Energetics of Hydrogen Storage Reactions: The Power of DFT

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ACKNOWLEDGEMENTS

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Outline

- Challenge
- Motivation
- Methodology
- $LaNi_5$, $LaNi_5H_7$: benchmark results
- $LaNi_5H_n$, $LaCo_5H_n$: can DFT predict preferred H sites, filling sequence, maximum H concentration?
- $LiNH_2 + LiH \leftrightarrow Li_2NH + H_2$: energetics of a novel hydrogen storage reaction
- Summary

Challenge

GM

"Gotta Have" Fuel Cell Vehicles

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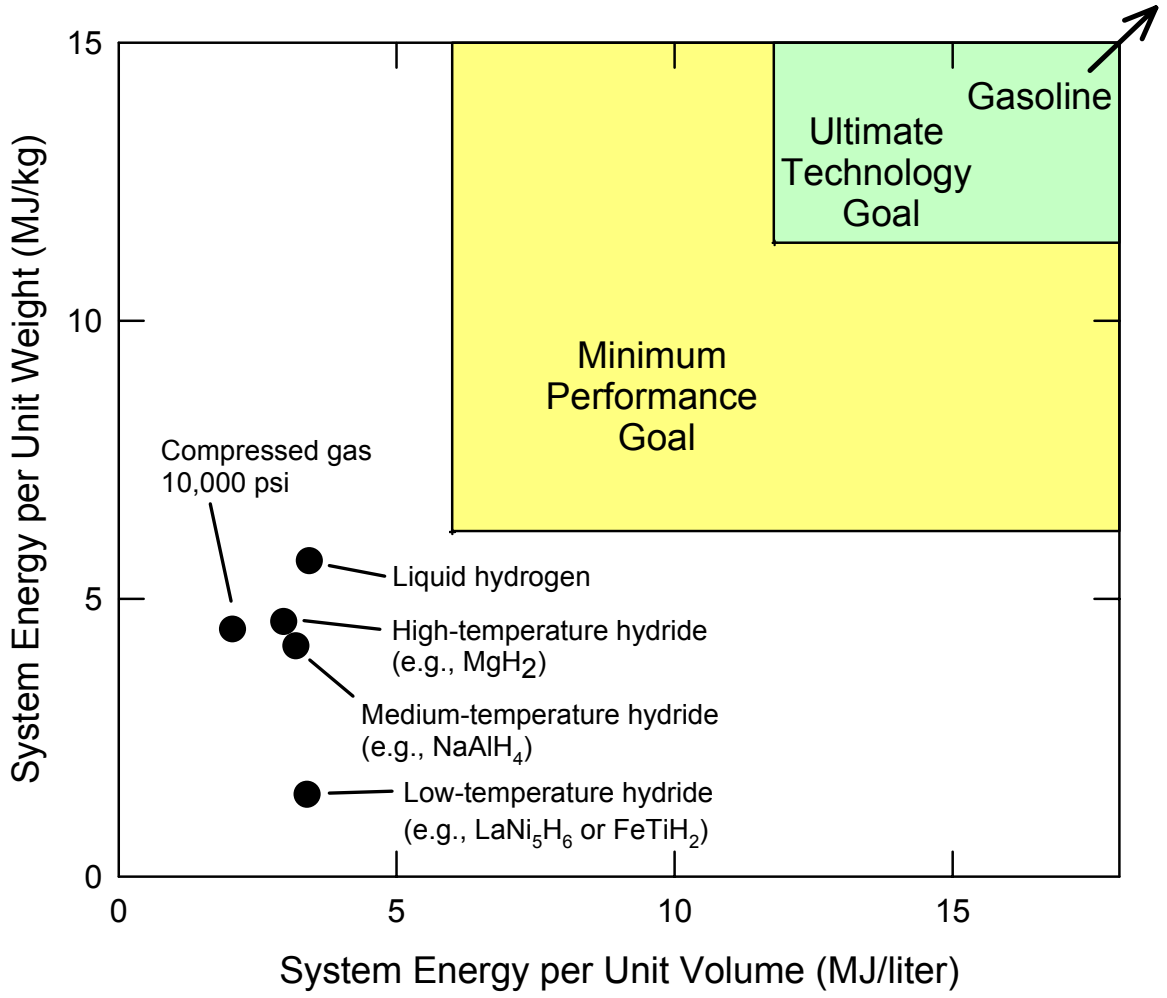
CHALLENGE (cont'd)
Gravimetric Energy Density vs. Volumetric Energy Density of Fuel Cell Hydrogen Storage Systems



CHALLENGE (cont'd)
HYDROGEN STORAGE PARAMETER GOALS

METRIC	GOAL
• System energy per unit weight for conventional vehicles with 300-mile range	> 6 MJ/kg
• System energy per unit volume for conventional vehicles with 300-mile range	> 6 MJ/ℓ
• Usable energy consumed in releasing H_2	<5 %
• H_2 Release Temperature	~80 ºC
• Refueling Time	<5 minutes
• H_2 Ambient Release Temp Range	-40/+45 ºC
• Durability (to maintain 80% capacity)	150,000 miles

Motivation

- Assess the capability of density functional theory (DFT) for modeling properties of solid hydrides, including electronic structure, enthalpies of formation, hydrogen site preferences, and maximum hydrogen occupancy

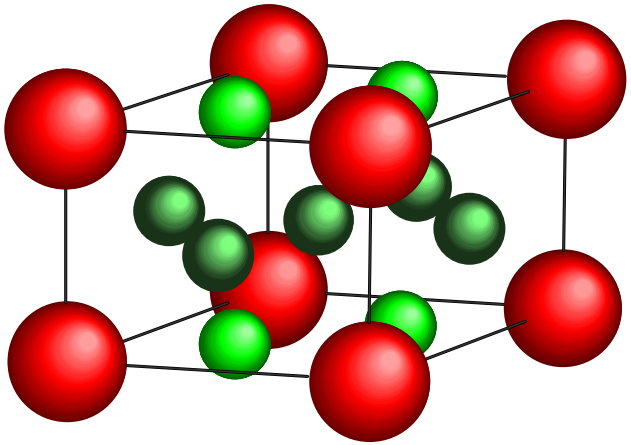
Calculational Methodology (briefly!)

- Vienna *ab initio* simulation package (VASP)
- Projector-augmented wave (PAW) potentials

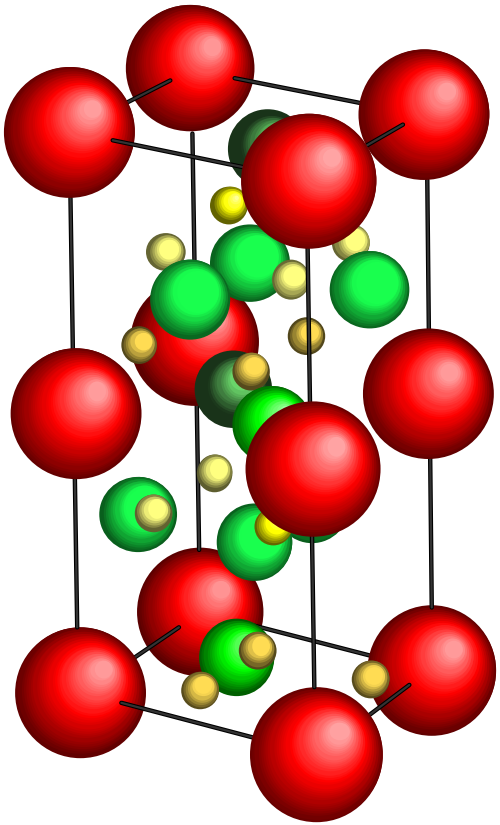
Benchmark Results: $LaNi_5$, $LaNi_5H_7$

$LaNi_5$ and $LaNi_5H_7$ Crystal Structures

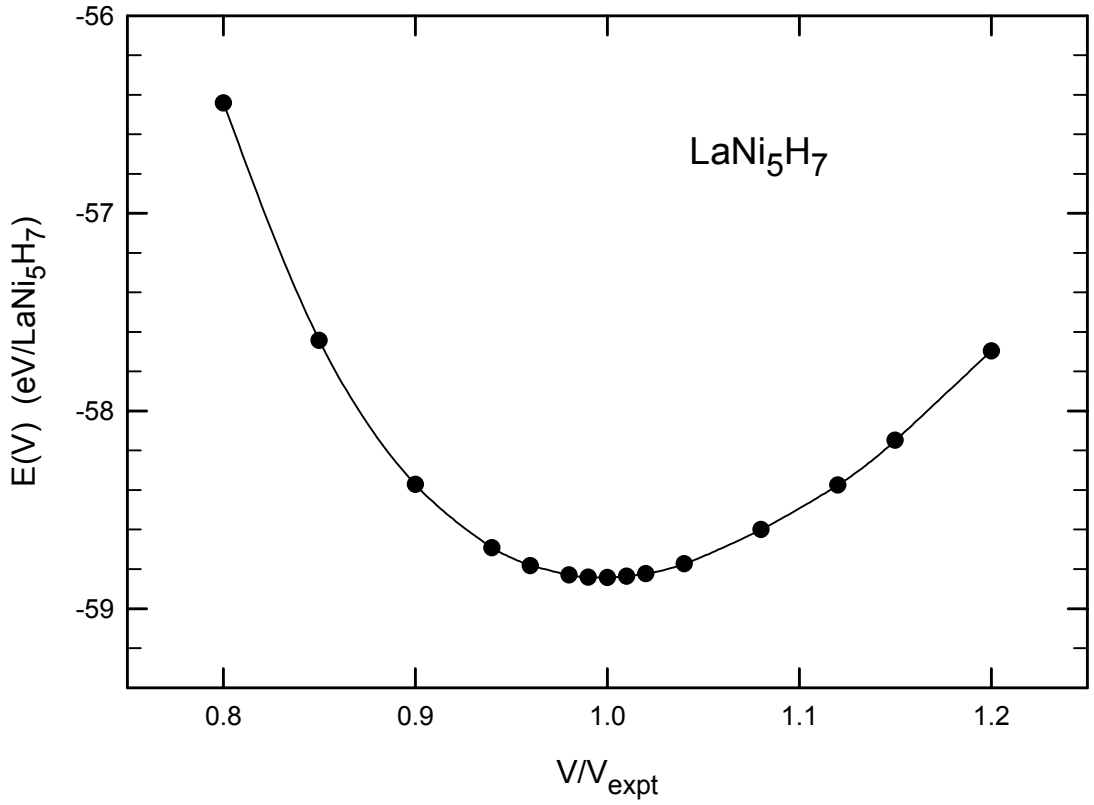
$LaNi_5$
hexagonal $CaCu_5$ P6/mmm



$(LaNi_5H_7)_2$
hexagonal $P6_3mc$



$LaNi_5H_7$: Energy vs Volume E(V)



Crystal Structure Parameters for $LaNi_5$ and $LaNi_5H_7$

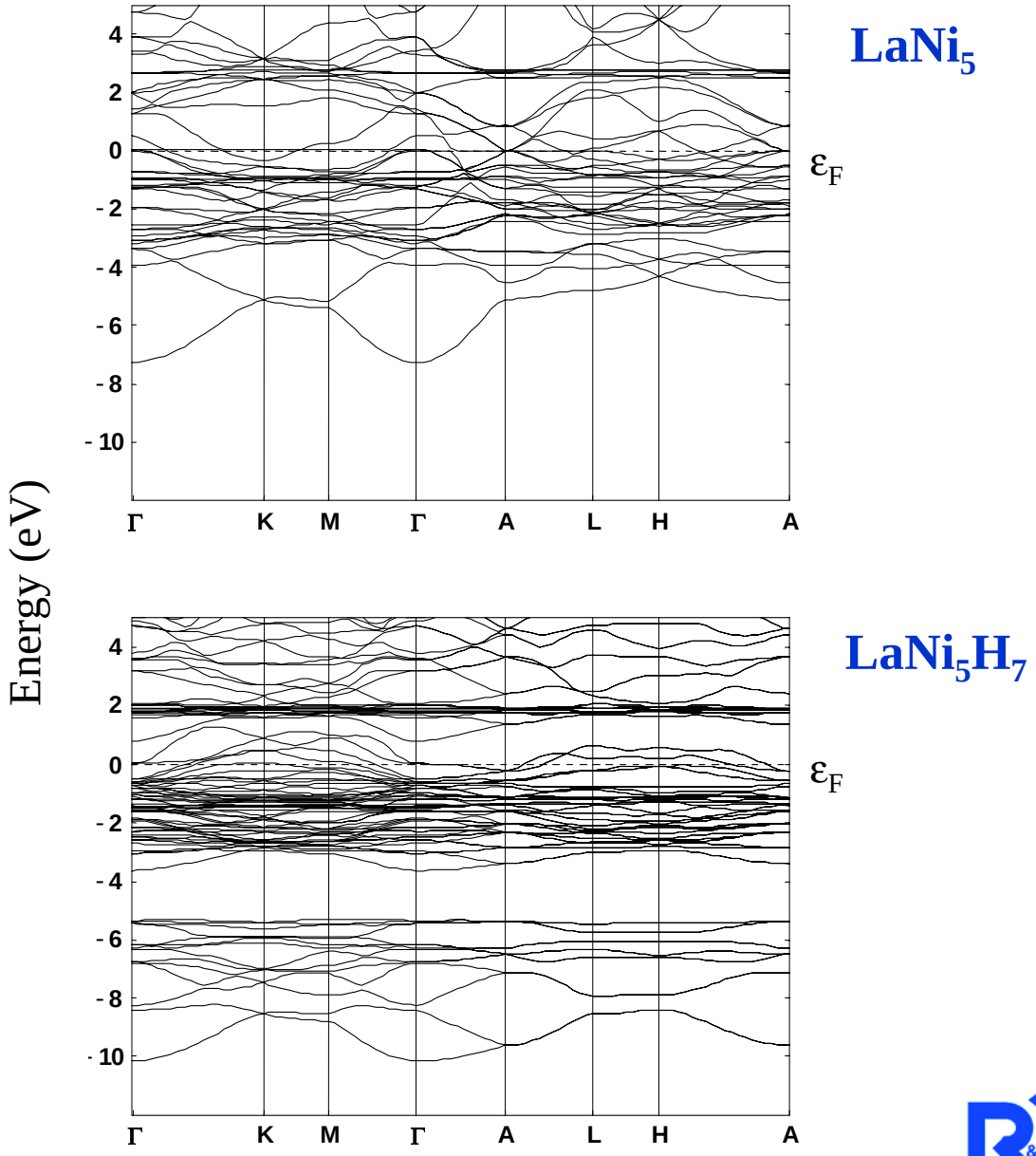
$LaNi_5$

	Calc	Expt
a (Å)	5.008	5.017
c (Å)	3.967	3.986
B (GPa)	135	137, 139

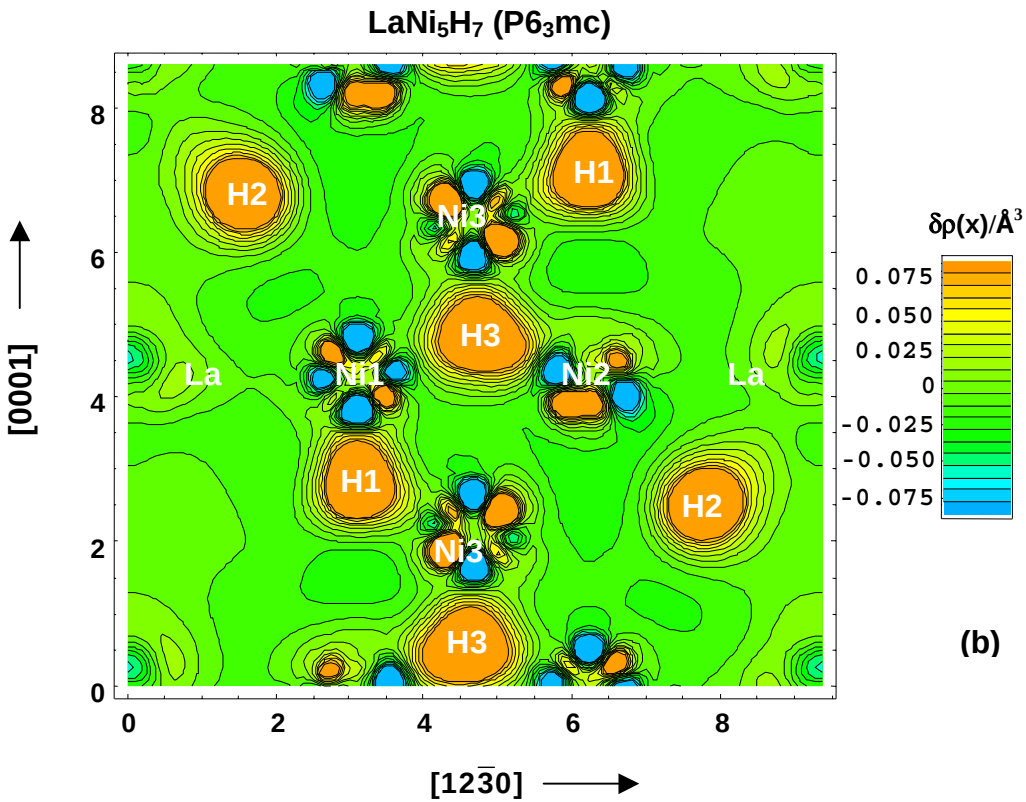
$LaNi_5H_7$

	Calc	Expt		Calc	Expt		Calc	Expt
			La (2a) z	0.0029	0.0218	H1 (2b) z	0.8221	0.8137
a (Å)	5.363	5.409	Ni1 (2b) z	0.0077	0.0024	H2 (6c) x	0.1508	0.1596
c (Å)	8.723	8.600	Ni2 (2b) z	0.4854	0.4889	z	0.2761	0.2804
			Ni3 (6c) x	0.4995	0.4975	H3 (6c) x	0.5058	0.5640
			z	0.2542	0.25	z	0.0630	0.0556

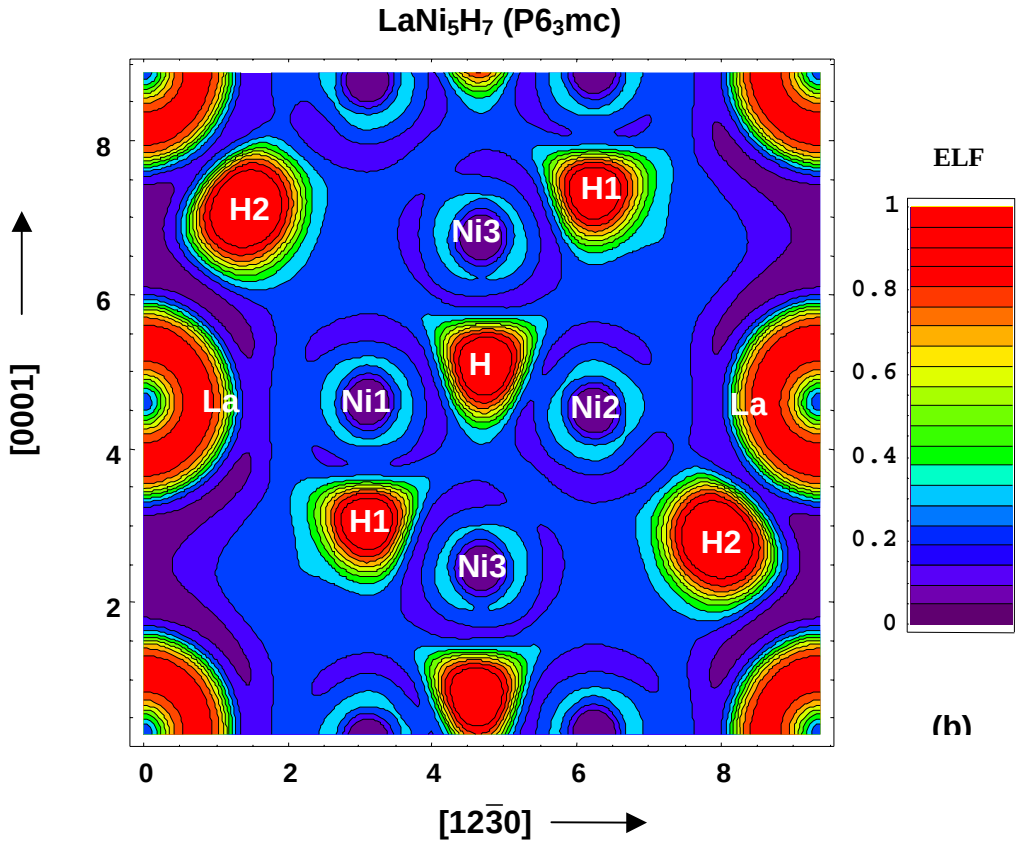
Band Structures of $LaNi_5$ and $LaNi_5H_7$



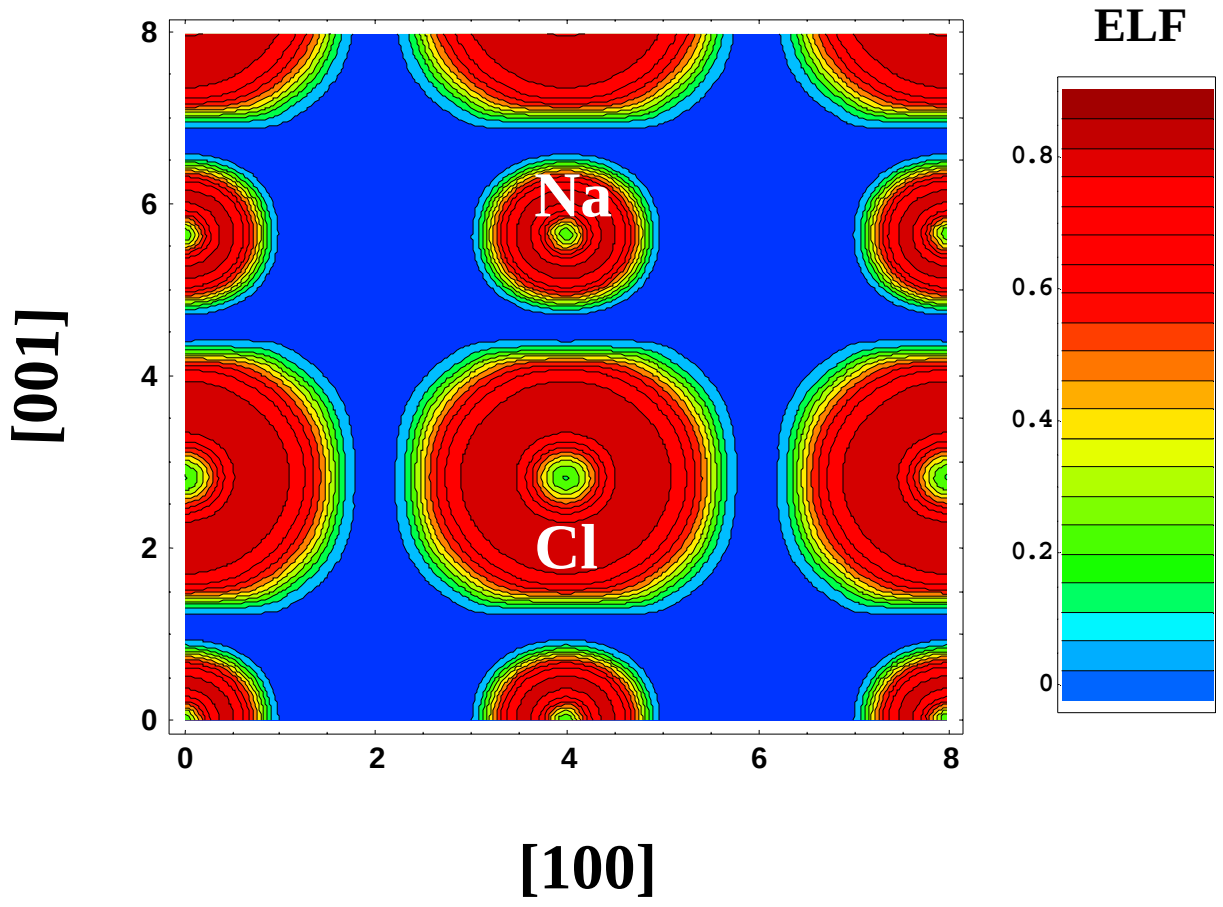
$\delta\rho = \rho(LaNi_5H_7) - \rho(LaNi_5H_0) - \rho$ (7H non-int)



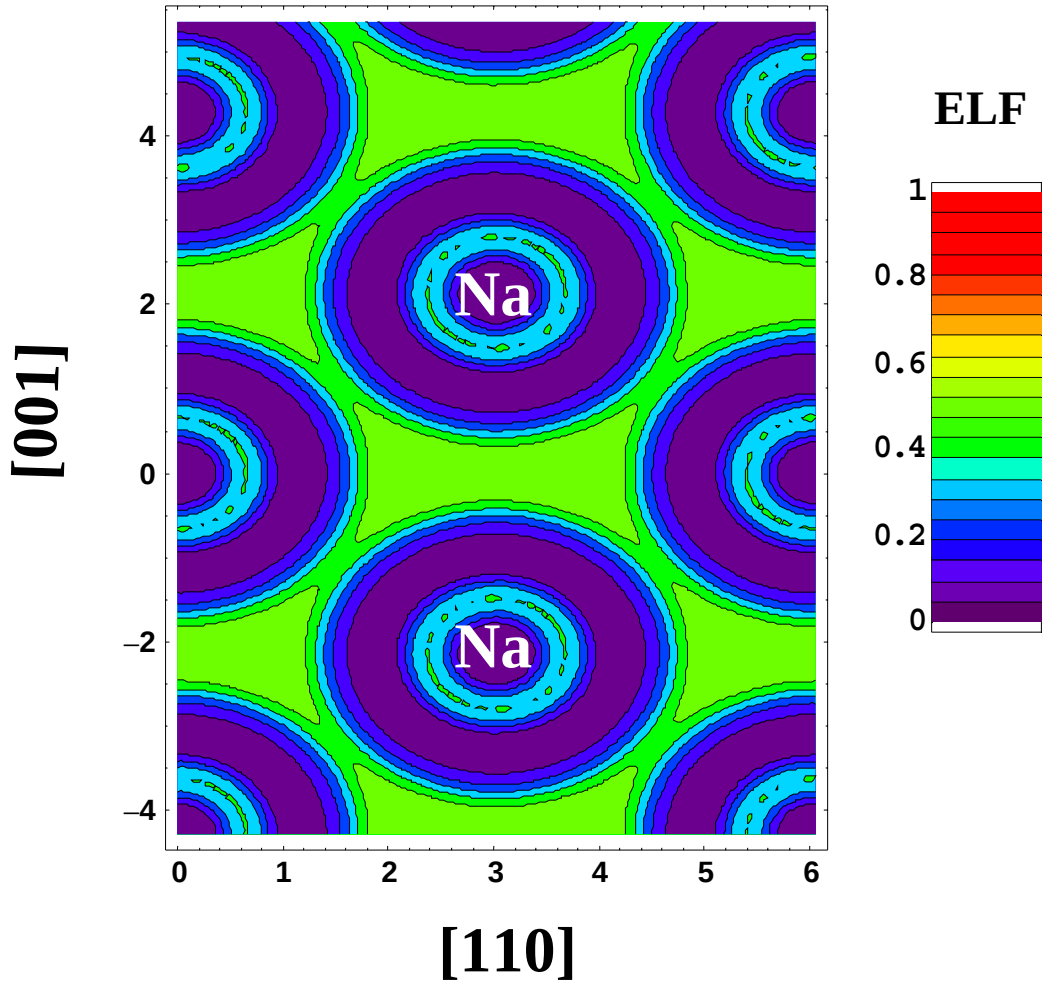
$LaNi_5H_7$ Electron Localization Function (ELF)



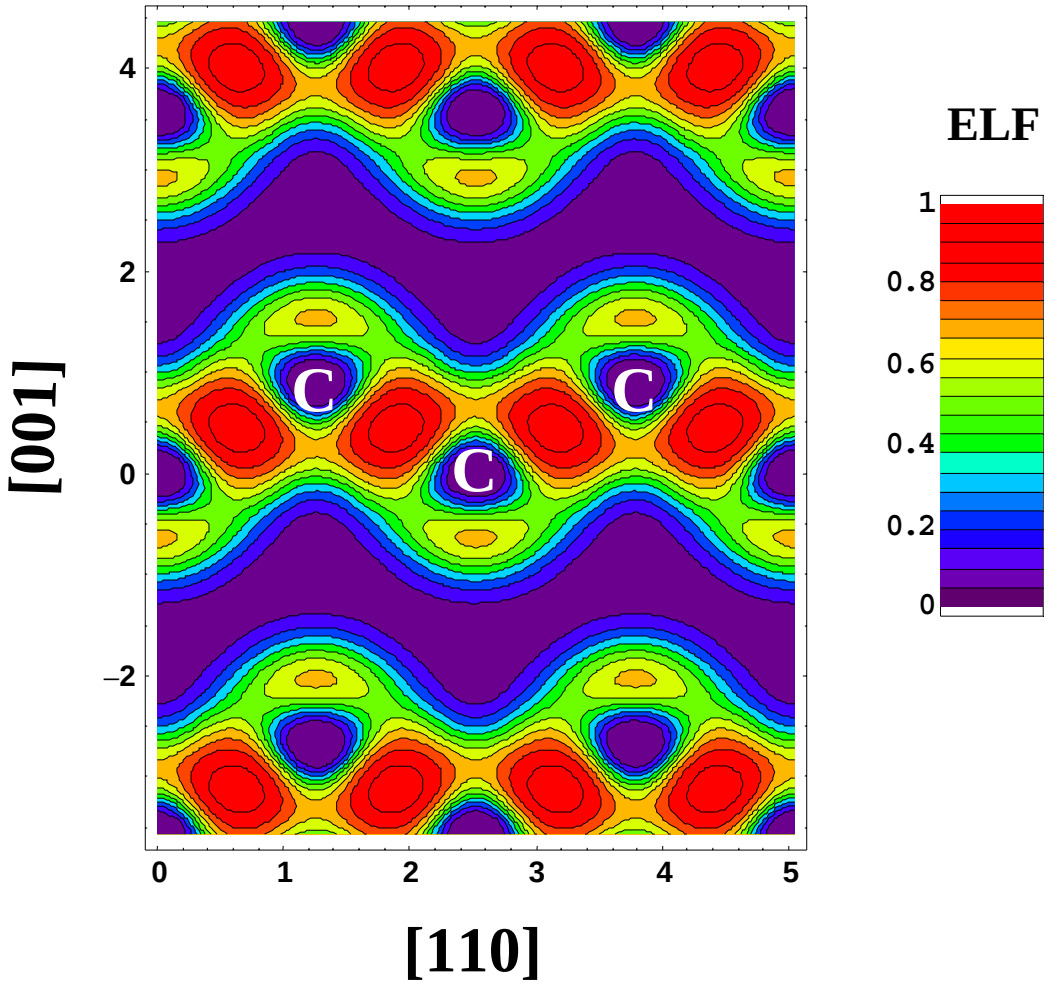
ELF for NaCl



ELF for Na Metal



ELF for Diamond



Enthalpies of Formation ΔH

$$\Delta H(LaNi_5H_7) = 2/7[E(LaNi_5H_7) - E(LaNi_5)\ ] - E(H_2)$$

$$= -40 \text{ kJ/mole } H_2$$

expt: -32 - -37

other calcs: -57 (1998); -45 (2001)

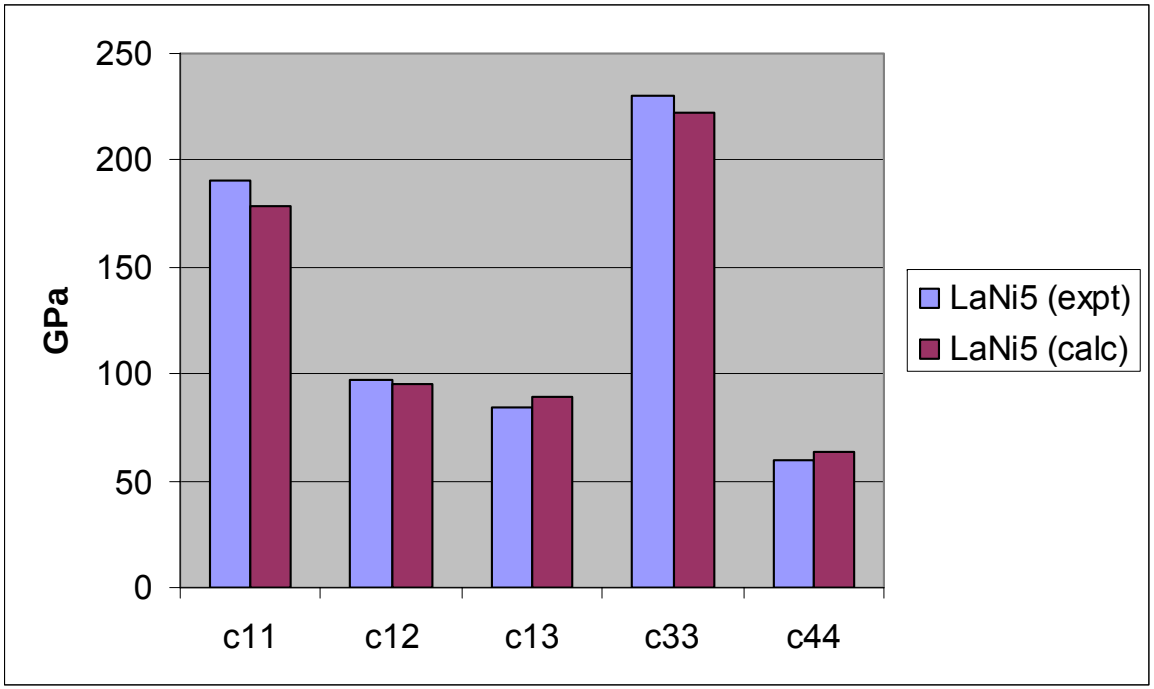
1 kJ/mole H_2 = 0.01 eV/H_2

$$\Delta H(LaNi_5) = E(LaNi_5) - E(La) - 5\,E(Ni)$$

$$= -168 \text{ kJ/mole } LaNi_5$$

expt: -159 ± 8; -166

Elastic Constants of $LaNi_5$



Results:
$LaNi_5H_n$, $LaCo_5H_n$

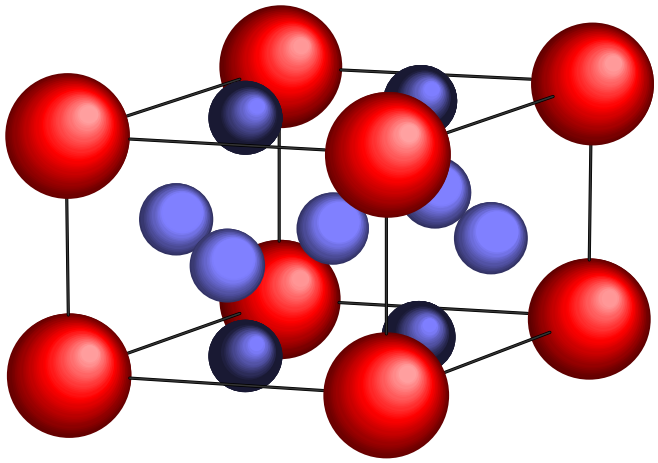
???

- For a given crystal structure, can DFT
  - identify the sites preferred by hydrogen?
  - establish the filling sequence of hydrogen sites?
  - provide an estimate of the maximum hydrogen concentration?

$LaCo_5$ and $LaCo_5H_4$ Crystal Structures

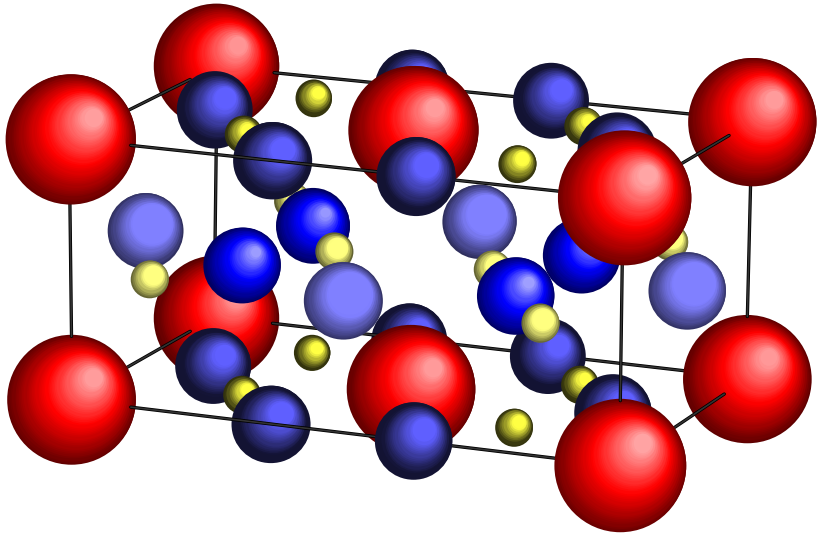
$LaCo_5$

hexagonal $CaCu_5$ P6/mmm



$(LaCo_5H_4)_2$

base-centered orthorhombic Cmmm



Strategy

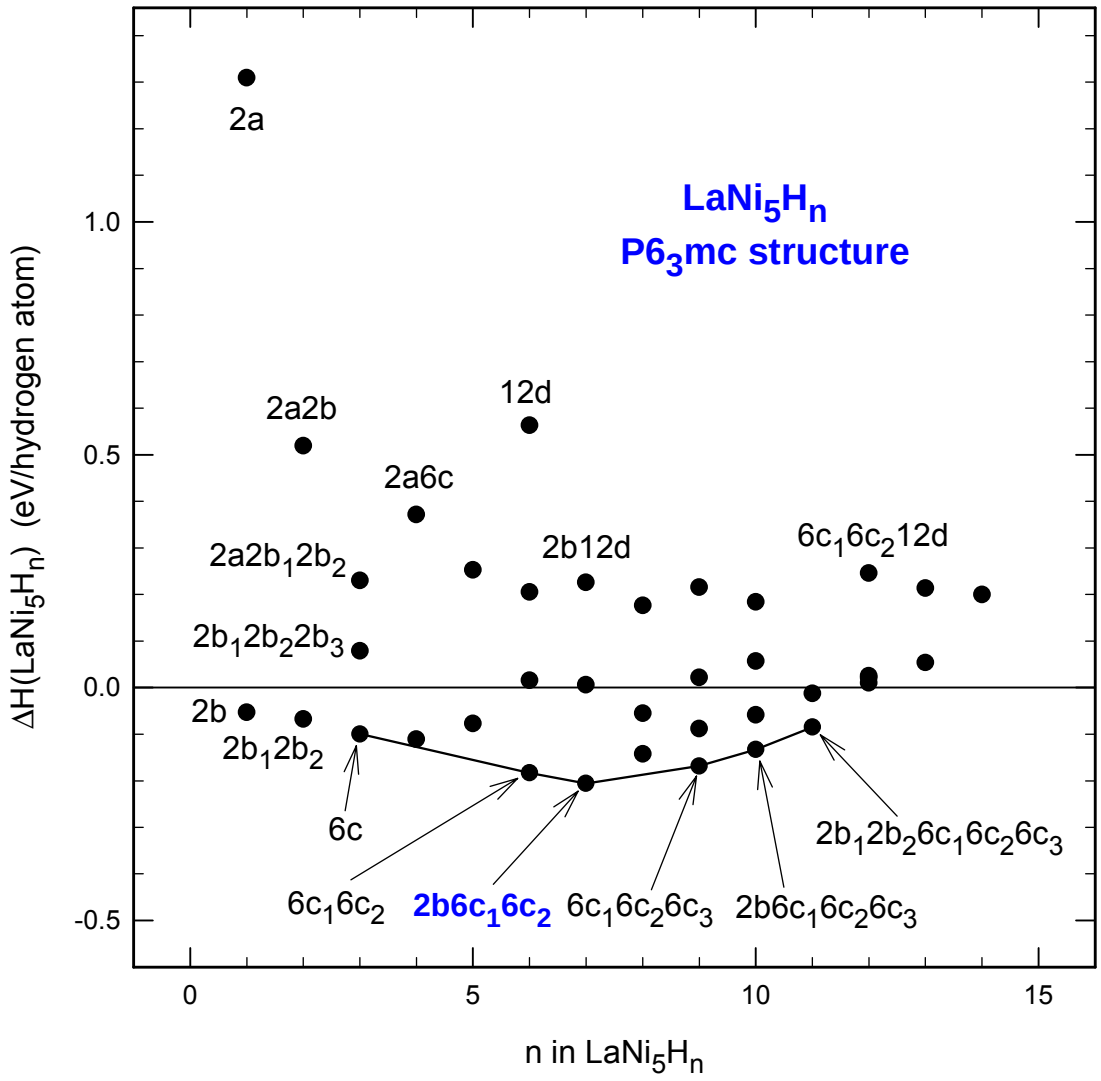
- Focus on $LaNi_5H_n$ ($P6_3mc$ structure) and $LaCo_5H_n$ (Cmmm structure)
- Calculate

  $\Delta H(LaNi_5H_n) = E(LaNi_5H_n) - E(LaNi_5) - (n/2)E(H_2)$

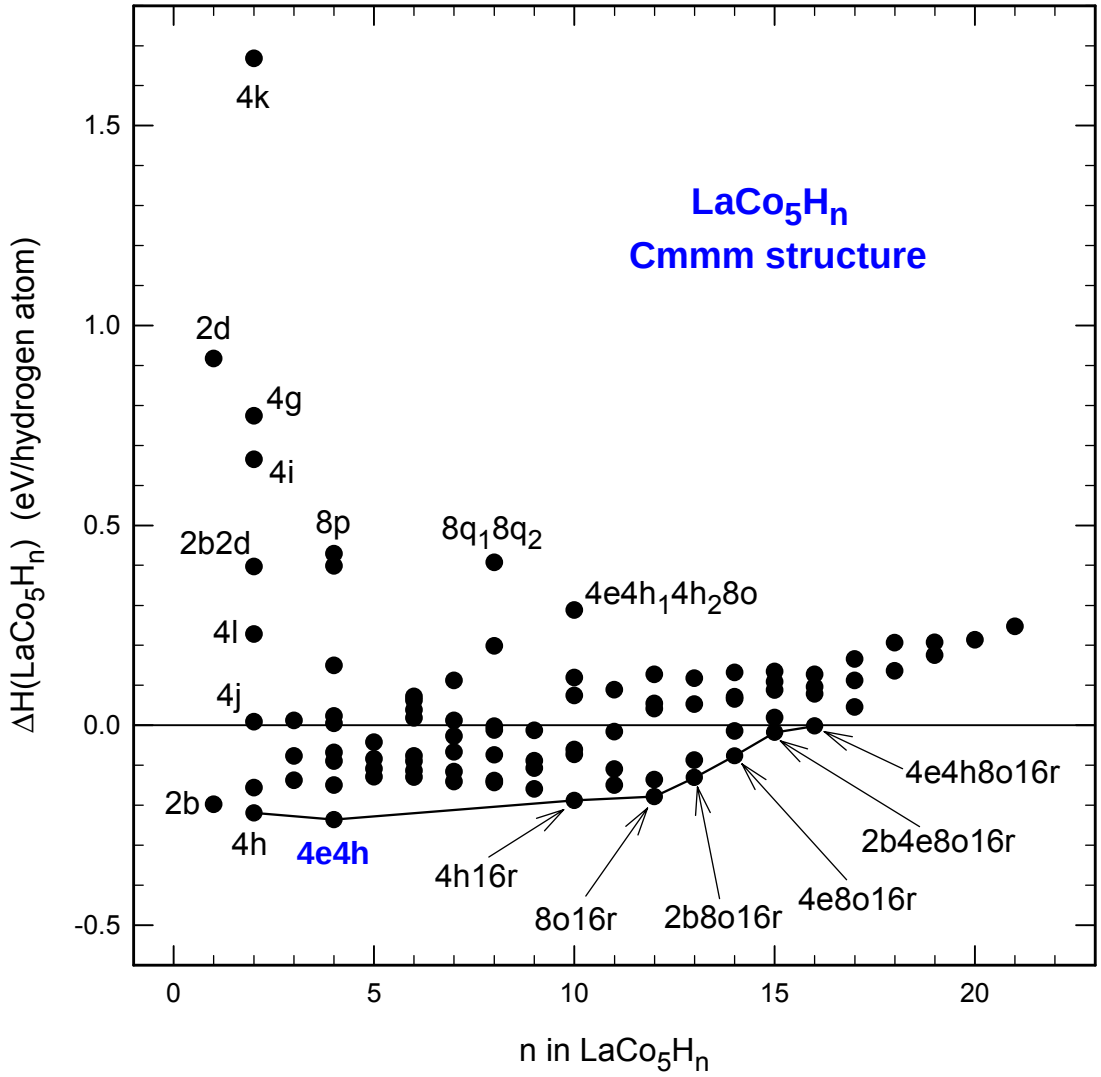
  $\Delta H(LaCo_5H_n) = E(LaCo_5H_n) - E(LaCo_5) - (n/2)E(H_2)$

  for various hydrogen configurations and occupancies
- Examined 38 hydrogen configurations in $LaNi_5H_n$, 93 configurations in $LaCo_5H_n$

Site-dependent Enthalpies of Formation in $LaNi_5H_n$



Site-dependent Enthalpies of Formation in $LaCo_5H_n$

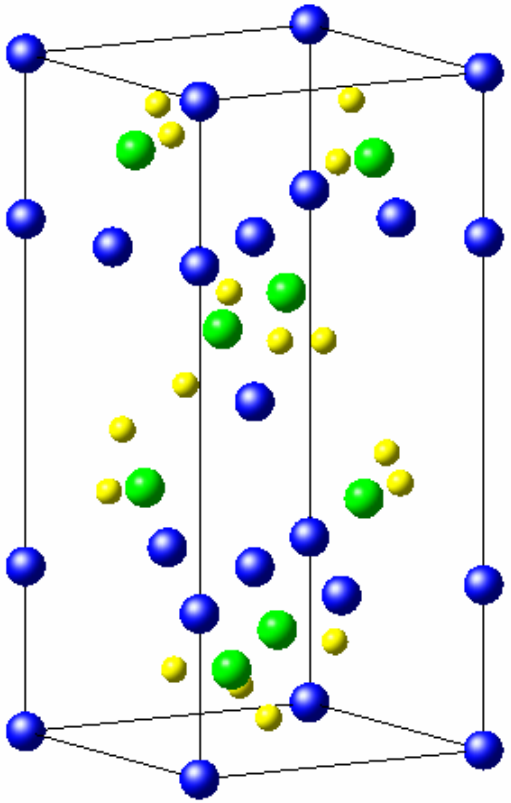


Energetics of a Novel Hydrogen Storage Reaction:

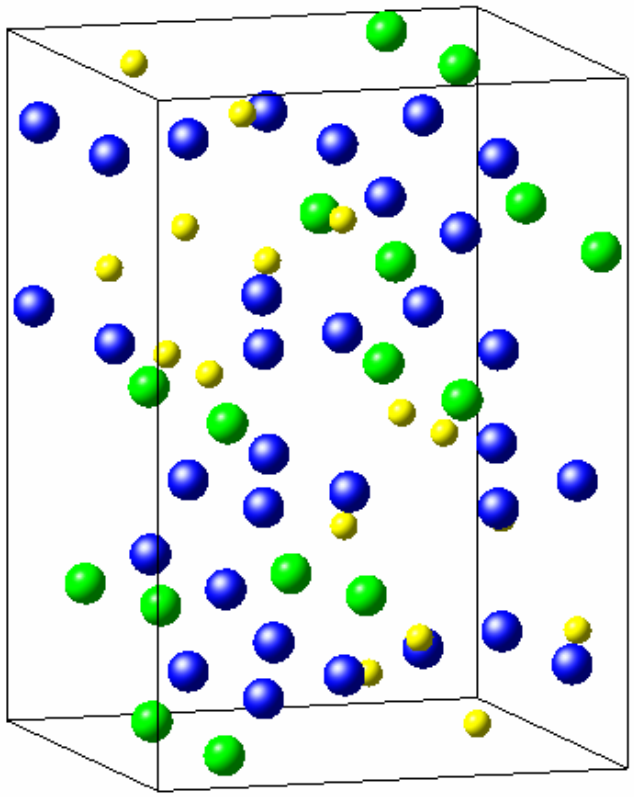
$$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2$$

Crystal Structures

$LiNH_2$ amide
tetragonal I-4

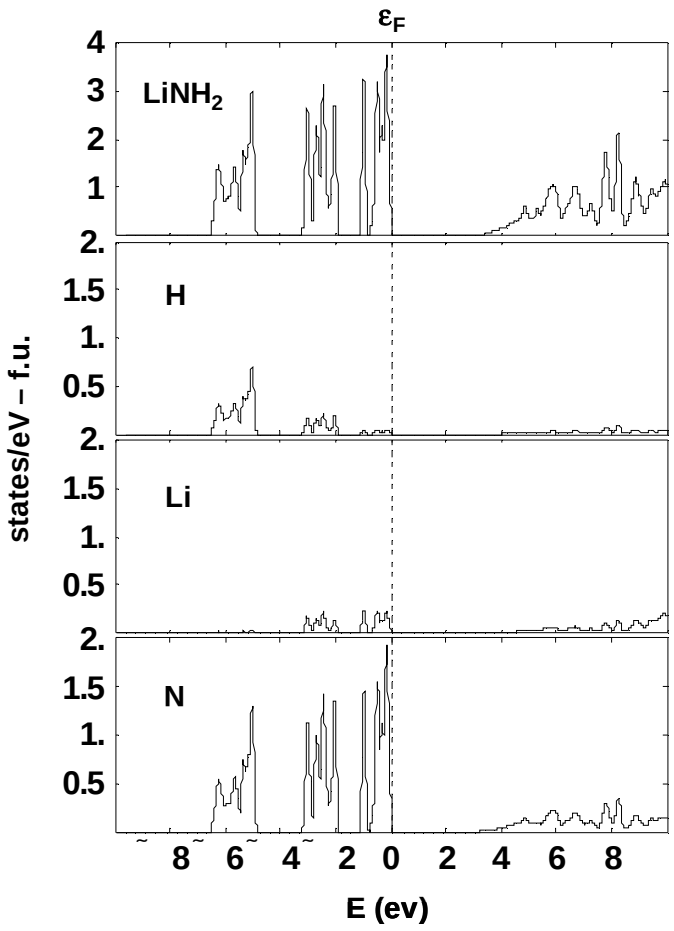


Li_2NH imide
orthorhombic Ima2

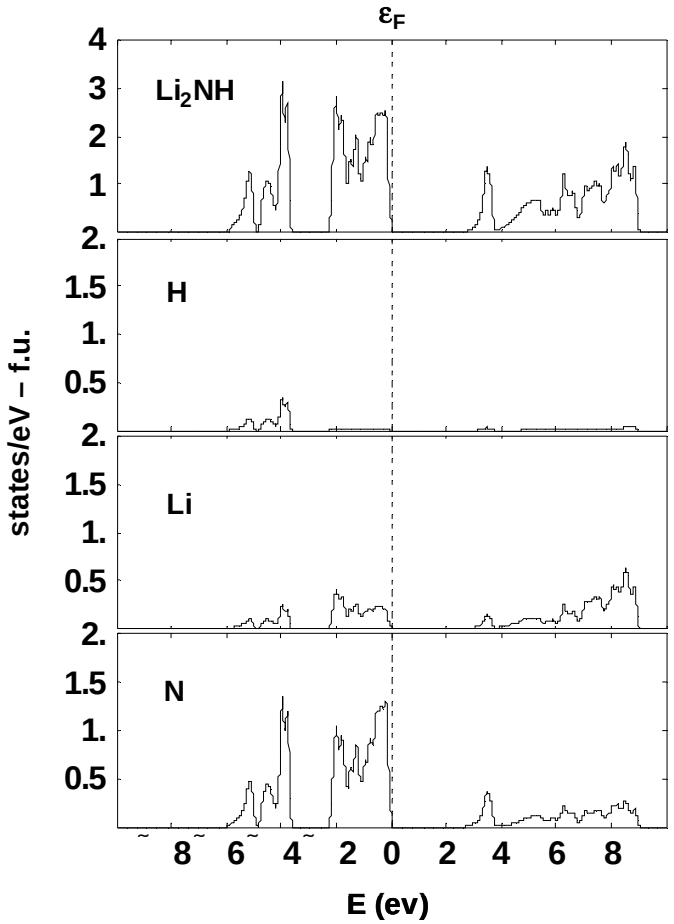


Densities of States

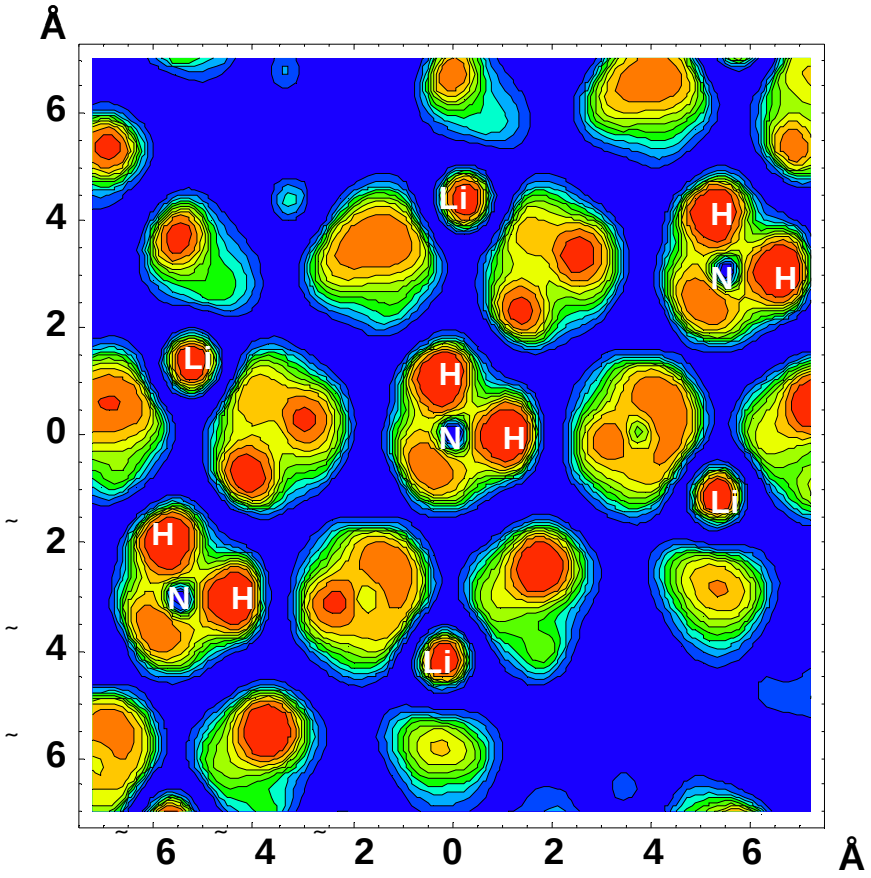
Li amide

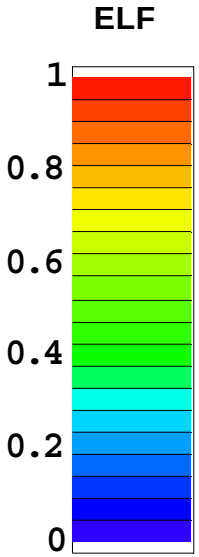


Li imide

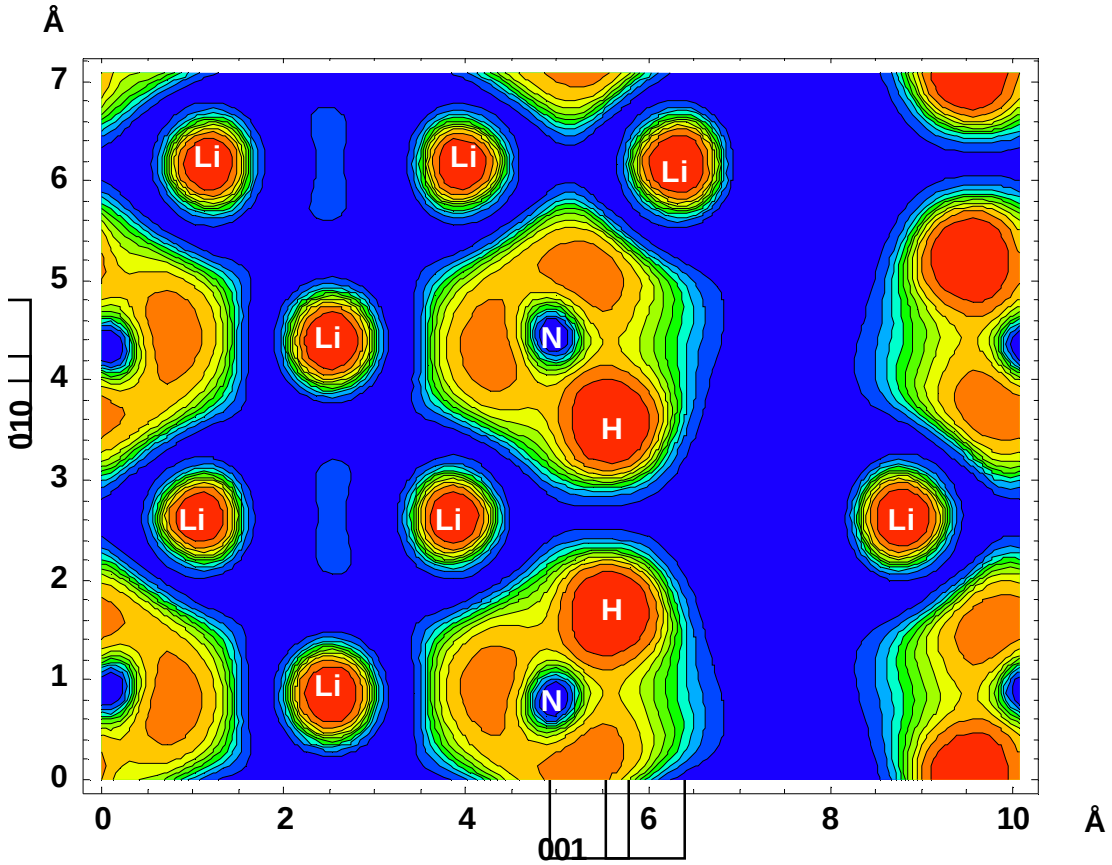


ELF for $LiNH_2$





ELF for Li_2NH



Enthalpies of Formation

T = 0:

$$\Delta H_0 = \Delta H_{el} + \Delta H_{ZPE}$$

$$\Delta H_0(LiNH_2) = \Delta H_{el}(LiNH_2) + \Delta H_{ZPE}(LiNH_2)$$

$$= [E_{el}(LiNH_2) - E_{el}(Li) - \tfrac{1}{2}E_{el}(N_2) - E_{el}(H_2)]$$

$$+ [E_{ZPE}(LiNH_2) - E_{ZPE}(Li) - \tfrac{1}{2}E_{ZPE}(N_2) - E_{ZPE}(H_2)]$$

T = 298K:

$$\Delta H_{298} = \Delta H_0 + \delta\Delta H_{298}$$

$$\delta\Delta H_{298}(LiNH_2) = E_{ph}(LiNH_2) - E_{ph}(Li)$$

$$- \tfrac{1}{2}[7/2\ kT + E_{vib}(N_2)] - [7/2\ kT + E_{vib}(H_2)]$$

Enthalpies of Formation ΔH_{298} and Reaction ΔH_R

	$LiNH_2$	LiH	Li_2NH
ΔH_{el}	-196	-84	-194
ΔH_{ZPE}	31	3	16
$\delta\Delta H_{298}$	-8	-4	-6
ΔH_{298} kJ/mole	-173	-85	-184
ΔH_{298} expt kJ/mole	-176	-91	-222

$$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2$$

$$\Delta H_R = \Delta H_{298}(Li_2NH) - \Delta H_{298}(LiNH_2) - \Delta H_{298}(LiH)$$

$$\Delta H_R(\text{components, expt}) = -222 + 91 + 176 = 45 \text{ kJ/mole}$$

$$\Delta H_R(\text{calc}) = -184 + 85 + 173 = 74 \text{ kJ/mole}$$

$$\Delta H_R(\text{direct expt}) = 66 \text{ kJ/mole}$$

$$\Rightarrow \Delta H_{298} \text{ expt } (Li_2NH) = -222 \text{ kJ/mole likely inaccurate}$$

Summary

- DFT is capable of accurately describing properties of metallically-bonded hydrides such as $LaNi_5H_n$ and $LaCo_5H_n$, as well as complex hydrides such as $LiNH_2$ and Li_2NH
- Large, growing body of DFT results on other systems: binary hydrides, $NaAlH_4$, $LiAlH_4$, $LiBH_4$, etc.

  Session U14: Modeling Thursday 3/24 8a

- No question regarding the power of DFT for known hydrides

  ** ***Going forward*****:** one goal is the imaginative use of DFT to spur discovery of technologically viable hydrogen storage materials