First Principles and Kinetic Monte Carlo Investigations of Pd-based Membranes for Hydrogen Separation

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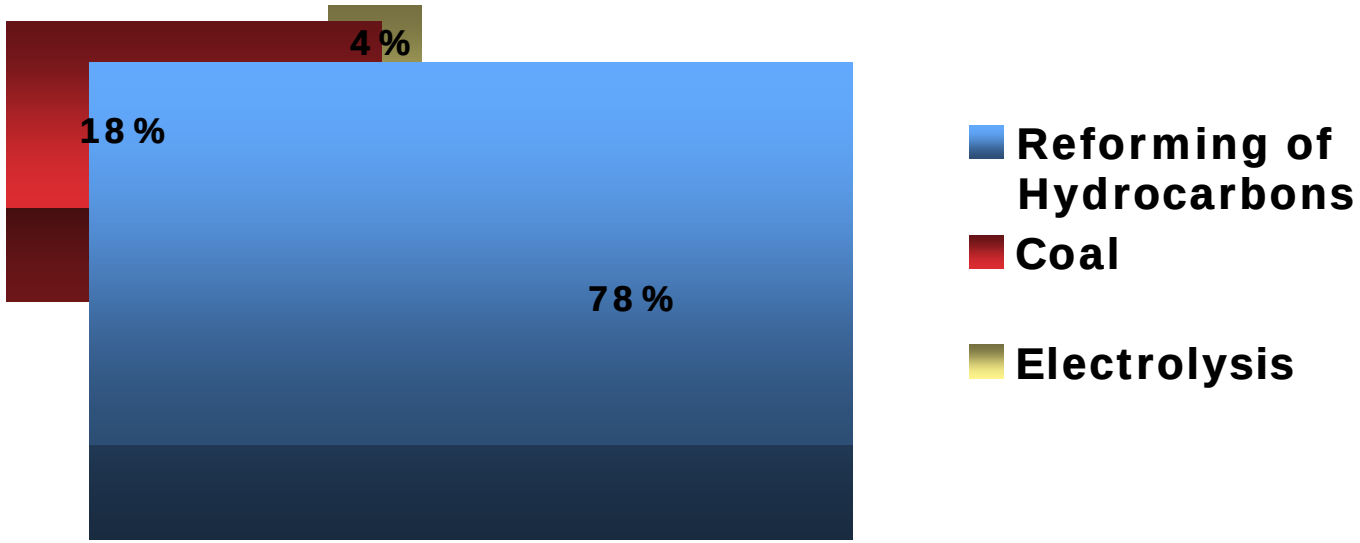
Hydrogen Production



Source: http://en.wikipedia.org/wiki/Hydrogen_economy

- Produced hydrogen is mixed with other gases like CO, CO_2, H_2S, heavy elements , etc
- Efficient separation processes is needed

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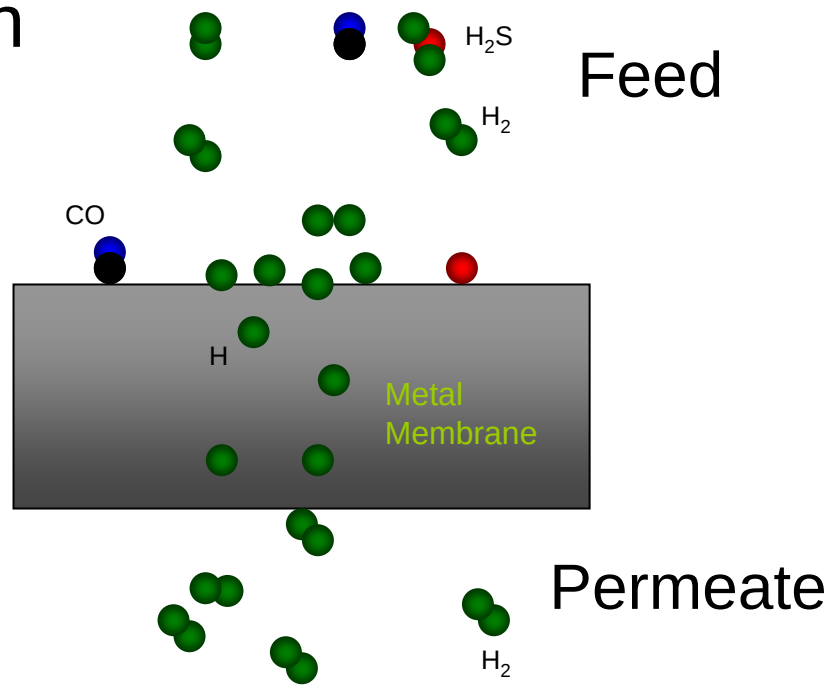
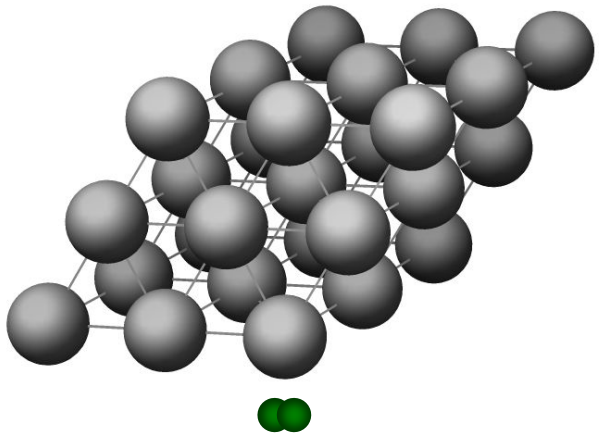
Hydrogen Separation Processes

- Metal Membrane Separation
  - Ease of operation
  - High purity (~99.9%)
  - Cost effective



- Pressure Swing Adsorption
  - Intermittent adsorption cycles
  - Multi-bed process requiring complex process control
  - High purity (~ 99% - 99.999%)
  - Relatively expensive

Hydrogen Separation Using Metal Membranes

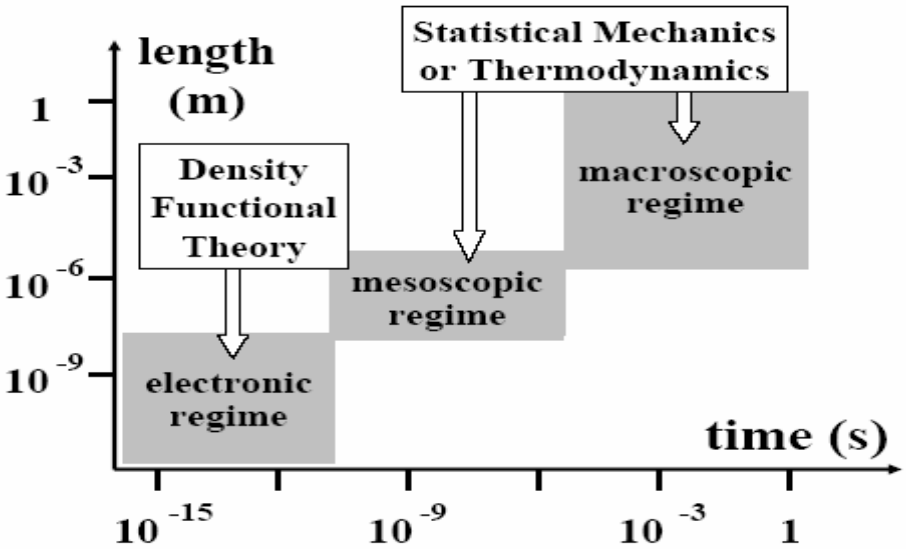


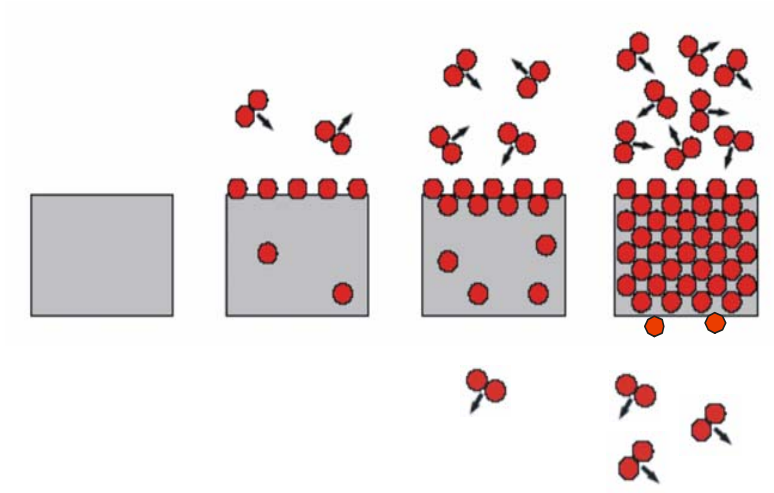
- Key Challenges:
  - High hydrogen flux
  - Tolerance to poisoning by adsorbates like S, CO etc
  - Resistant to stable hydride formation

Objective

- Long term goal: First principles approach towards developing new membranes
- Develop an atomistic understanding of membrane-adsorbate interactions
- Identify the mechanisms of hydrogen separation over Pd-based membranes
- Study sulfur and CO poisoning
- Create a framework towards bottom-up formulation of improved membrane materials

First Principles Approach





- Utilizing elementary step insights to obtain macroscopic information

First Principles Approach

- Ab-initio calculations using DFT (Nobel Prize 1998)
  - Accurate adsorption energies, elementary step activation barriers and pre-exponential factors
  - Accurate diffusion barriers
- Kinetic Monte Carlo
  - Macroscopic observables from ab-initio calculations
    - Flux, diffusivity, …
  - Rate-limiting steps

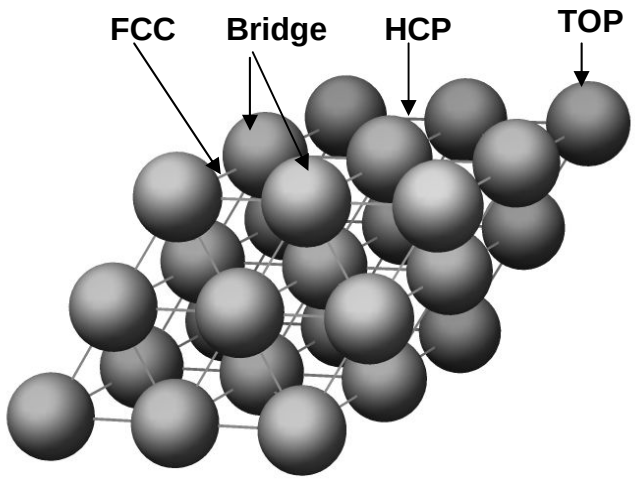
Why First Principles Approach?

- These tools are ideally suited for the system
  - Accurate analysis of elementary step mechanisms via DFT
    - Importance of covalent metal/H interactions
    - Limited number of manageable elementary steps
    - Fairly well-defined system
    - Mild conditions
  - Efficient kinetic algorithms (KMC) to relate elementary step information to macroscopic observables

DFT Studies: H on Pd (111) Surface

Adsorption energy:

$E_H = E_{H+slab} - (1/2\ E_{H2} + E_{slab})$



Adsorption Energy in eV (1 eV = 100 KJ/mol)

Species	On-top	Bridge	FCC	HCP
H	-0.05	-0.52	-0.70	-0.64

Dissociation of H_2 in <u>non-activated</u> on clean Pd

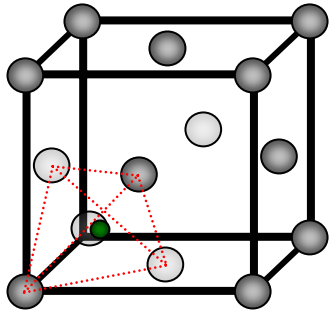
Hydrogen preferentially adsorbs in three-fold hollow sites

DFT: H at Pd Interstitial Sites

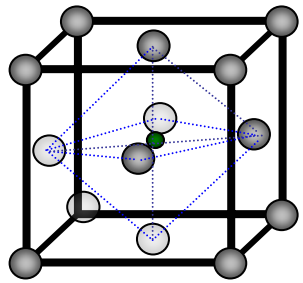
Adsorption energy:

$$E_H = E_{H+slab} - (1/2\ E_{H2} + E_{slab})$$

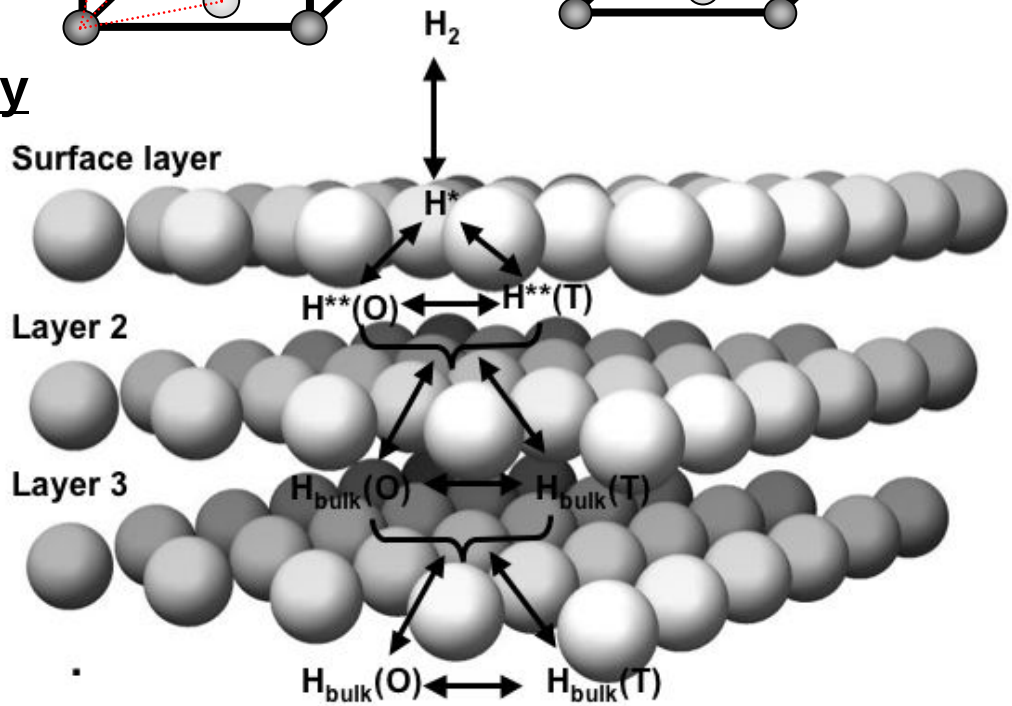
Tetrahedral



Octahedral

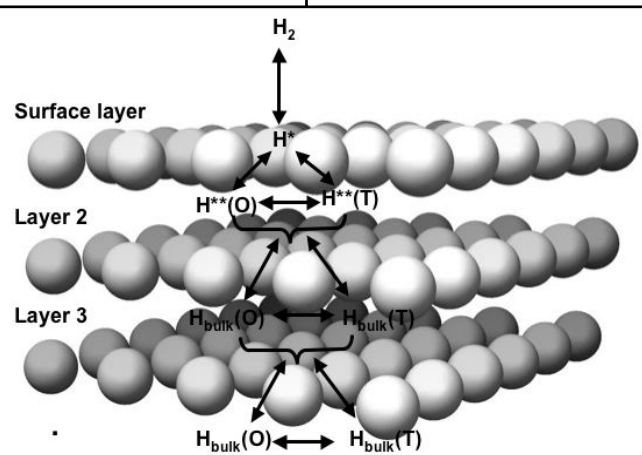


Site	Binding Energy
Tetrahedral (L2)	-0.22 eV
Octahedral (L2)	-0.35 eV
Tetrahedral (B)	-0.08 eV
Octahedral (B)	-0.14 eV



DFT: Elementary Step Kinetic and Thermodynamic Parameters

Elementary step	$E_{activation}$ eV/atom	ΔH eV/atom	A /site/sec
$1/2H_2 + * \rightarrow H*$	0.06	-0.70	10^{8} (a)
$H* \rightarrow 1/2H_2 + *$	0.76	0.70	10^{11}
$H* + ** \rightarrow H**(T) + *$	0.48	0.48	10^{11}
$H* + ** \rightarrow H**(O) + *$	0.35	0.35	10^{11}
$H**(O) \rightarrow H_{bulk}(O) + **$	0.21	0.21	10^{11}
$H**(O) \rightarrow H_{bulk}(T) + **$	0.27	0.27	10^{11}
$H_{bulk}(O) \rightarrow H_{bulk}(T)$	0.17	0.06	10^{11}
$H_{bulk}(T) \rightarrow H_{bulk}(O)$	0.11	-0.06	10^{13}



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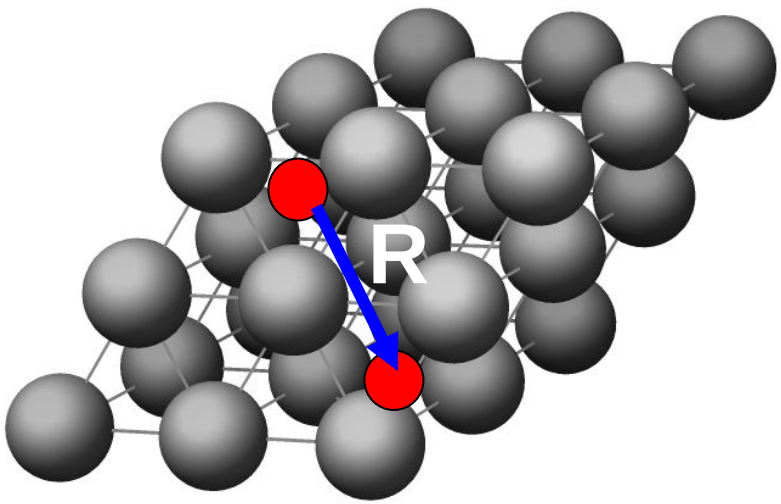
KMC Simulations to Relate the Elementary Step Mechanism to Macroscopic Observables

- Test the accuracy of the approach
- An important observable is diffusivity
- Need to relate the macroscopic transport coefficient D to the mean square distance of atomic migration
  - DFT and KMC to calculate tracer diffusivity



$$D = \lim_{t\to\infty}\left[\frac{1}{6n_H t}\sum_{m=1}^{n_H}\left\langle \left\|\mathbf{R}(t)-\mathbf{R}(0)\right\|^2\right\rangle_m\right]$$

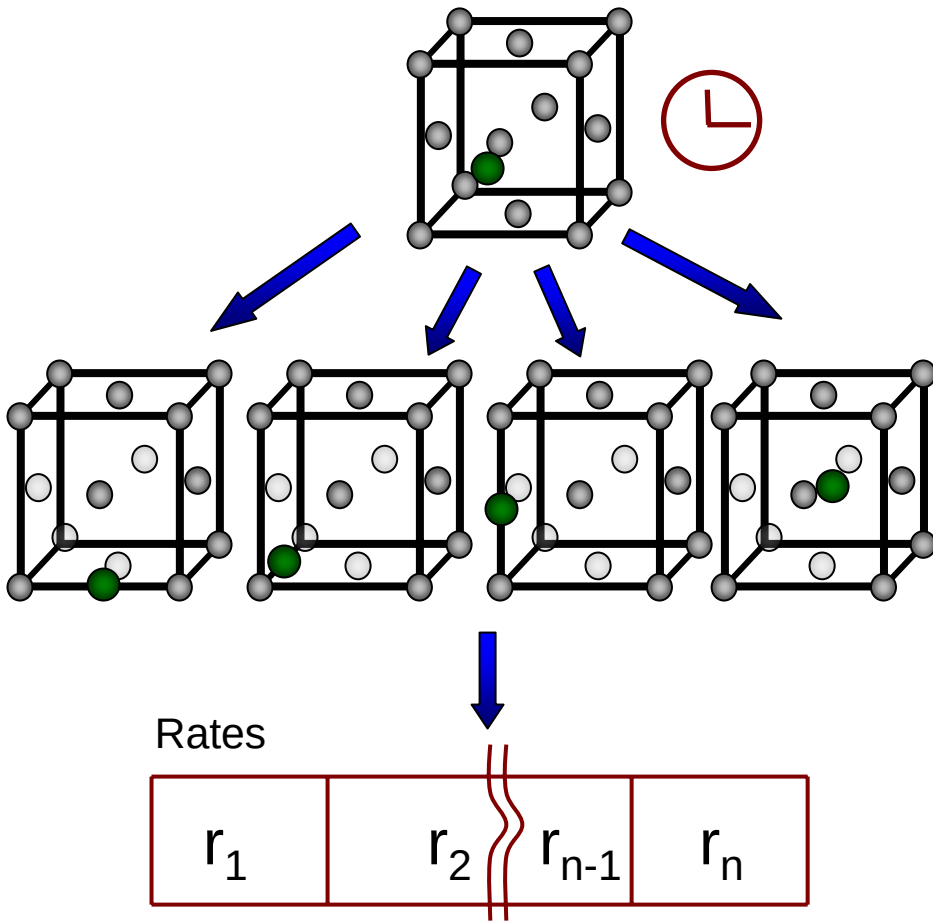
P. Kamakoti, Science, 2005

Kinetic Monte Carlo

Start
Set T, P, system configuration
Time = 0.0

Identify all possible events that can occur

List the events and the corresponding rates



N-fold way method A. B. Bortz, M. H. Kalos, and J. L. Lebowitz, J. Comput. Phys. **17**, 10 (1975)

Kinetic Monte Carlo

Generate event probabilities:

$$P_i = \frac{r_i}{\sum r_i}$$

Generate a random number ξ_1

Implement the event for which

$$\sum_{k=1}^{i-1} P_k \le \xi_1 < \sum_{k=1}^{i} P_k,\ 0 \le \xi_1 \le 1$$

Increment time

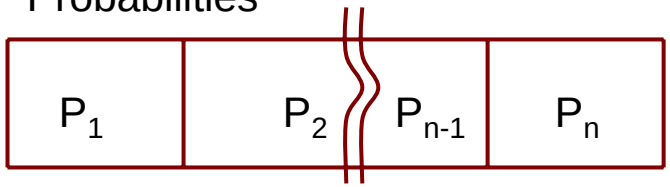
$$time = time - \frac{\ln(\xi_2)}{\sum r_i}$$

Convergence?

Yes → Stop

No → Repeat

Probabilities



N-fold way method A. B. Bortz, M. H. Kalos, and J. L. Lebowitz, J. Comput. Phys. **17**, 10 (1975)

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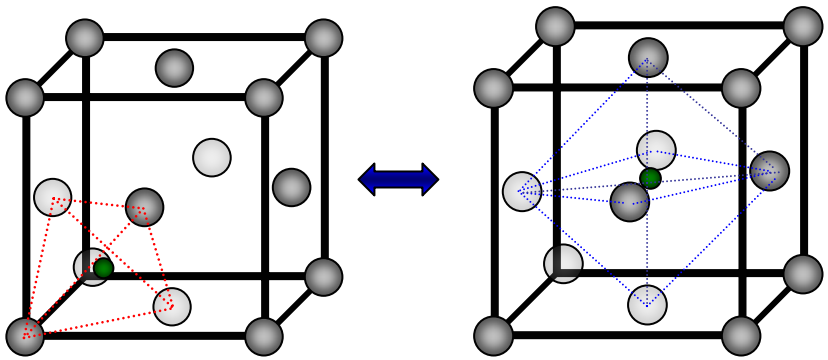
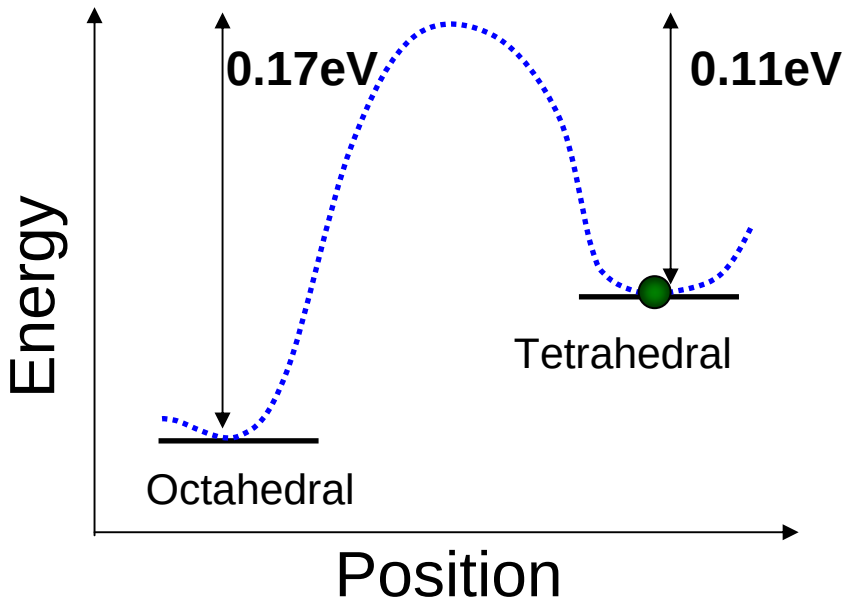
KMC: Hydrogen Diffusion through Bulk

Events: Site hopping from one site to another





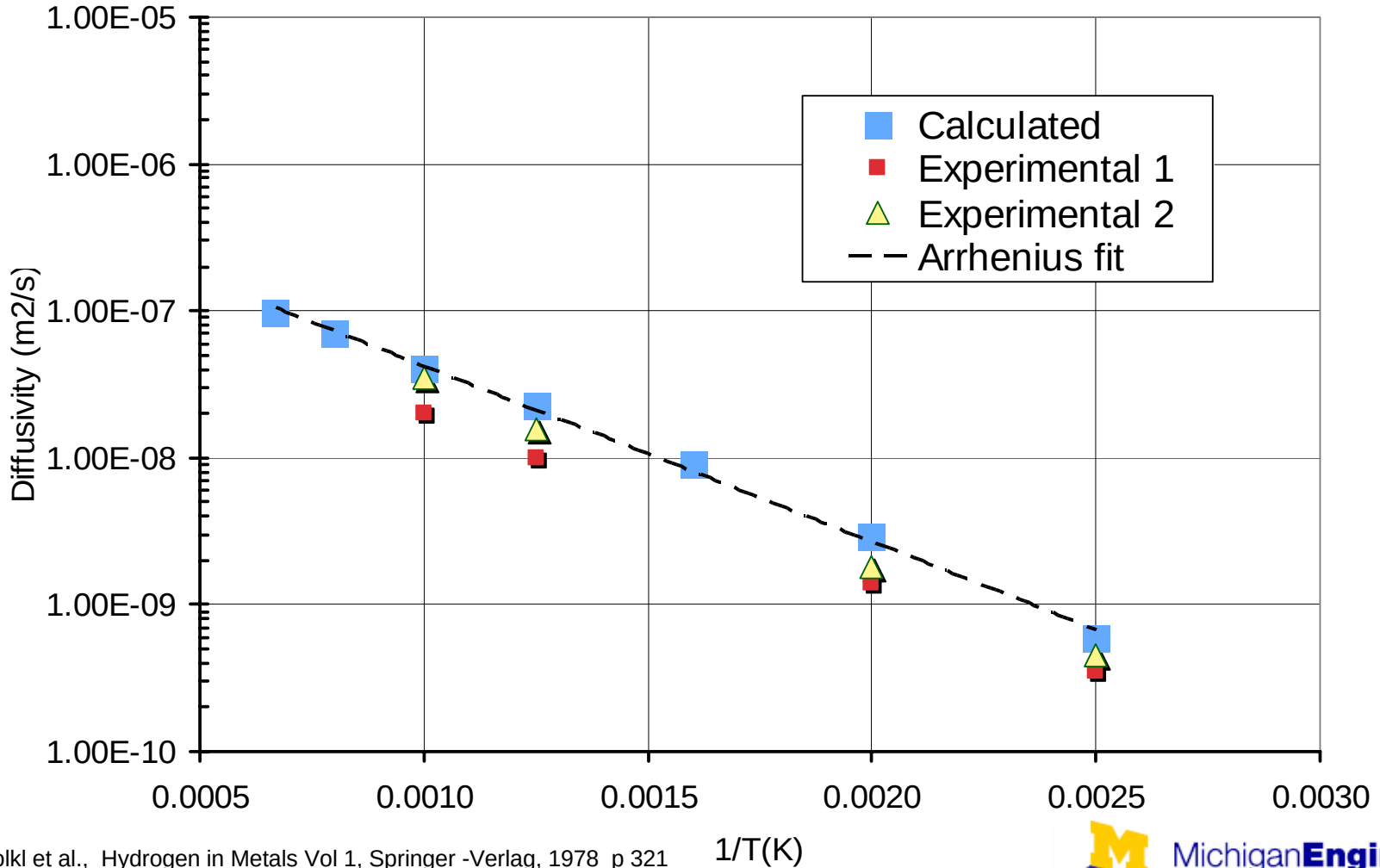
$$r_{T\to O} = Ae^{(-E_m/kT)}$$

$$A = \left(\frac{\prod_{i=1}^{3} \omega_{O,i} \sinh(\beta h \omega_{T,i}/2)/(\beta h \omega_{T,i}/2)}{\prod_{i=1}^{2} \omega_{TS,i} \sinh(\beta h \omega_{TS,i}/2)/(\beta h \omega_{TS,i}/2)} \right)$$

All the rate parameters and the lattice constant evaluated from first principles

KMC Calculated Diffusivity: Comparison with Experiments

$$D = 6.604 \times 10^{-7} e^{(\underline{-0.23eV}/kT)} m^2/s$$



1. Volkl et al., Hydrogen in Metals Vol 1, Springer -Verlag, 1978 p 321
2. Wicke et al., Hydrogen in Metals Vol 2, Springer -Verlag, 1978 p 73

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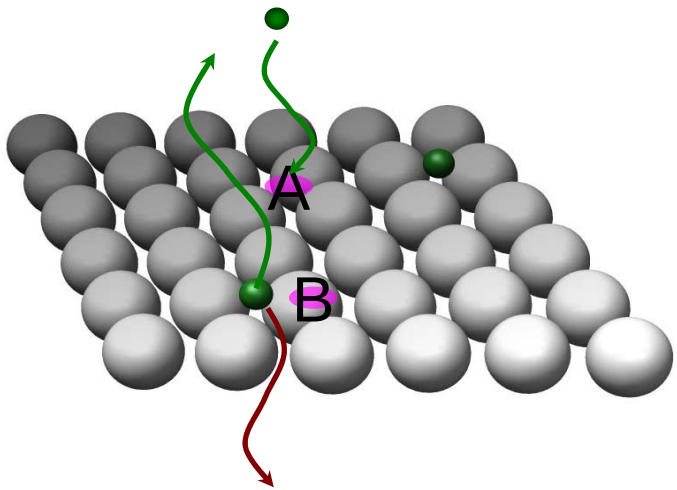
KMC: Pd Surface Effects

- **<u>Not obvious that diffusion through bulk is flux-limiting</u>**

- **<u>Surface KMC simulations</u>**
  - *Loop over all sites and evaluate the events at each type of site.*
- ***Events***
  - *A. Free site*
    - *Adsorption of H* →

$$r_{ads} = A_{ads} e^{\Delta S/k} e^{(-E_{ads}/kT)} P_{H_2}$$

$$= s \frac{P_{H_2}}{\sqrt{2\pi M_{H_2} kT}}$$

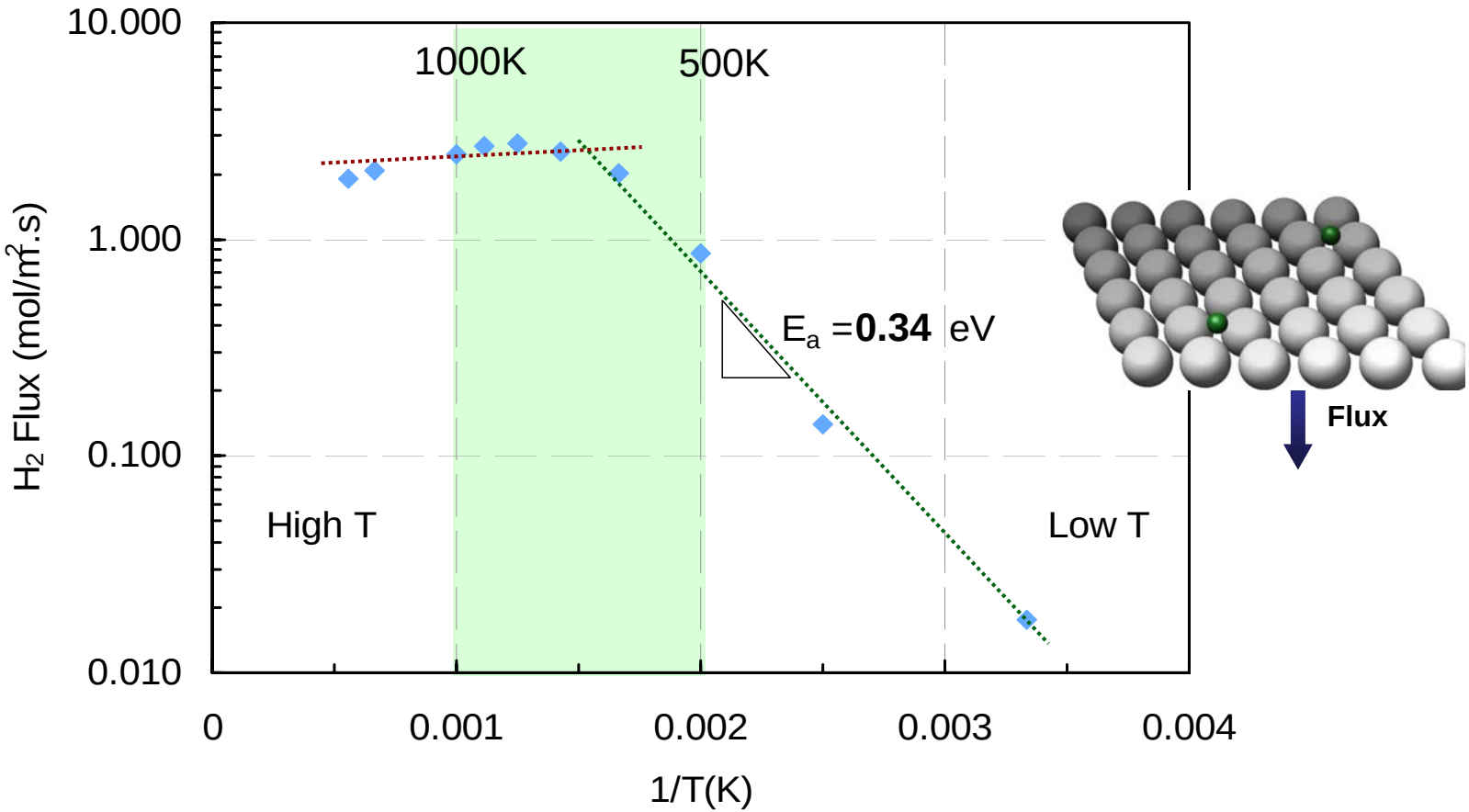


  - *B. H-occupied site*
    - *Desorption of H*
    - *Diffusion of H to subsurface layers* →

$$r_{O \to T} = A e^{(-E_m/kT)}$$

E_m = 0.35 eV, A = 10^{11}

KMC: Hydrogen Flux Through Surface Vs Temperature



At operating temperatures H atom diffusion from top to the second layer is rate-limiting

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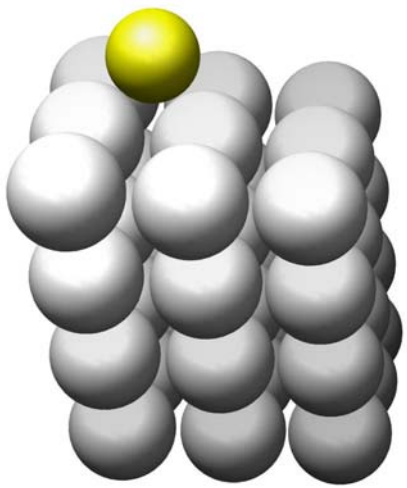
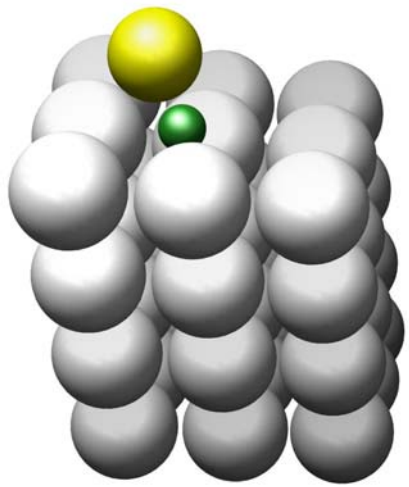
Surface Vs Bulk Diffusion Limitations

- Ongoing studies
- Preliminary results
  - Rate of diffusion from the top Pd layer to the layer bellow the top layer:
    - Rate = A exp(-Ea/kT) [H*] (Ea = 0.34 eV, A = 10^{11} 1/s)
  - Diffusion flux through Pd bulk
    - Flux = D [C_{H2}]/length (D = 6.6×10^{-7}exp (-0.23/kT))
- For thin membranes (length < 1µm) the flux is limited by the diffusion of H from the <u>Pd surface to the layer below</u>.
- For thicker membranes, <u>bulk diffusion</u> is flux-limiting step

What is the effect of Sulfur?

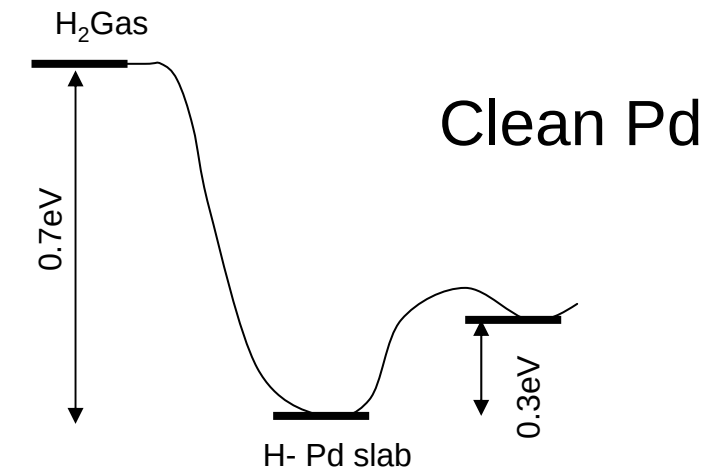


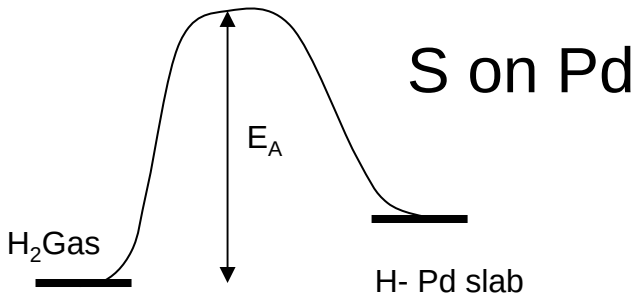


- S binds very strongly on Pd
  - Binding energy ~ -5.25 eV
- Co-adsorption of S and H
  - Adsorption of H is endothermic (0.14 eV)
  - Compared to un-poisoned Pd (-0.7 eV)

Insights from Ab-initio Calculations of S over Pd

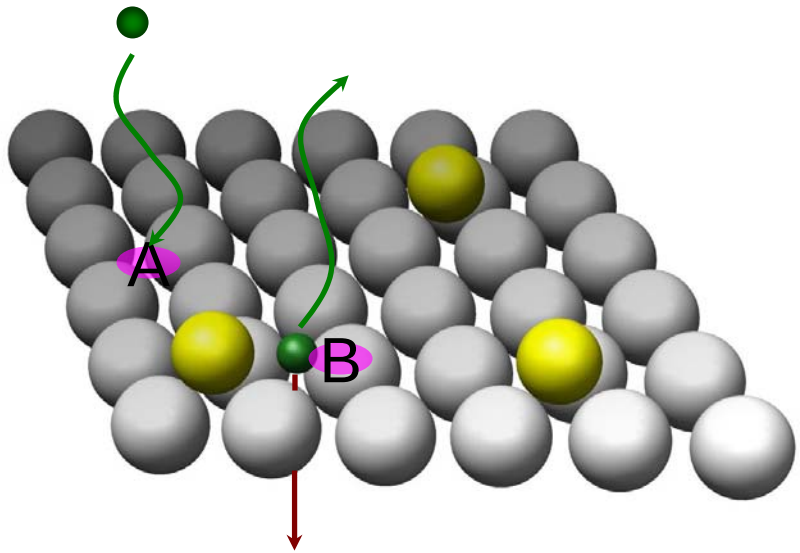
- Adsorption of H on S-covered Pd is endothermic
- Energy barriers for dissociation are large
  - Ea ~ 0.1eV -0.8 eV, function of proximity to S atom





KMC: H Adsorption and Diffusion in Presence of S

- Surface KMC simulations
  - Loop over all sites and evaluate the events at each type of site.
- <u>Events</u>
  - A. Free site :
    - Adsorption of H
  - B. H-occupied site:
    - Desorption of H
    - Diffusion of H to subsurface layers
  - C. Sulfur occupied sites:
    - Frozen



Adsorption Rate Expression in Presence of S

$$k_{ads} = A_{ads} e^{\Delta S / k} e^{(-E_a / kT)}$$

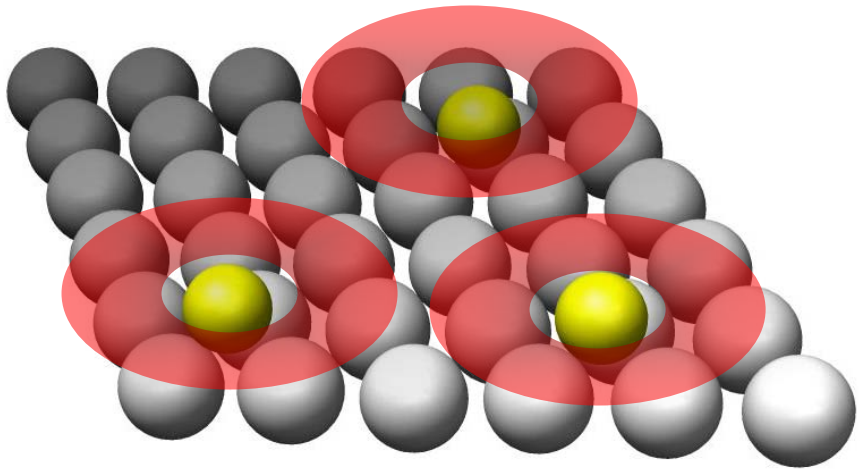
<u>Using DFT calculations</u>

Close to Sulfur

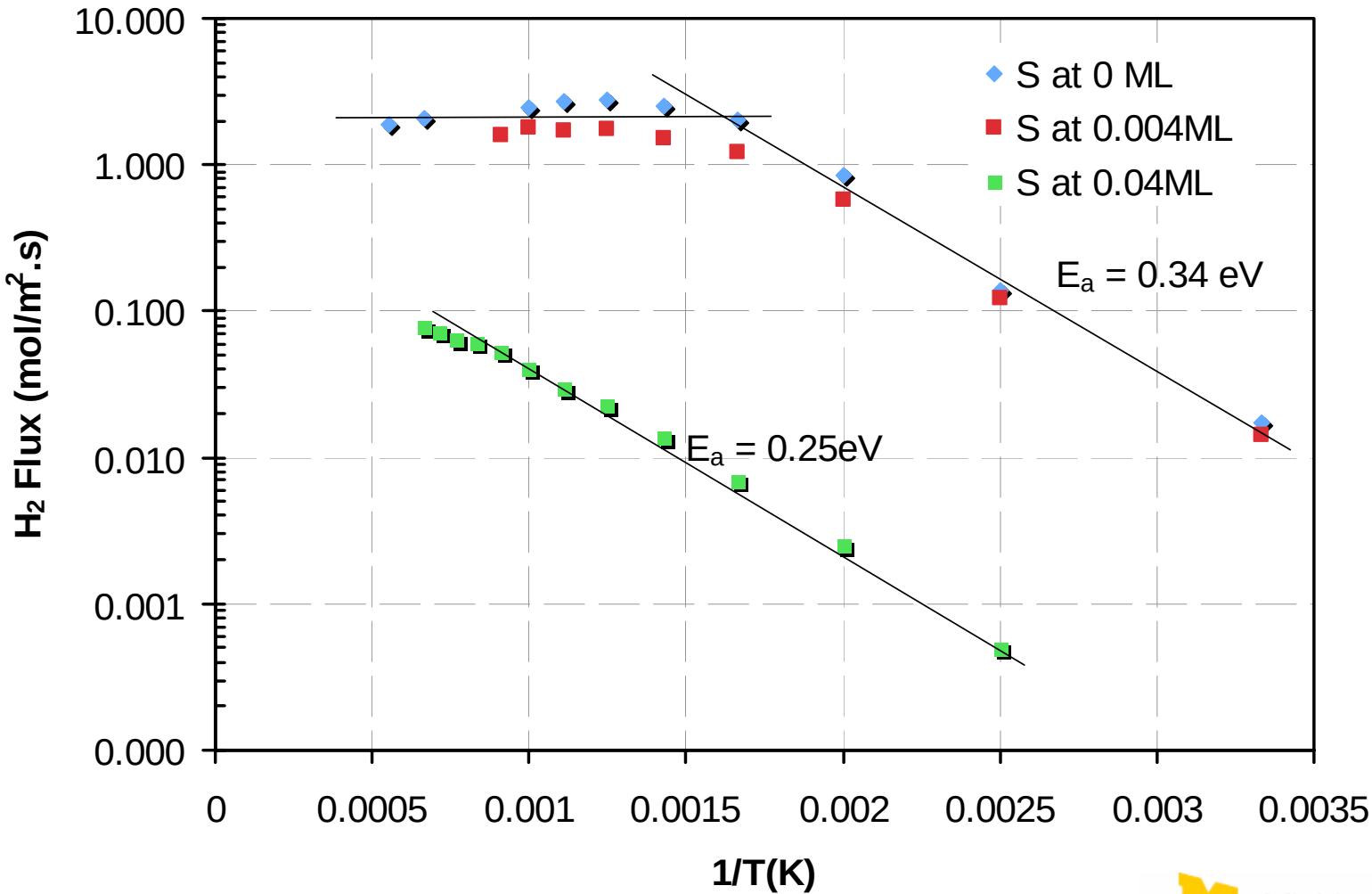
E_a **= 0.50 eV**

Red shaded region

E_a **= 0.25 eV**



KMC: Diffusion Rate in Presence of S



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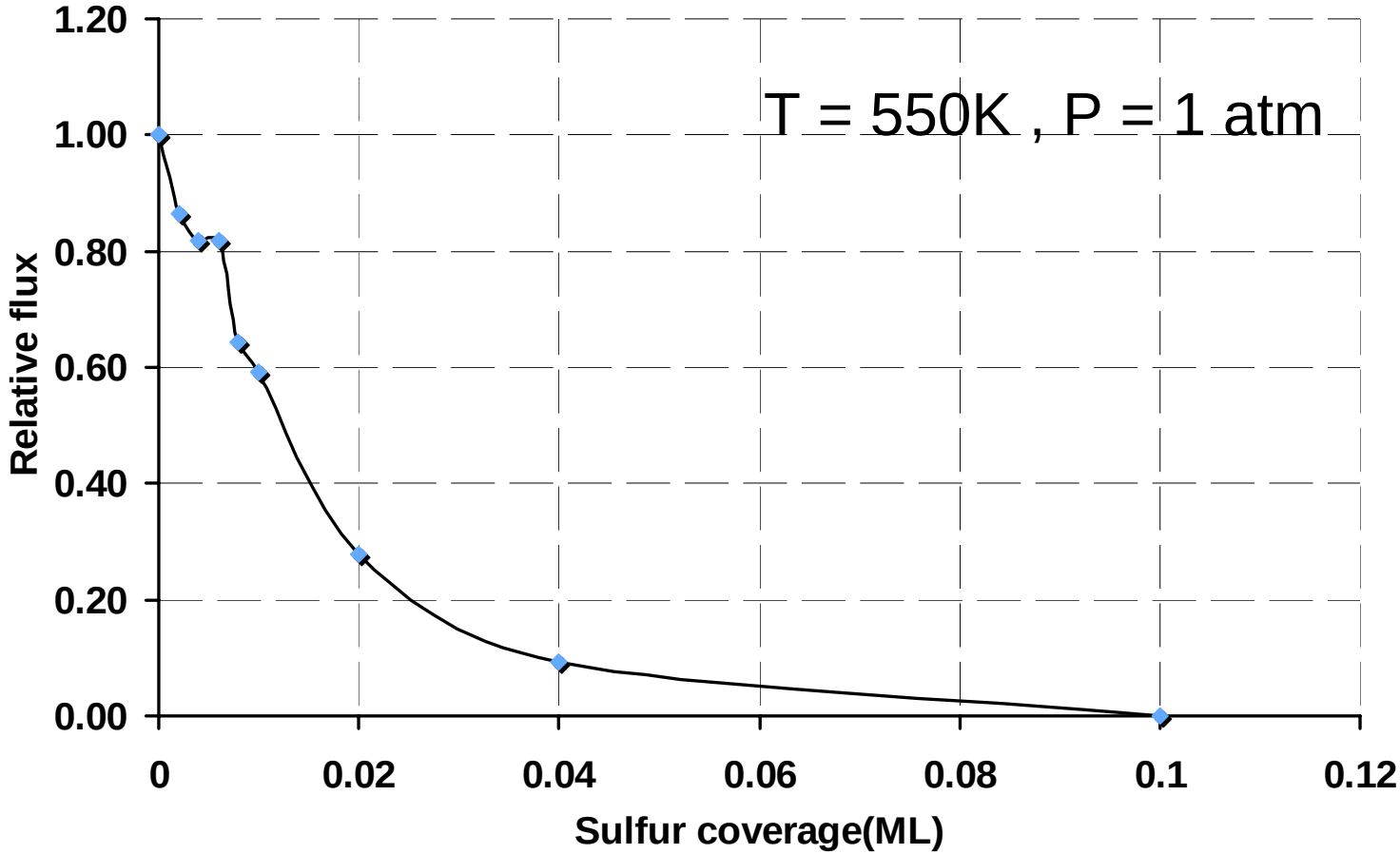
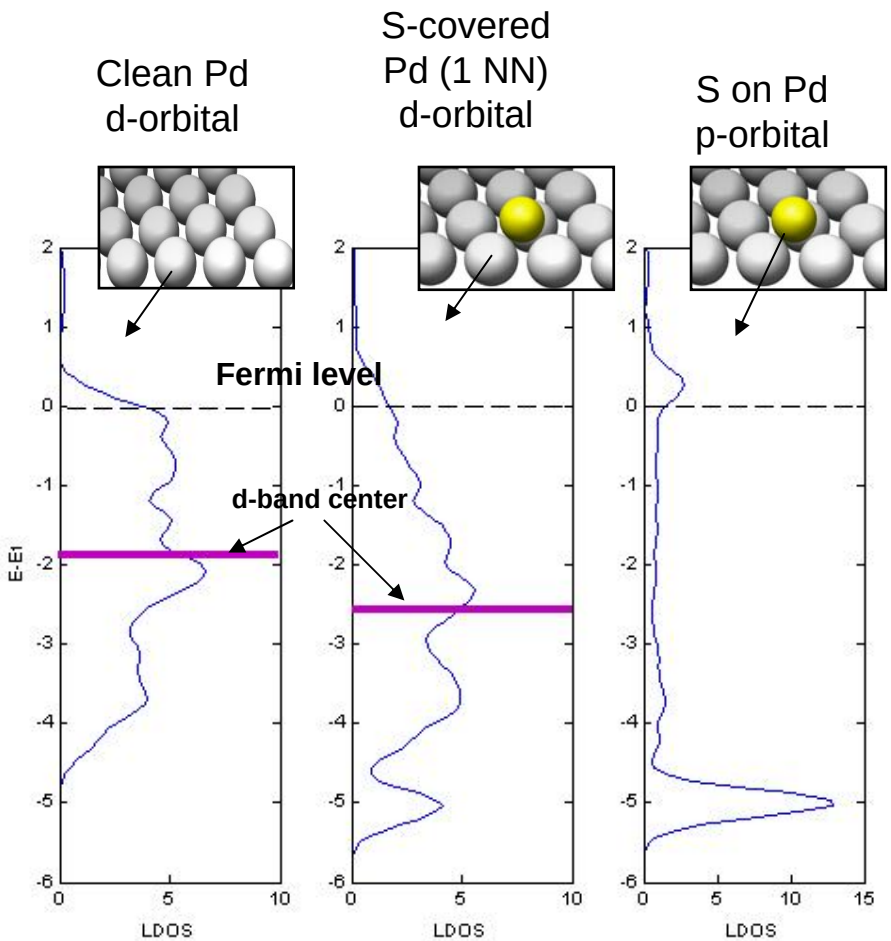
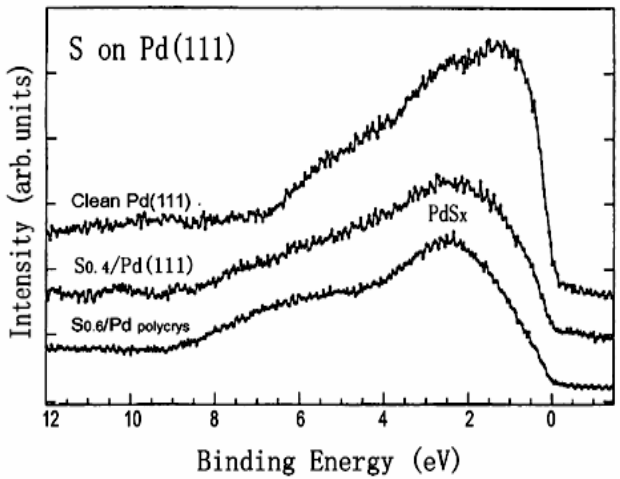
Effect of S Coverage on H Flux



Electronic Density of States Analysis





Rodriguez, J. A.; Chaturvedi, S.; Jirsak, T. Chem. Phys. Lett. 1998, 296 (3/4), 421-428

Conclusions

- Bottom-up approach incorporating insights from quantum chemical calculations can yield valuable information pertaining to hydrogen separation over metal membranes
- Interaction of poisoning agents with metal surface can be elucidated clearly
- Opens up a whole new dimension of rational bottom up design of novel metal membranes resistant to poisoning agents

Acknowledgements

Joydeep Mukherjee

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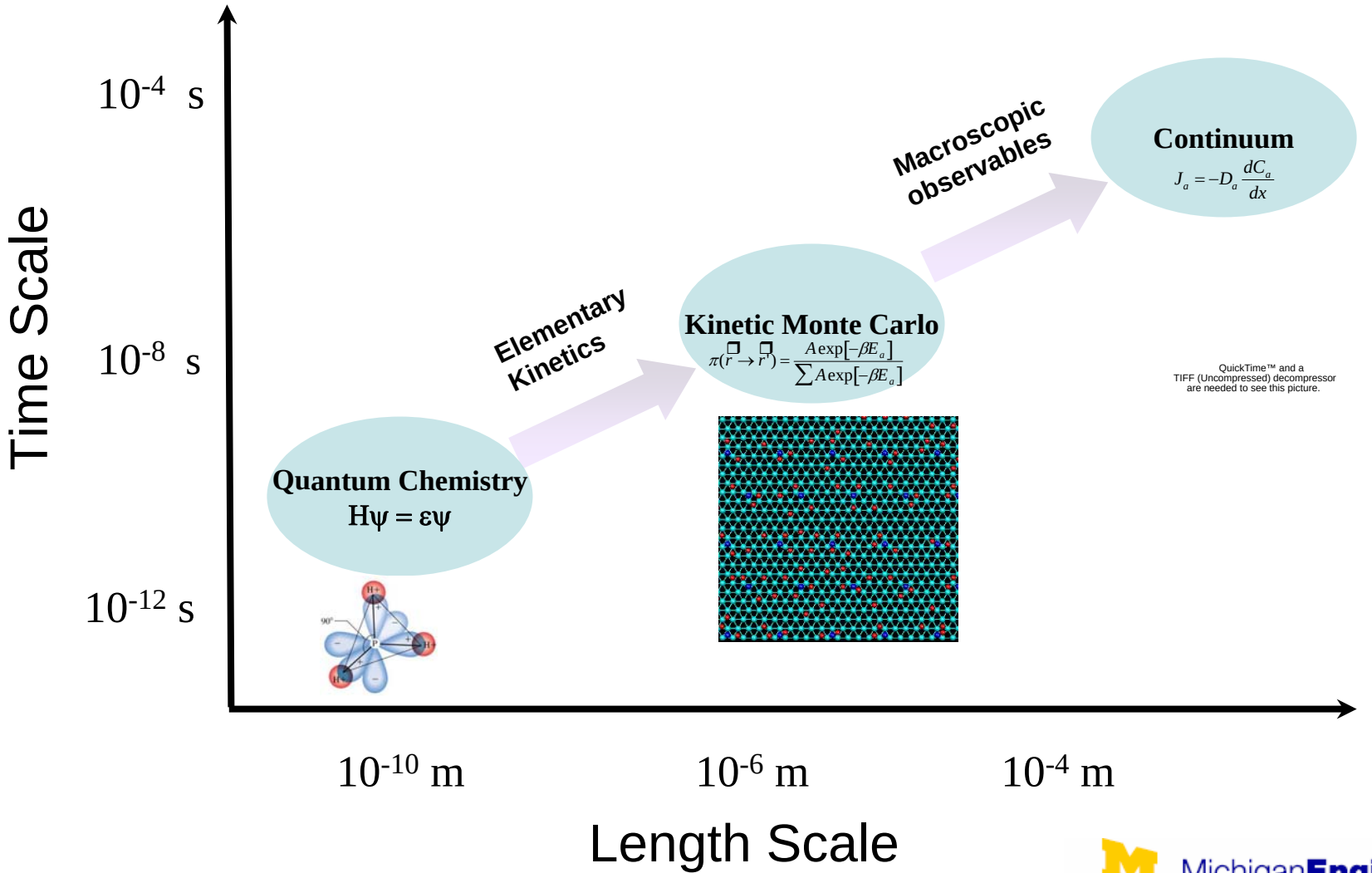
Approach



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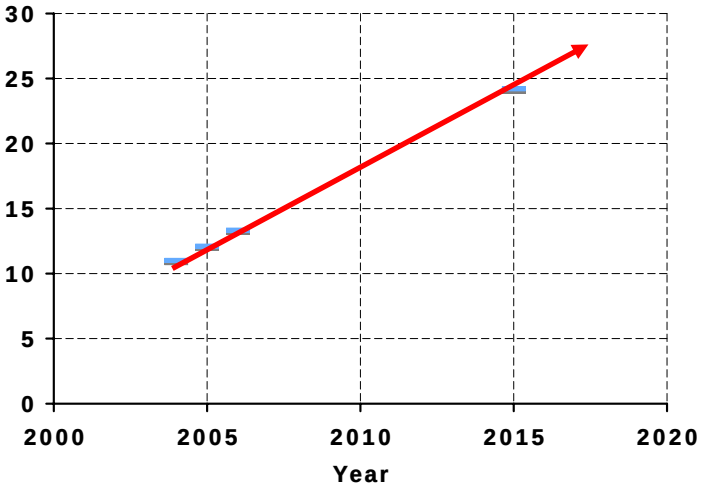
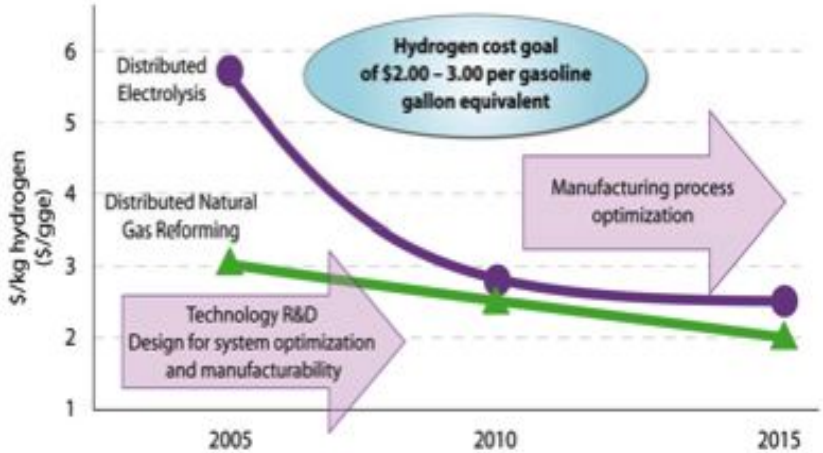
Road to Hydrogen Economy



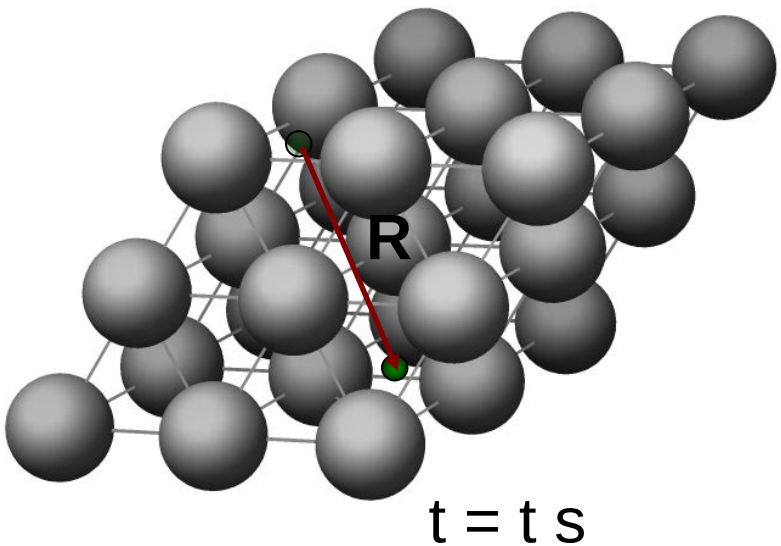


Economic Value ~ $ 135 Billion (2005)

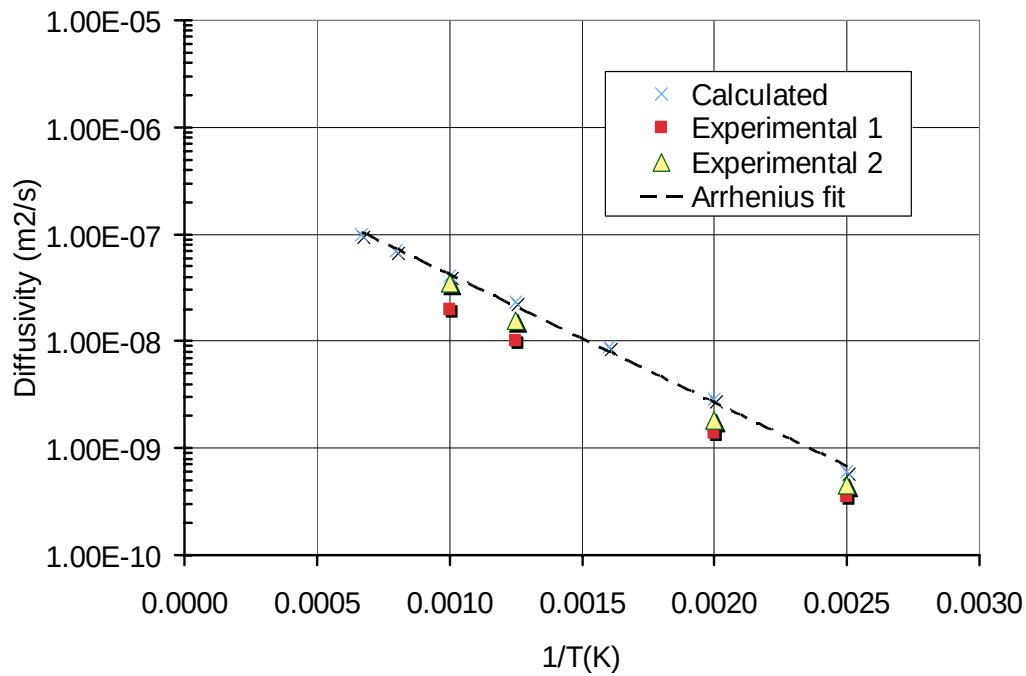
Need :

Cost effective hydrogen production processes

Hydrogen Diffusion:Comparison with Experiments



$$D = 6.604 \times 10^{-7} e^{(-0.23eV/kT)} m^2/s$$



Einstien's expression:

$$D = \lim_{t \to \infty} \left[\frac{1}{6 n_H t} \sum_{m=1}^{n_H} \left\langle \left\| \mathbf{R}(t) - \mathbf{R}(0) \right\|^2 \right\rangle_m \right]$$

1. Volkl et al., Hydrogen in Metals Vol 1, Springer -Verlag, 1978 p 321
2. Wicke et al., Hydrogen in Metals Vol 2, Springer -Verlag, 1978 p 73

Rate Limiting Step

Rate of H_2 dissociation

$$r_{ads} = A_{ads} e^{\Delta S/k} e^{(-E_{ads}/kT)} P_{H_2}$$

$$= s \frac{P_{H_2}}{\sqrt{2\pi M_{H_2} kT}}$$

Rate of Diffusion Step

$$r_{O\to T} = A e^{(-E_m/kT)}$$

$$A = \left(\frac{\prod_{i=1}^{3} \omega_{O,i} \sinh(\beta h \omega_{O,i}/2)/(\beta h \omega_{O,i}/2)}{\prod_{i=1}^{2} \omega_{TS,i} \sinh(\beta h \omega_{TS,i}/2)/(\beta h \omega_{TS,i}/2)} \right)$$

At 500K, 1 atm

$$r_{ads} \sim 3 \times 10^8 / site / \sec$$

$$r_{O\to T} \sim 10^8 / site / \sec$$

Which is the rate limiting step?

Summary

- Sulfur binds very strongly on the Pd surface
- Sulfur alters the energy landscape for hydrogen dissociation pathways
- Drastic reduction of hydrogen permeate flux at S-coverages > 0.04 ML

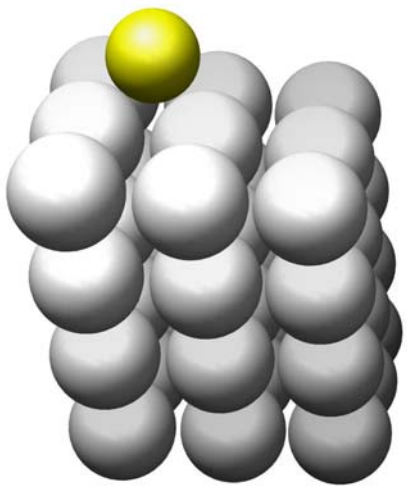
What is the underlying reason behind these effects?

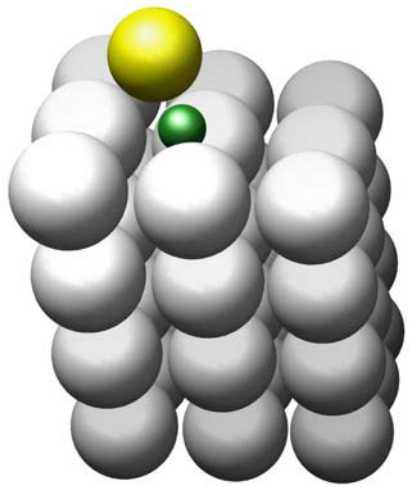
Summary

- Hydrogen dissociation **Non-activated** over clean Pd
- Hydrogen diffusion rate limiting at **low** temperatures
- Hydrogen adsorption rate limiting at **high** temperatures

What happens when Sulfur is adsorbed on Pd?

Effect of Sulfur on Hydrogen Separation



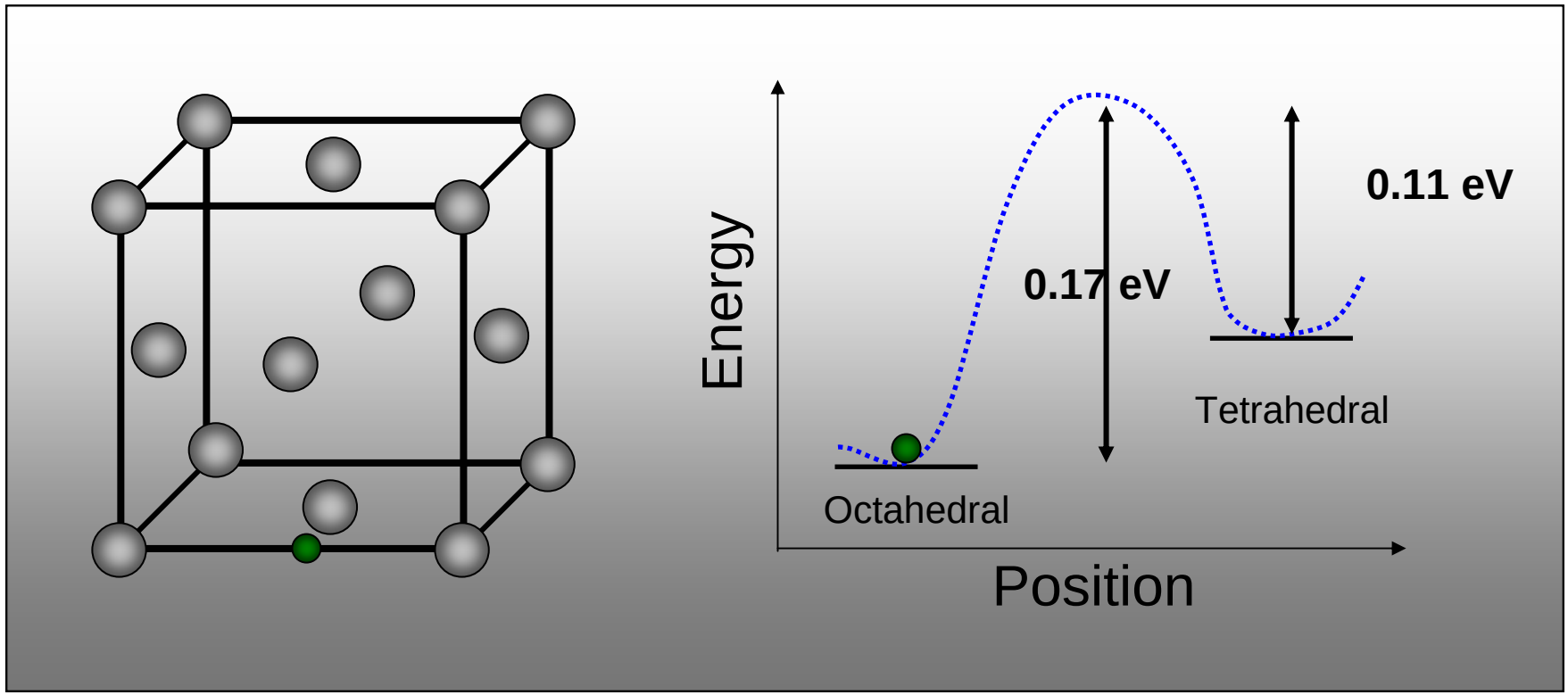


- Sulfur binds very strongly on Pd
  - **Binding energy ~ 5.25 eV**
- Co-adsorption of hydrogen is disfavored
  - Adsorption slightly **endothermic** (0.14 eV)

Diffusion Barriers

Extensively investigated before

NEB calculations to find transition states and diffusion barriers : Ke X, Kramer G J, Phys Rev B, 66(2002)



Ab-Initio Density Functional Theory

Solve Kohn-Sham Equations

$$\left(-\frac{1}{2}\nabla^2+\left[\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+\mathrm{V_{XC}}(\mathbf{r})-\sum_{\mathrm{A}}^{\mathrm{M}}\frac{\mathrm{Z_A}}{|\mathbf{r}-\mathbf{r}_A|}\right]\right)\psi_{\mathrm{i}}=\varepsilon_{\mathrm{i}}\psi_{\mathrm{i}}$$

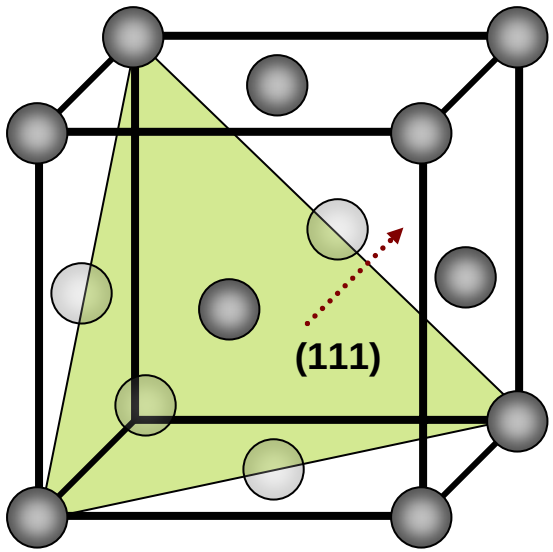
Total energy
Molecular structure
Electronic structure

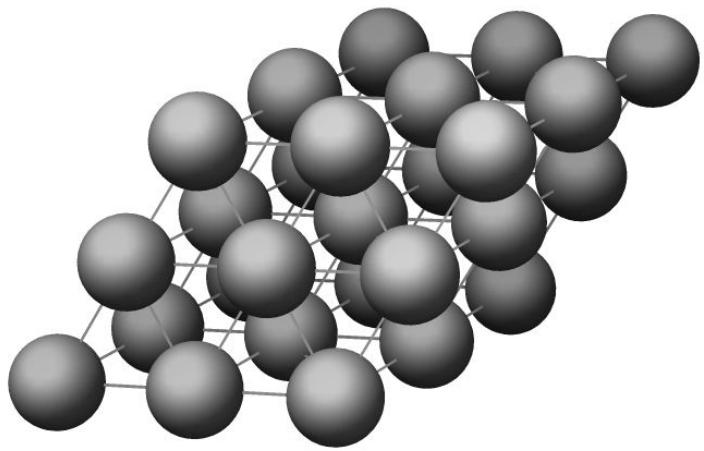
Nudged elastic band
Transition states,
Activation energies for barriers, PES

Nobel prize in Chemistry in 1998
It is an important tool for surface chemistry, chemistry, materials physics

Calculations on Pd (111)

- Calculation were performed using DACAPO
- GGA PW 91, plane wave cutoff 350 eV, Converged with Monkhorst Plank k-points



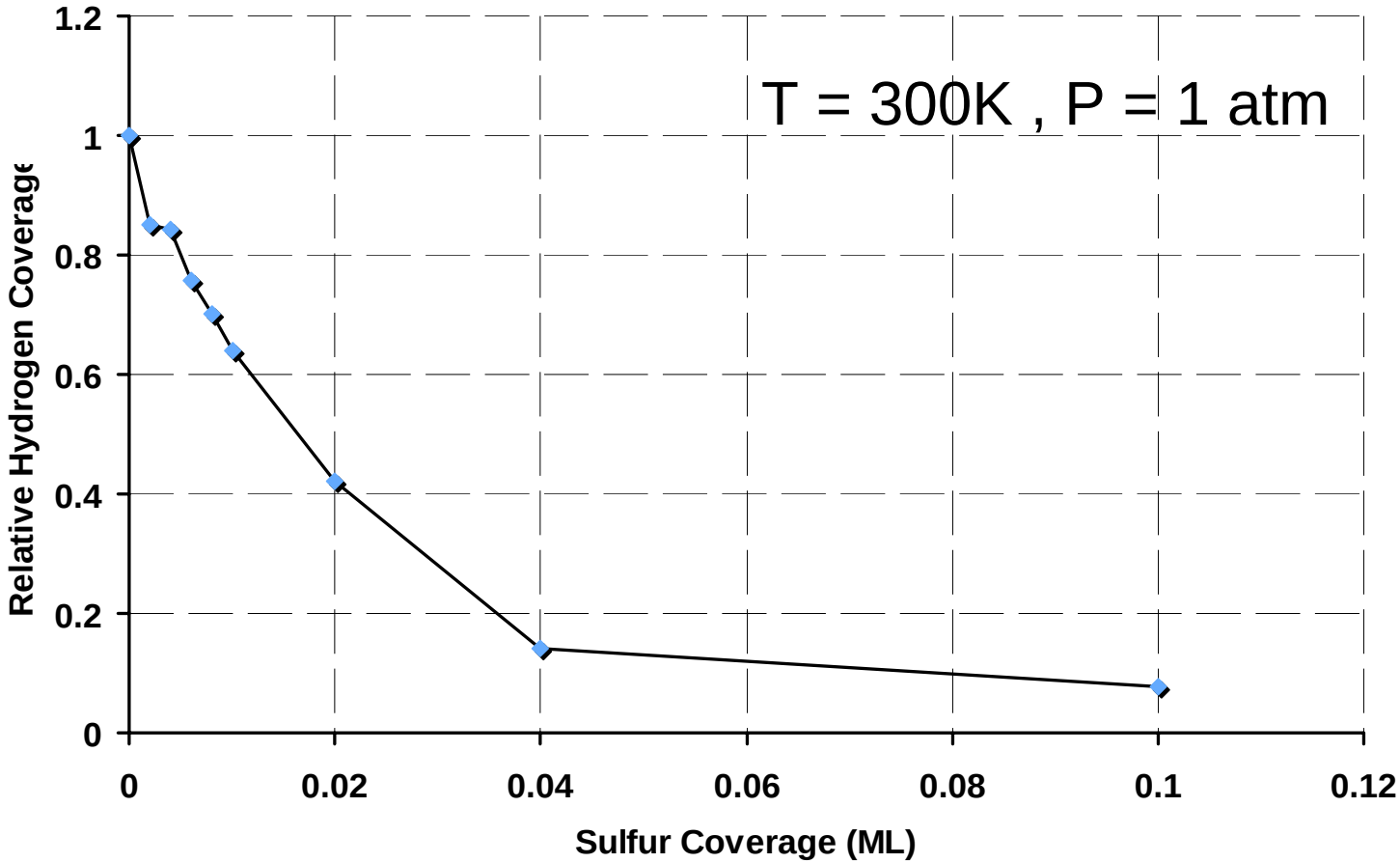


<u>Lattice constant</u>

Experimental : 3.89 Å

Calculated : 3.97 Å

Effect of S Coverage on Surface H Coverage



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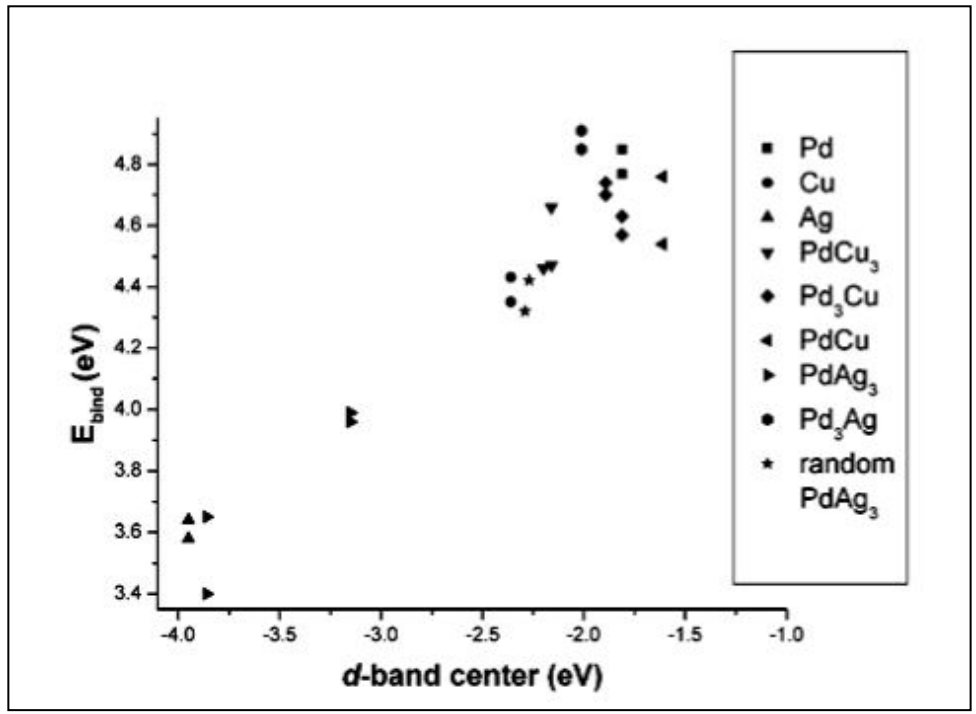
Possible Remedies

- Alloying
  - Pd-Cu
  - Pd-Ag

- Co-adsorption of other species that will favor the adsorption of H in the presence of S



Alfonso et al. Surface Science 546 (2003) 12–26

First Principles and Kinetic Monte Carlo Investigations of Pd-based Membranes for Hydrogen Separation

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