

# Numerical modeling of hydrogen/deuterium absorption in transition-metal alloys

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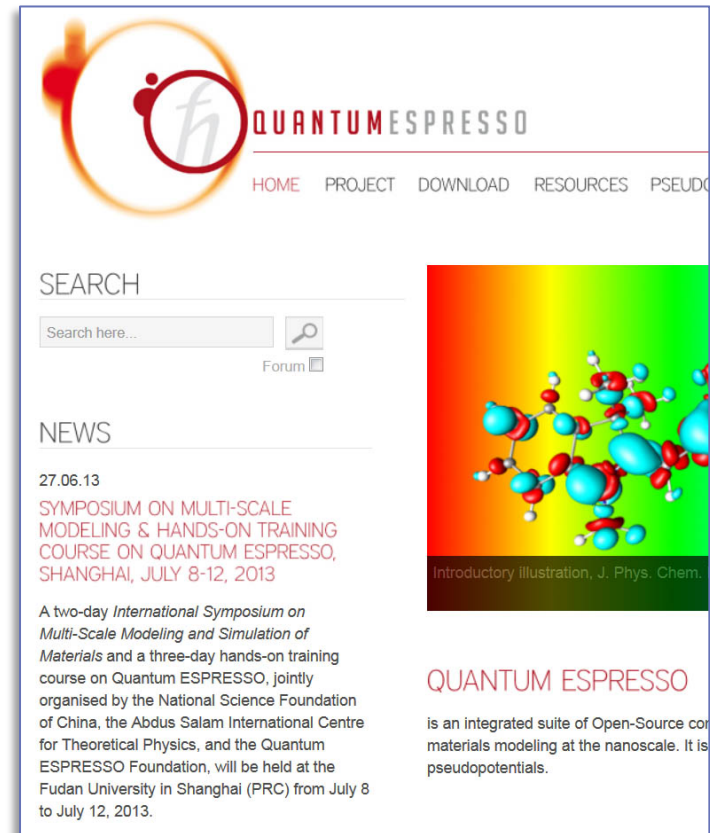


# QuantumEspresso

- **Electronic structure calculations and material modeling based on density functional theory (DFT):**

<http://quantum-espresso.org>

- **APPLICATIONS:**  
**condensed matter physics,**  
**chemistry / pharmaceutical**



The screenshot shows the Quantum Espresso website homepage. At the top left is the logo, a stylized 'h' inside a circle with a red and orange gradient. To the right of the logo is the text 'QUANTUM ESPRESSO'. Below this is a navigation menu with links: HOME, PROJECT, DOWNLOAD, RESOURCES, and PSEUDO. A search bar is located below the navigation menu, with the text 'SEARCH' above it and 'Search here...' inside the input field. To the right of the search bar is a magnifying glass icon and the text 'Forum'. Below the search bar is a 'NEWS' section. The first news item is dated '27.06.13' and is titled 'SYMPOSIUM ON MULTI-SCALE MODELING & HANDS-ON TRAINING COURSE ON QUANTUM ESPRESSO, SHANGHAI, JULY 8-12, 2013'. The text below the title describes a two-day international symposium and a three-day hands-on training course on Quantum ESPRESSO, jointly organized by the National Science Foundation of China, the Abdus Salam International Centre for Theoretical Physics, and the Quantum ESPRESSO Foundation, held at Fudan University in Shanghai (PRC) from July 8 to July 12, 2013. To the right of the news section is a large image of a molecular structure with a red, yellow, and green gradient background. Below the image is the text 'Introductory Illustration, J. Phys. Chem.'. Below the image is the text 'QUANTUM ESPRESSO' and a short description: 'is an integrated suite of Open-Source code for materials modeling at the nanoscale. It is based on pseudopotentials.'



# Nuclear active environment (NAE)

**1. High H:Pd loading ratio**

**2. Presence of dopants  
or impurities**

**3. Structural morphology:  
(voids, cracks, dislocations,  
surface morphology)**



# Figures of merit

- Figures of merit to explore the variations in physical properties:
  - Hydrogen adsorption energy
  - Hydrogen-Hydrogen separation



# Nuclear active environment (NAE)

## 1. High H:Pd loading ratio

Figure of merit: **adsorption energy**

## 2. Presence of dopants or impurities

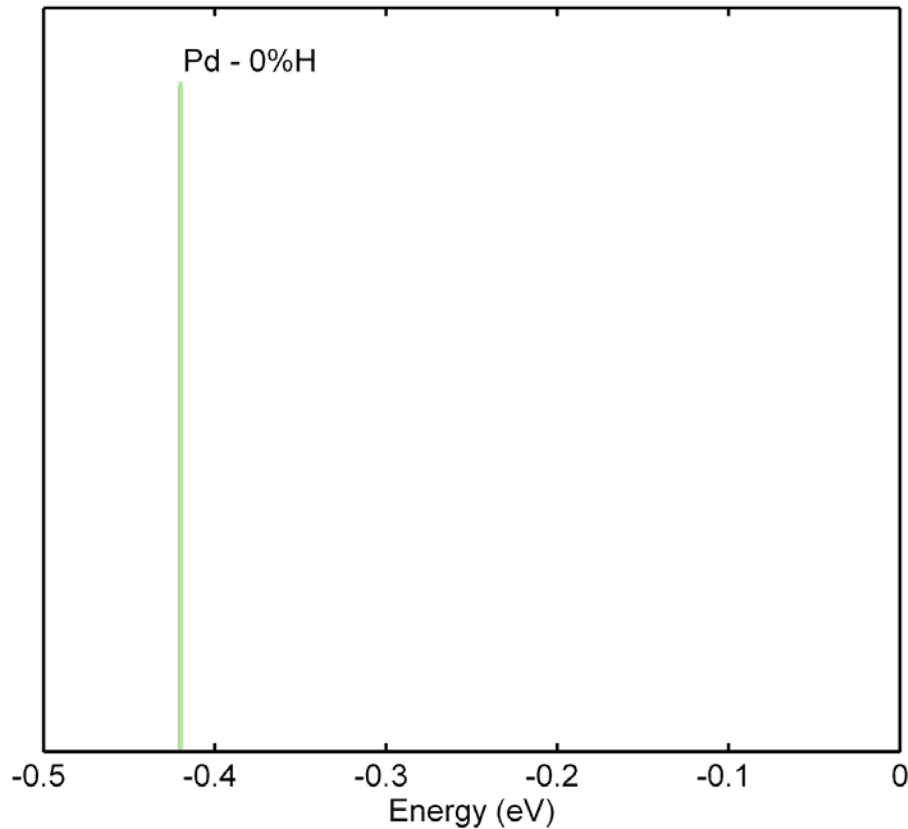
Figure of merit: **adsorption energy**

## 3. Structural morphology: (voids, cracks, dislocations, surface morphology)

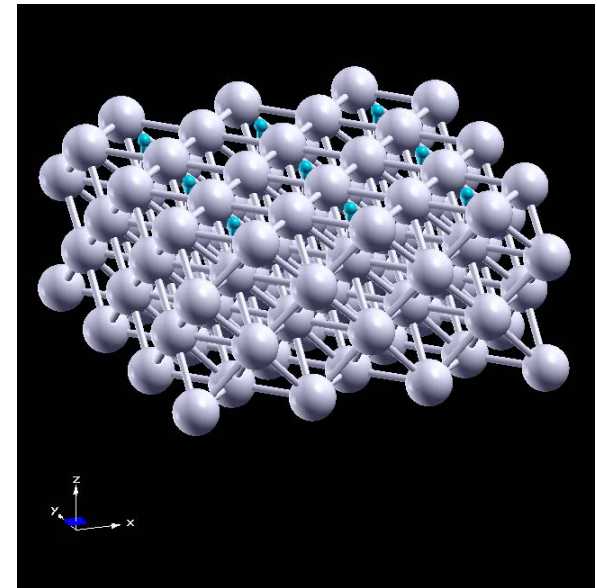
Figure of merit: **H-H separation**



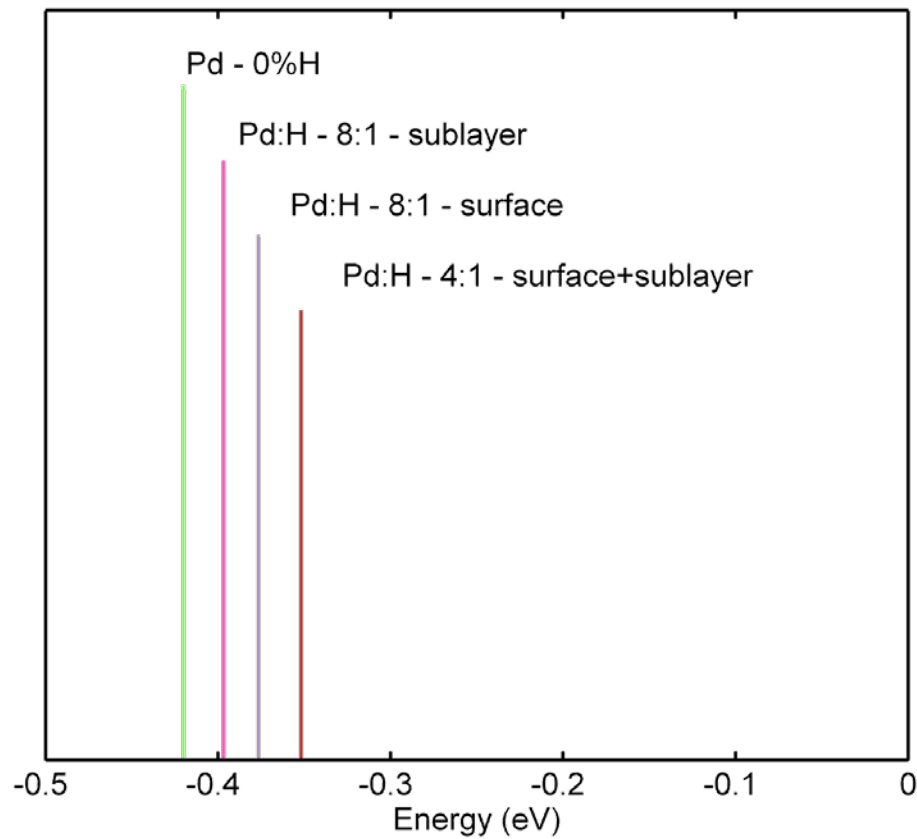
# Adsorption energy



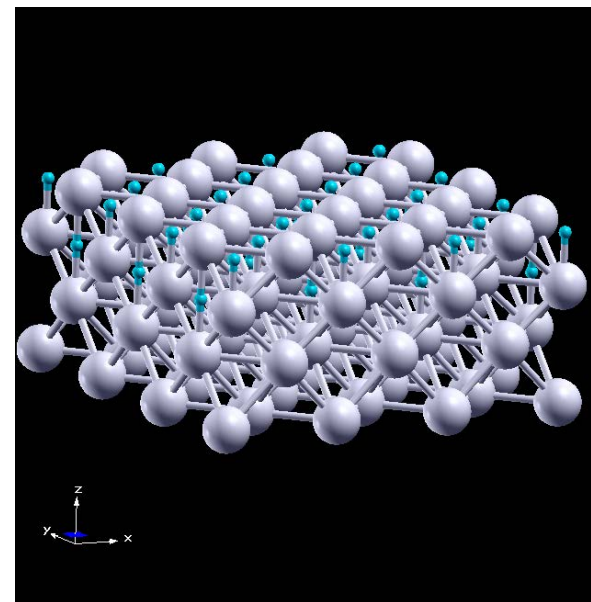
- (100) Pd surface modeled as slab:



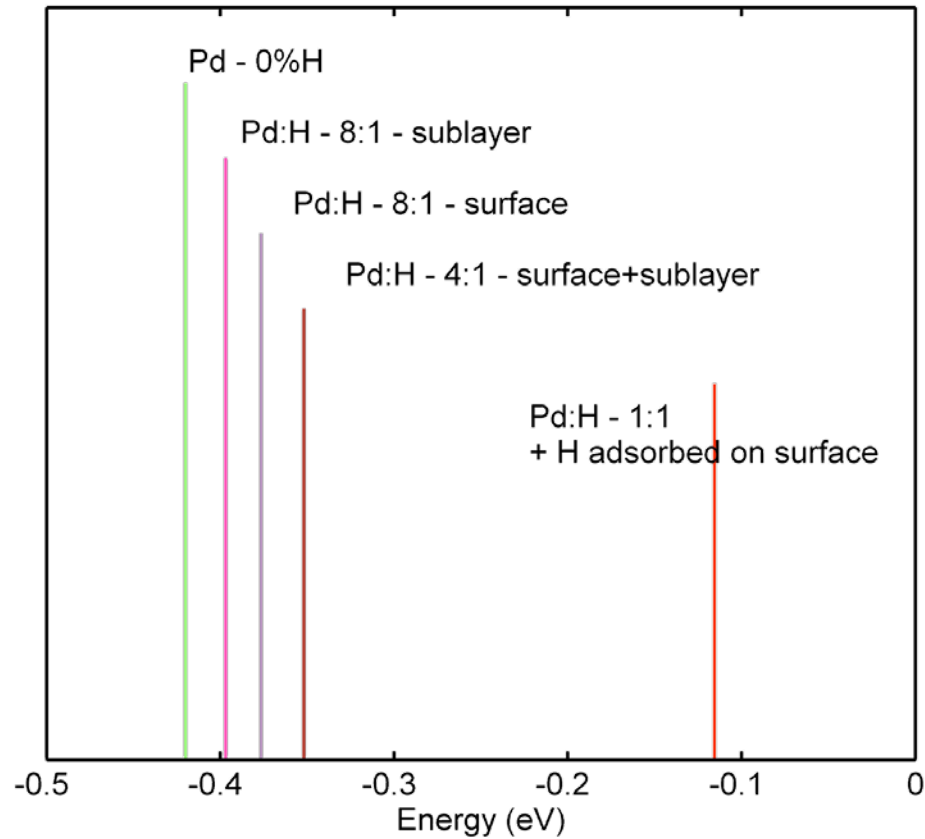
# Adsorption energy



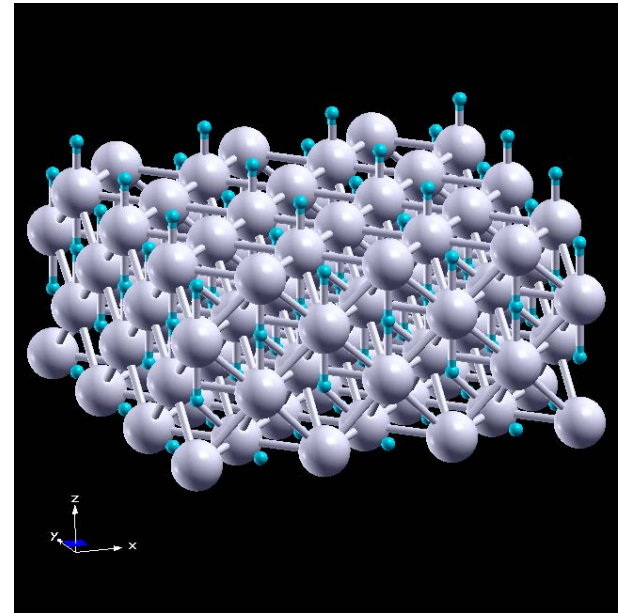
- (100) surface modeled as slab:



# Adsorption energy



- (100) surface modeled as slab:





# Results: H loading ratio

- Loading of palladium with hydrogen reduces adsorption energy\*

\* Similar results reported by M. Johansson et al “Hydrogen adsorption on palladium and palladium hydride at 1 bar”, Surf. Science 604 (2010) 718-729

- As a result: mobile atomic hydrogen weakly binded to the surface and available for reaction



# Results: H loading ratio

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\* Similar results reported by M. Johansson et al “Hydrogen adsorption on palladium and palladium hydride at 1 bar”, Surf. Science 604 (2010) 718-729

- As a result: mobile atomic hydrogen weakly binded to the surface and available for reaction
- ...there is another way to lower adsorption energy



# Nuclear active environment (NAE)

## 1. High H:Pd loading ratio

Figure of merit: **adsorption energy**

## 2. Presence of dopants or impurities

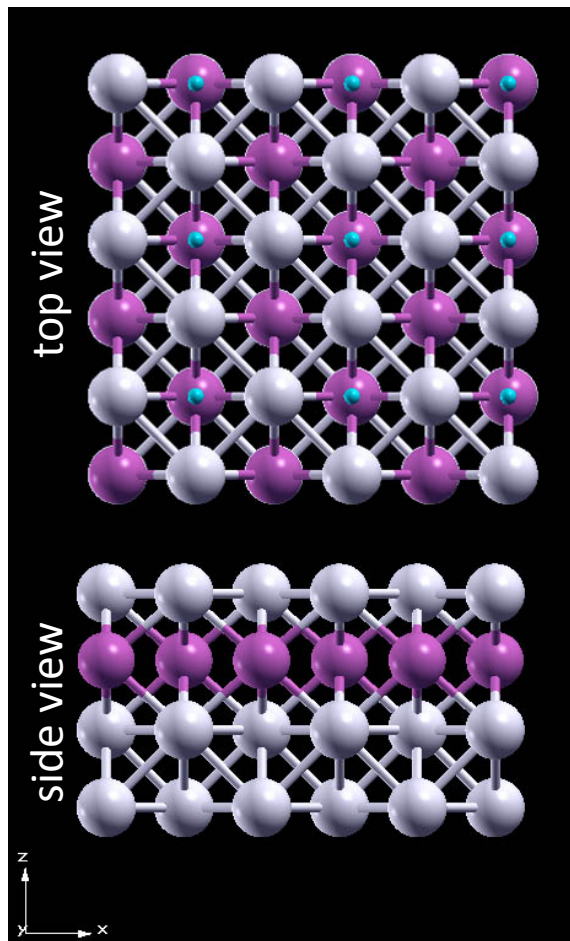
Figure of merit: **adsorption energy**

## 3. Structural morphology: (voids, cracks, dislocations, surface morphology)

Figure of merit: **H-H separation**



# Presence of dopants (near-surface alloys - NSA)



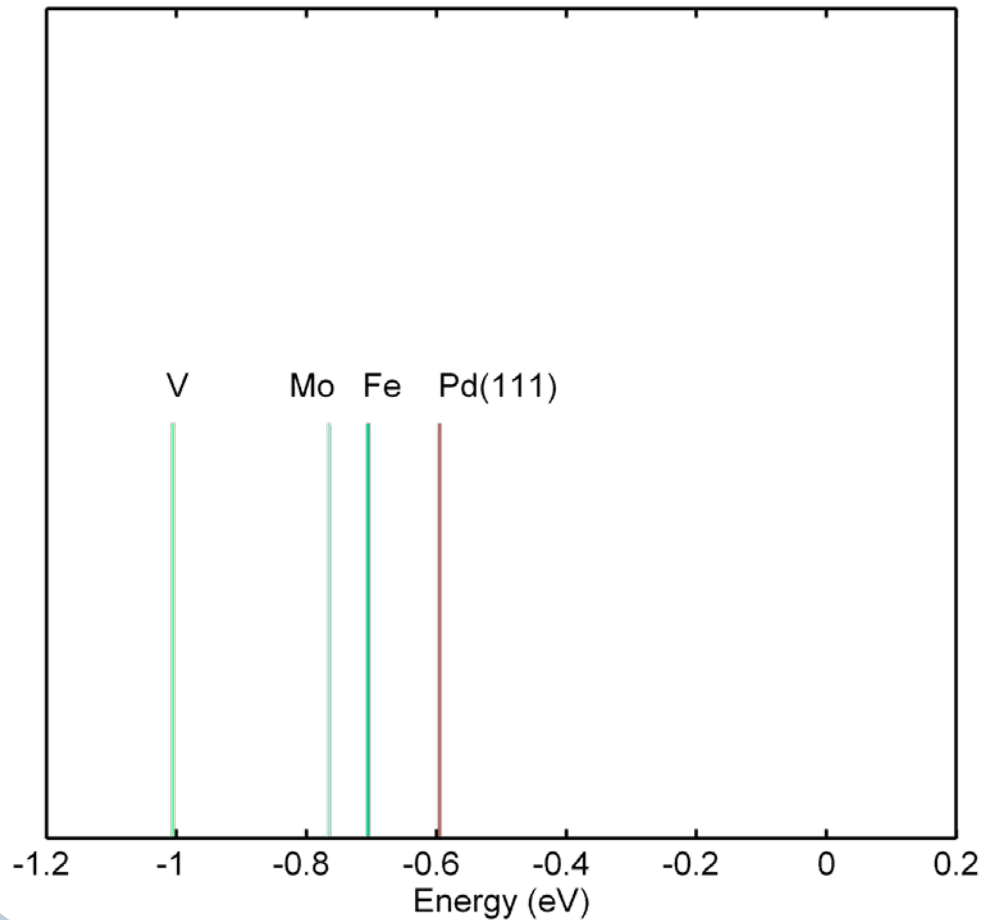
← Host (Pd)  
← Solute (Rh)

- **X/Y: X-solute, Y-host (Rh/Pd)**
- Near surface solute concentration is different from bulk
- $H_2$  dissociation energy remains low
- Adsorption energy is reduced
- Result: mobile atomic hydrogen weakly bound to the surface and available for reaction.

J.Greeley M.Mavrikakis, "Alloy catalyst designed from first principles", Nature Mat. Vol3,(2004) pp.810-812



# Near-surface alloys

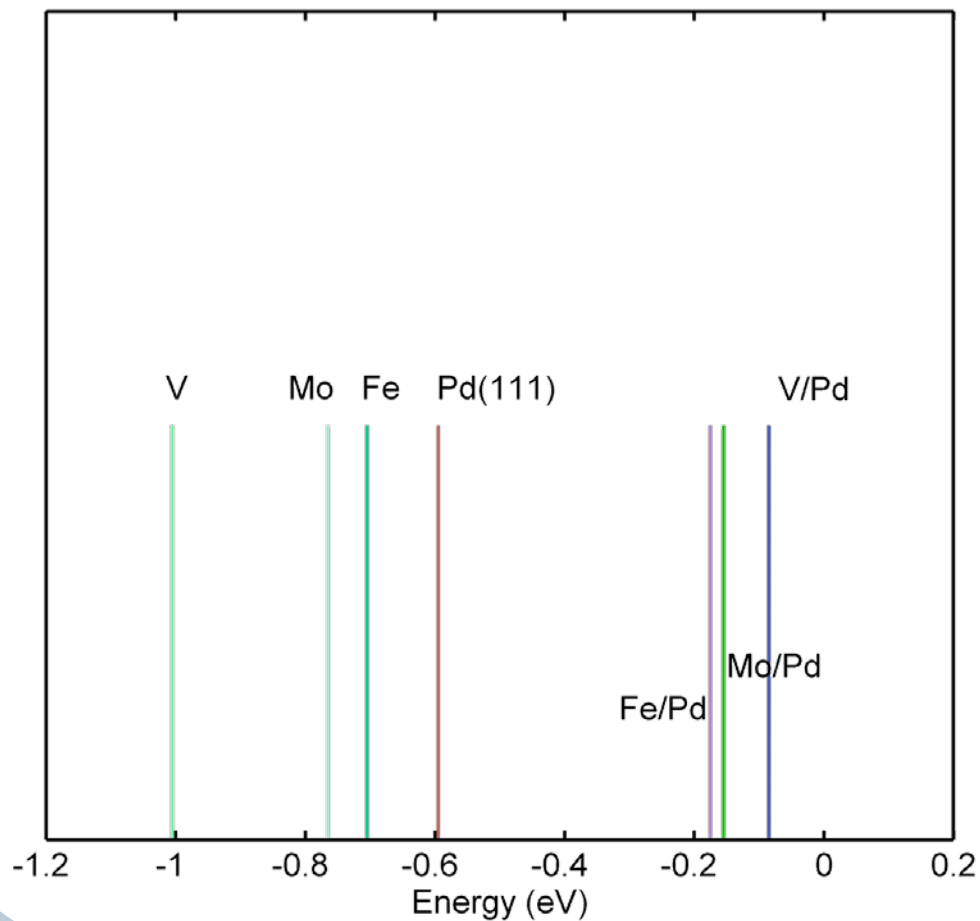


V  
Mo  
Fe  
Pd (111)

J.Greeley M.Mavrikakis, "Alloy catalyst designed from first principles", Nature Mat. Vol3,(2004) pp.810-812



# Near-surface alloys

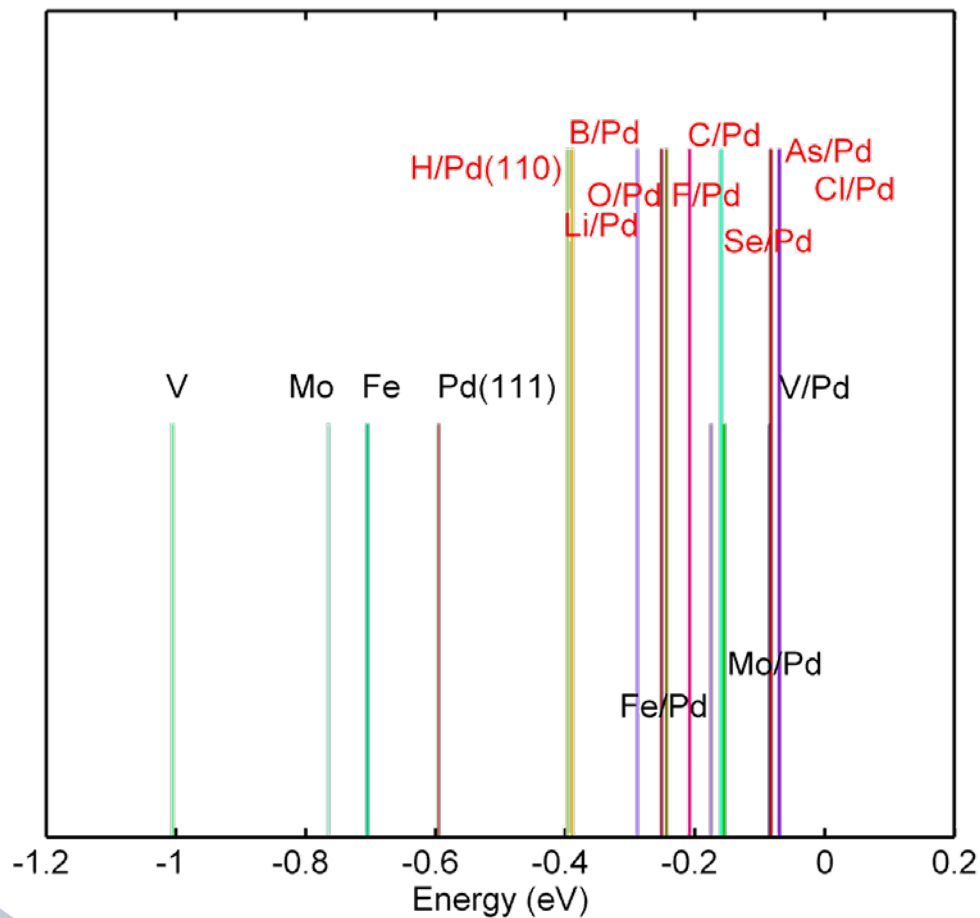


V  
Mo  
Fe  
Pd (111)  
Fe/Pd  
Mo/Pd  
V/Pd

J.Greeley M.Mavrikakis, "Alloy catalyst designed from first principles", Nature Mat. Vol3,(2004) pp.810-812



# Near-surface alloys



V	H/Pd
Mo	Li/Pd
Fe	B/Pd
Pd (111)	O/Pd
Fe/Pd	F/Pd
Mo/Pd	C/Pd
V/Pd	Se/Pd
	As/Pd
	Cl/Pd



# Results: presence of dopants

- Substitutional or interstitial sublayer doping reduces hydrogen adsorption energy.
- If reaching high hydrogen loading ratios is impossible, sublayer doping can be used to reduce adsorption energy to allow hydrogen to move more freely along the surface





# Nuclear active environment (NAE)

## 1. High H:Pd loading ratio

Figure of merit: **adsorption energy**

## 2. Presence of dopants or impurities

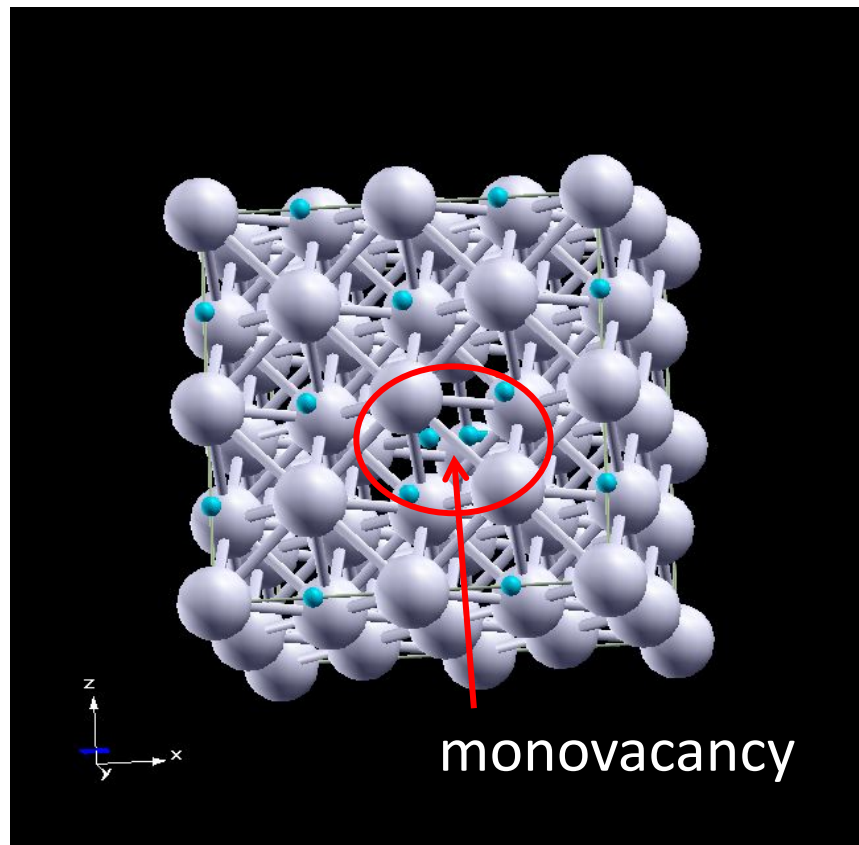
Figure of merit: **adsorption energy**

## 3. Structural morphology: (voids, cracks, dislocations, surface morphology)

Figure of merit: **H-H separation**

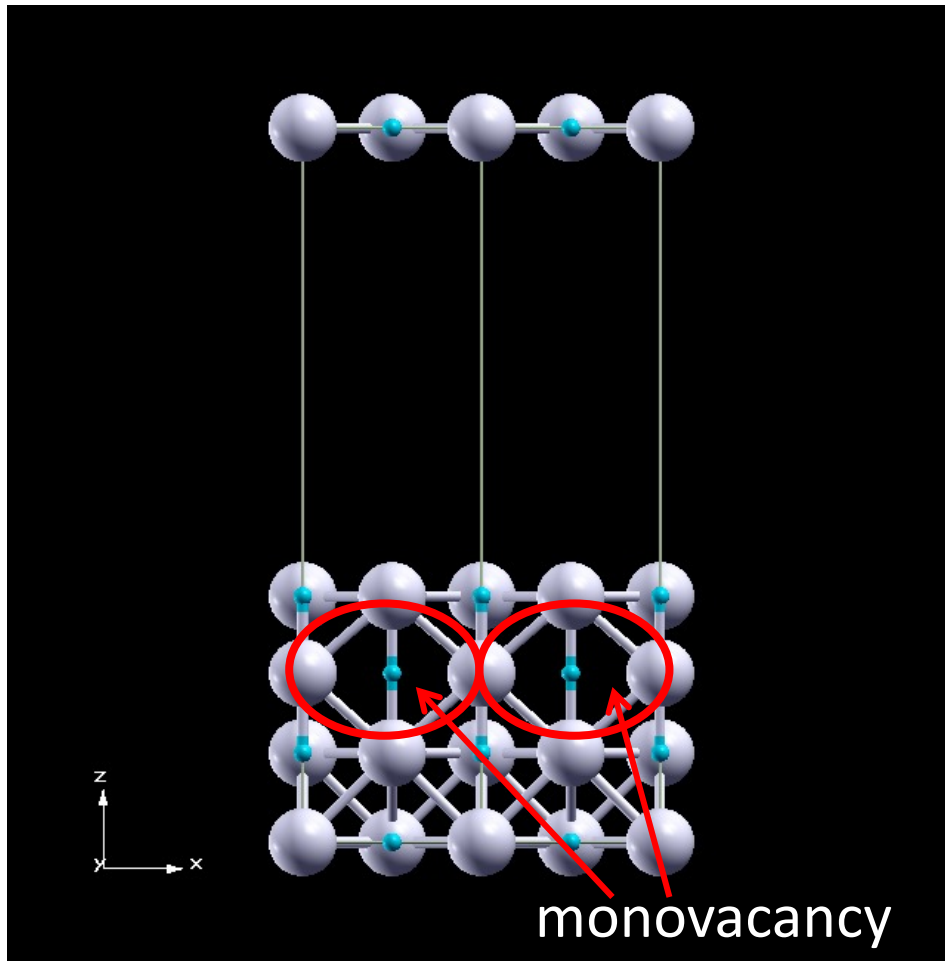


# Structural morphology: monovacancy in bulk (P. Hagelstein, 2012)



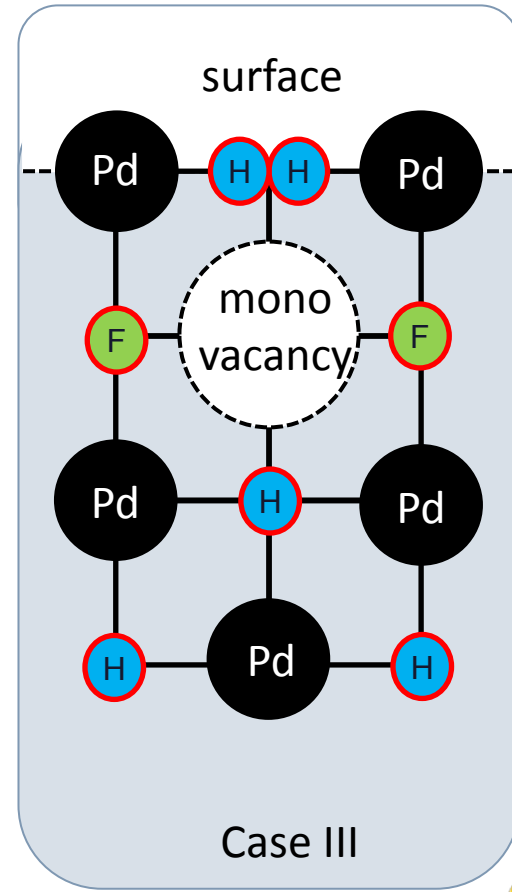
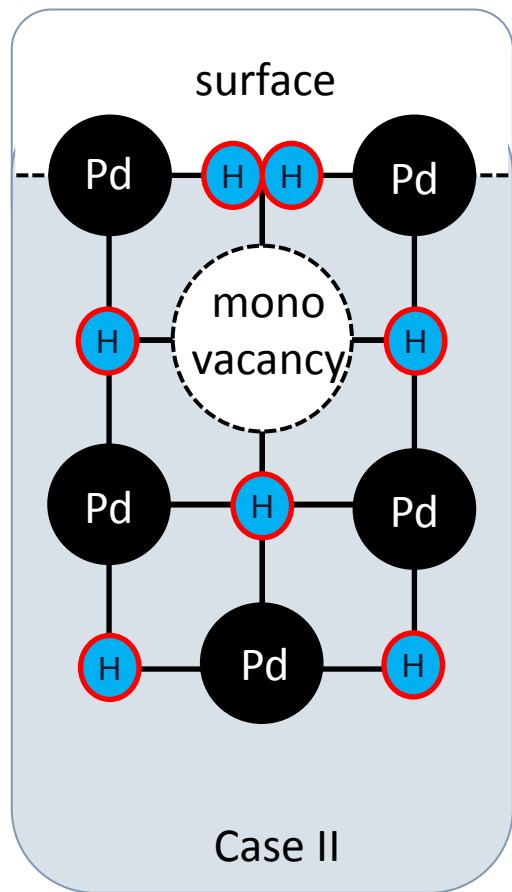
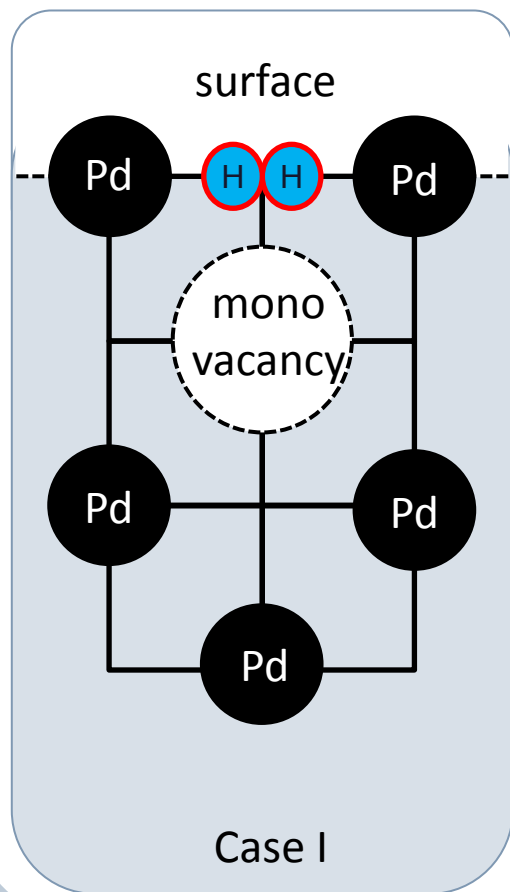
- PdH fcc
- Pd is replaced with H
- H comes from octahedral site to form H<sub>2</sub> molecule
- Change H<sub>2</sub> position and H-H separation within the cell to find minimum of total energy
- **H-H separation close to 1 Angstrom**

# Monovacancy in subsurface layer

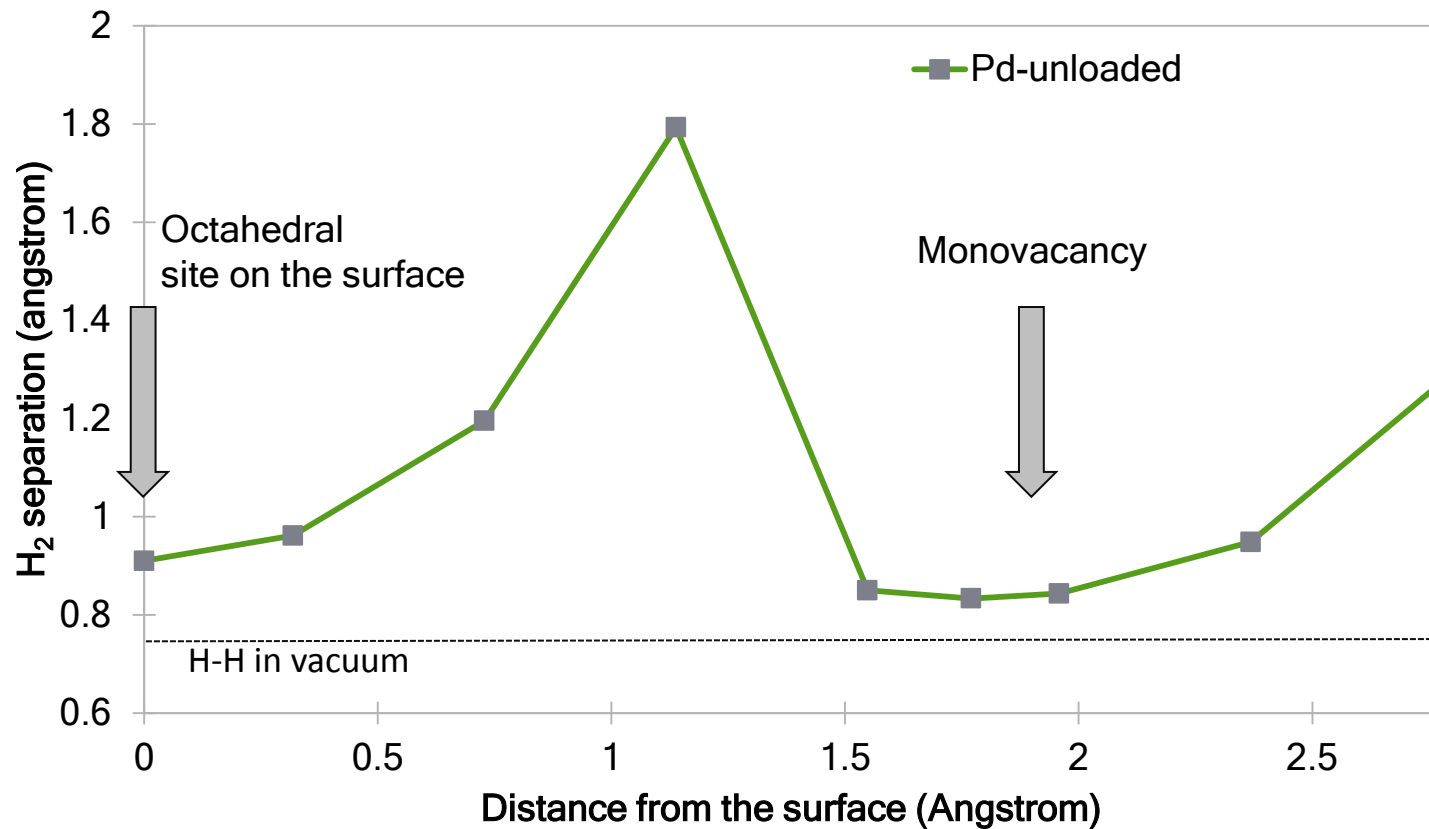


- PdH fcc (100) plane
- Pd is missing in sublayer
- H<sub>2</sub> molecule comes into octahedral site from above and progresses towards the monovacancy
- H<sub>2</sub> separation is 0.72 Å

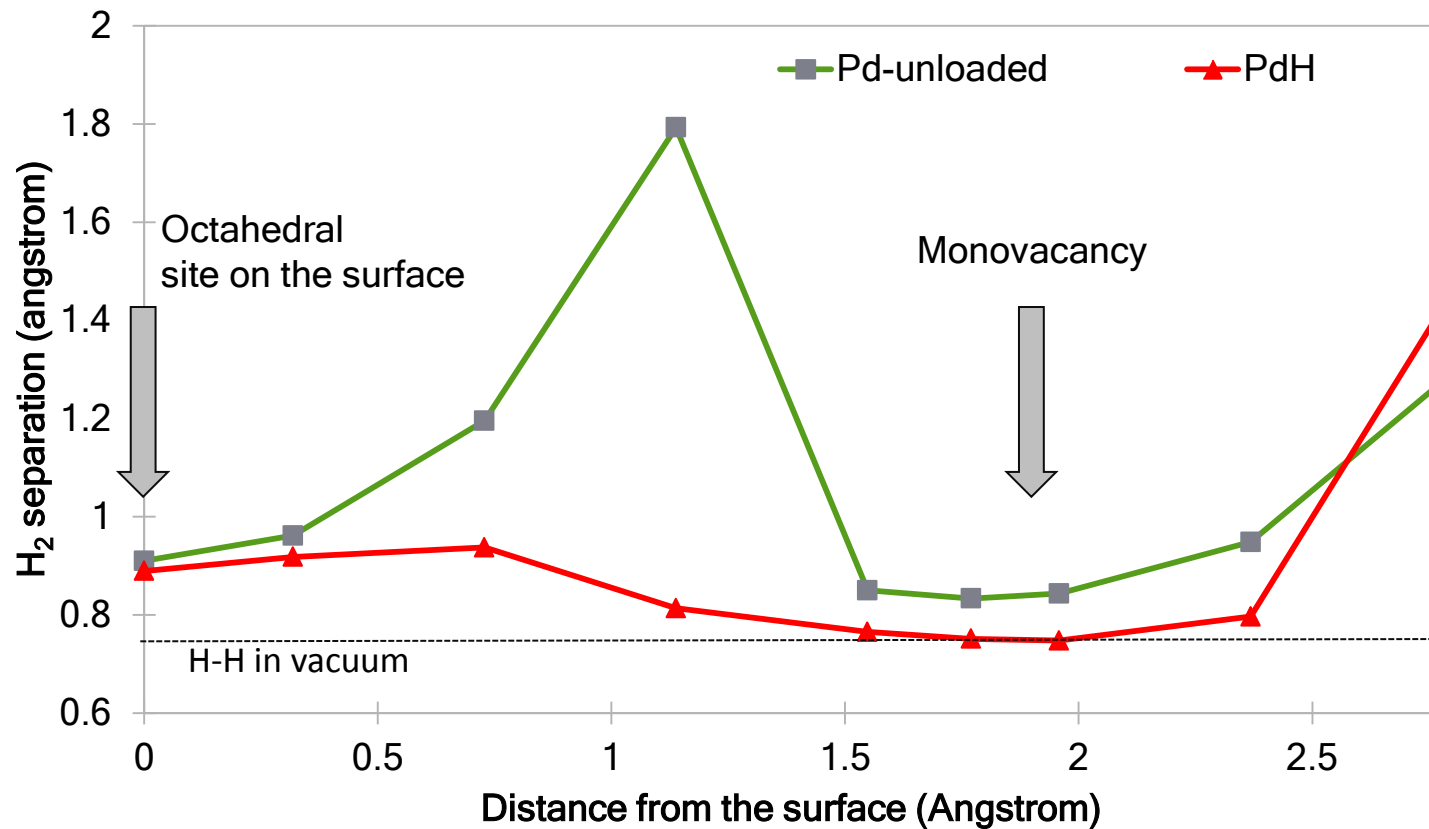
# Monovacancy in subsurface layer



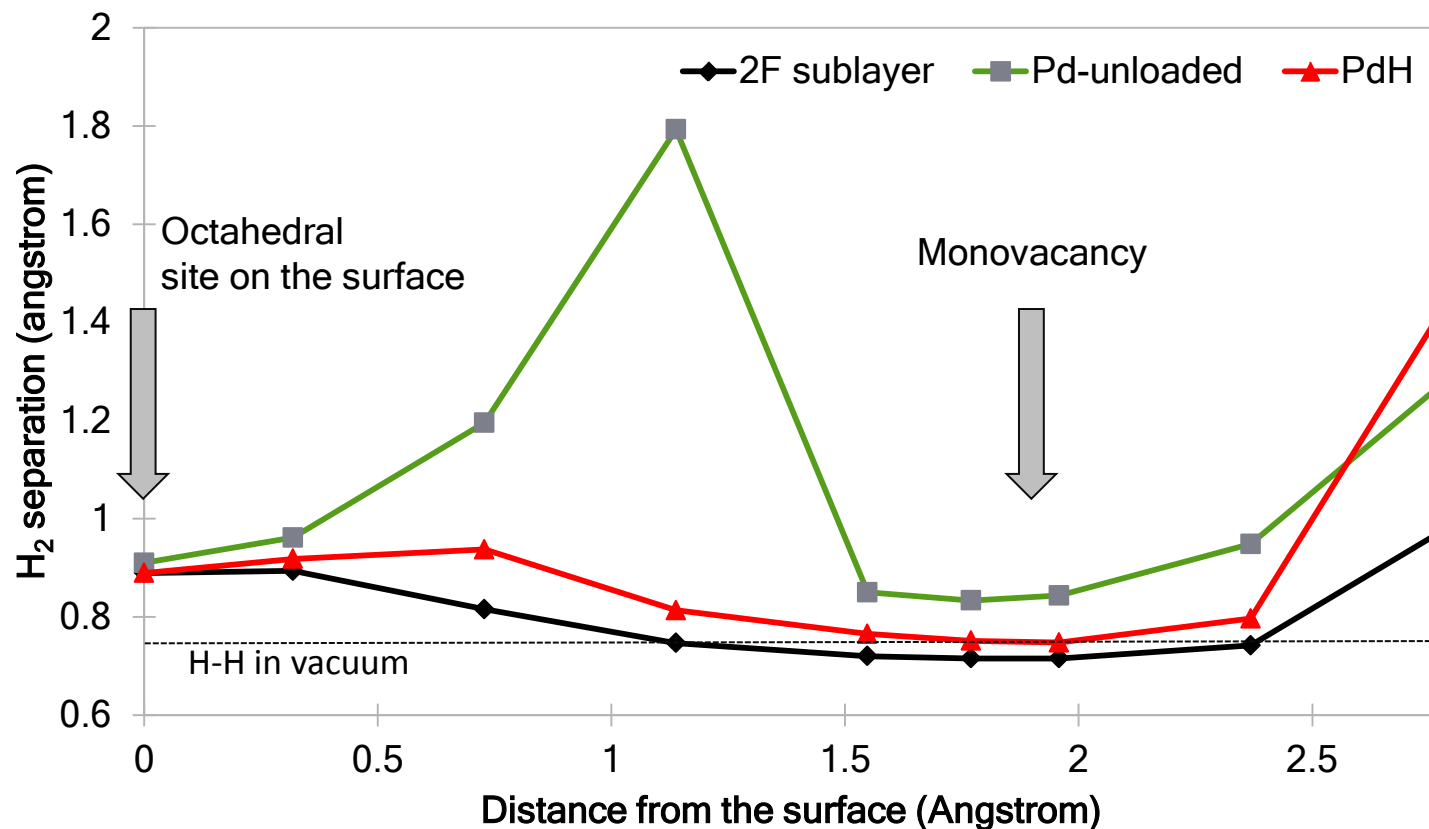
# Monovacancy in subsurface layer case I – pure Pd



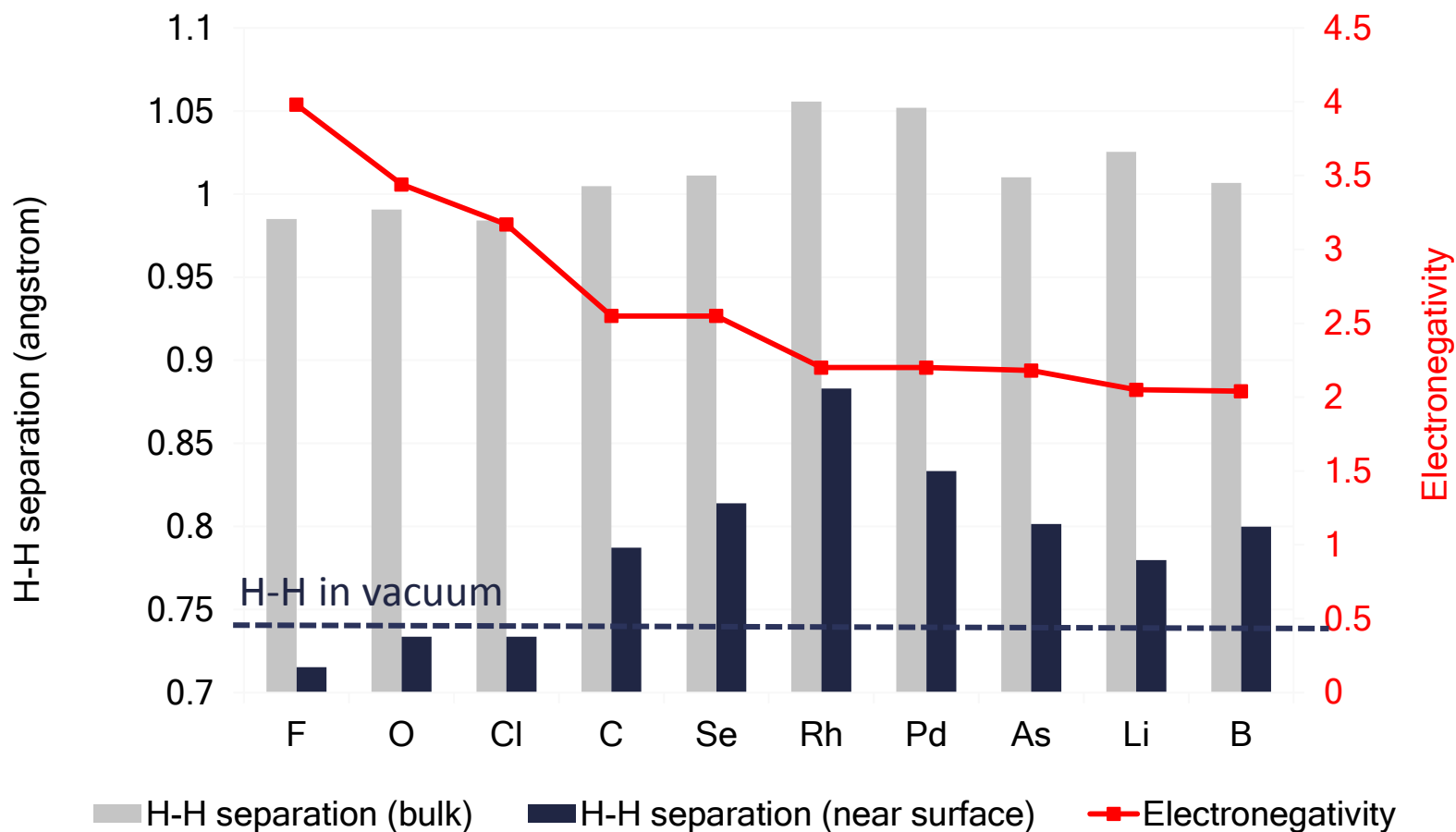
# Monovacancy in subsurface layer case II – PdH



# Monovacancy in subsurface layer case III – F/PdH



# Effect of electronegativity





# Results: surface morphology

- H-H separation can be decreased by high Pd:H loading or by doping the sublayer
- H-H separation at monovacancy depends on electronegativity of doping elements and can reach **0.72 Angstrom**



# Conclusions

- QuantumEspresso allows quick scan of potential NAE in transition-metal alloys
- Hydrogen loading is confirmed to reduce adsorption energy in the same way as near-surface alloys.

High H:Pd ratio  
or NSA

Low adsorption  
energy

H is mobile

High probability  
of reaction

- H-H separation can be decreased by introducing:
  - defects
  - chemical dopants (electronegativity effect)

