Using numerical simulations to better understand the Cold Fusion Environment

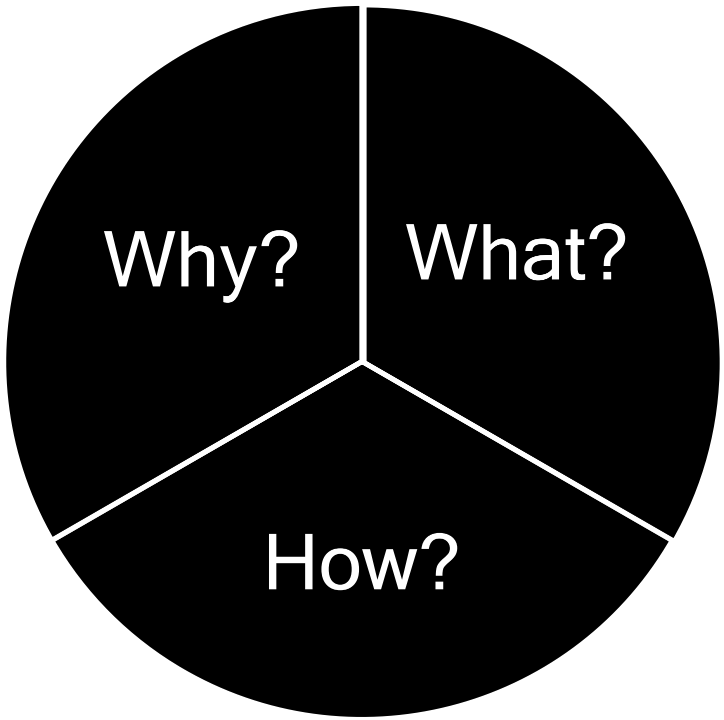
Coolescence LLC
Boulder, Colorado, U.S.A.

Outline

- Why? What? How?
- Numerical simulations:
  - Density functional theory
  - Software evaluation
  - Modeling (effect of etch on exposed crystal planes on the surface)*

*) Modeling results on hydrogen absorption inside near surface voids in the presence of impurities were presented at ICCF-18, Missouri, 2013

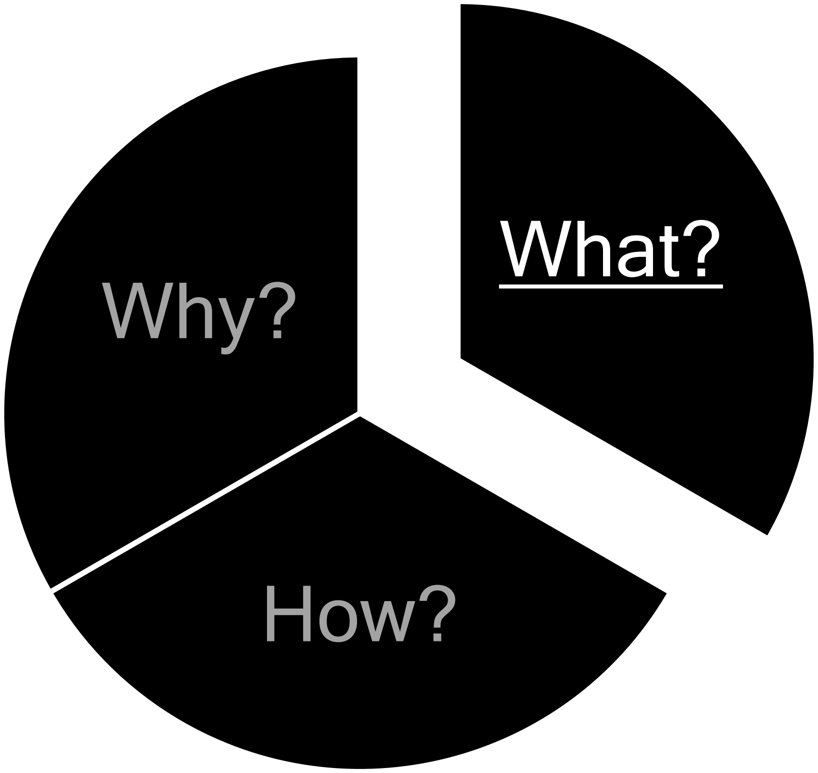
Numerical simulations



Why? - reasons

- To better understand
  - Study the important parameters (hydrogen loading, crystallographic composition, surface morphology, chemical composition, magnetic properties, etc.)
- To save time and resources
  - Model chemical environment of wide variety of material systems
- To enhance the effect
  - Through further optimization of important material parameters

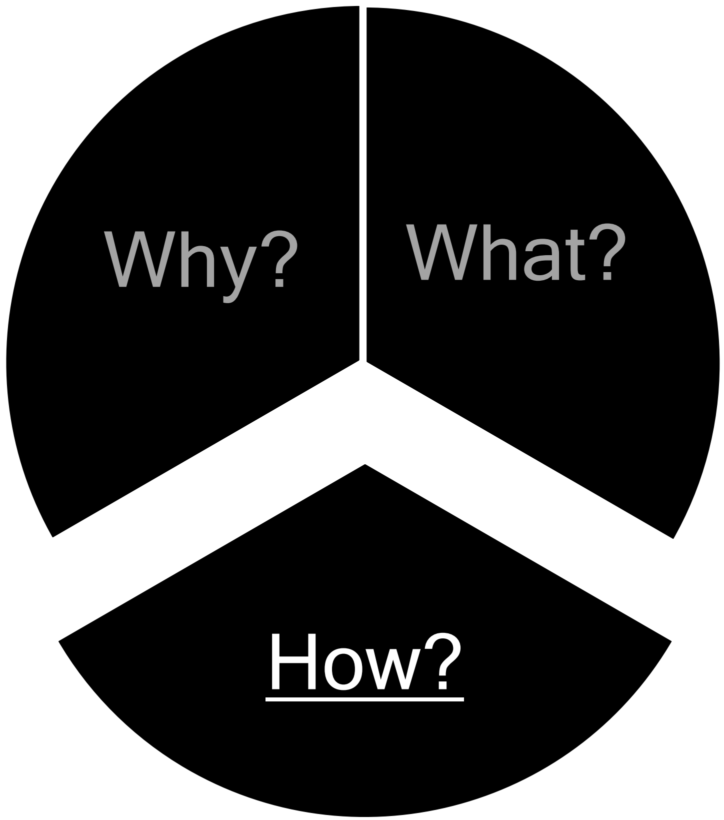
What? are we going to study (parameters)



What? - parameters

- Hydrogen/Deuterium adsorption and absorption conditions
- Surface morphology/crystallography/chemistry
- Change of physical (measurable) properties of Pd alloy material

How? are we going to solve (methods)



How? - methods

- **Electronic structure calculations and material modeling based on density functional theory (DFT), molecular dynamics (MD) from first principals and classical:**

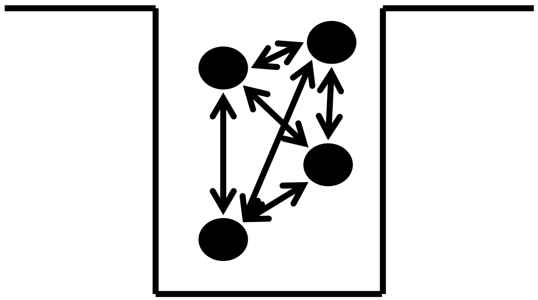
  - PWscf (QuantumEspresso)
  - ABINIT
  - VASP
  - CASTEP
  - ADF
  - ATK (Quantum Wise)
  - …

Part I
Theory

What is DFT?

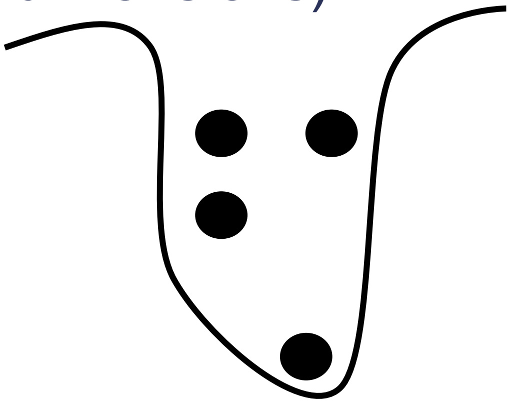
Quantum Mechanics

- Schrödinger equation describes many-body problem
- Solving for wave function (3N dimensions)



DFT

- Kohn-Sham equations for single noninteracting particles in effective potential
- Solving for electron density (3 dimensions)



Hohenberg-Kohn theorems

Theorem I

- **Ground state properties of a many-electron system are uniquely determined by an electron density**

electron density defines potential => potential defines solution of SE => wave function => one-to-one mapping between wave function $\psi_i(\mathbf{r})$ *and electron density* $n(\mathbf{r})$

Theorem II

- **Electron density that minimizes energy of the overall functional is the true electron density**

This true electron density corresponds to the full solution of SE

What is functional?

- FUNCTION: g(x)
  - example:

$$g(x) = \sin(x) + 2x - e^x$$

- FUNCTIONAL: F[g(x)]
  - example: definite integration operator:

$$F[g] = \int_a^b g(x)dx$$

Hohenberg-Kohn theorems

Theorem I

- Ground state properties of a many-electron system are uniquely determined by an electron density (n)

Theorem II

- Electron density that minimizes energy of the overall functional is the true electron density

$$E[n] = E_{N-e}[n] + T[n] + E_{e-e}[n] =$$

$$= \int V_{N-e}(\vec{r})n(\vec{r})d\vec{r} + F_{HK}[n]$$

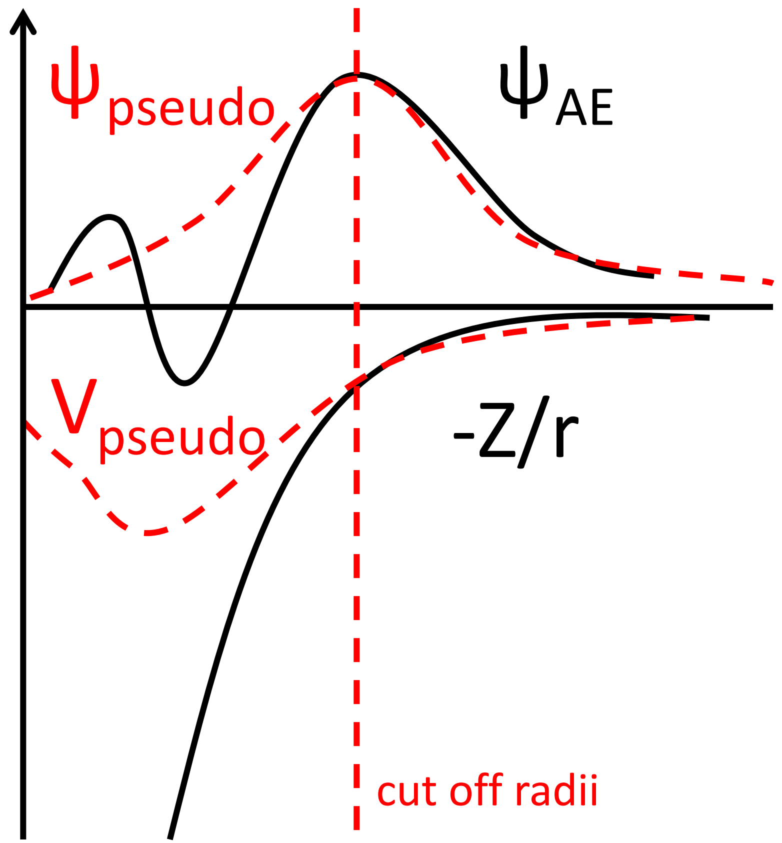
$$E_{ground} = \min_{n(\vec{r})}\left\{F_{HK}[n(\vec{r})] + \int V_{N-e}(\vec{r})n(\vec{r})d\vec{r}\right\}$$

Approximations

- To close gap between many-body Schrödinger system and Kohn-Sham equations we need to know exchange-correlation functional (term that includes all many-body interactions)
  - Local density approximation (LDA) based on electron density at each location
  - Generalized gradient approximation (GGA) based on electron density and its gradient
  - Empirical functionals

Approximations

- The pseudopotential is an effective potential constructed to replace the atomic all-electron potential (full-potential) such that core states are eliminated and the valence electrons are described by pseudo-wavefunctions with significantly fewer nodes



What DFT can and cannot predict?

DFT can predict

- Electron density
- Total energy
- Lattice constant
- Bond length
- Vibrational frequencies
- Phonon frequencies

DFT cannot predict

- Excited state energies
- Wave functions
- Band structure
- Superconductivity
- Excitons
- Electronic transport

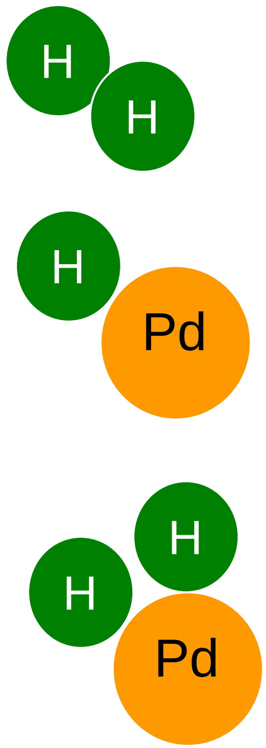
With approximations / using other methods

- Band structure
- Density of states
- Fermi surface
- Electronic transport

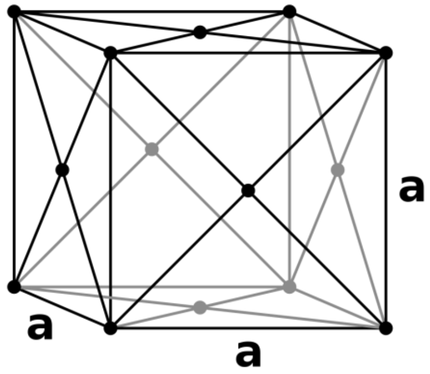
Part II
Evaluation

Evaluation of our DFT simulations

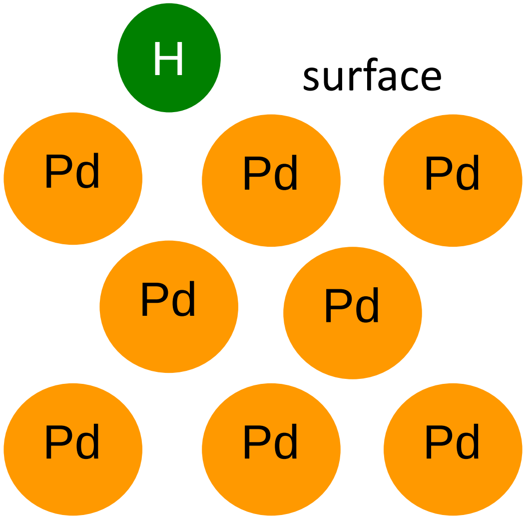
Binding Energy



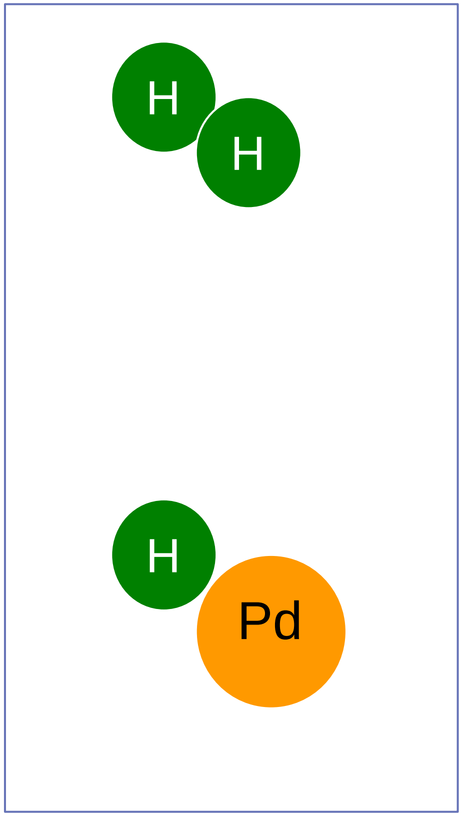
Lattice parameters

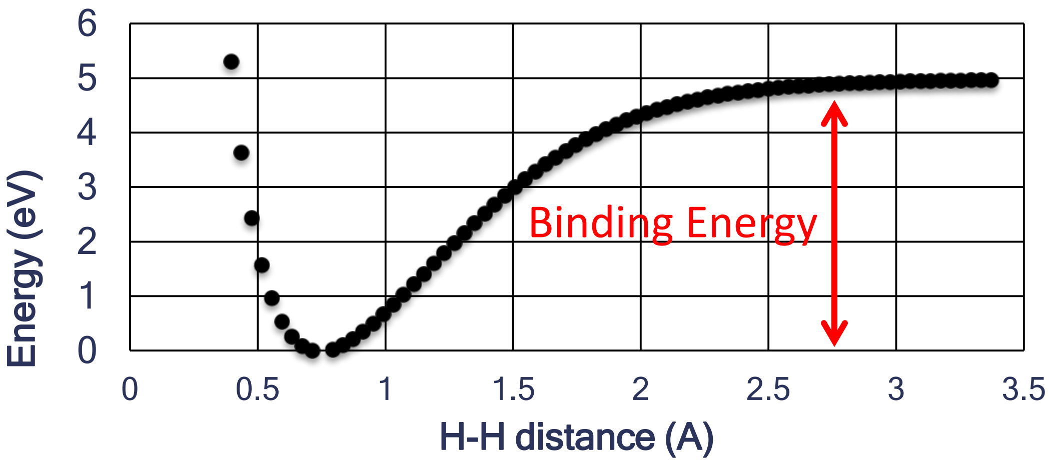


Adsorption Energies



Evaluation. Binding energy H_2 and PdH

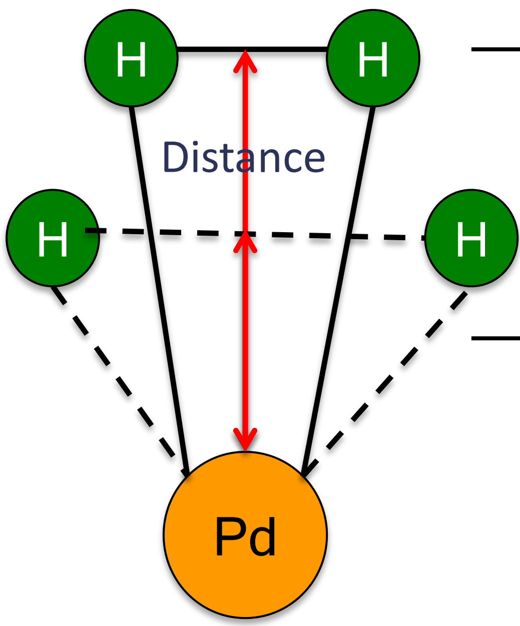


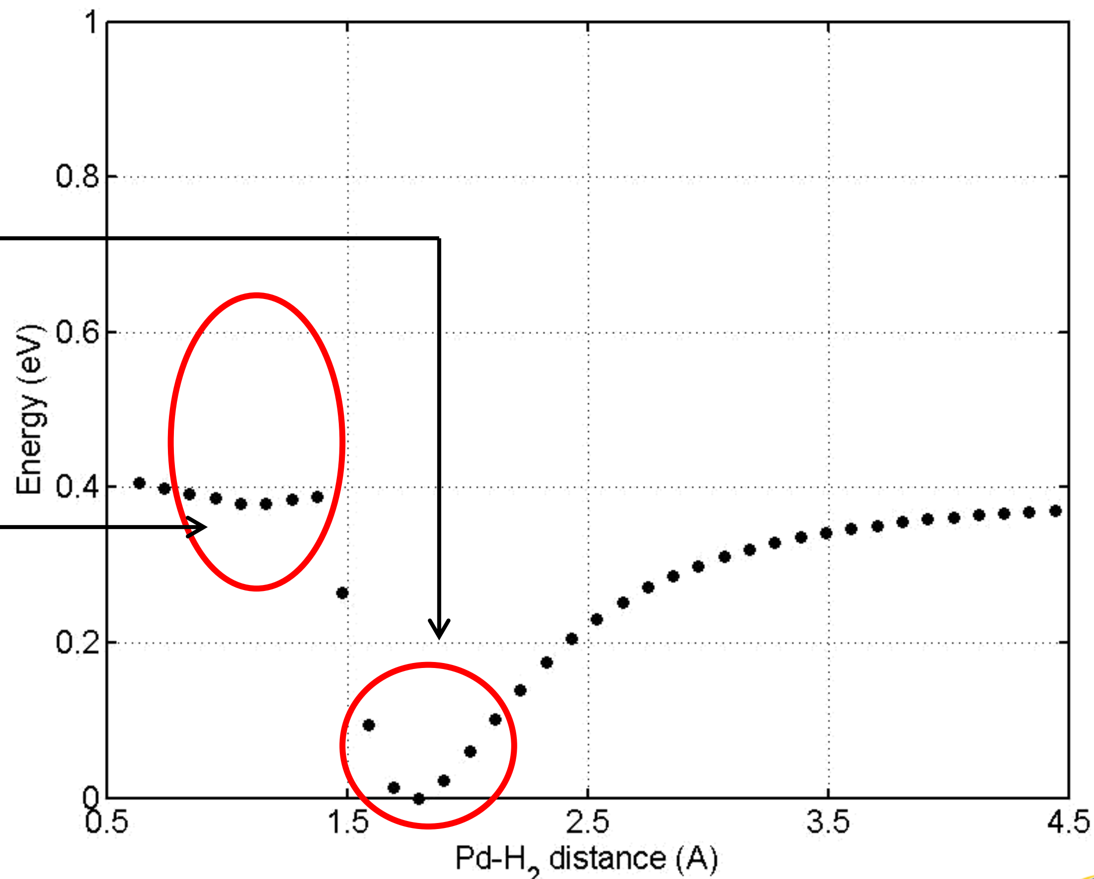


	H-H	Pd-H
Binding energy (eV) reference / calculated	4.52 / **4.97**	2.34 / **2.12**
Separation (A) Reference /calculated	0.74 / **0.75**	1.55 / **1.57**

Evaluation. Binding energy. Pd-H_2

Effect of using different pseudopotentials
valence electrons distribution





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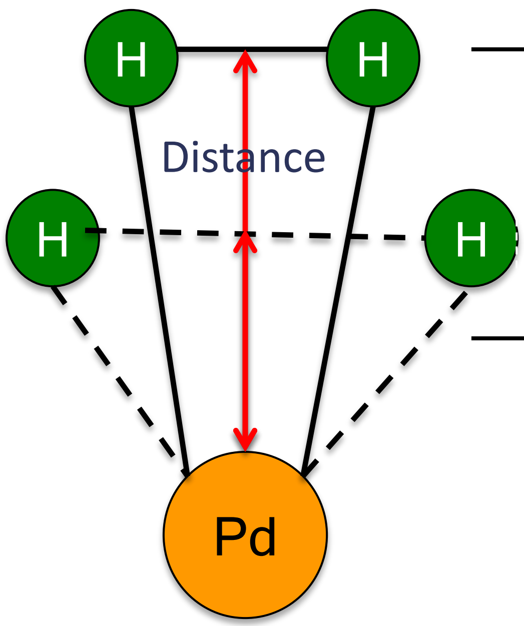
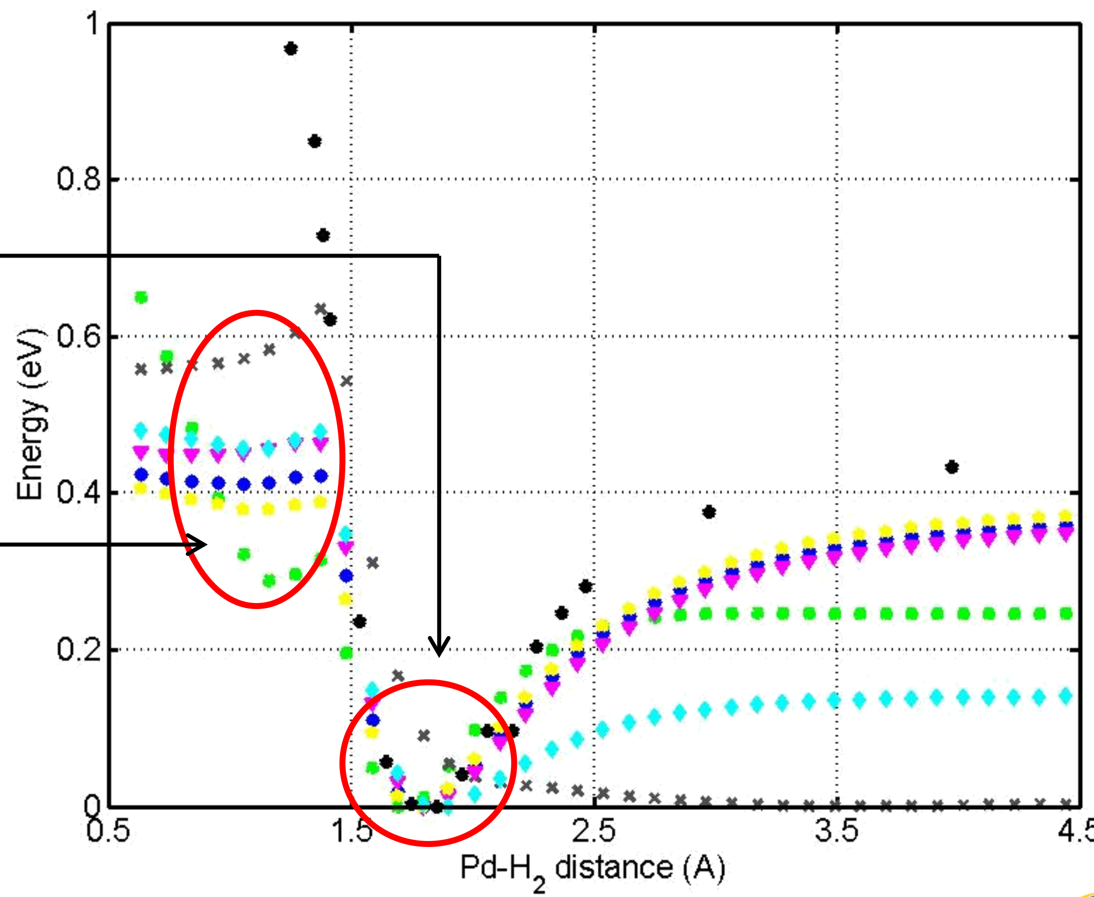
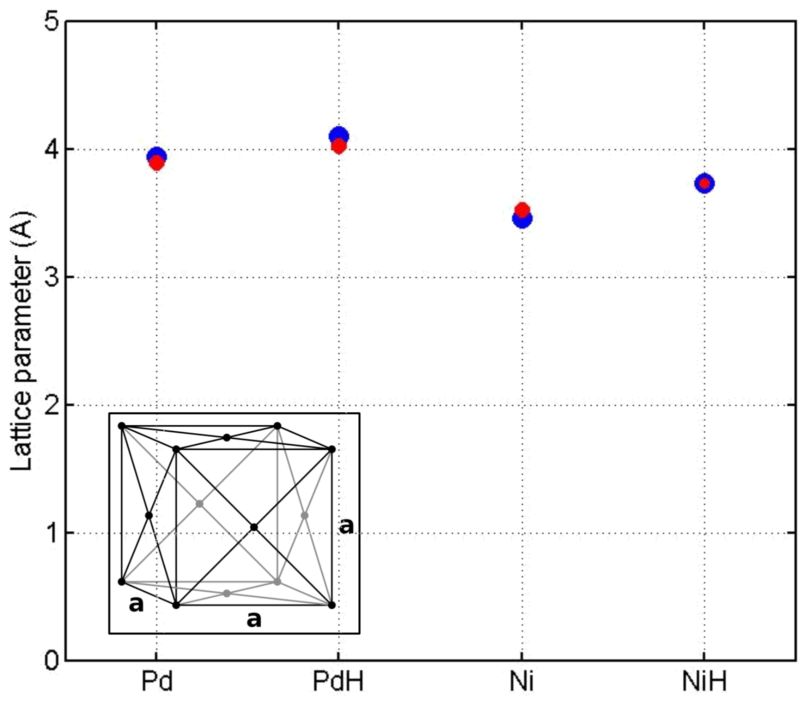


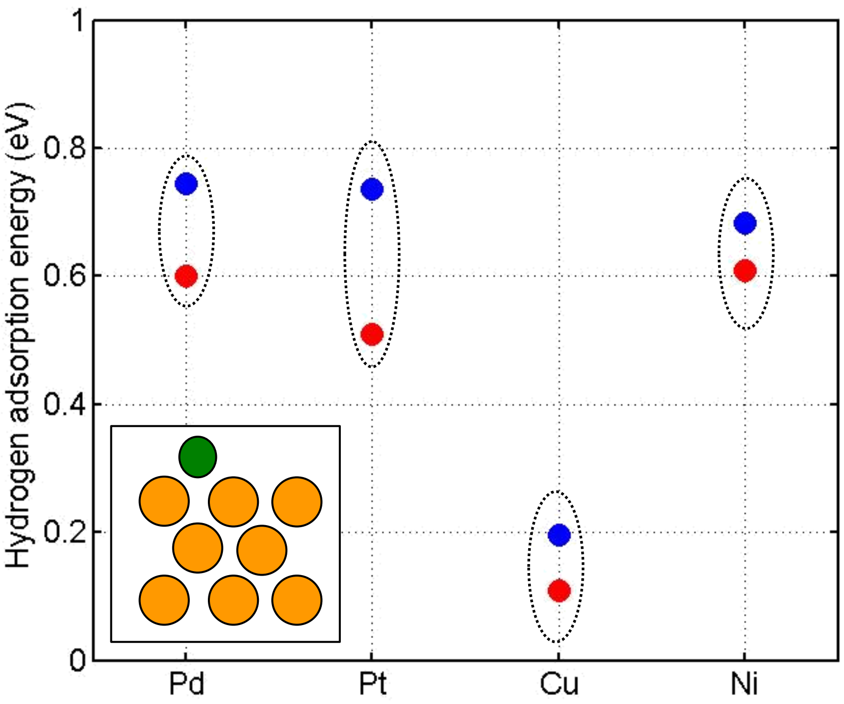


Evaluation. Lattice parameters and hydrogen adsorption energies

Calculated within DFT
Experimentally measured



Accurate within <0.1A



Accurate within ~0.2 eV

Evaluation summary

- Quantum Espresso and ADF DFT codes were evaluated.
- The results on bulk and surface calculations are in close agreement with references

Part III
Modeling

Modeling

H_2/D_2 in Palladium/Nickel alloys

High H/D loading ratio

- Change in screening potential
- Adsorption energy function of loading ratio
- Change in transport properties in PdH

Defects, Crystallography

- Atomic and molecular absorption in cracks/ voids etc
- Preferential hydrogen adsorption through crystallographic planes

Impurities, Etch

- Change in adsorption energy
- Selective adsorption

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- Selective adsorption

Effect of etch on exposed crystal planes on the surface

- Vittorio Violante (ENEA, Italy)* emphasized the importance of (100) crystal plane orientation in successful LENR replications

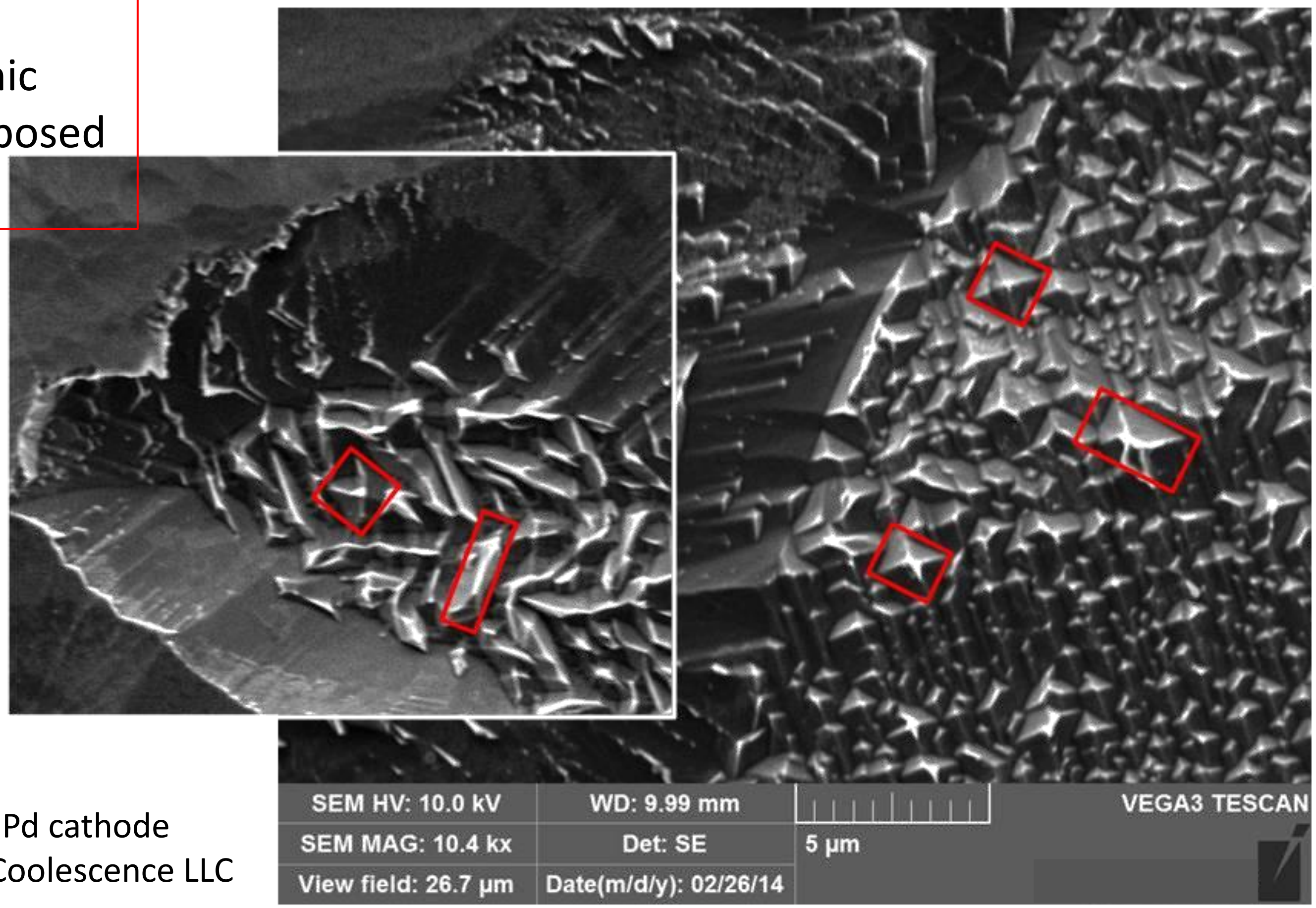
  *) V. Violante, E. Castagna, S. Lecci, M. Sansovini, G. Hubler, D. Knies, K. Grabowski, M. McKubre, F. Tanzella, C. Sibilia, Z. Del Prete, T.Zilov "Evolution and Progress in Material Science for Studying the Fleischmann and Pons Effect (FPE)"

- Cathode fabrication is a multi-step process that involves etch and annealing
- Etch and annealing affect the crystallographic composition of the cathode surface

Pd cathode fabricated at Coolescence LLC

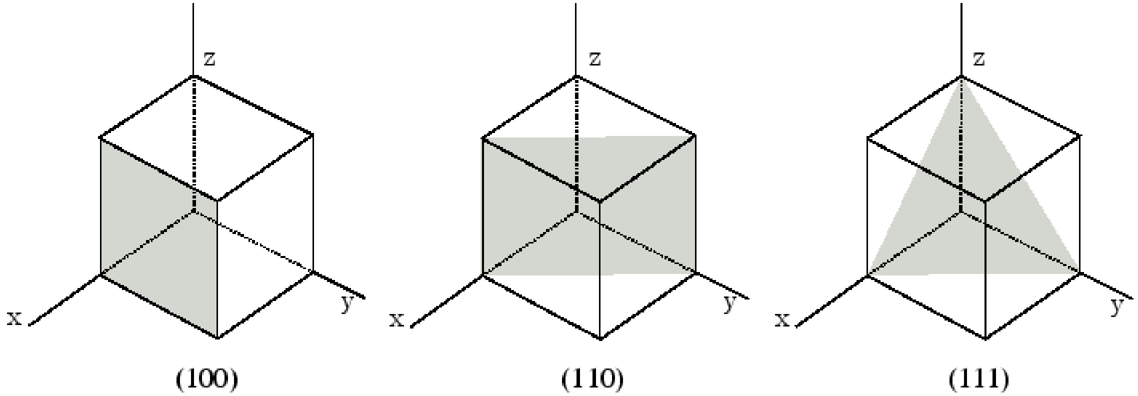
Effect of etch on exposed crystal planes on the surface

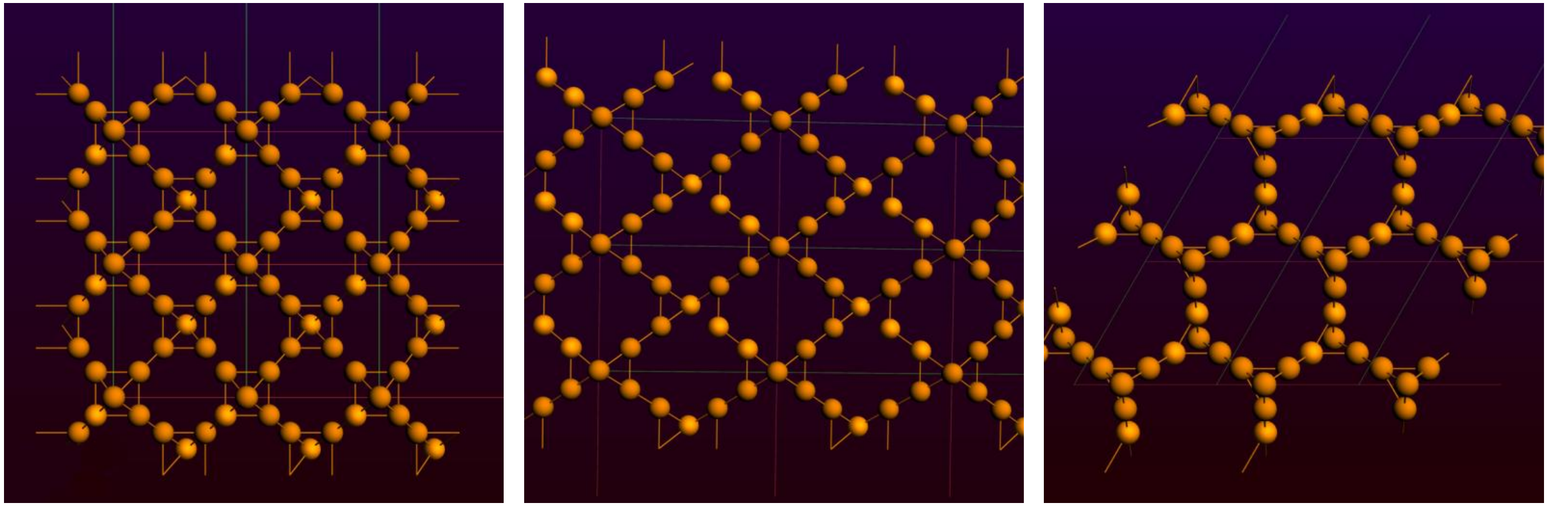
Different crystallographic planes are exposed by the etch



SEM image of Pd cathode fabricated at Coolescence LLC

Effect of etch on exposed crystal planes on the surface

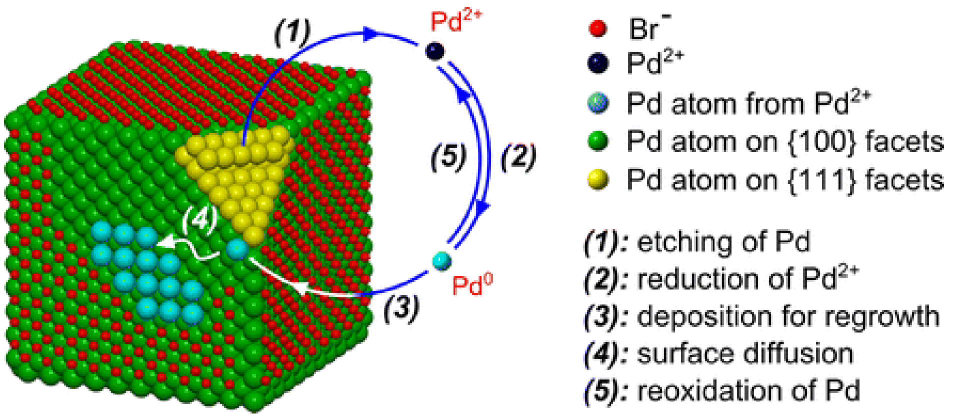




Effect of etch on exposed crystal planes on the surface

- Adsorption energy depends on crystallographic plane

- Possible implications:
  - anisotropic etch;
  - variation in impurities concentration (grain surface vs boundaries).



M.Liu et al "Transformation of Pd nanocubes into Octahedra with controlled sizes by maneuvering the rates of etching and regrowth", J. Am. Chem. Soc. 2013, 135, 11752-11755

Effect of etch on exposed crystal planes on the surface

Simulations set up

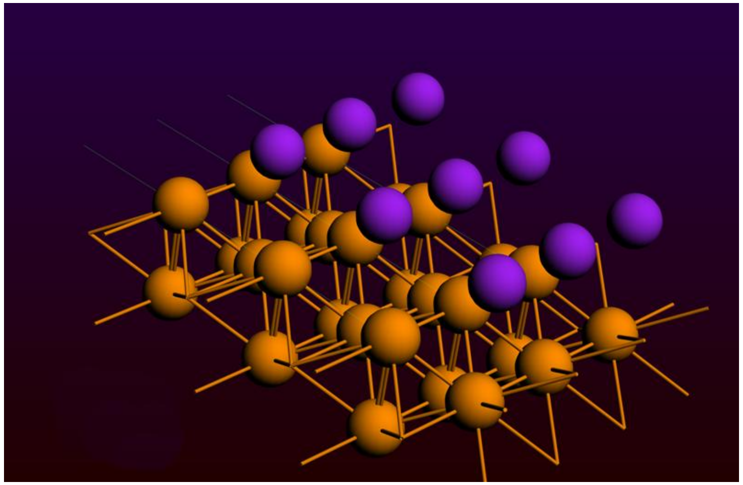
- Elements: H, Br, Cl, F, I
- Adsorption sites: (100), (110), (111)

$\underbrace{\hphantom{Elements: H, Br, Cl, F, I; Adsorption sites: (100), (110), (111)}}_{\text{15 data points}}$

- Pd surface is constructed as a slab.
- Adsorption energy:

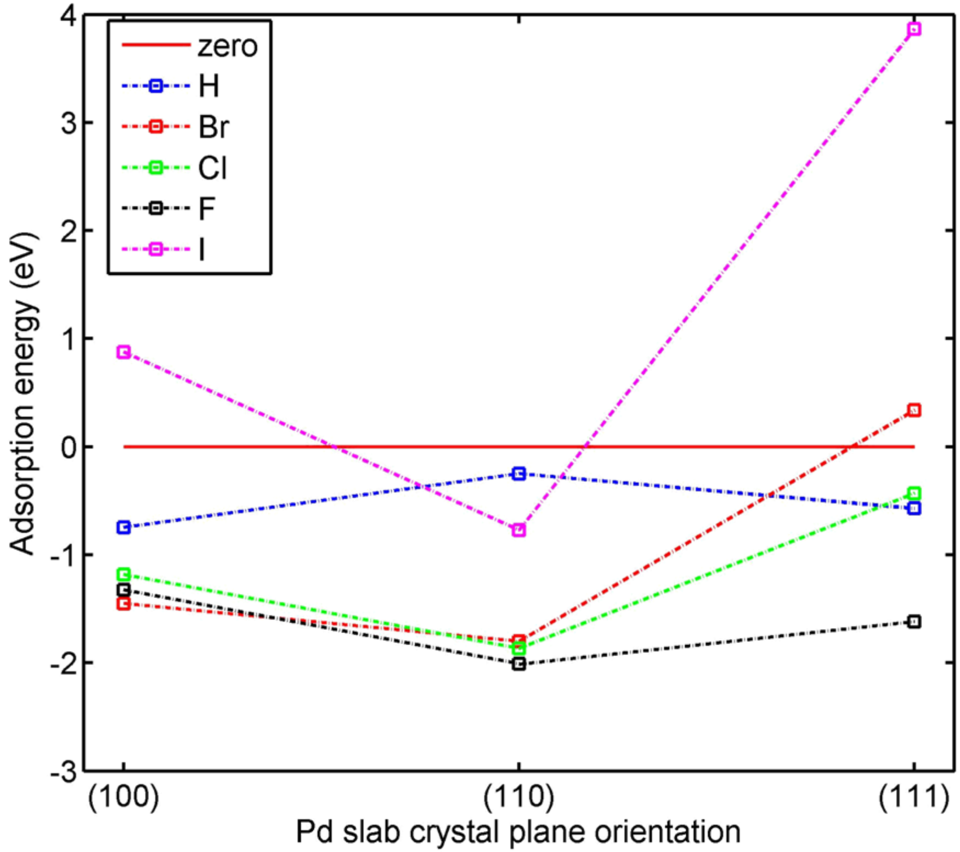
$$E_{ads} = E_{surf+H} - E_{surf} - \frac{1}{2}E_{H_2}$$

Does adsorption energy depend on crystallographic plane?



Iodine adsorbed on (100) four-folded site

Simulations result



- H will preferentially adsorbs on (100), (111)
- Br,Cl,F,I will adsorb on (100), (110)
- Halogens may interfere/compete with hydrogen adsorption sites on Pd surface

Modeling summary

- Wet etch on Pd cathode can be highly anisotropic to affect different crystal planes exposure on the surface
- Halogens may interfere/compete with hydrogen adsorption sites on Pd surface
- Molecular dynamics simulation may help better understand the selective adsorption on metal surface

Overall conclusions

- DFT-based codes are powerful and versatile tools to study material properties and bulk/surface chemistry.
- DFT can:
  - help to understand the particularities of different material configurations
  - predict certain material properties
  - suggest material characteristics