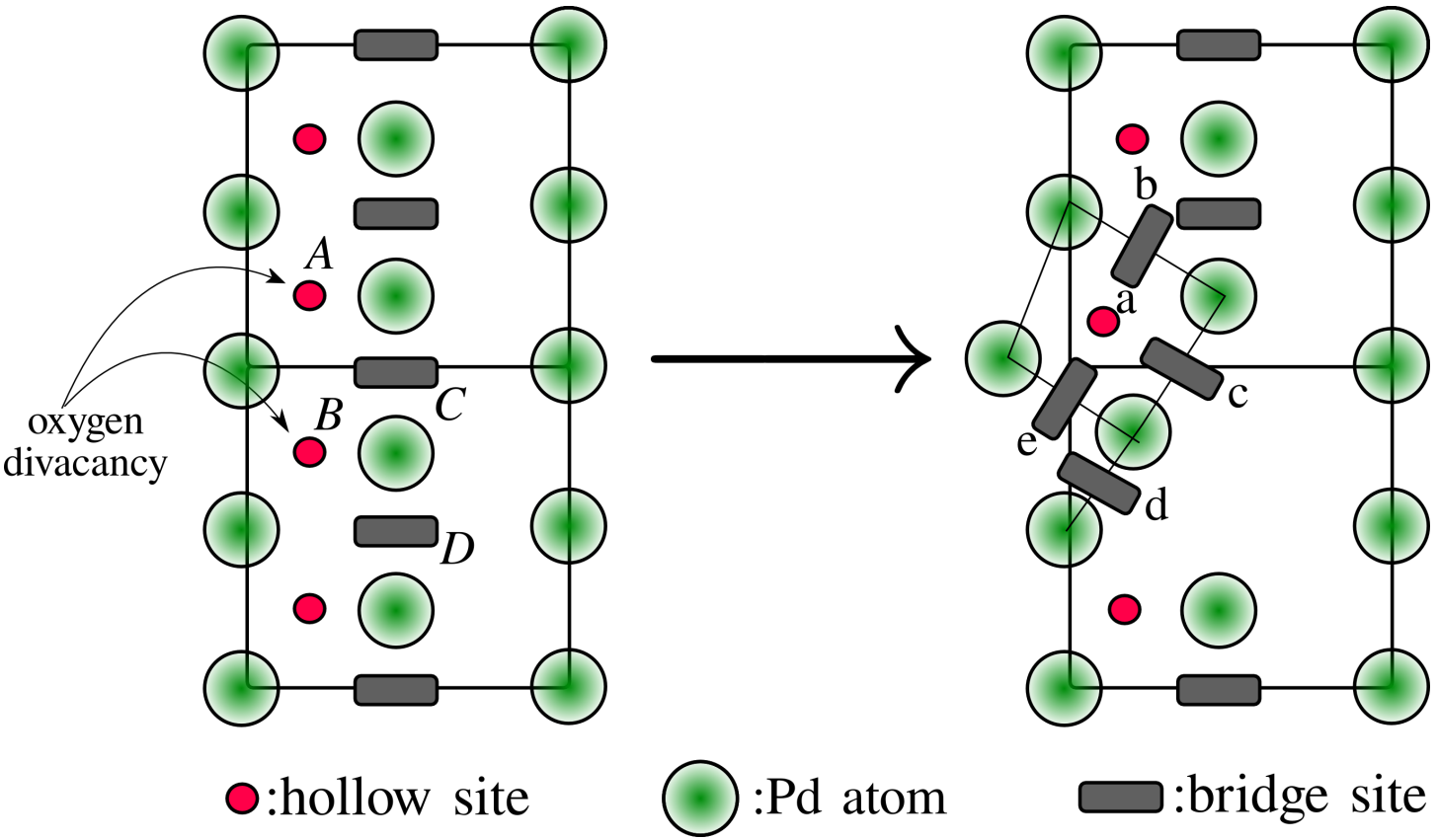




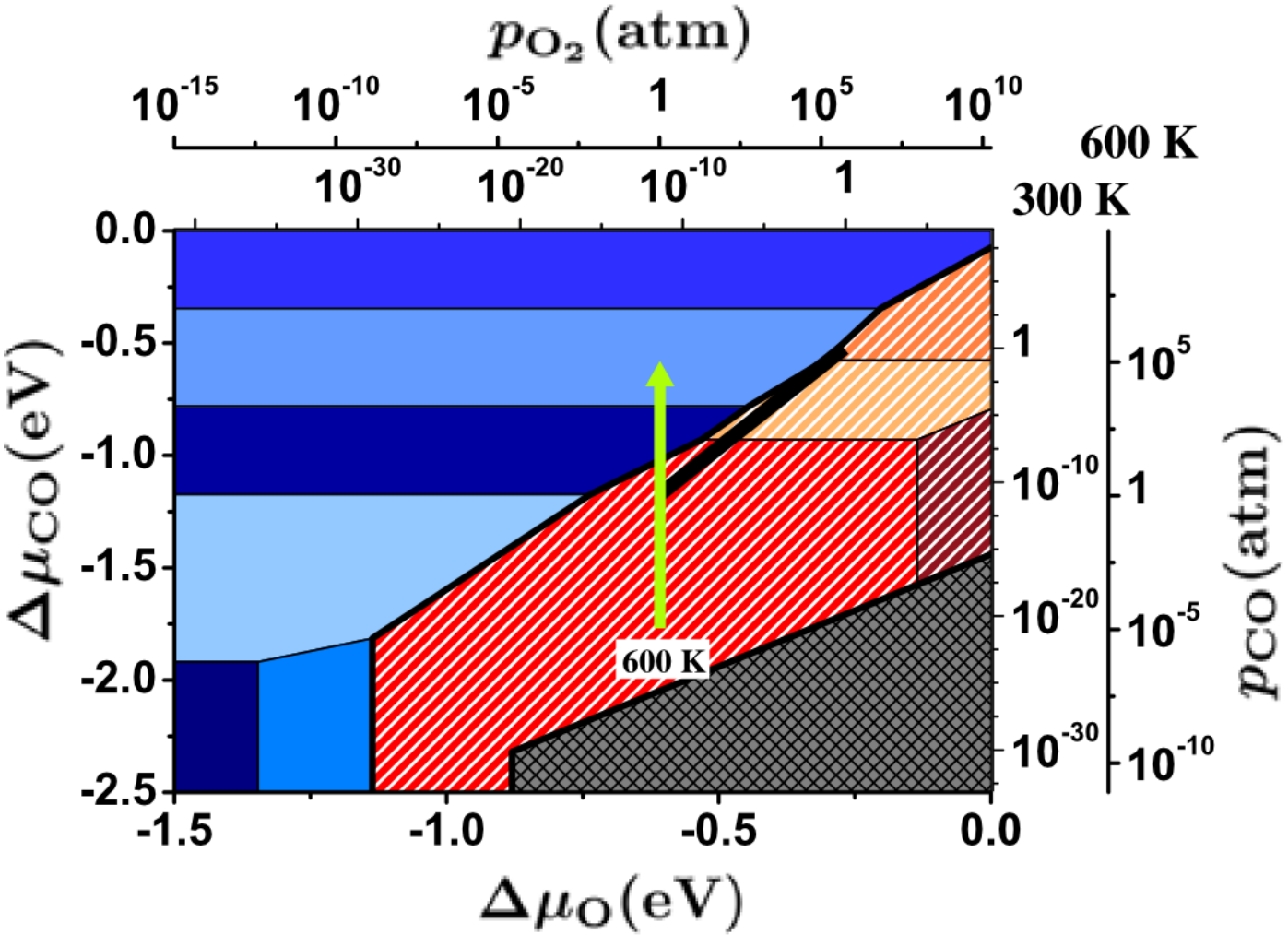
- Palladium atoms move to substrate hollow positions

Reconstruction rule

- map reconstruction back to discrete positions



Refined oxide stability boundary[7]



[7] Rogal *et al* (2008), PRB **77**, 155410

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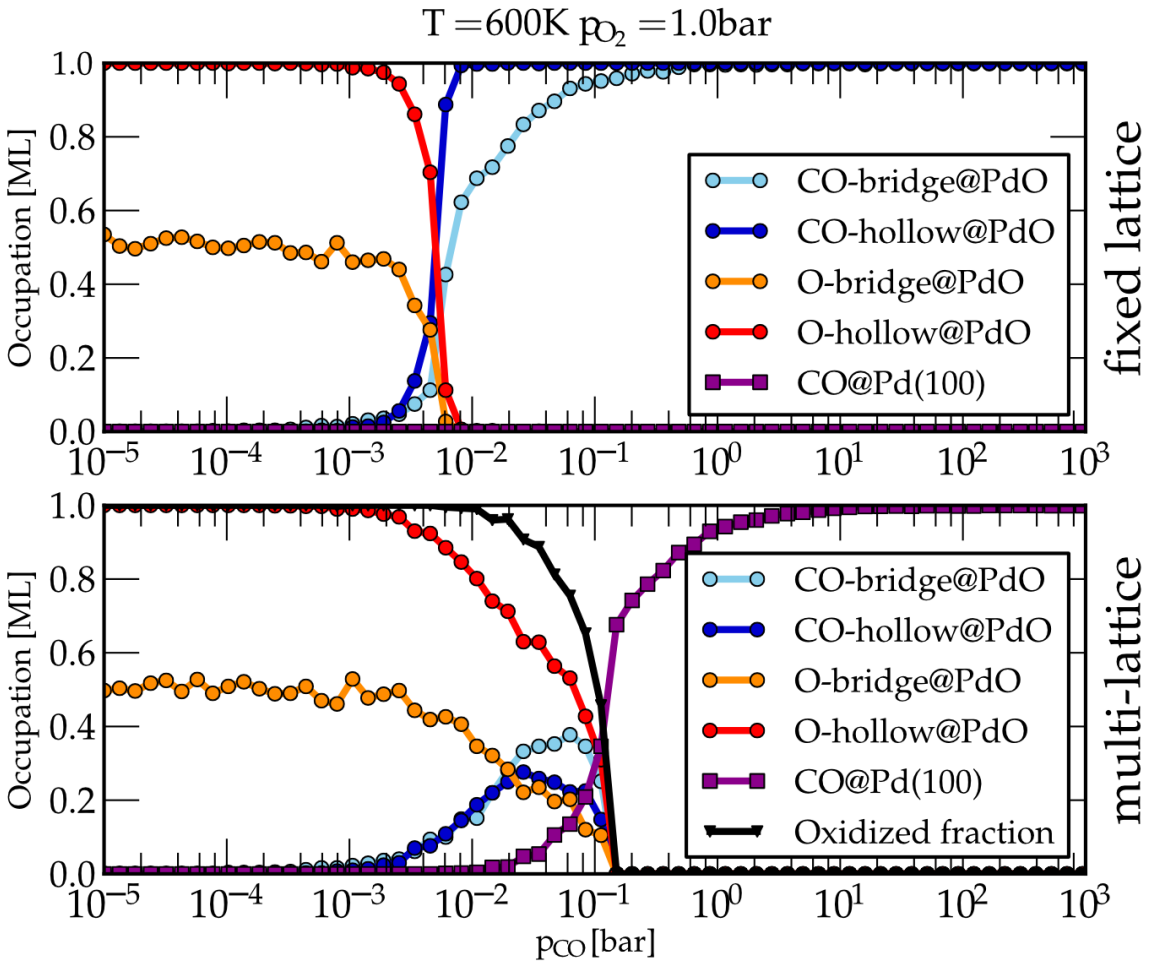

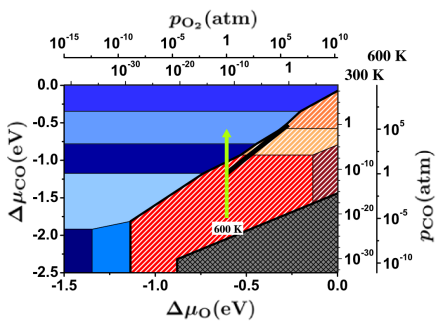

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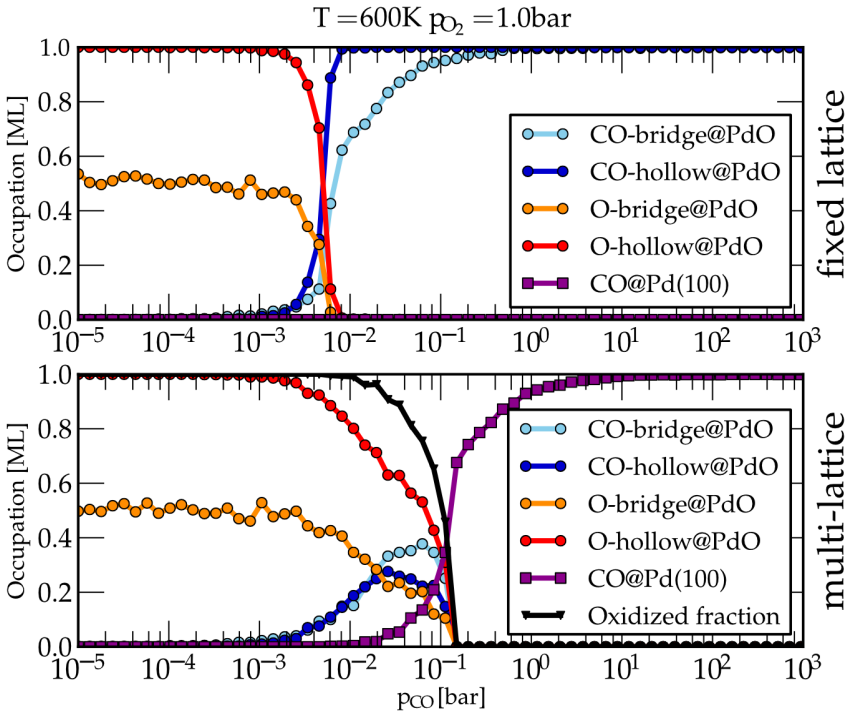

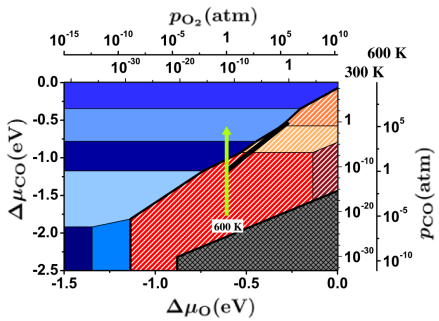

Present status

- uses only guessed rates constants for new processes not considered in the preceding 1p-kMC from Rogal *et al.*
- considers only the onset of oxide destruction

[7] Rogal *et al* (2008), PRB **77**, 155410

Summary

- DFT+kMC important tool to predict model catalyst behavior
- Multi-lattice kinetic Monte Carlo actually *works*
- Palladium surface oxide under reactive conditions

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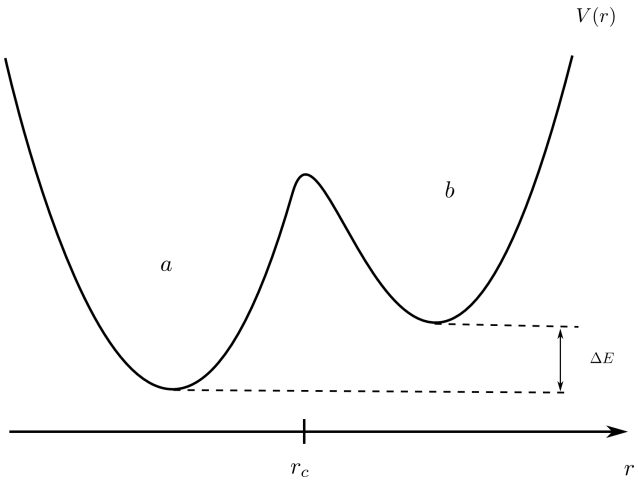
Thank you for your attention

Transition State Theory



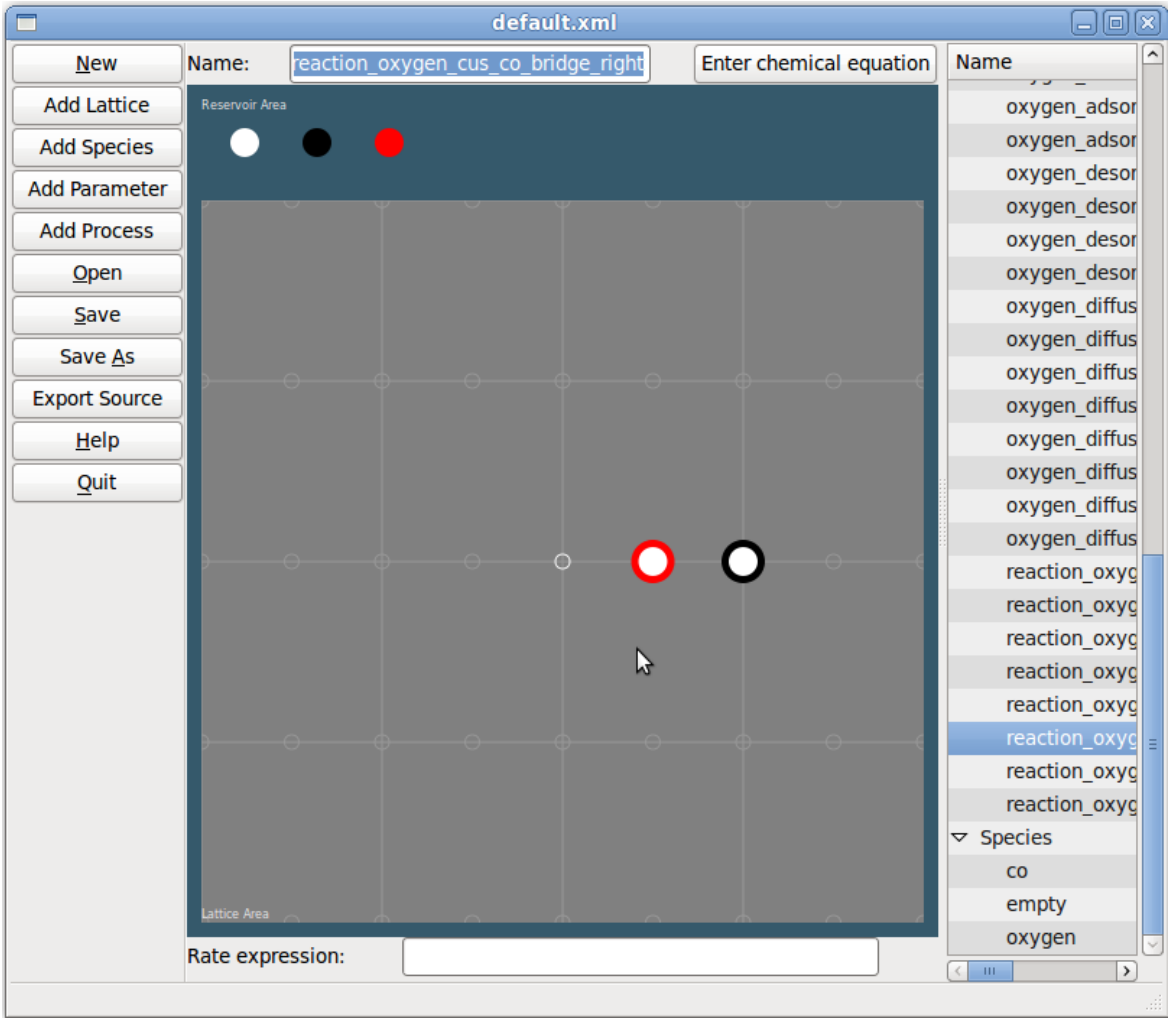
harmonic approximation

- flux-over-population

$$k_{\mathrm{TST}} = \frac{\int \mathrm{d}r\, \mathrm{d}p\, \frac{p}{m} \delta(r - r_c) \Theta(p) \mathrm{e}^{-\beta H}}{\int \mathrm{d}r\, \mathrm{d}p\, \mathrm{e}^{-\beta H}}$$

$$k_{\mathrm{TST}} = (\beta h)^{-1}\, \mathrm{e}^{-\beta \Delta G}$$

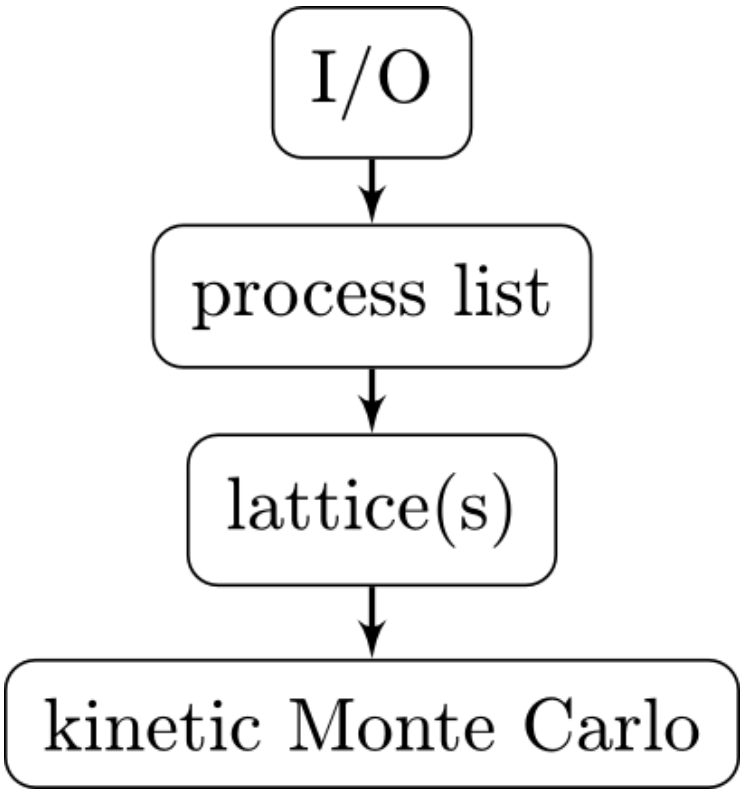
KMOS GUI[8]



[8] http://mhoffman.github.com/kmos

kMC modularization

- divide program parts based on degree of reusability



Oxide patching rule

- reversing the initial oxide destruction