First-Principles Studies of He Diffusion and Clustering in Pd

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He Bubbles in Metals

Nucleation, Growth, and Interaction:

Multi-scale simulations needed

This atomistic study focuses on the nucleation stage.

Purposes: Accurate determination of the energetics of relevant configurations from first-principles

Provide input parameters for the rate equations and continuum models

Better understanding of microscopic processes

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

Density Functional Theory

Hohenberg and Kohn, 1964; Kohn and Sham, 1965
(1999 Nobel Prize in Chemistry)

For interacting electrons in an external potential, the total energy is a functional of the density, $n(\vec{x})$

$$\mathrm{E}\,[n] = T_0[n] + \int V_{ext}(\vec{x})\, n(\vec{x})\, \mathrm{d}^3x + \frac{e^2}{2} \iint \frac{n(\vec{x})\, n(\vec{x}')}{|\,\vec{x} - \vec{x}'\,|}\, d^3x\, d^3x' + E_{xc}[n]$$

= kinetic + potential + electrostatic + exchange-correlation

$E_{xc}[n]$: exact form unknown

(Local approximation; Generalized gradient approximation)

Density Functional Theory (Continued)

Minimize $E[n]$ with respect to $n(\vec{x})$: $\dfrac{\delta E}{\delta n} = 0$

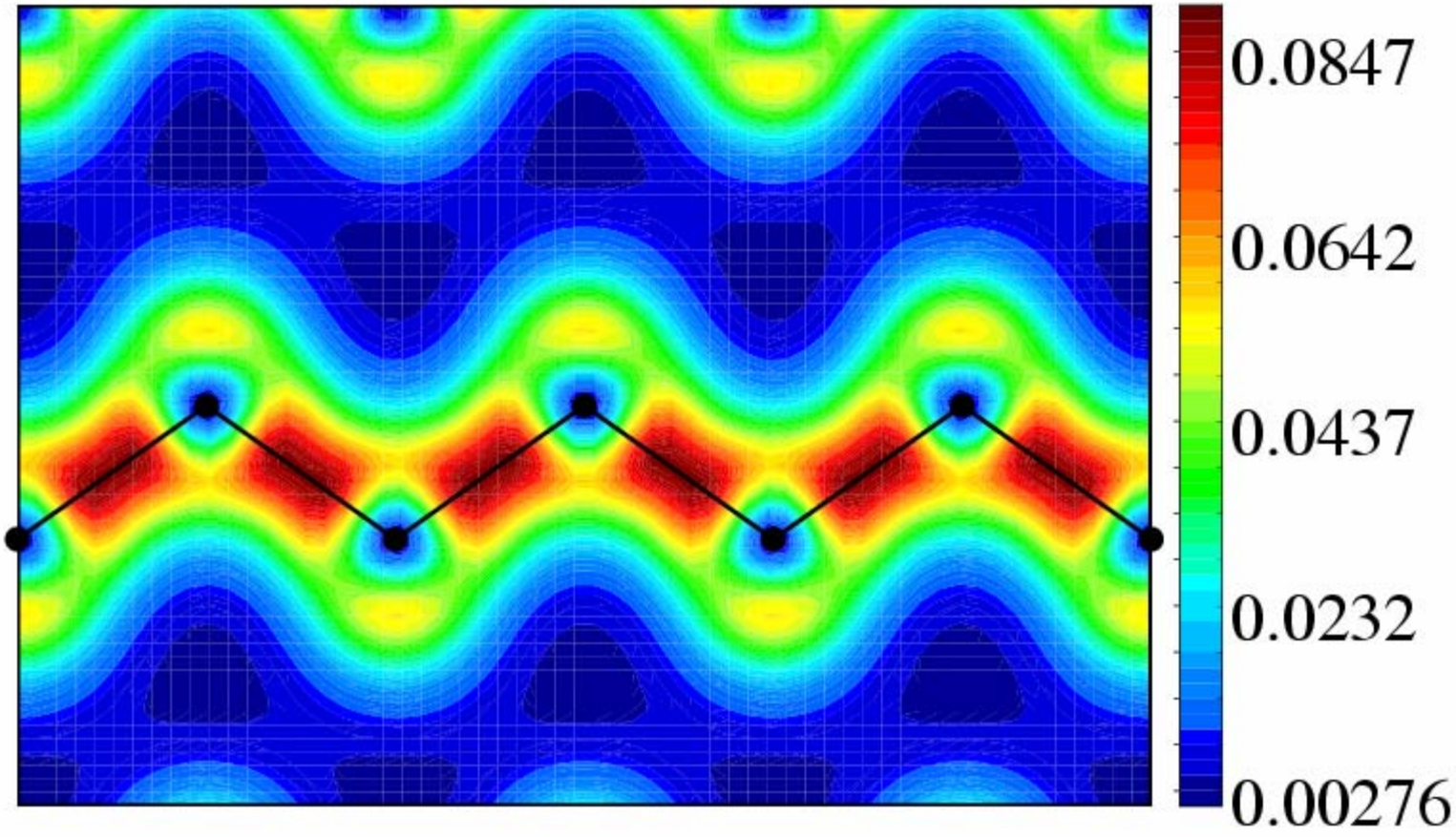
One obtains a set of one-particle equations which can be solved self-consistently.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(\vec{x}) \right] \psi_i(\vec{x}) = E_i \psi_i(\vec{x})$$

with $$n(\vec{x}) = \sum_i^N |\psi_i(\vec{x})|^2$$

$$V_{eff}(\vec{x}) = V_{ext}(\vec{x}) + e^2 \int \frac{n(\vec{x}')}{|\vec{x} - \vec{x}'|} d^3x' + \frac{\delta E_{xc}[n]}{\delta n}$$

Charge density in Si (110 plane)



Calculational Methods and Details

- Density functional theory (LDA or GGA)
- Projector Augmented Wave (PAW) method
- Plane wave basis
- Supercells containing 32 Pd atoms
- Energy cutoff: 390 - 520 eV
- System investigated so far:
  H/He in perfect Pd crystal and Pd with a lattice vacancy

Caution:

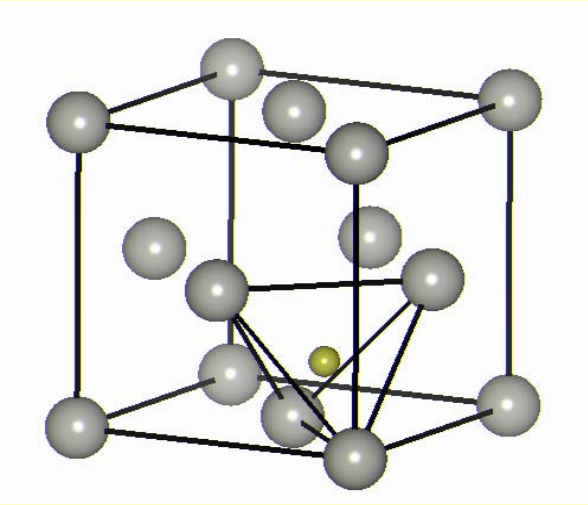
Local density approximation (LDA) or generalized gradient approximation (GGA) is not perfect to describe the van der Waals interaction.

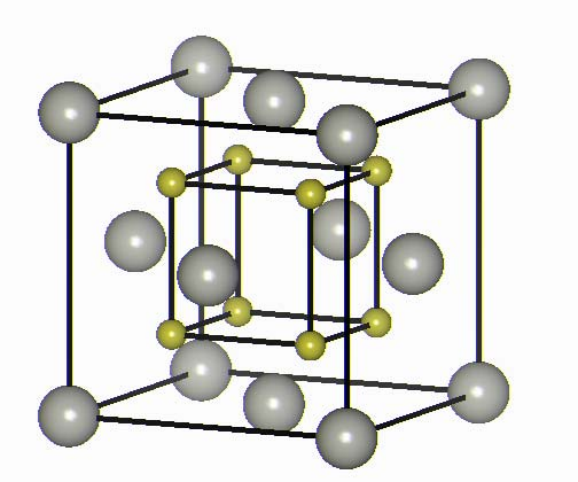
Fcc He solid

	Calculation	Experiment
Lattice constant	4.12 Å	3.91 Å
Cohesive energy	0.031 eV/atom	0.028 eV/atom

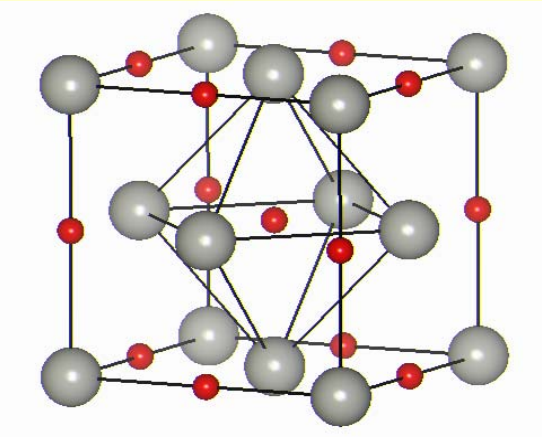
Interstitial Sites in an FCC Lattice

Tetrahedral

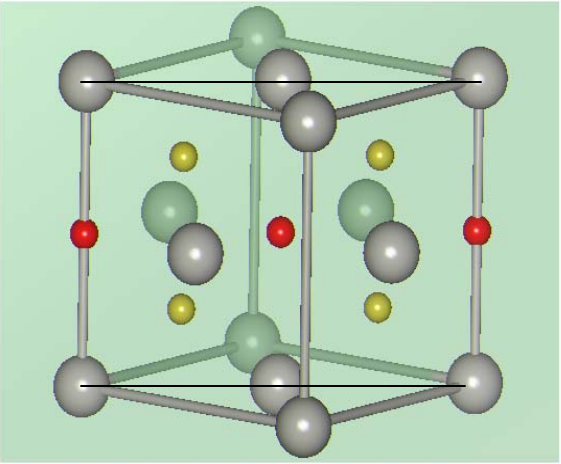


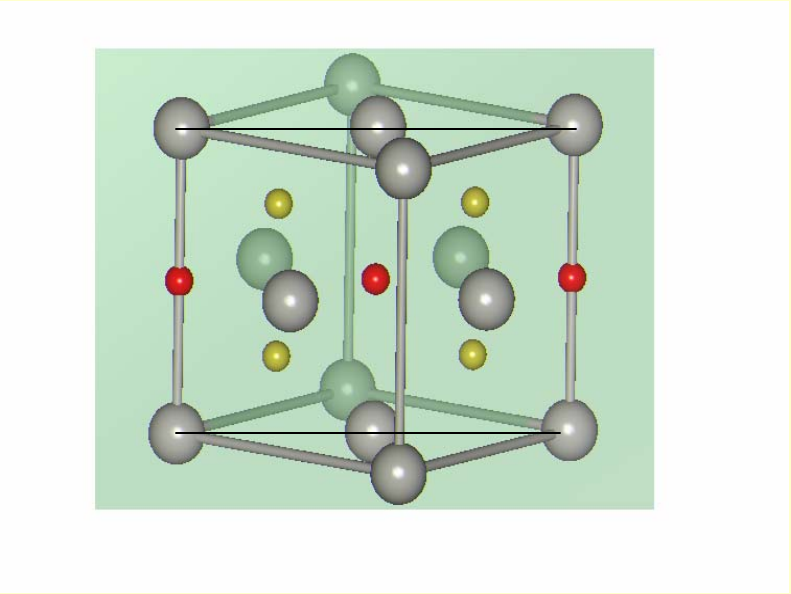


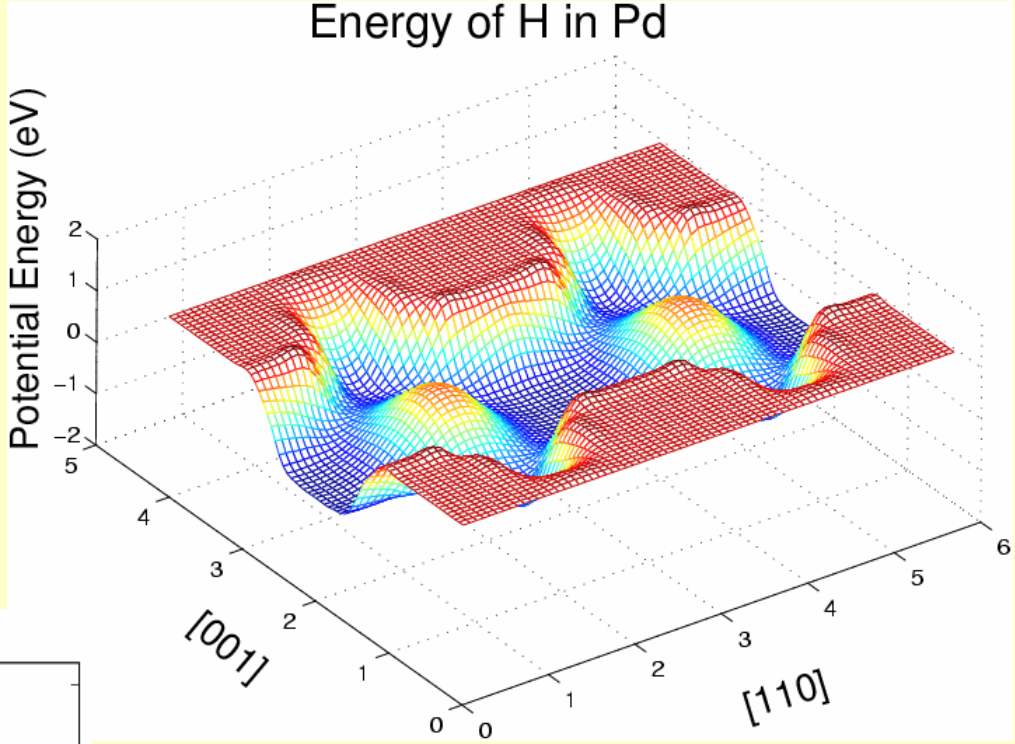
Octahedral

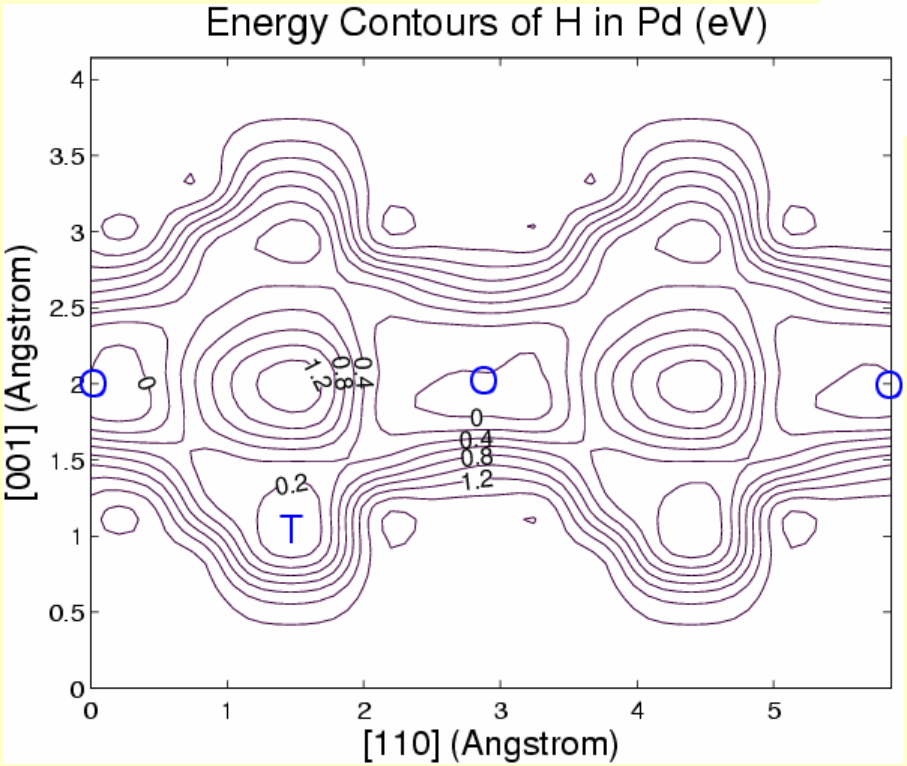


<110> plane







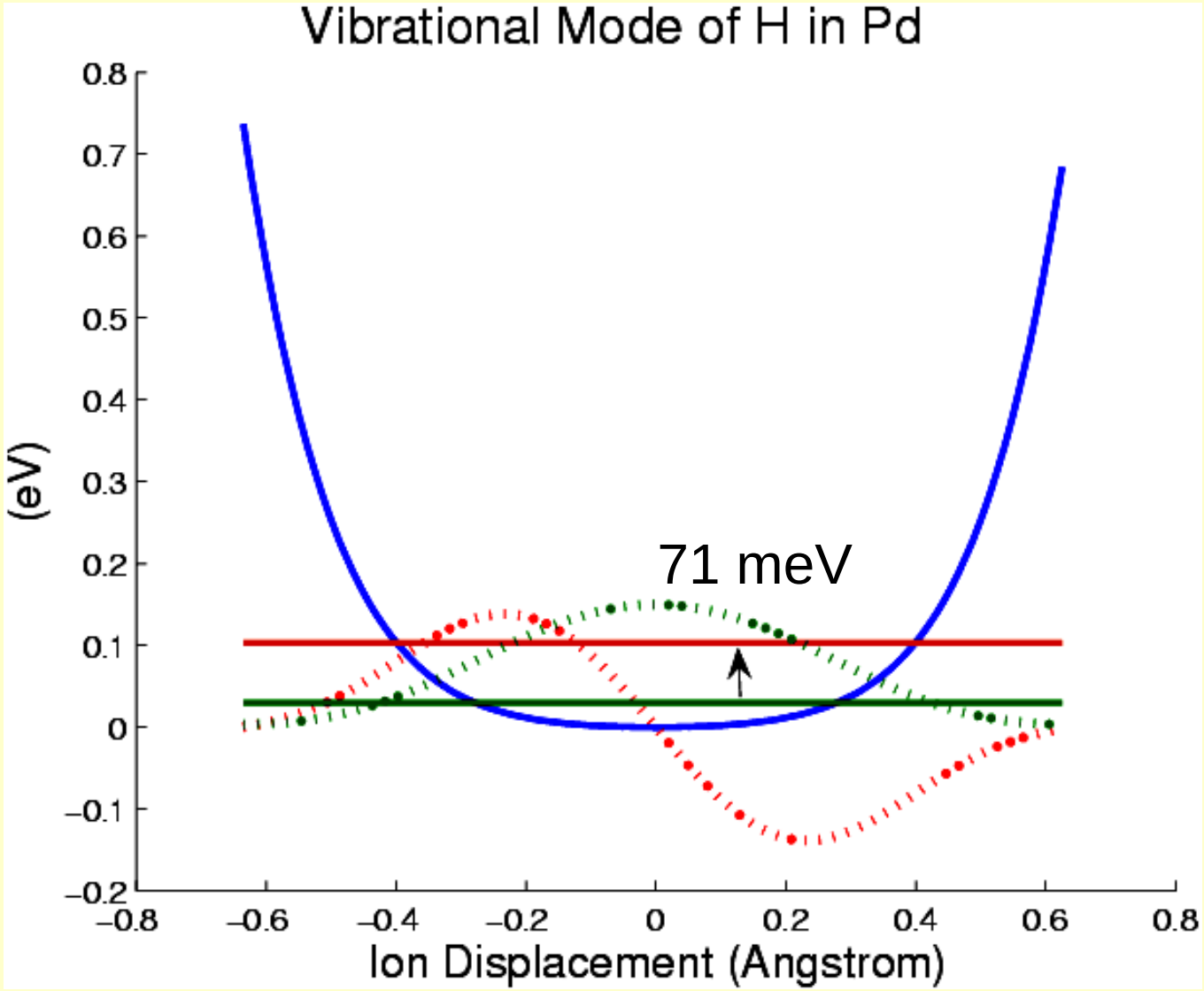


Preferred site: Octahedral

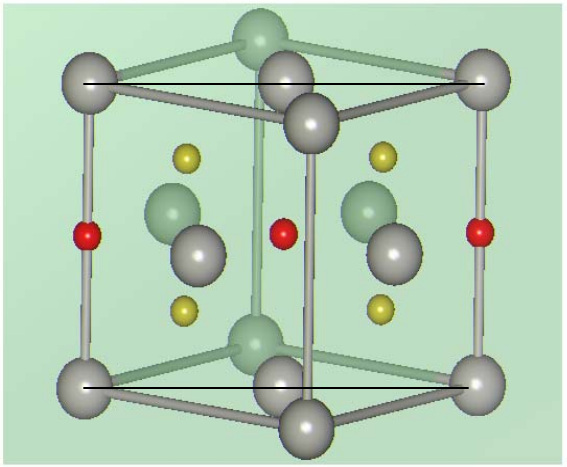
Diffusion path: O – T – O

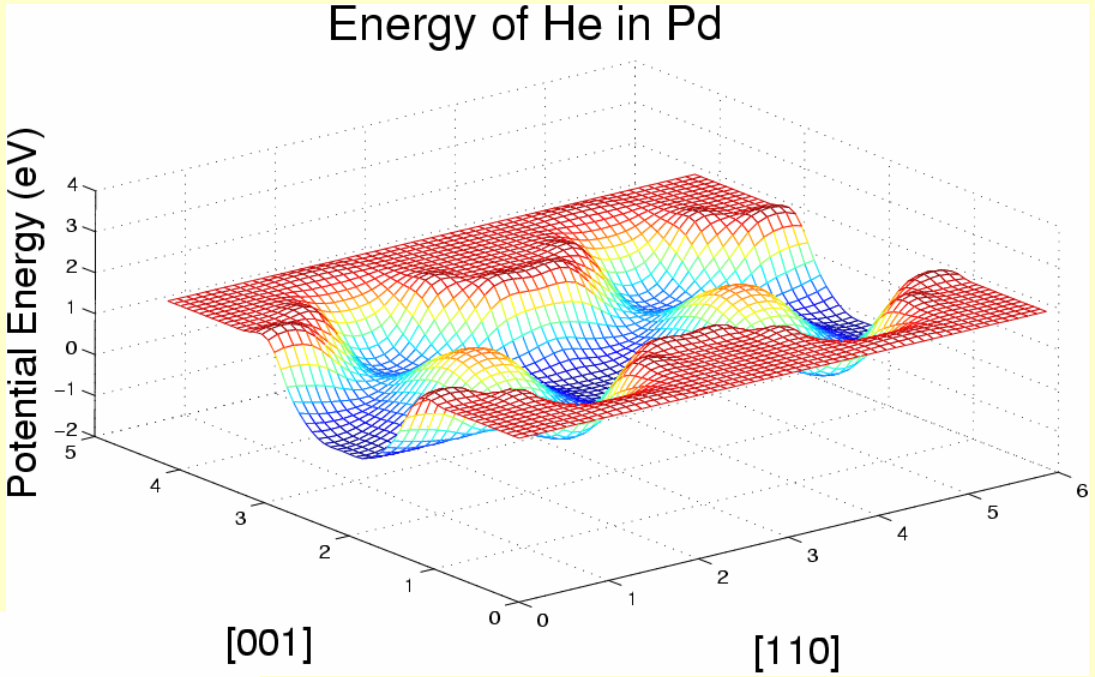
Diffusion barrier ¼ 0.35 eV

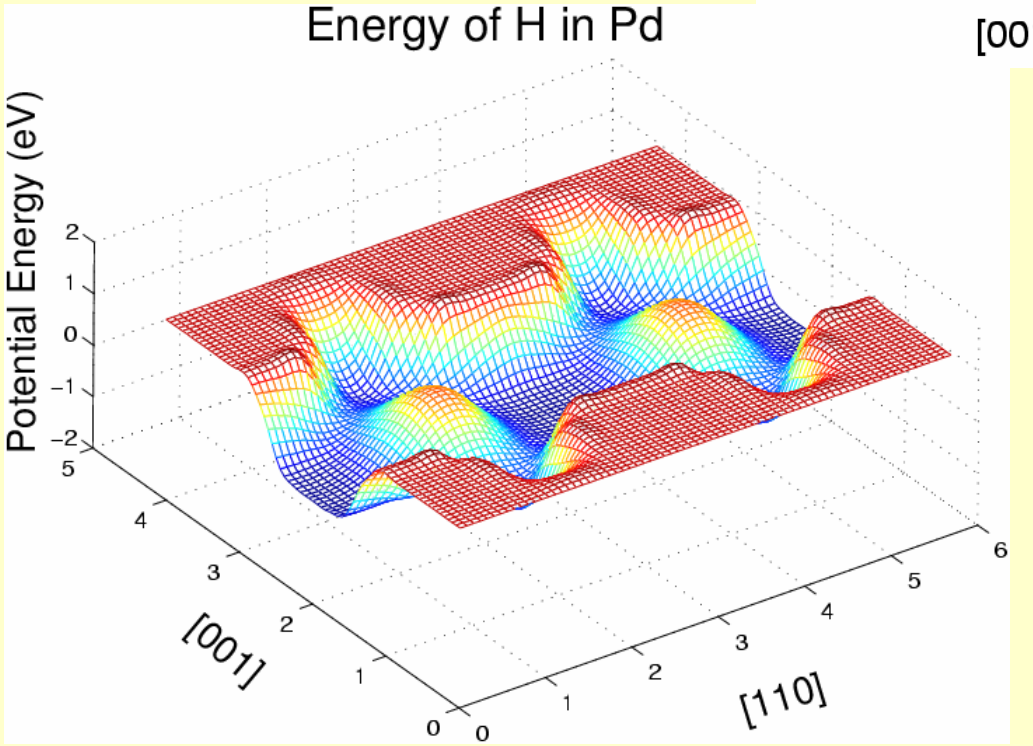
(no Pd relaxation)



Expt. 60 - 70 meV (Rush et al. 1984)







He in Pd (similar to H)

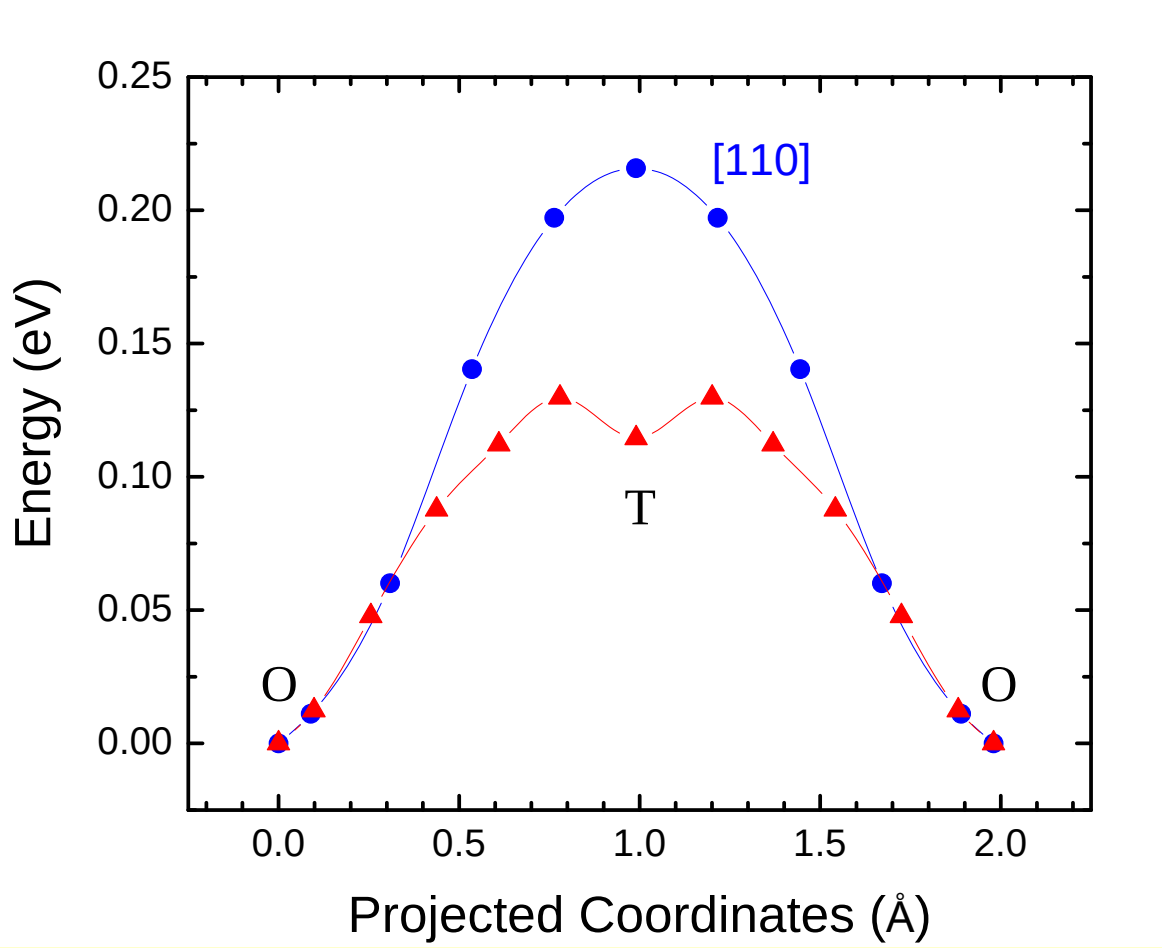
Preferred site: Octahedral

Diffusion path: O – T – O

Diffusion barrier ¼ 0.5 eV
(0.35 eV for H)
no Pd relaxation

Including nearest-neighbor Pd relaxations

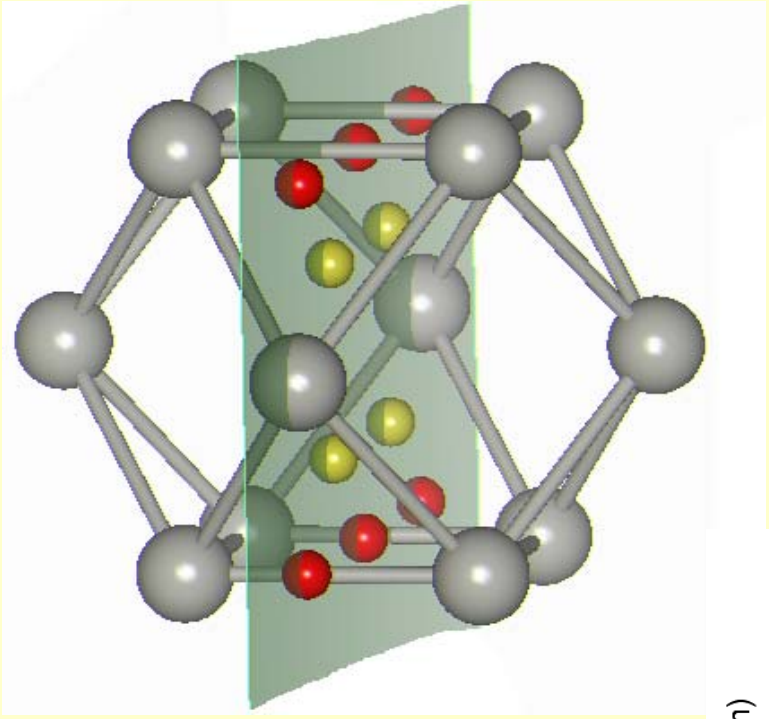
The shape of the He potential energy surface does not change, but the barrier is much reduced.

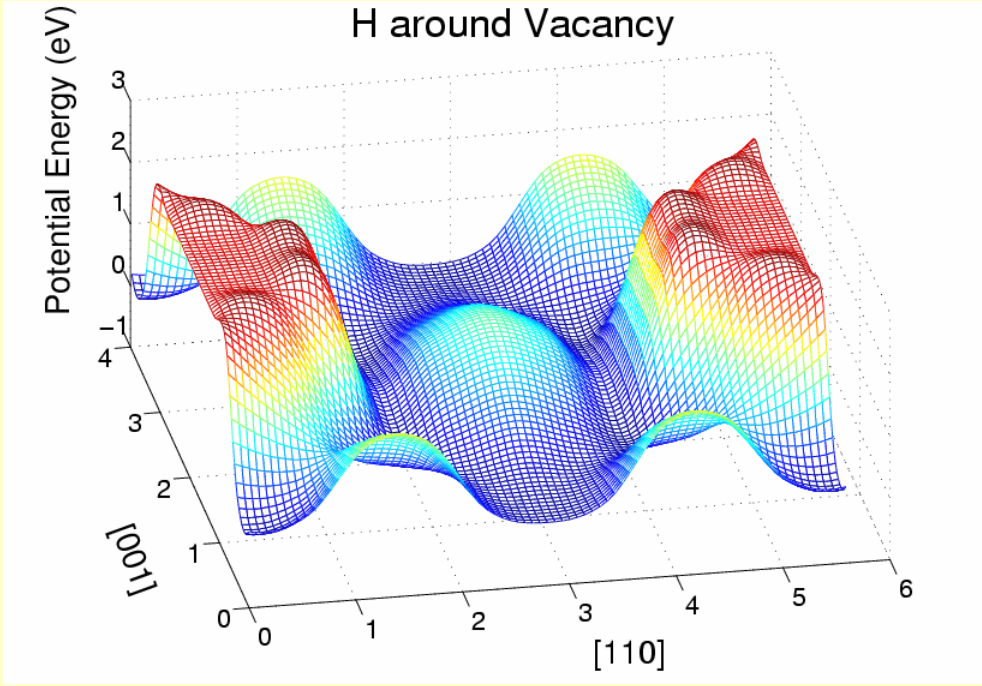


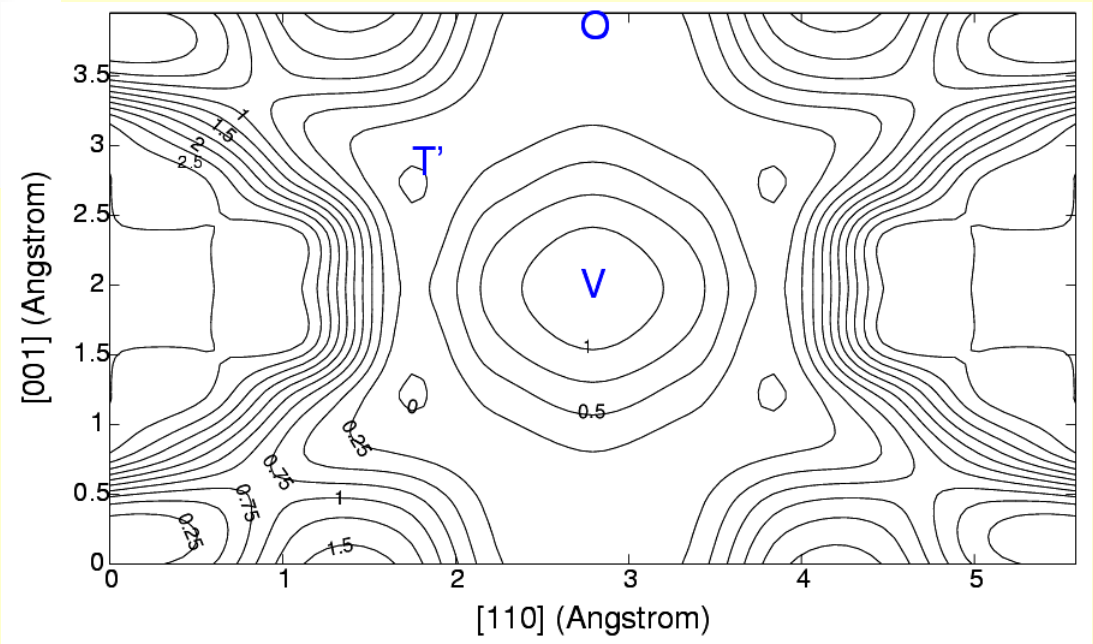
Diffusion barrier:
0.13 eV
(lower limit)

Interstitial He is very mobile.

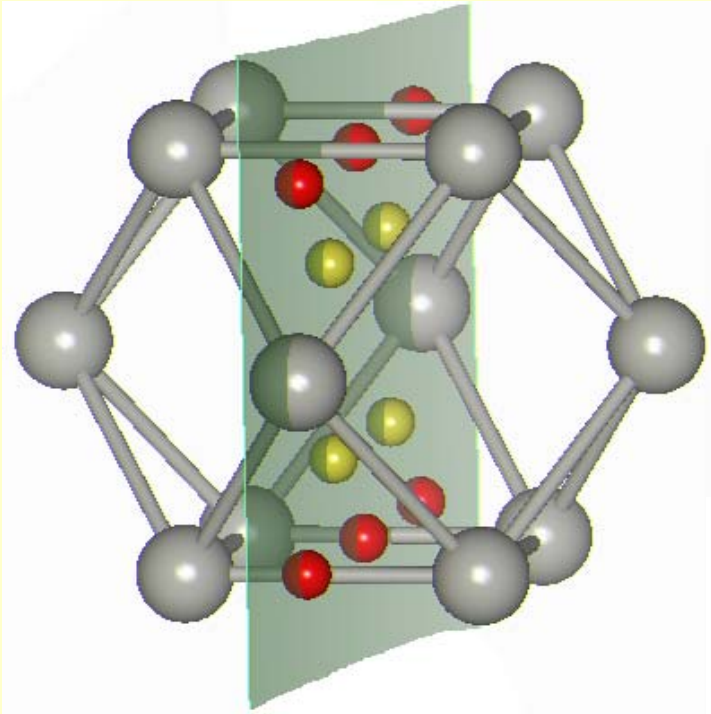
H near the Vacancy

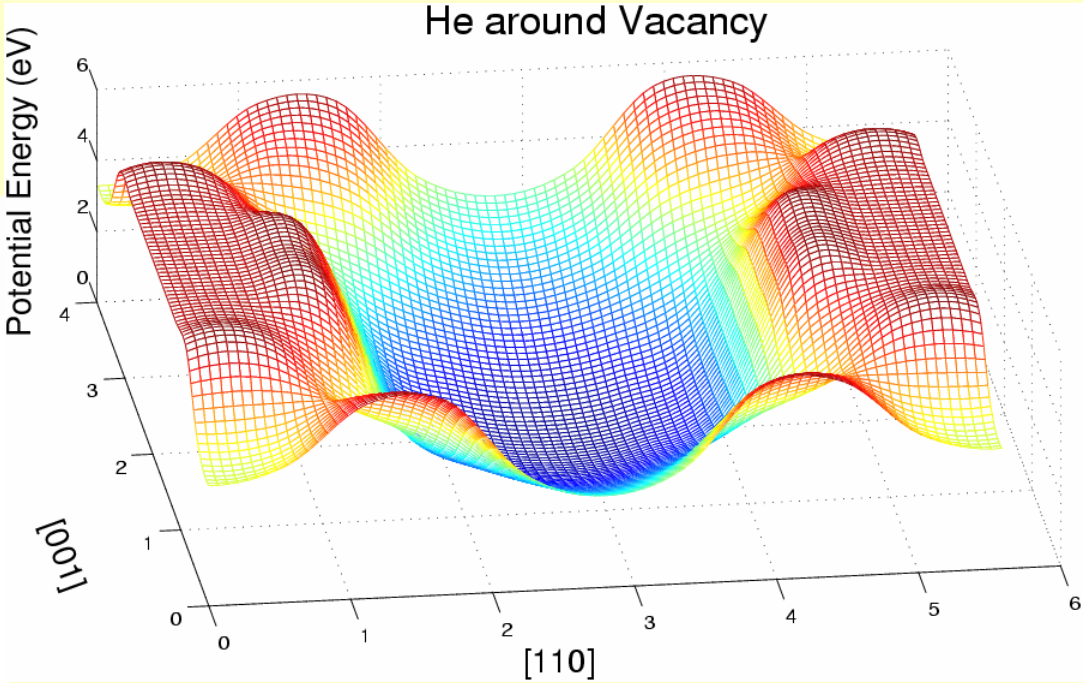


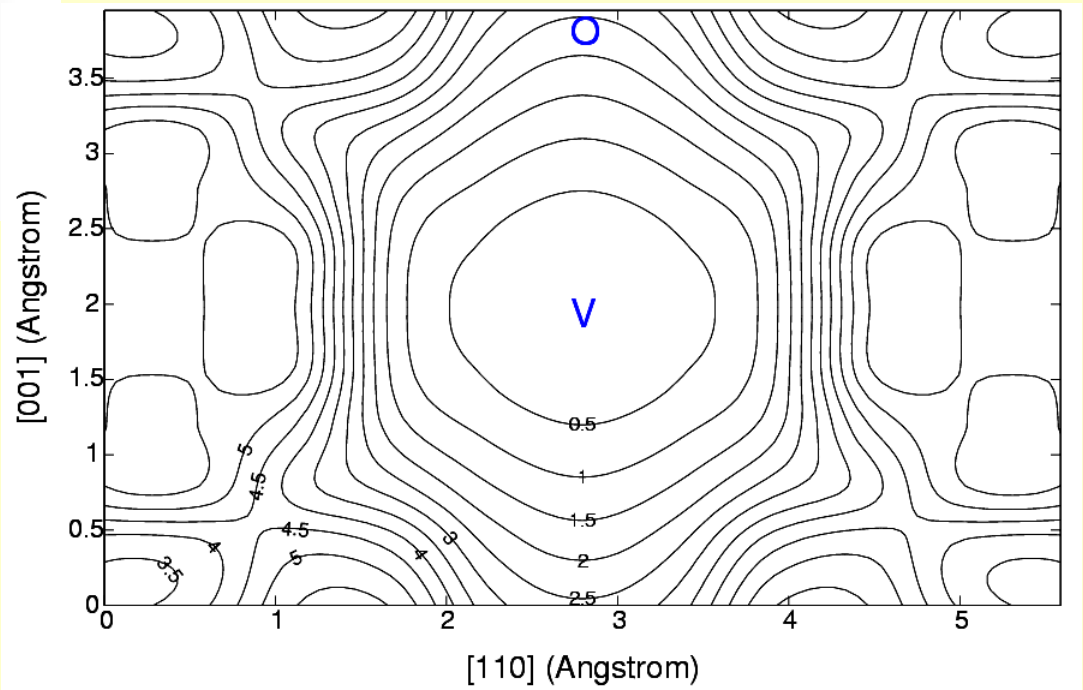




He near the Vacancy



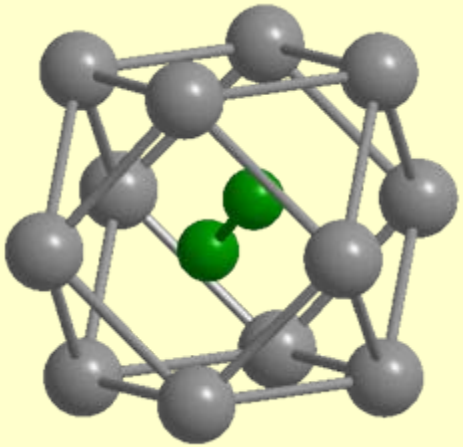




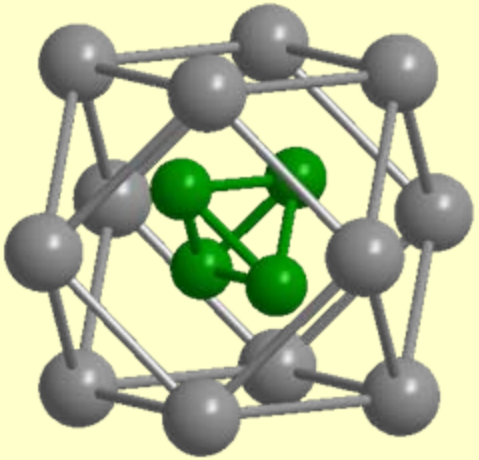
Energy of H and He in Pd (in eV, with respect to atoms)		
	H	He
Pd32	-3.33	3.62
Pd31Vac	-3.74	0.97
Trapping Energy	-0.41	-2.65

- With a trapping energy of 0.4 eV, interstitial H in Pd prefers a site near the vacancy.
- With a trapping energy of 2.6 eV, interstitial He in Pd strongly prefers occupying the vacancy site.

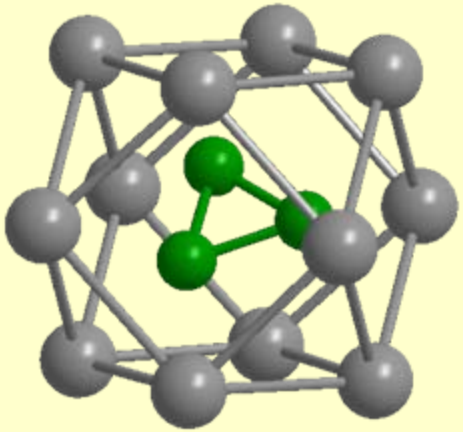
Helium Clusters at a Lattice Vacancy



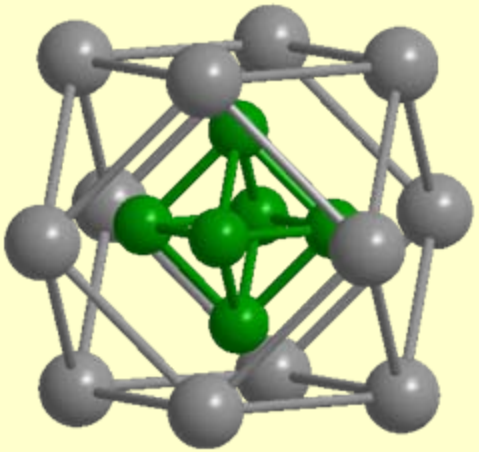
N = 2



N = 4



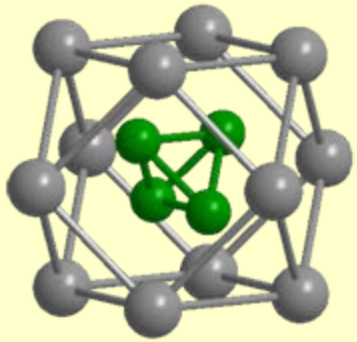
N = 3

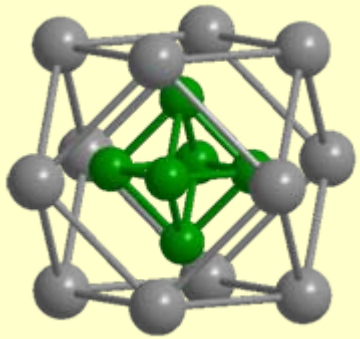


N = 6

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

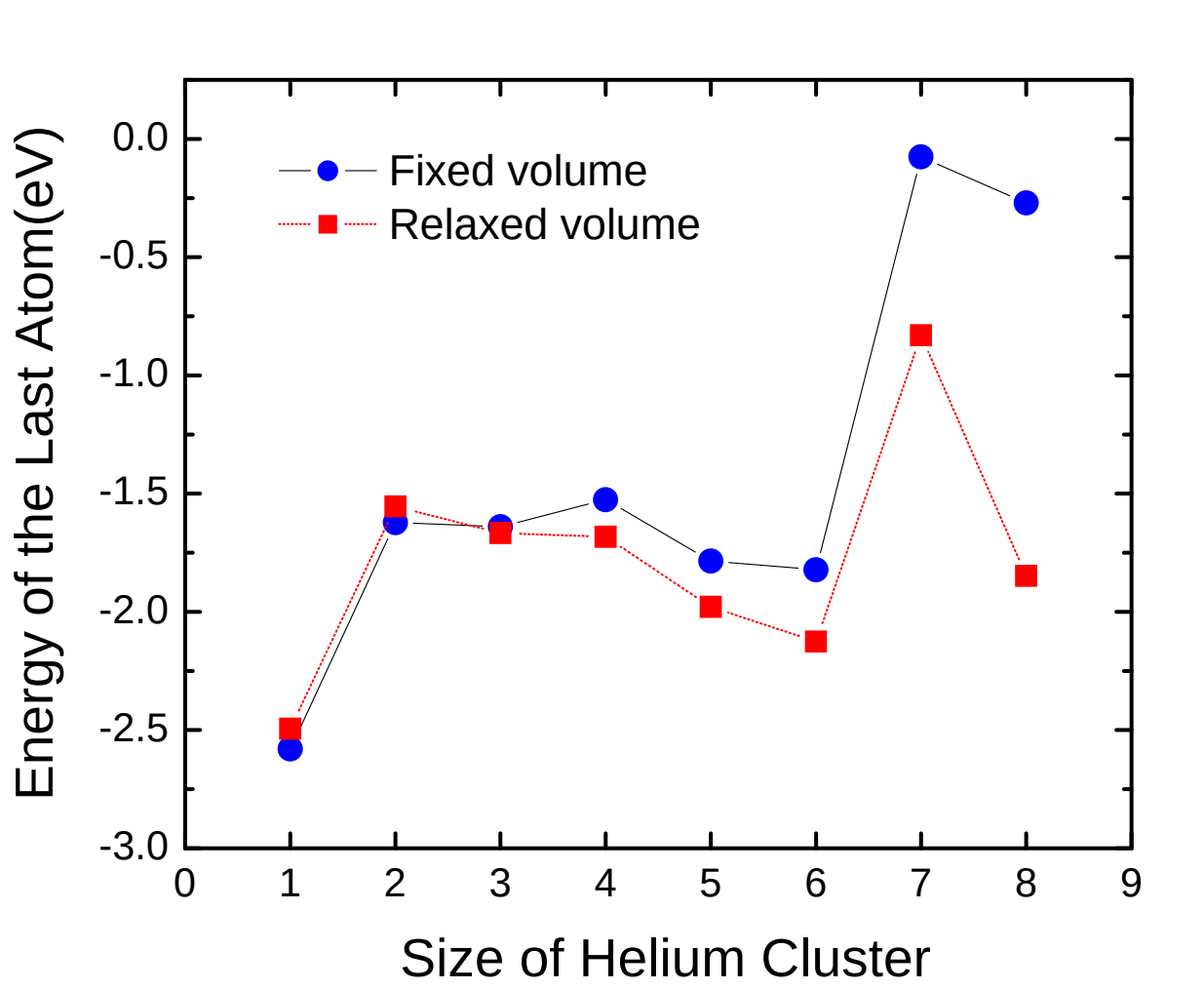
Initial state	Final state	Energy gain
Empty vacancy	1 He	2.6 eV
1 He	2 He	1.6 eV
2 He	3 He	1.6 eV
3 He	4 He	1.5 eV
4 He	5 He	1.8 eV
5 He	6 He	1.8 eV





It is energetically favorable for He atoms to aggregate at the vacancy site.

Energy of the last He atom
(with respect to interstitial site)



Large energy gain for the first He

Vacancy site will be populated.

Conclusion

- Interstitial He has a low diffusion barrier in Pd.
- Large energy gain for the first He to go into the vacancy site; vacancy capture is not relevant for cluster growth.
- Energetically favorable to form a cluster as large as eight atoms at the vacancy site.
- Nearest-neighbor He-He separation in the cluster is about 1.6 – 1.8 Å, much smaller than that in the solid (2.8 Å).

Future Work

- He cluster in a perfect crystal
- Multiple vacancies – nano He bubble
- Preferred shape of the nano bubble
- Growth of the nano bubble by emitting Pd self-interstitial atoms