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 / pharmatheutical

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

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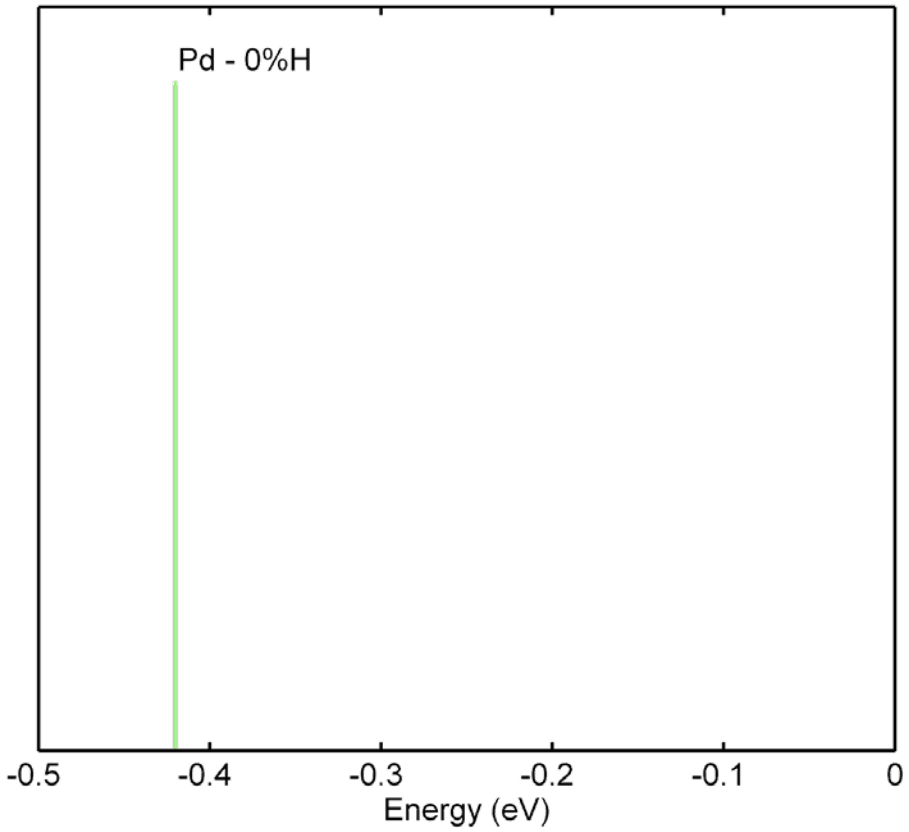
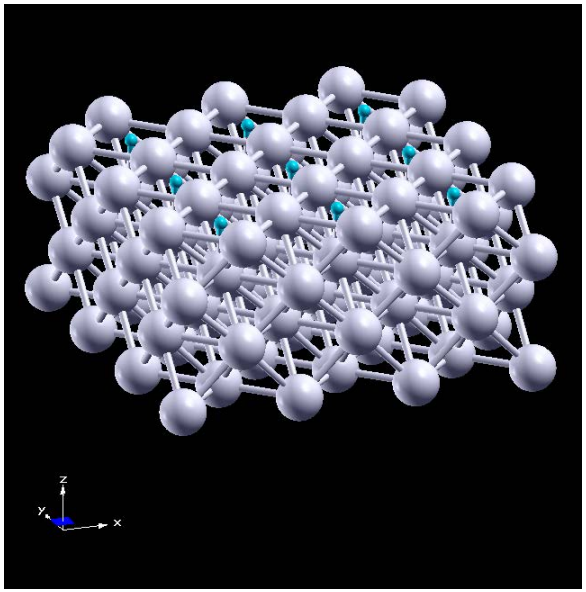
Figure of merit: **H-H separation**

Adsorption energy



- (100) Pd surface modeled as slab:



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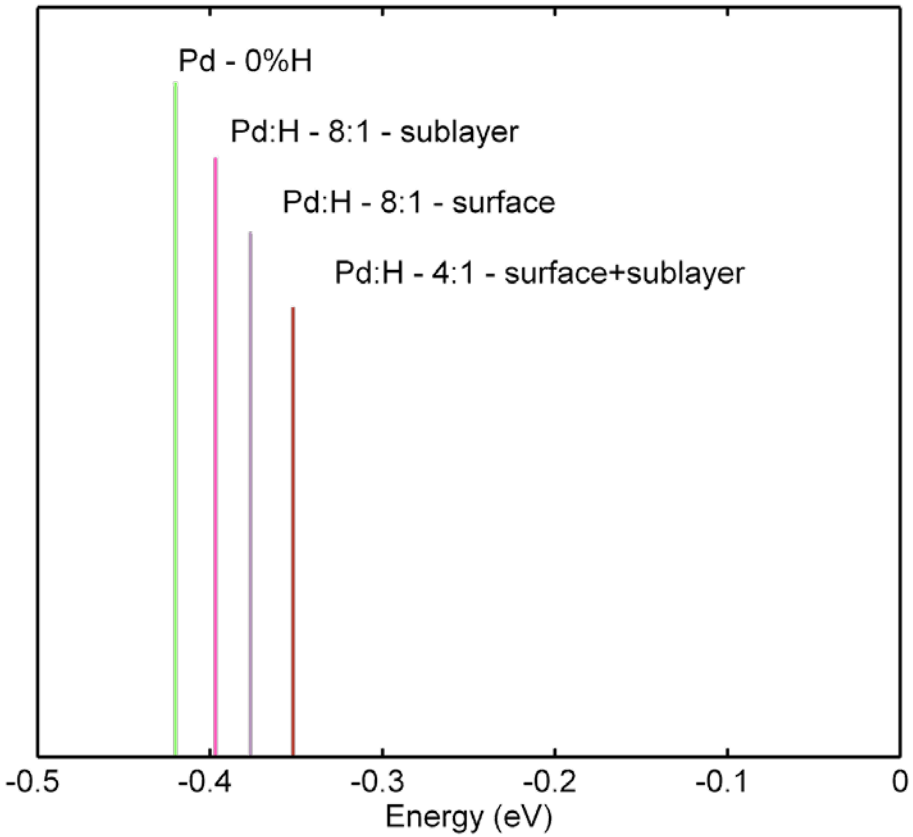

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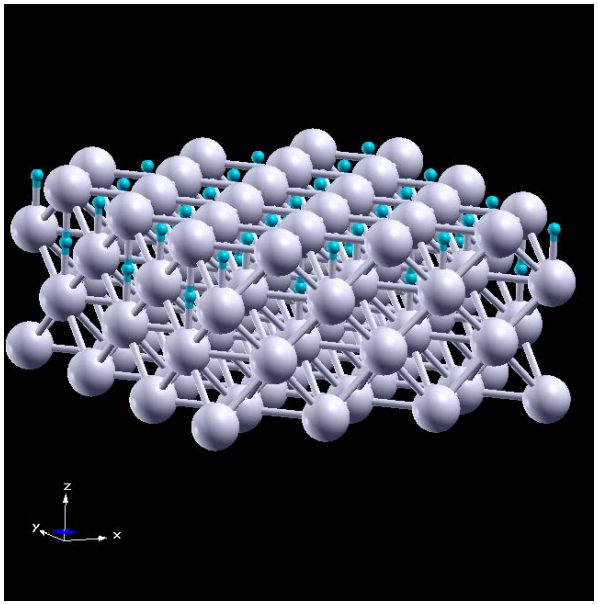
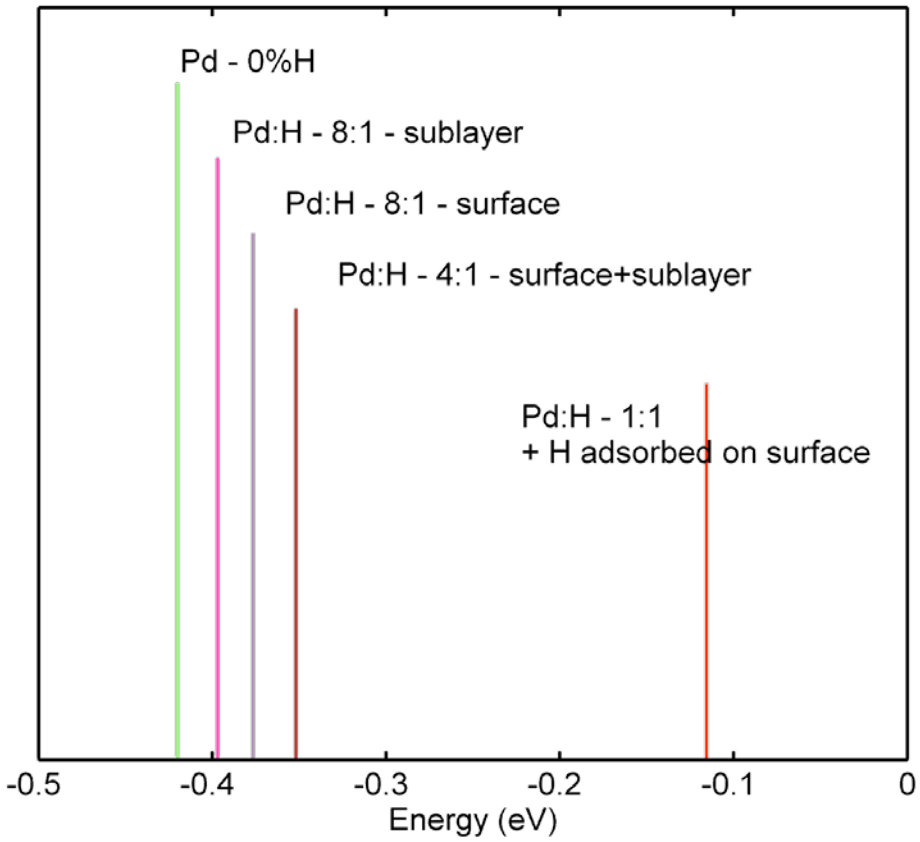


Adsorption energy



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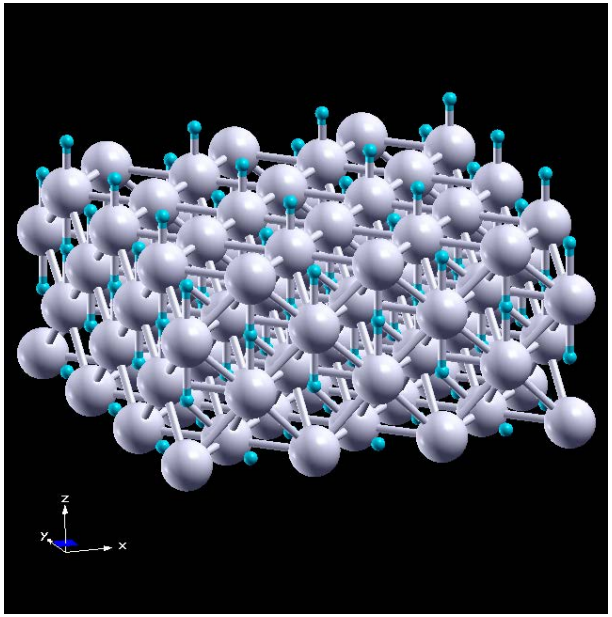

Results: H loading ratio

- 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

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

- …there is another way to lower adsorption energy

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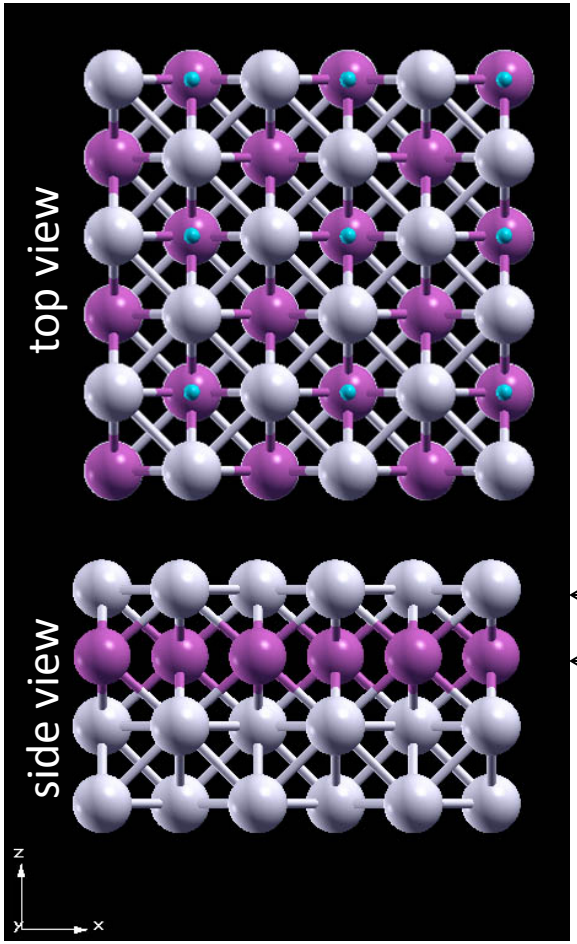
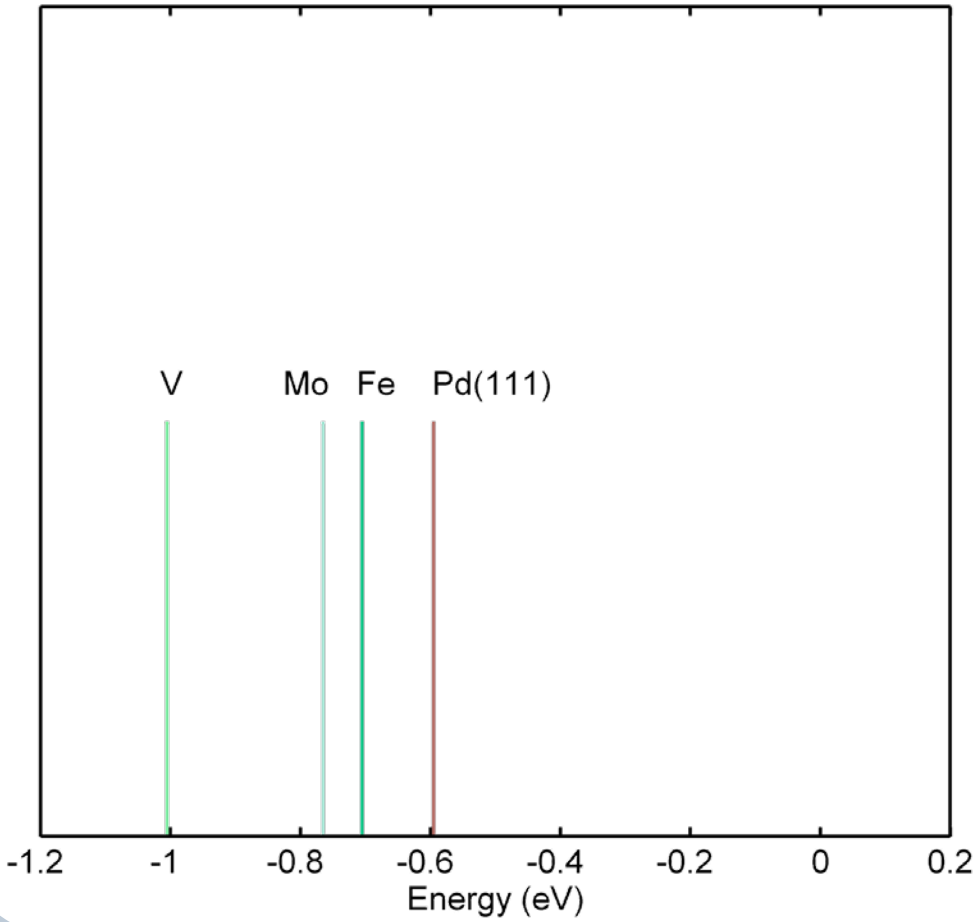
Presence of dopants (near-surface alloys - NSA)



- **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 binded 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)

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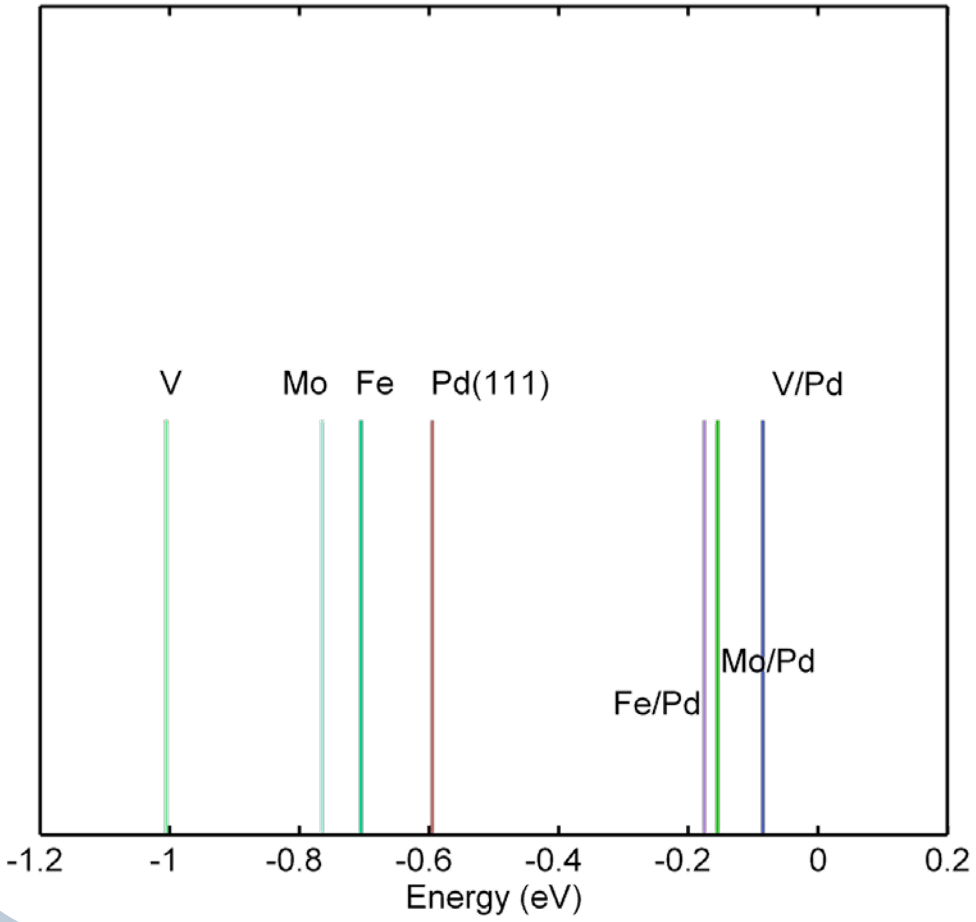
Near-surface alloys



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

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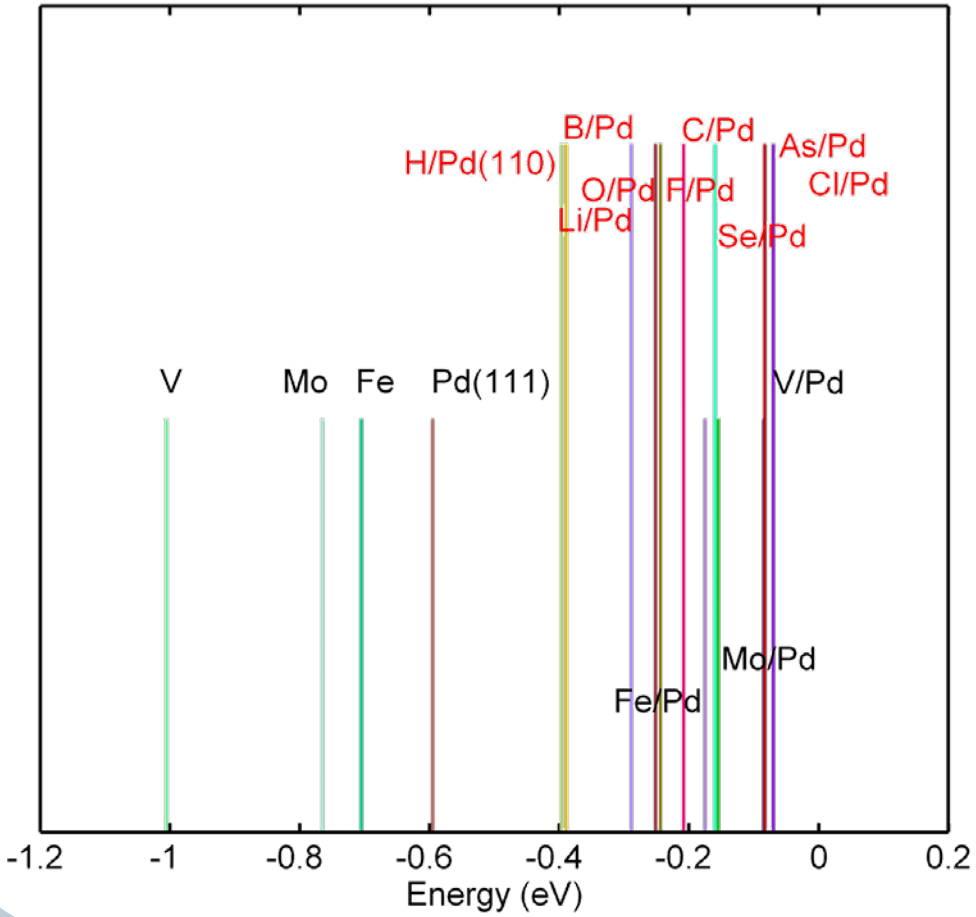
Near-surface alloys



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

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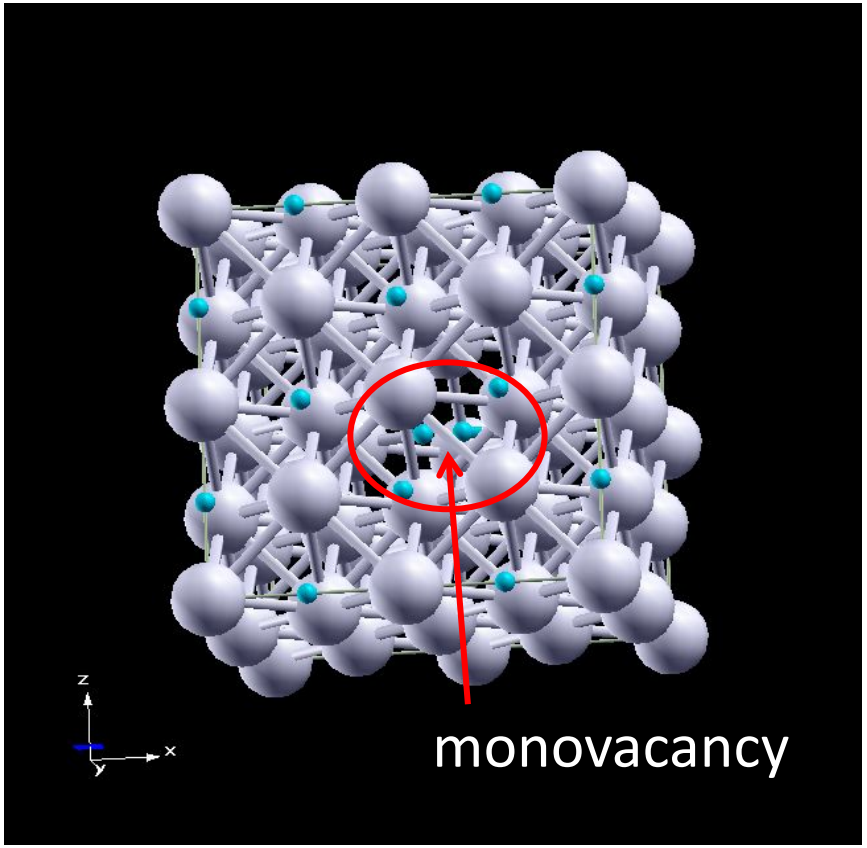
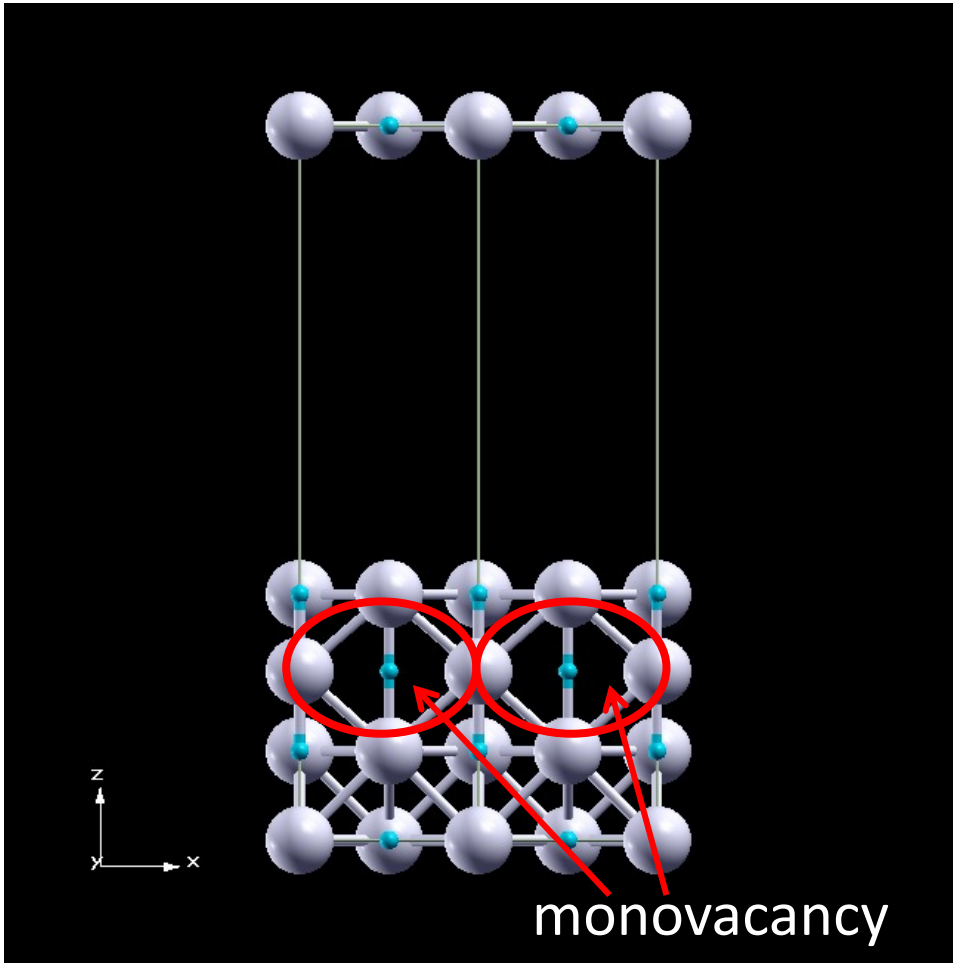
Figure of merit: **H-H separation**

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



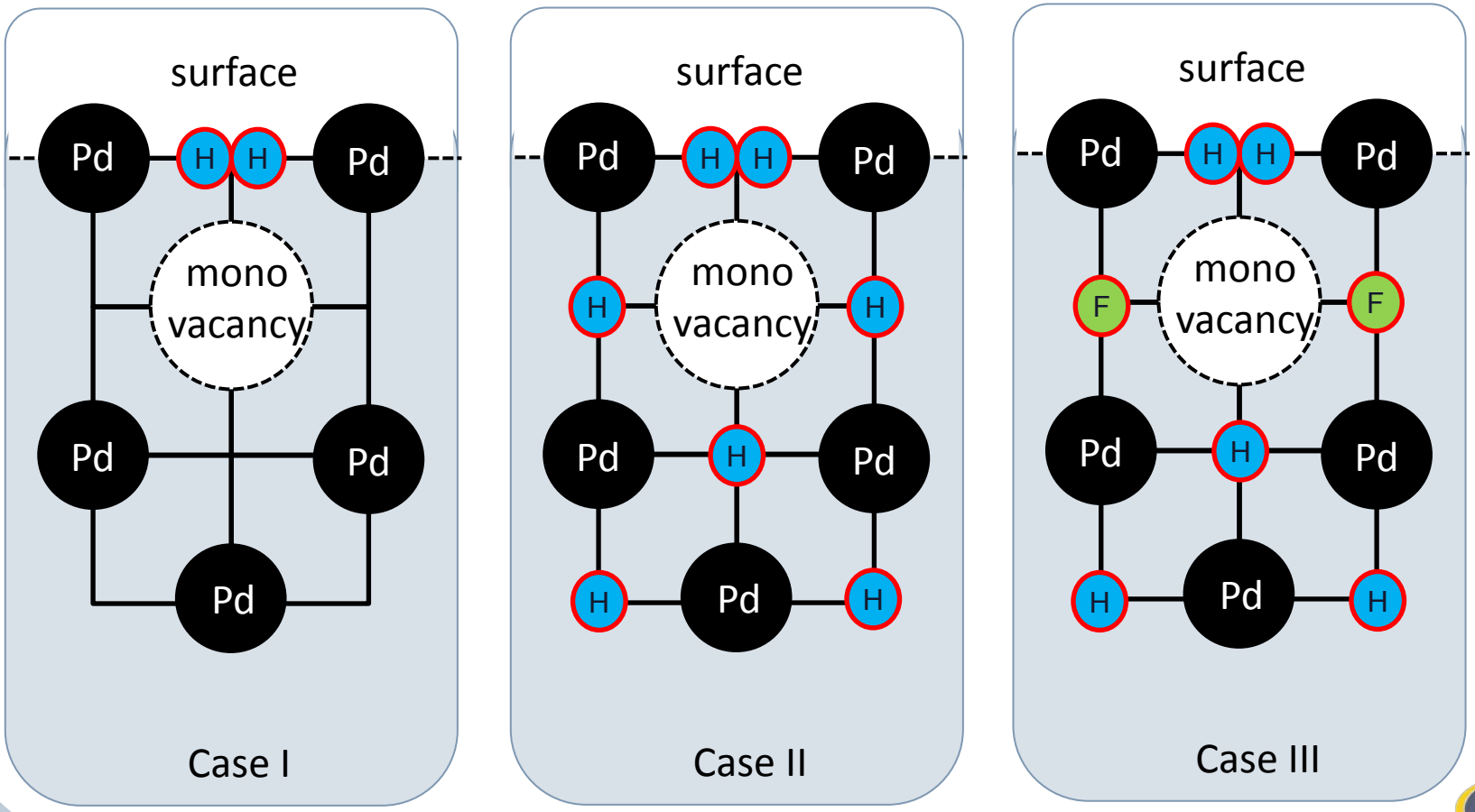
- PdH fcc
- Pd is replaced with H
- H comes from octahedral site to form H_2 molecule
- Change H_2 position and H-H separation within the cell to find minimum of total energy
- **H-H separation close to 1 Angstrom**

Monovacancy in subsurface layer

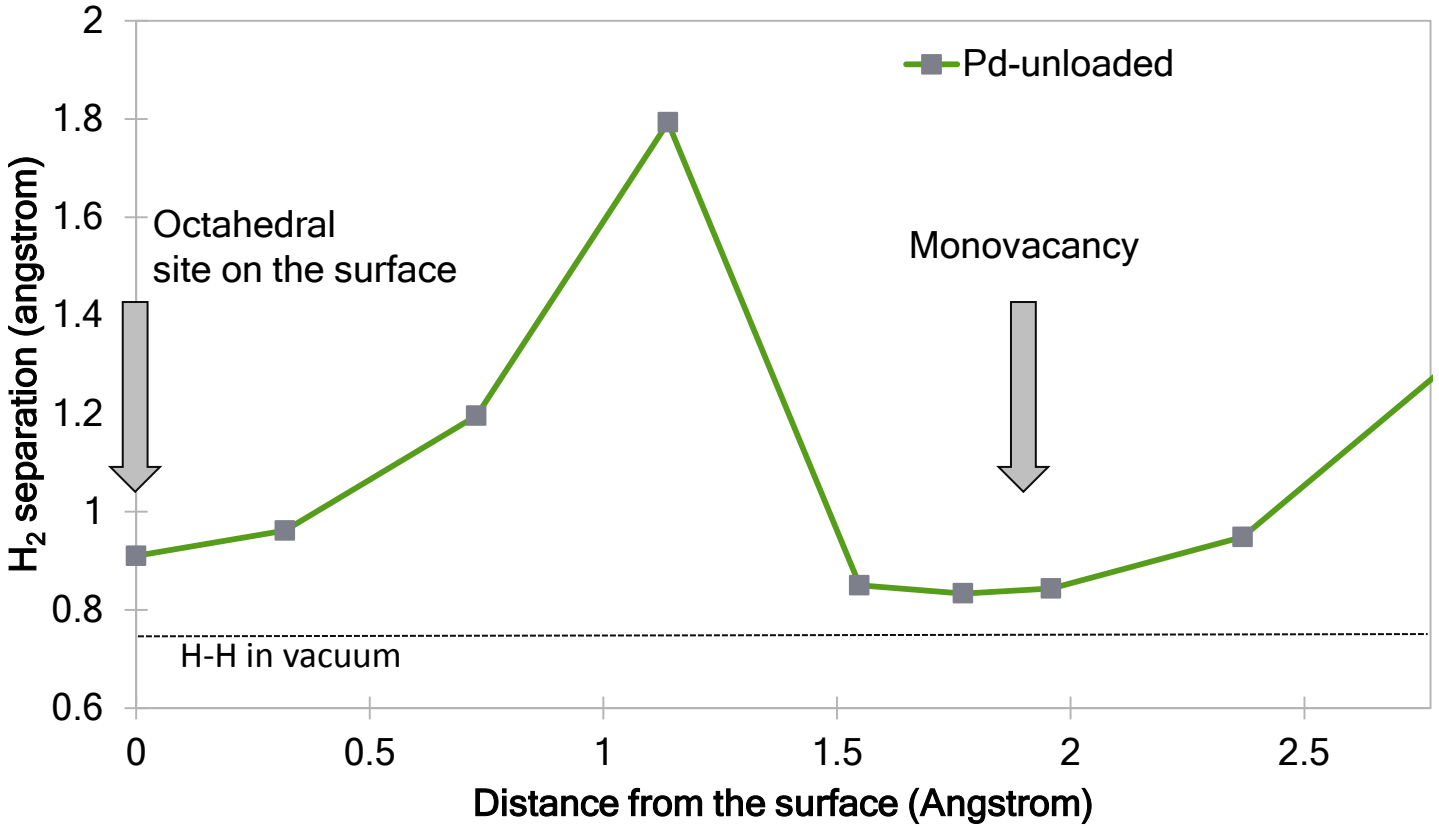


- PdH fcc (100) plane
- Pd is missing in sublayer
- H_2 molecule comes into octahedral site from above and progresses towards the monovacancy
- **H_2 separation is 0.72 A**

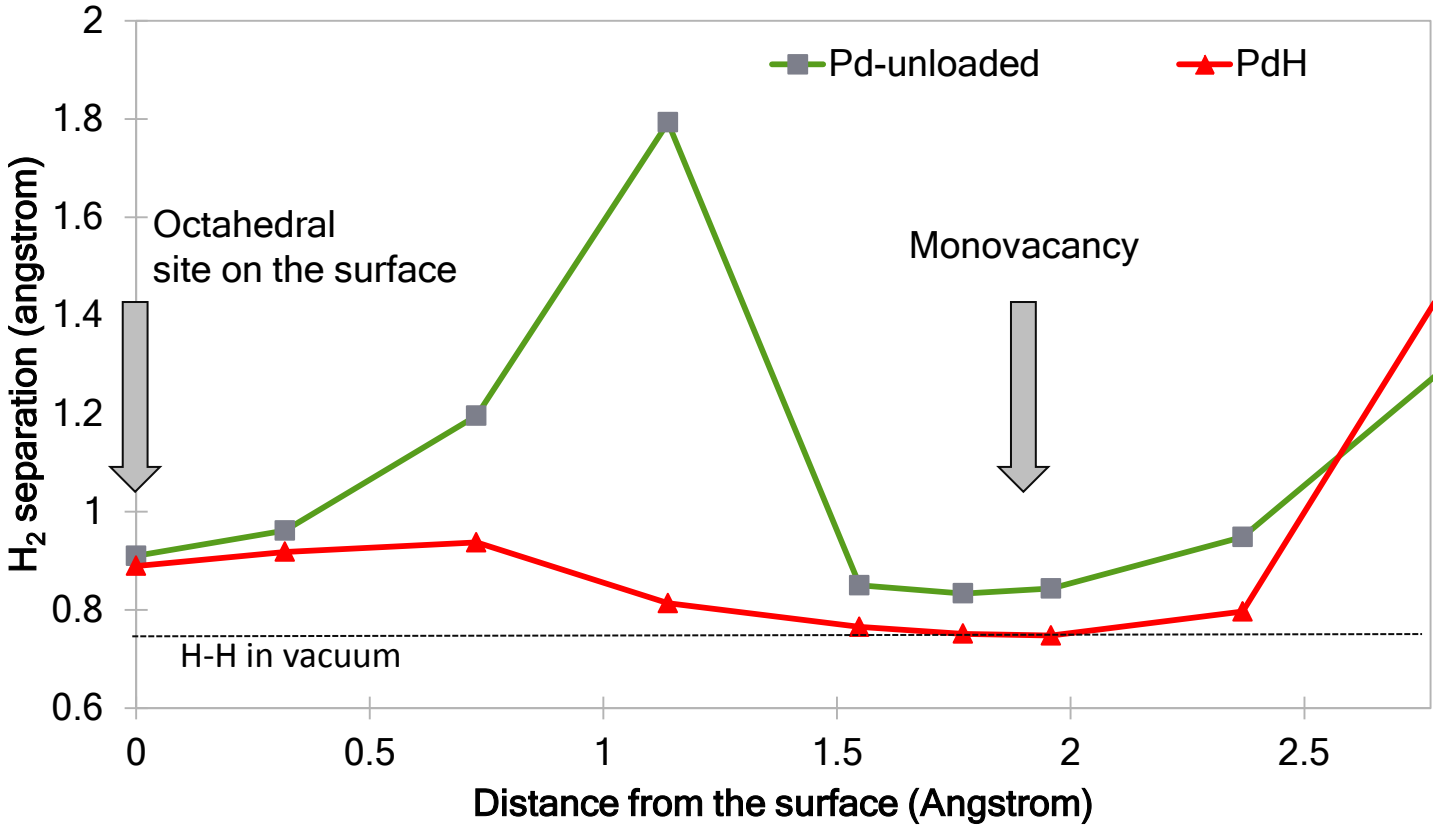
Monovacancy in subsurface layer



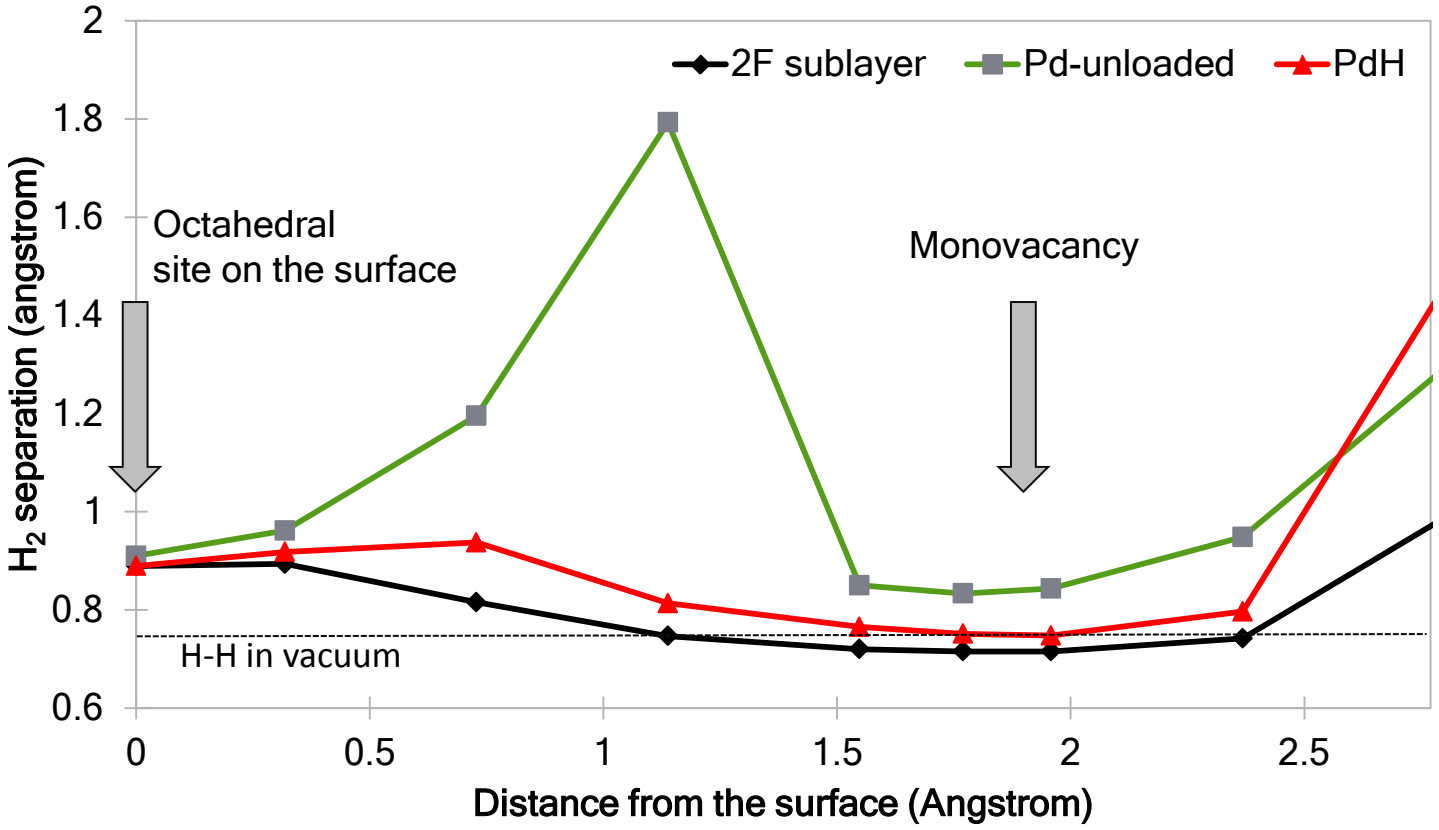
Monovacancy in subsurface layer case I – pure Pd



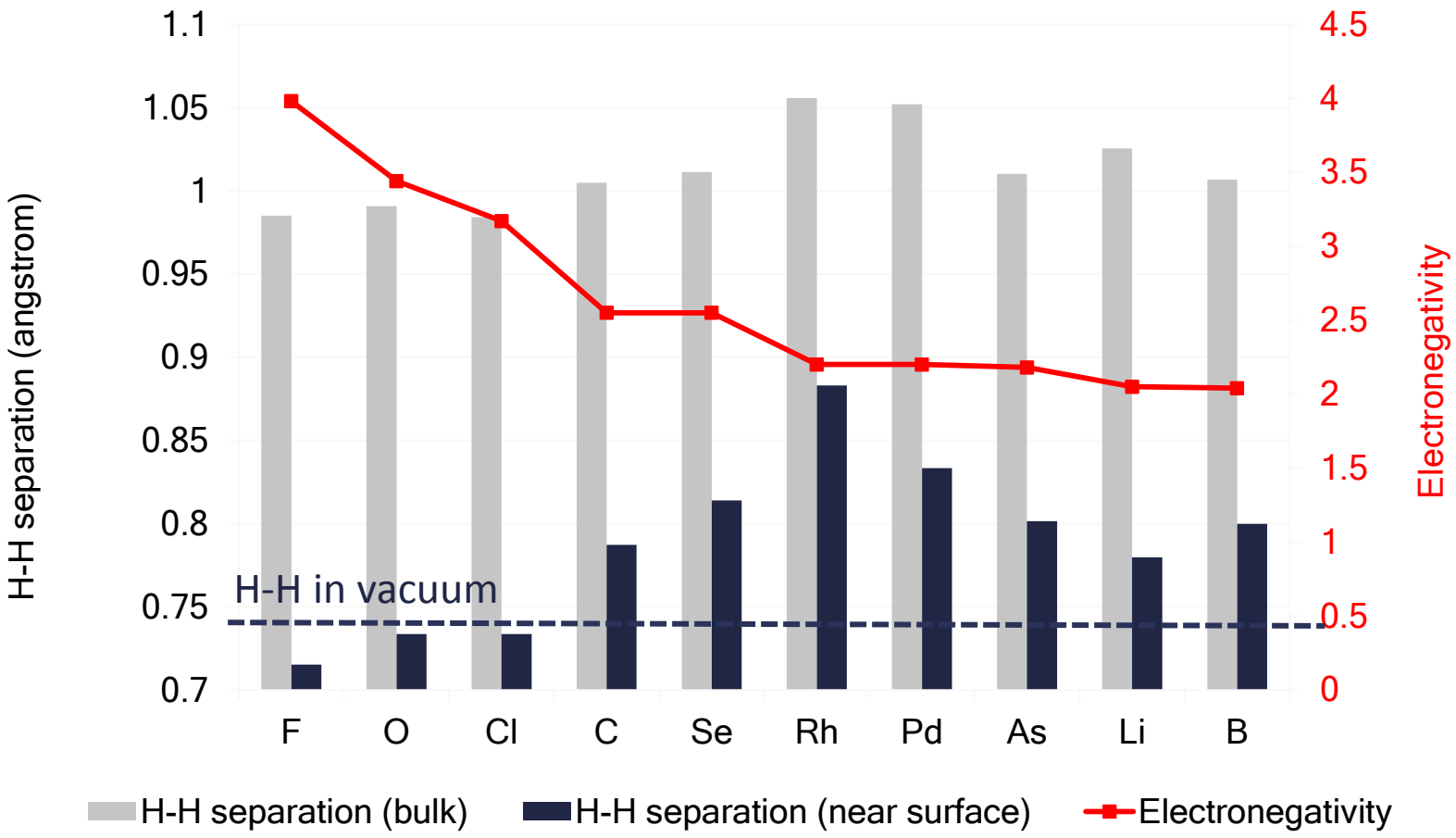
Monovacancy in subsurface layer case II – PdH



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

- QantumEspresso 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.

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