Electronic and Energetic Properties of Helium in Pd Tritide: PdT_x ($0 \leq x \leq 1$)

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Focus of This Report

From first-principles:

- to accurately determine the energetics of interstitial He and H in Pd metal
- to better understand the interaction mechanisms among different species
- Provide input parameters for the rate equations and continum models

Outline

- Theoretical Methods
- He in Pd vs. H in Pd
- He in PdT_x where $0 \leq x \leq 1$
- Small He cluster in a defect-free Pd lattice with and without H
- Conclusion

Standard models for "First-Principles" Calculations

Inputs: Atomic number

Atomic arrangements

Ground-state properties:

Density functional theory

("One-particle" equations for the many-body problem)

Pseudopotential Methods

Calculational Methods

- Density functional theory with GGA
- Projector Augmented Wave (PAW) method
- Plane wave basis (VASP code)
- Energy cutoff: 390 - 520 eV
- Supercell containing 32 Pd atoms
- Diffusion path and barrier is studied by efficient nudged elastic band (NEB) method

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- **He in Pd vs. H in Pd**
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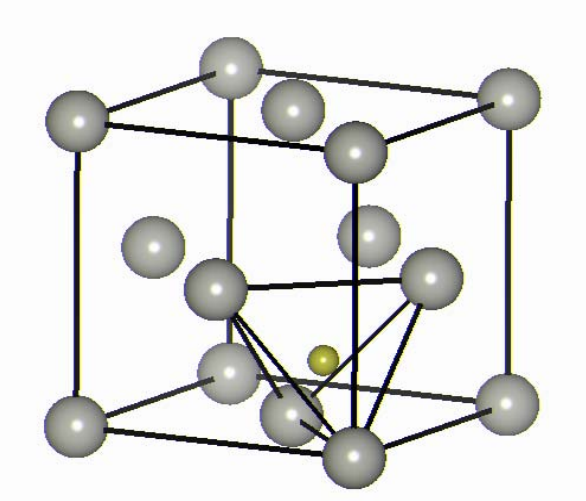
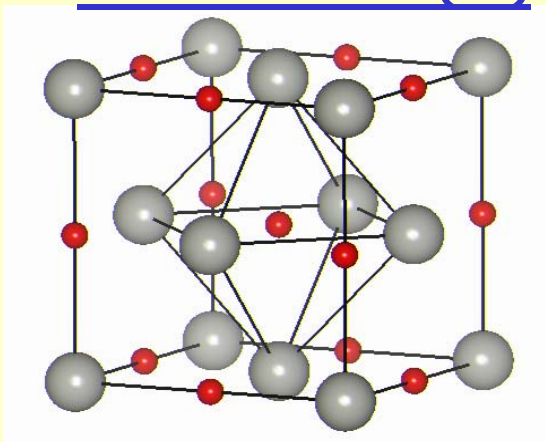
Interstitial Sites in an FCC Lattice

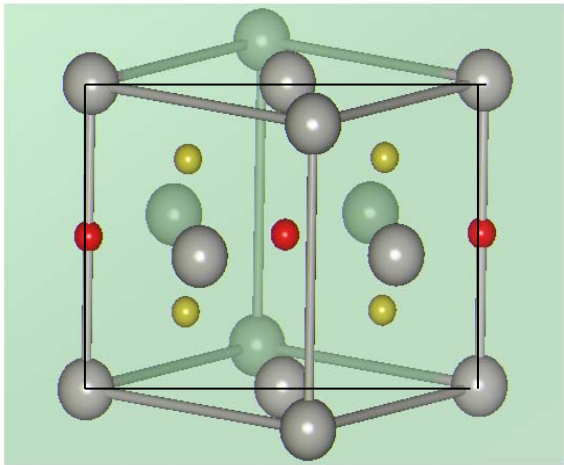
Tetrahedral (T)



Octahedral (O)

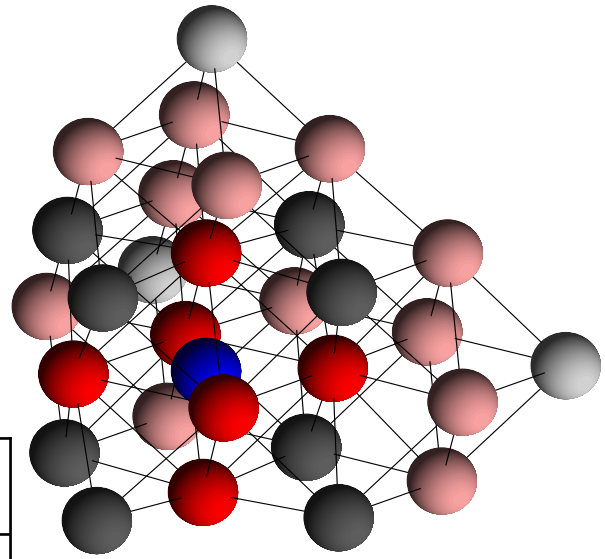


<110> plane



Both He and H energetically Prefer the O site than the T site in the Pd lattice

Lattice Distortions



He at the octahedral site:

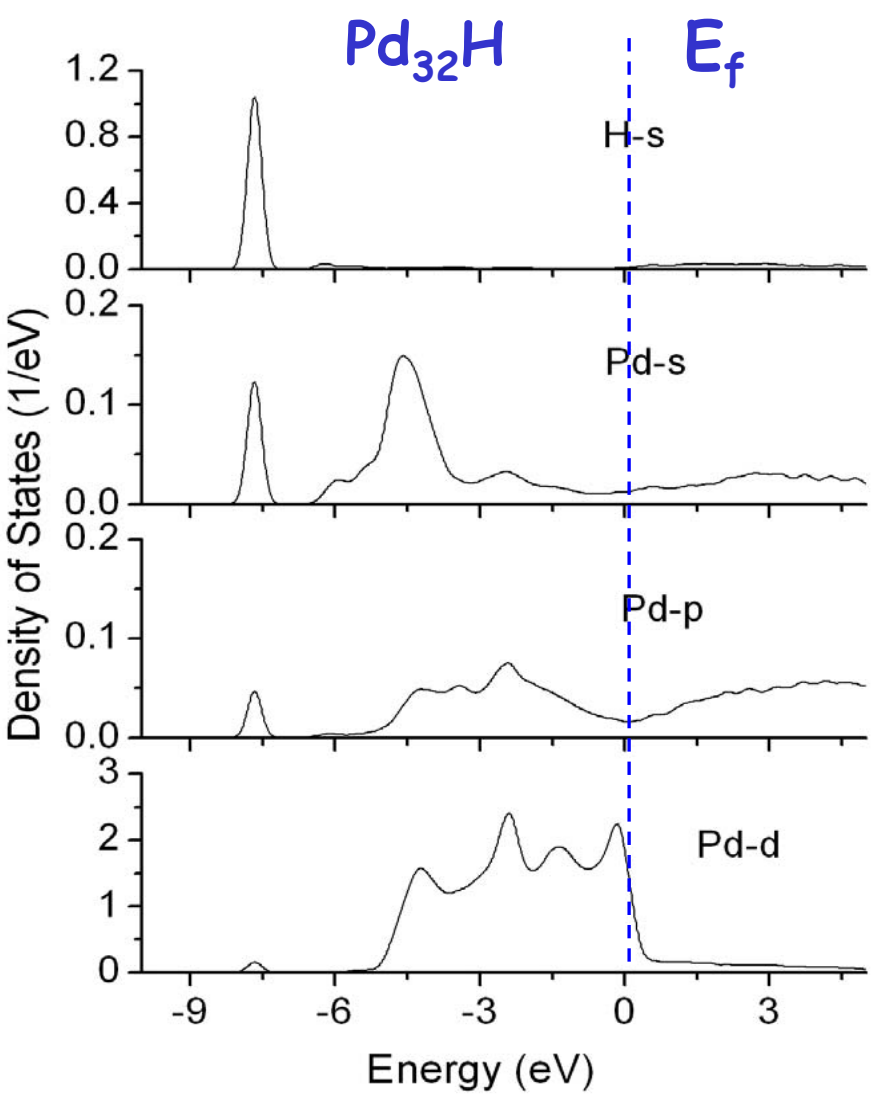
x	y	z	direct.	Δd/a	color
0.23	0.5	0.75	{100}	3.87%	Red (nn)
0.25	0.25	0.5	{111}	0.06%	Grey (nnn)
0.25	1	0.75	{100}	0.95%	light red (3rd)
1	1	1	{100}	0.40%	light grey (4th)

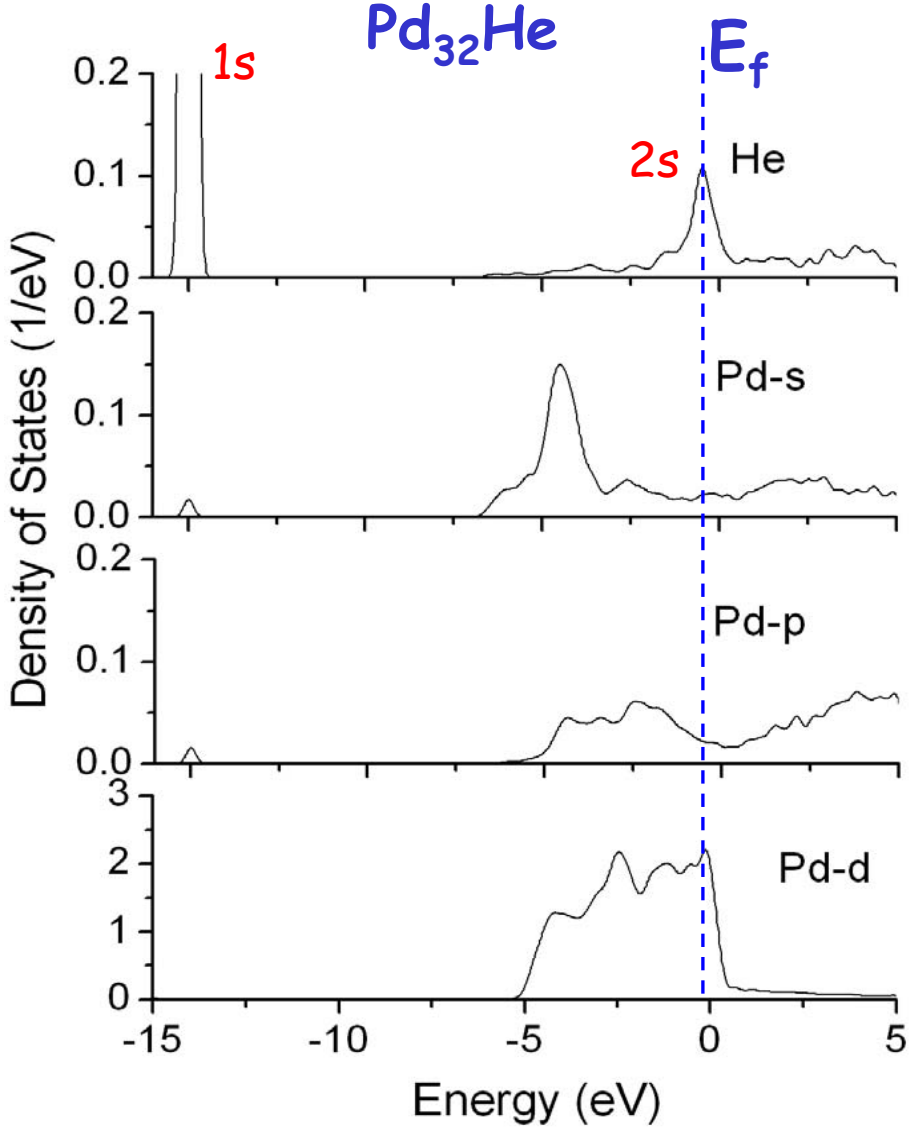
H at the octahedral site:

x	y	z	direct.	Δd/a	color
0.23	0.5	0.75	{100}	0.62%	Red (nn)
0.25	0.25	0.5	{111}	0.44%	Grey (nnn)
0.25	1	0.75	{100}	0.11%	light red (3rd)
1	1	1	{100}	0.09%	light grey (4th)

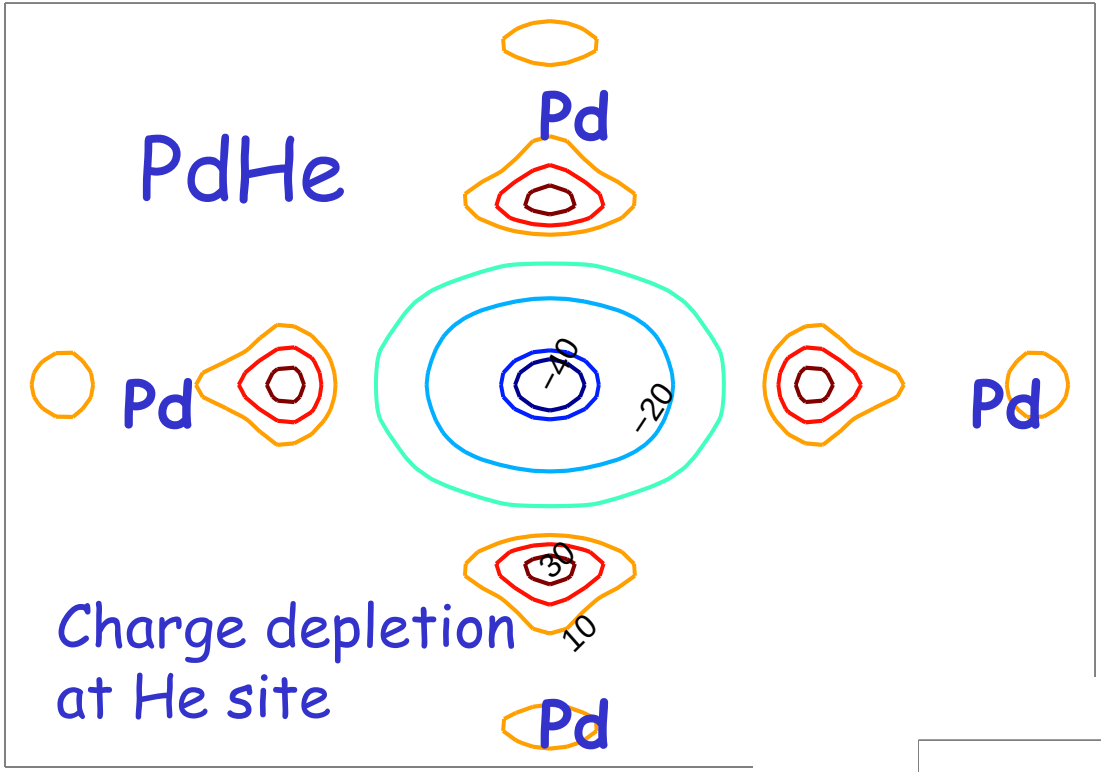
a is lattice constant

Projected density of states (PDOS)





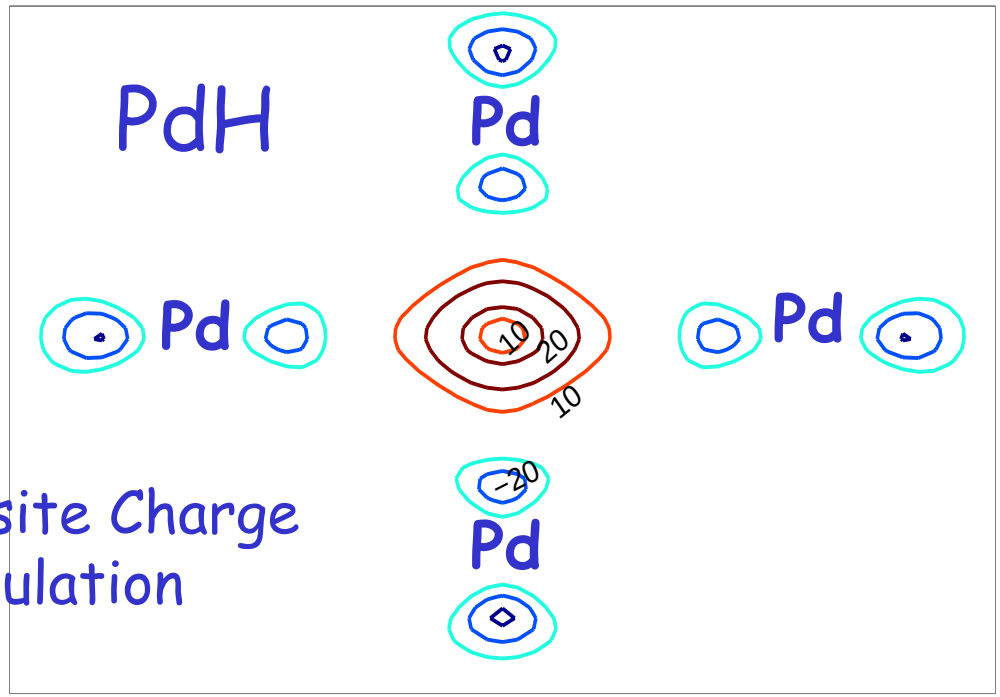
Charge Density Difference



Charge depletion at He site

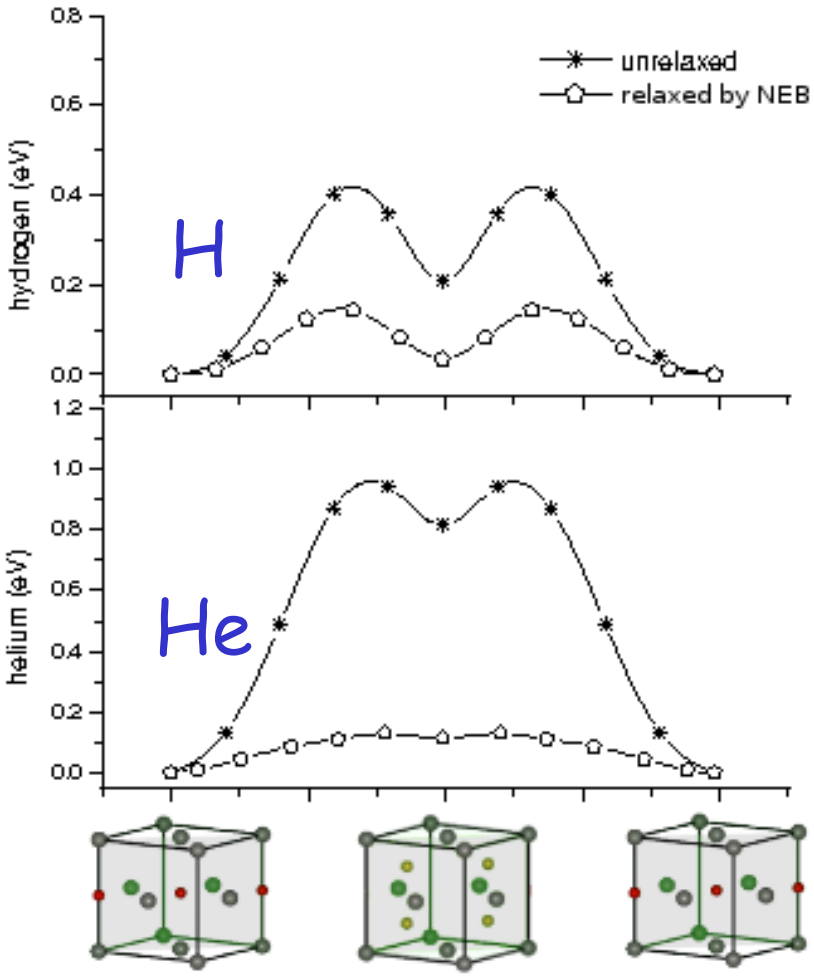
$\Delta\rho = \rho(PdHe) - \rho(Pd) - \rho(He)$

$\Delta\rho = \rho(PdH) - \rho(Pd) - \rho(H)$



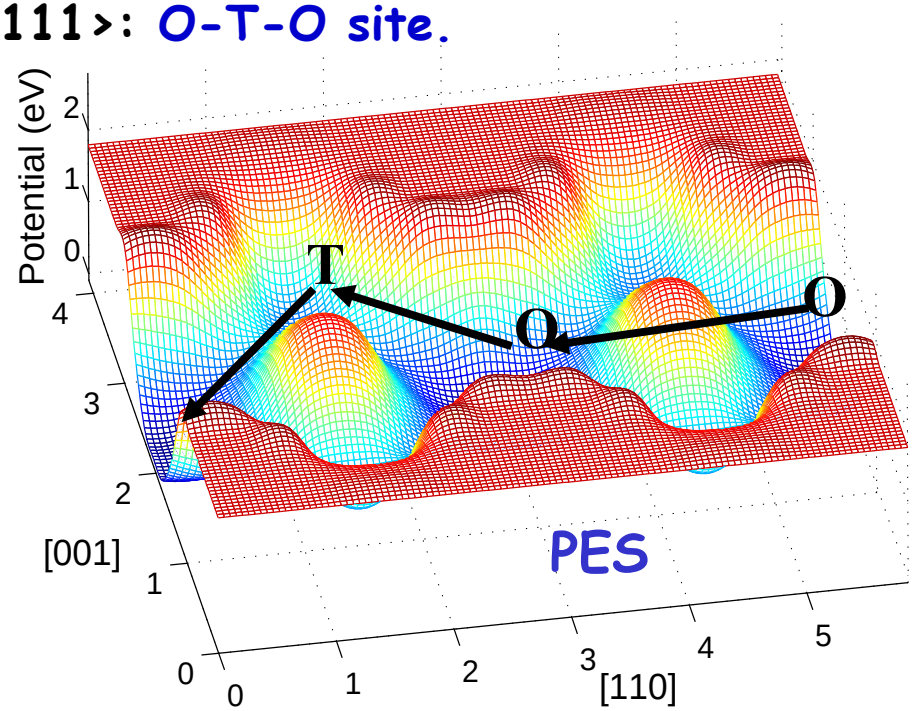
At H site Charge accumulation

He and H diffusion in Pd



<110>: directly between two O-O sites.

<111>: O-T-O site.



For both H and He, the minimum energy diffusion path is O –T-O; the local metal lattice distortion has big effects on the diffusion barrier.

Zero-point energy (ZPT) corrections

	Octahedral	Tetrahedral	TS
Hydrogen	0.08	0.19	0.16
Tridium	0.04	0.11	0.09
^{3}He	0.08	0.08	0.08
^{4}He	0.07	0.07	0.08

- ZPT has a larger effect on H than on He.
- H diffusion barrier increases from 0.16 to 0.21 eV
- He diffusion barrier remains about the same

Hydrogen Expt. ZPE = 0.06 - 0.07 eV (Rush et al. 1984)

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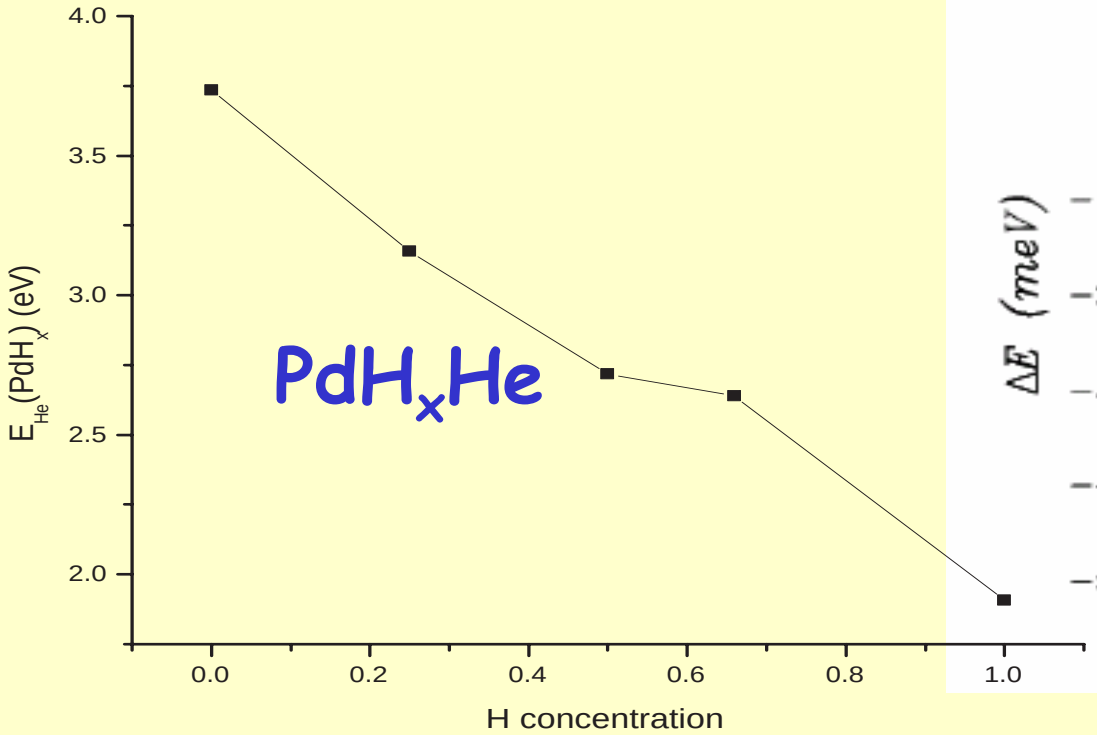
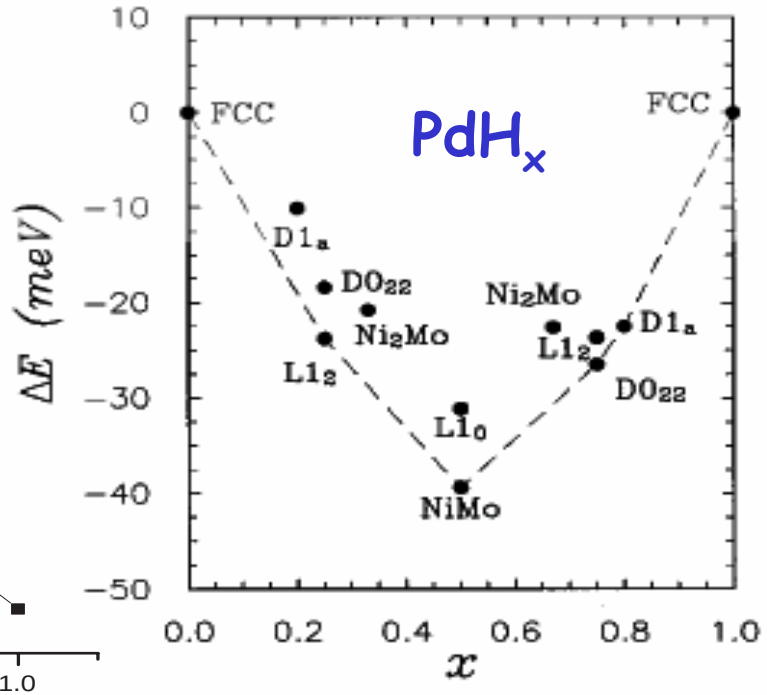
Energetics of He in PdH_x



*Yan Wang, et al. PRB **53**, 1 (1996)*

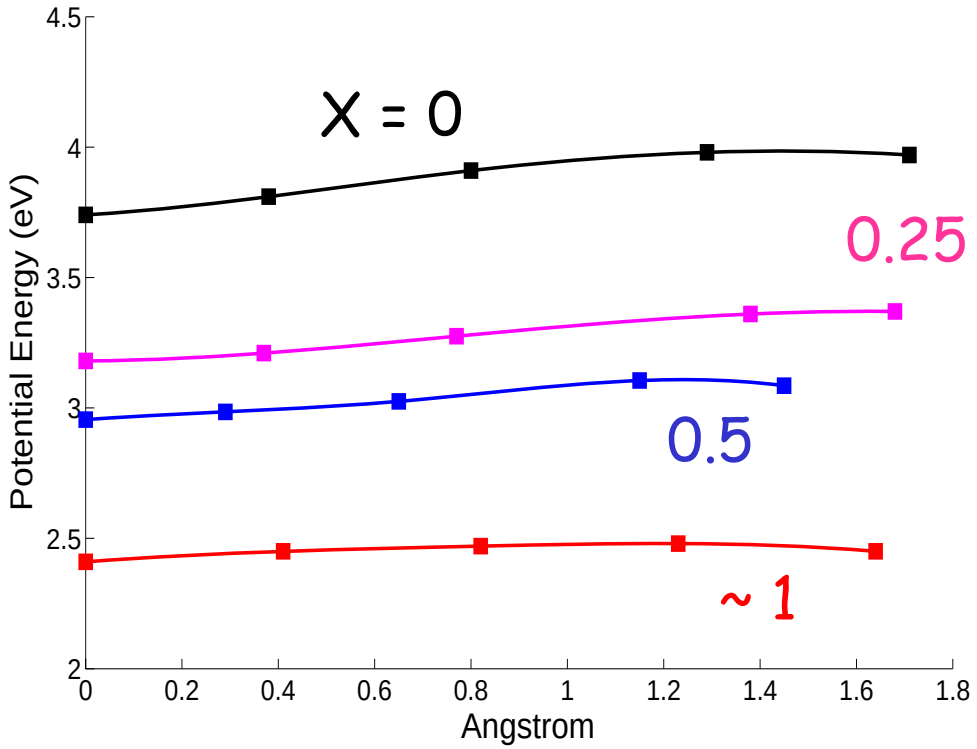


$$E_{He} = E(PdH_xHe) - E(PdH_x) - E(\text{He atom})$$

He prefers empty octahedral sites. The energy of He decreases when more H atoms present in Pd.

He Diffusion in PdH_x

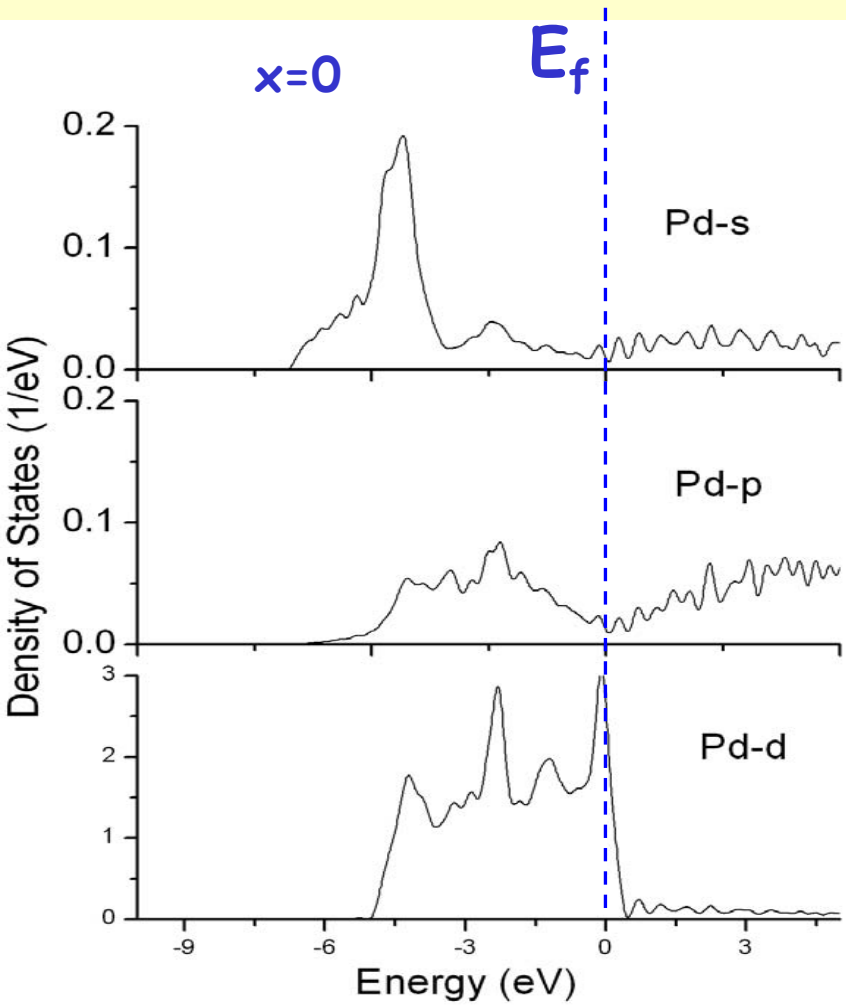
x	0	0.25	0.5	0.67	0.75	~ 1
O (eV)	3.74	3.18	2.96	2.64	2.7	2.41
T (eV)	3.97	3.37	3.09	2.77	2.83	2.45
ΔE_{T-O}	0.23	0.19	0.13	0.13	0.13	0.04

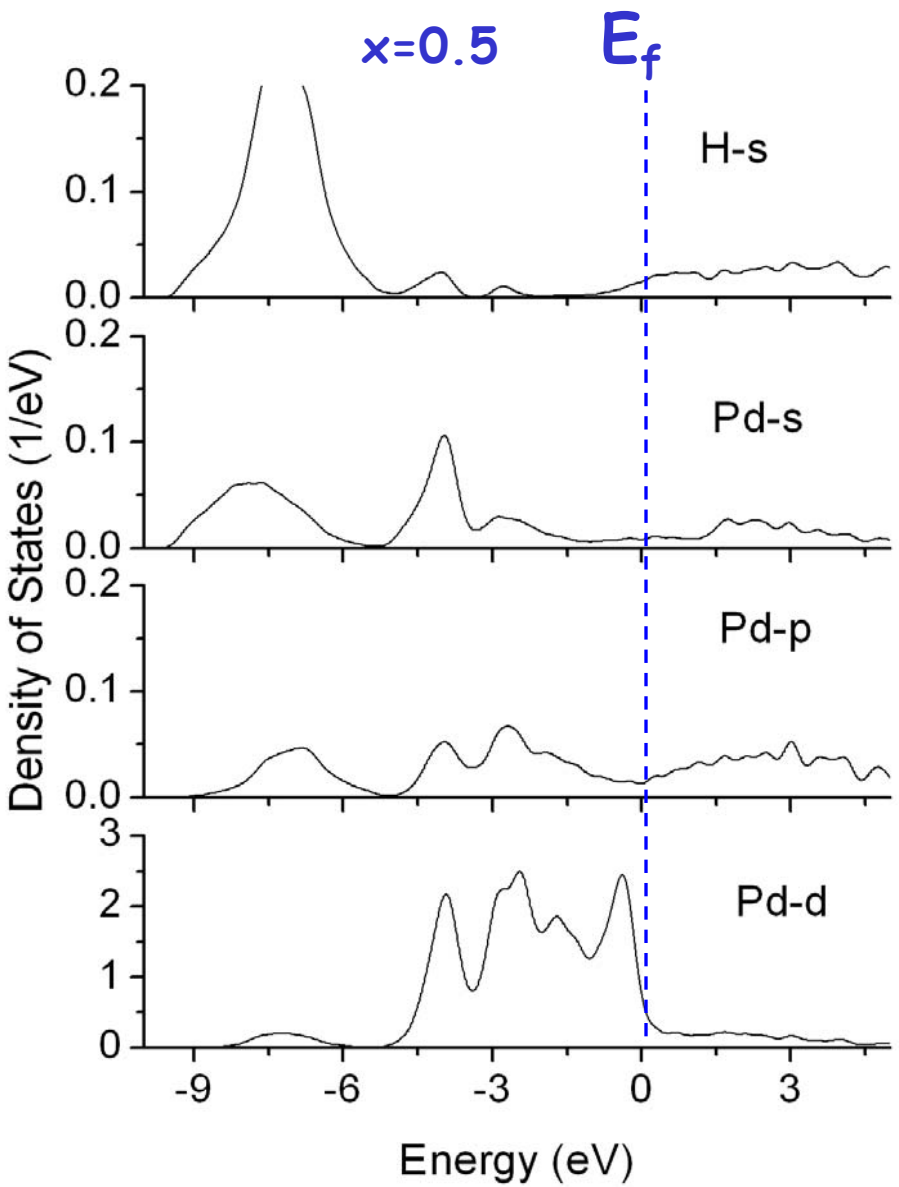


The existence of H modifies the energetics of He in the Pd metal.

PDOS

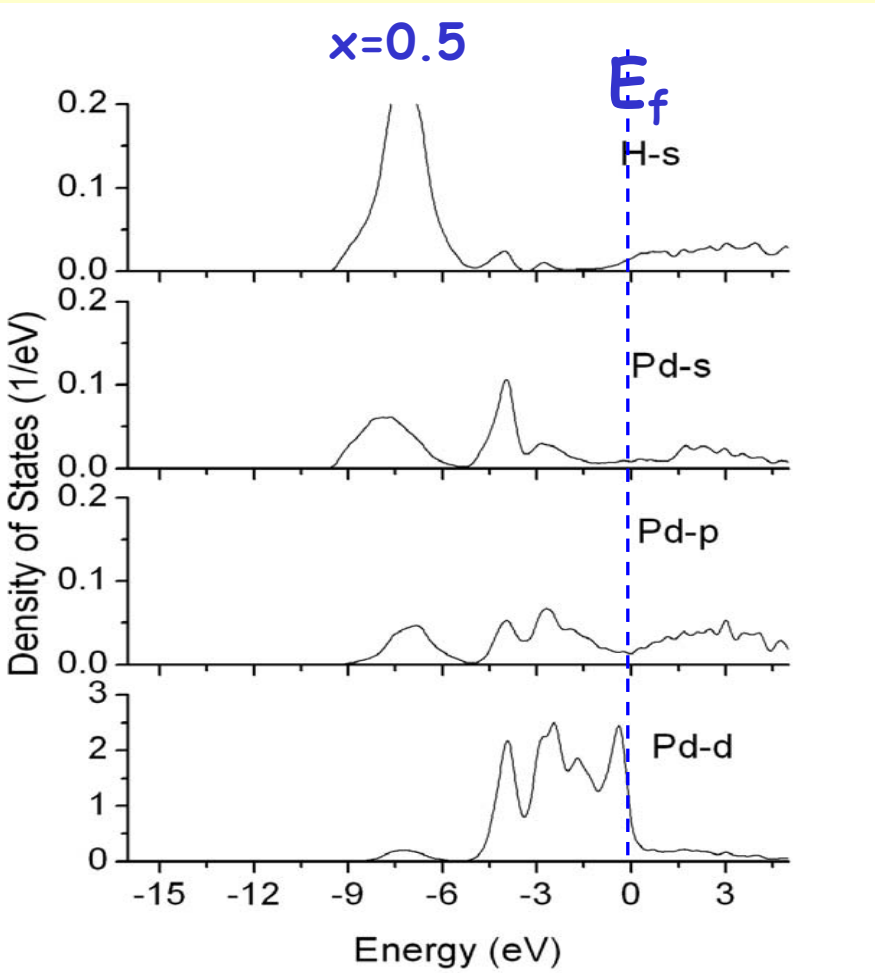
PdH_x

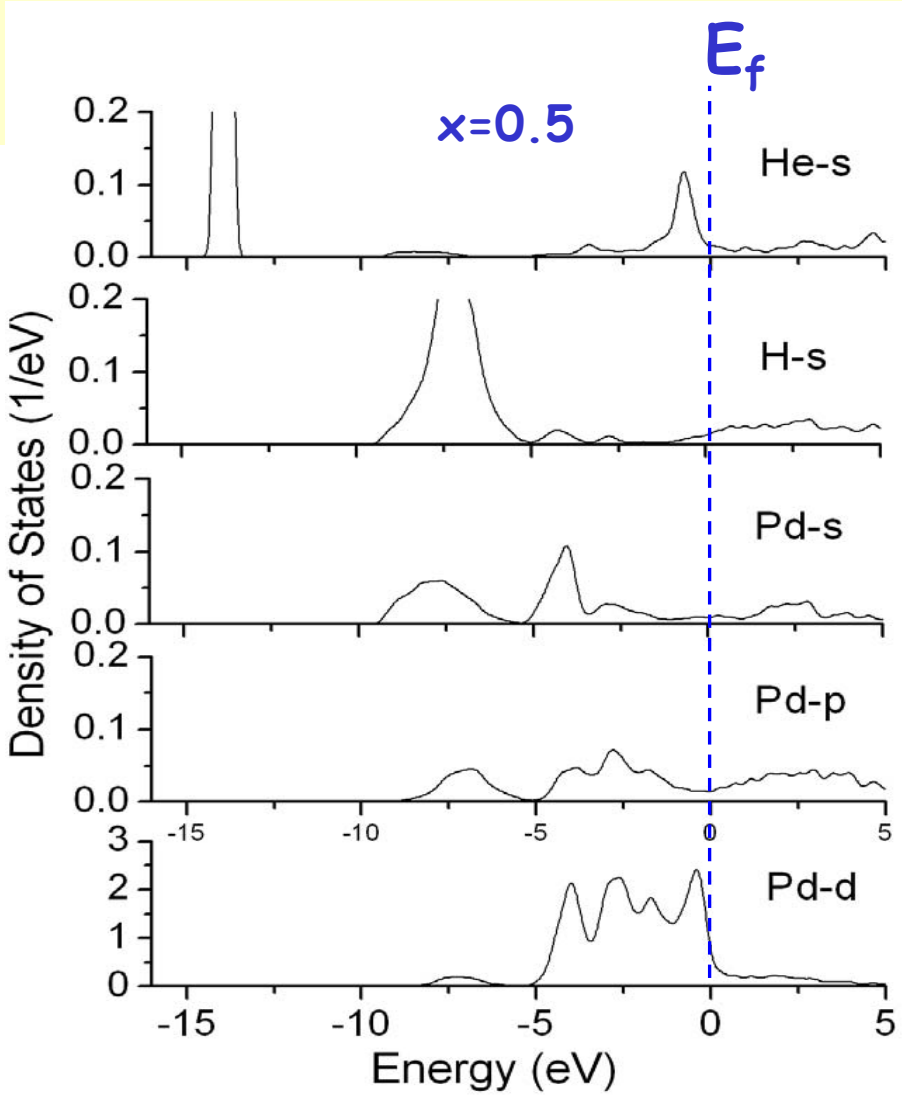

x=0
E_f
Pd-s
Pd-p
Pd-d
Density of States (1/eV)
Energy (eV)


x=0.5
E_f
H-s
Pd-s
Pd-p
Pd-d
Density of States (1/eV)
Energy (eV)

PDOS

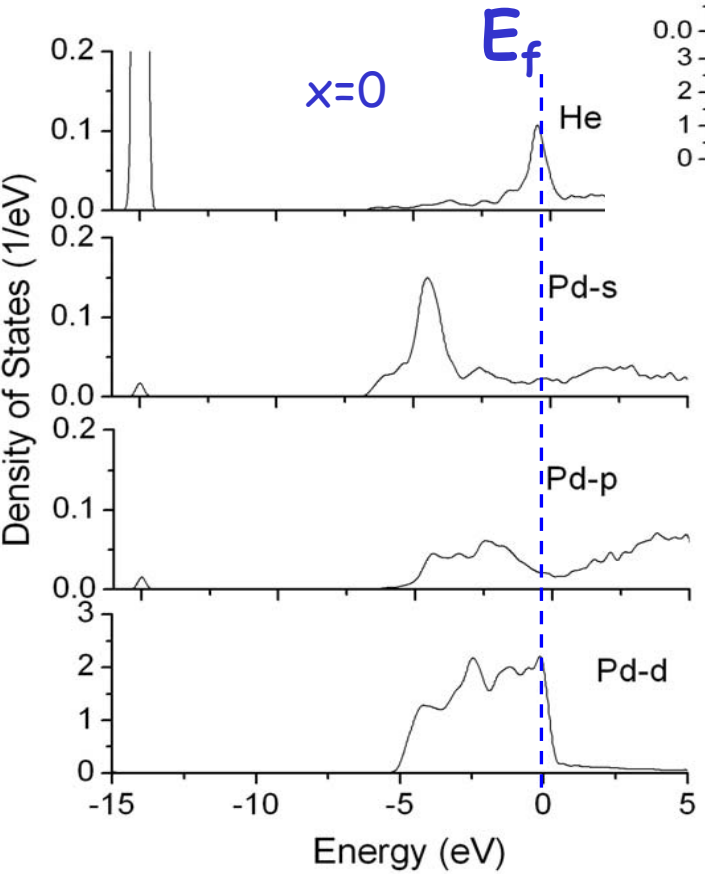
$PdH_{0.5}$ vs. $PdH_{0.5}He$

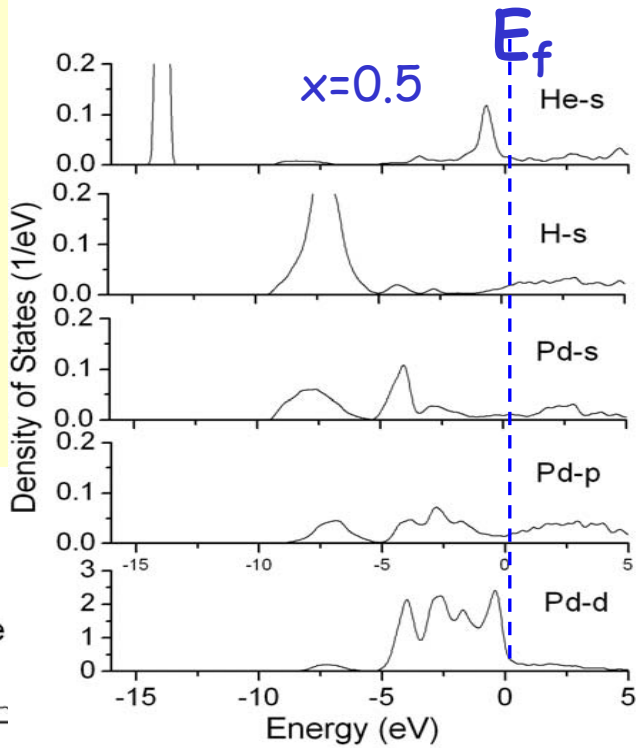


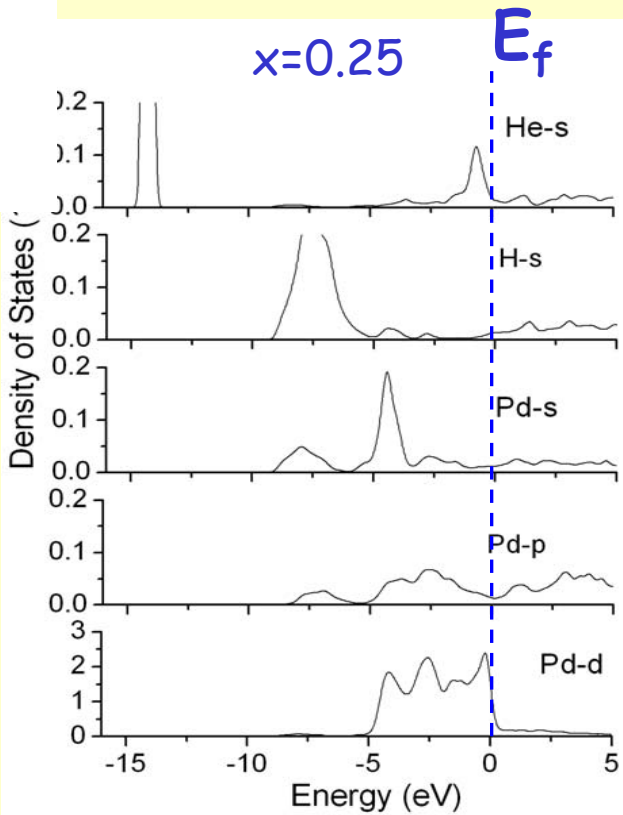


PDOS

PdH_xHe


x=0
E_f
He
Pd-s
Pd-p
Pd-d
Density of States (1/eV)
Energy (eV)


x=0.5
E_f
He-s
H-s
Pd-s
Pd-p
Pd-d
Density of States (1/eV)
Energy (eV)


x=0.25
E_f
He-s
H-s
Pd-s
Pd-p
Pd-d
Density of States (
Energy (eV)

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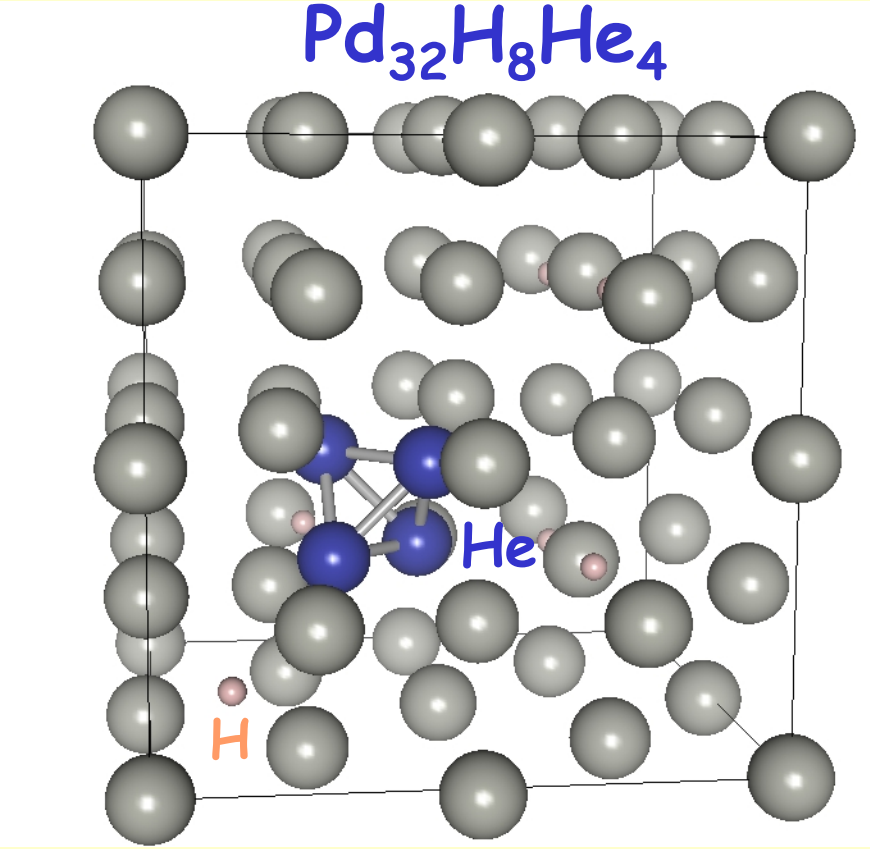
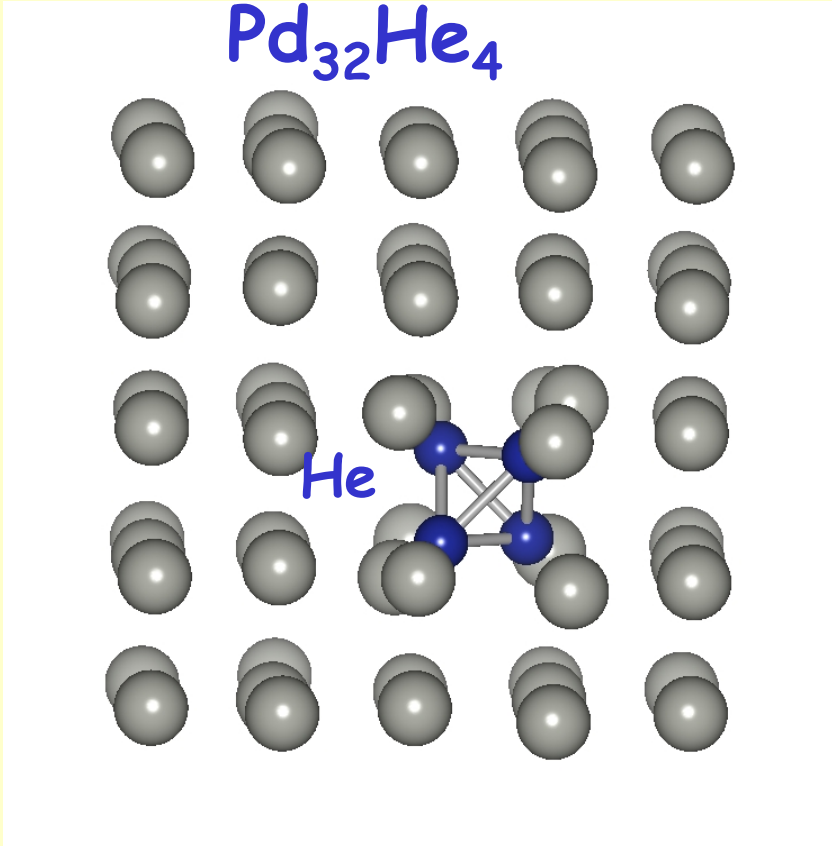
n = 4



Pd



He-He separation:
1.77~1.82 Å

He-He separation:
~ 1.79 Å

He cluster leads to local lattice distortions

Energy gain when moving one more He atom from the O site to the existing He:

Initial state	Final state	Energy gain	
		$Pd_{32}He_n$	$Pd_{32}H_8He_n$
empty O site	1 He	3.6	3.2
1 He	2 He	0.6	0.4
2 He	3 He	1.5	1.2
3 He	4 He	2.6	1.8

It is energetically favorable for He atom to aggregate together at interstitial regions.

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- Interstitial He and H interact differently with Pd metal lattice. He has a low diffusion barrier in PdH_x systems.
- The coexistence of H atoms affects the energetics of He in Pd metal.
- Forming and the growth of a He cluster is energetically favorable in Pd with and without the presence of H.
- He-He separation in the cluster is about 1.8 Å, similar to that found in systems with Pd vacancies, but much smaller than that in the solid (2.8 Å).

Future Work

- Effect of H presence on He clustering around the vacancy
- Multiple vacancies – nano He bubble
- Preferred shape of the nano bubble
- Growth of the nano bubble by emitting Pd self-interstitial atoms