

# ***“Insights” from simulation on the electronic and thermodynamic properties of novel light-metal amidoboranes***

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B. Kerkeni, S. A. Shevlin &  
Z. X. Guo

Department of Chemistry  
University College London  
Gower St  
London  
WC1E 6BT  
United Kingdom



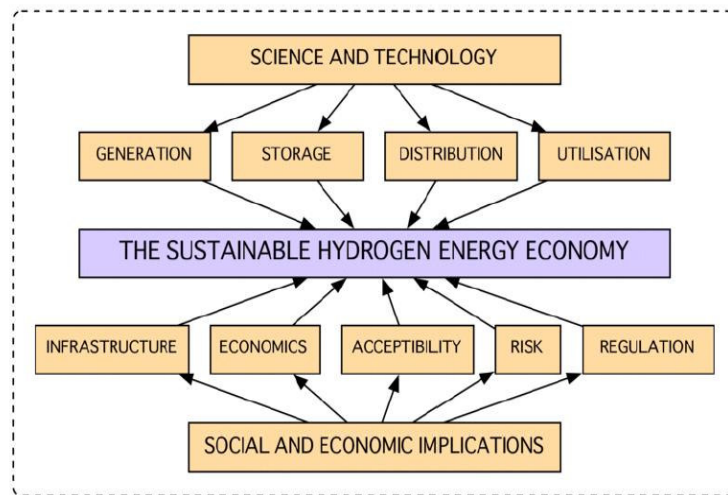
# Contents

- 1: Hydrogen as a clean fuel and storage issues
- 2: Simulation methodology
- 3: Ammonia borane
- 4: Metal amidoboranes (Li, Na, Mg)
- 5: Conclusions

# 1: Hydrogen as a fuel

- UK is seeking international commitment to cut emissions of CO<sub>2</sub> by 20% by 2020
- In order to achieve this, need to switch from fossil to “clean” fuels
  - Especially for vehicular applications
- Hydrogen, with a high energy density of 119 MJ/Kg, is the favourite replacement
- Prime issue for hydrogen applications are:
  - Storage (safe and efficient)

*THE SUPERGEN INITIATIVE*



# 1: Storage requirements

- Target for hydrogen storage systems is to allow vehicles to drive 480 km range
  - This requires storing 5.6 kg H<sub>2</sub>
  - 2 kWh/kg H<sub>2</sub> storage (6 wt.%)
- Other targets are:
  - Compactness
  - Low cost
  - Near room temperature operation
  - Allow easy refuelling and safe operation
- Thus favoured solution is storage in solid systems (R&D in the use of novel condensed-phase hydride materials)
- However, currently no material meets all these requirements

## 2: Simulation & Hydrogen storage

- How can simulation aid research into hydrogen storage materials?
  - Determine  $H_2$  binding energies
  - Determine activation barriers for  $H_2$  release
- A quantity of interest is the electronic *binding energy* of  $H_2$  to the substrate

- This is defined as:

$$E_{\text{Bind}}(H_2) = E_{\text{Tot}}(X) + E_{\text{Tot}}(H_2) - E_{\text{Tot}}(X + H_2)$$

$E_{\text{Tot}}(X + H_2)$  is energy of the total system

$E_{\text{Tot}}(X)$  is energy of system after  $H_2$  removed  $E_{\text{Tot}}(H_2)$  is energy of isolated  $H_2$

- The more positive  $E_{\text{bind}}$ , the more strongly  $H_2$  bound
- For practical applications, want  $E_{\text{bind}}$  between 0.2 and 0.7 eV/ $H_2$

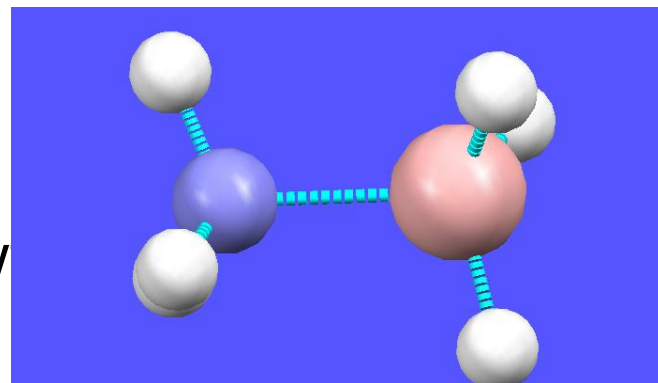
## 2: Methodology

- We performed density functional theory simulations using VASP
- A plane wave basis set is used, with a cutoff of 450 eV
- $\Gamma$ -point sampling is sufficient for both systems used
- PAW used to treat core electrons, with the PBE xc-functional
- Climbing Nudged Elastic Band method used for barrier calculation, with transition state structures re-relaxed with the dimer method
- To check results, we performed PBE and B3LYP calculations using GAUSSIAN03 with the 6-311G++(d,p) basis set

Both PBE calcs give similar results to within 1/100 eV

# 3: Ammonia borane ( $\text{NH}_3\text{BH}_3$ )

- Prototype system: ammonia borane (**AB**,  $\text{NH}_3\text{BH}_3$ ), as it has a large hydrogen storage capacity of 19.6 w %
- Unfortunately, by itself it does not meet targets
  - it is too **unstable** w.r.t. dehydrogenation
  - Has got side products



● B

● N

○ H

	$E_{\text{Bind}}$	$E_{\text{Bind}} + \text{ZPE}$	$\Delta G(\text{R.T})$	XC
$\text{NH}_3\text{BH}_3$	0.075	-0.227	-0.532	PBE
	-0.100	-0.418	-0.701	B3LYP



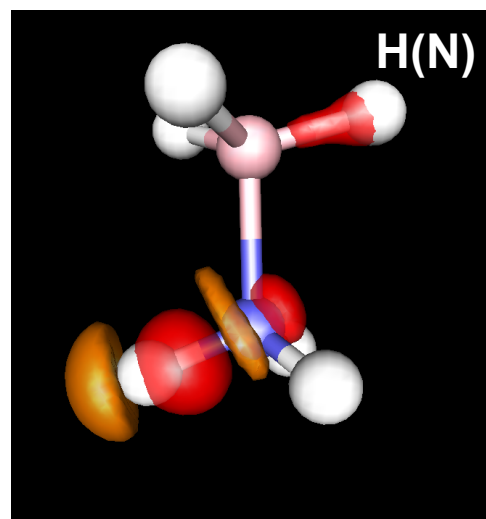
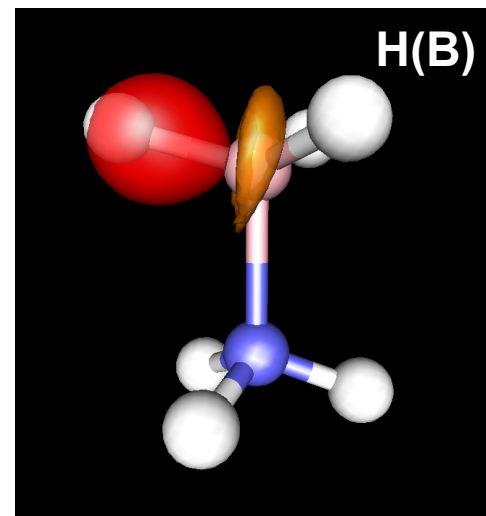
Unstability?

# 3: Binding of hydrogen

- We look at the binding of H atoms to **AB**, via calculation of the charge density difference

$$\text{CDD} = \rho(\text{NH}_3\text{BH}_3) - \rho(\text{NH}_2\text{BH}_3) - \rho(\text{H})$$

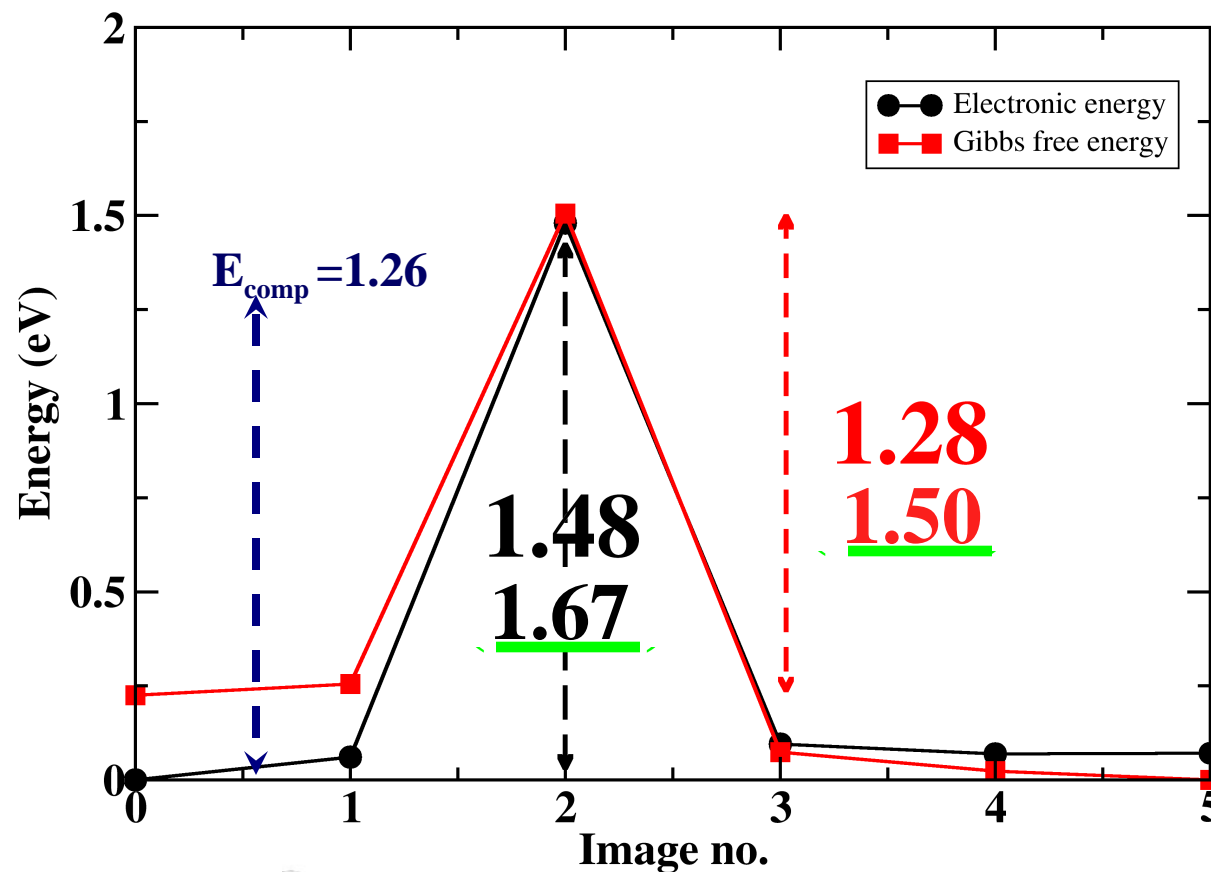
- The H atom that is bound to the B atom [H(B)] withdraws electron density from the bond
- We can therefore consider it negatively charged
- In contrast, H(N) positively charged
- The molecule as a whole is **thermodynamically destabilised against neutral H<sub>2</sub> release**



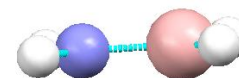
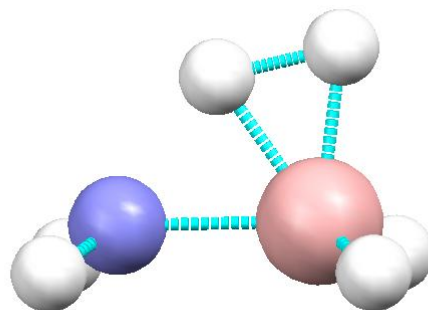
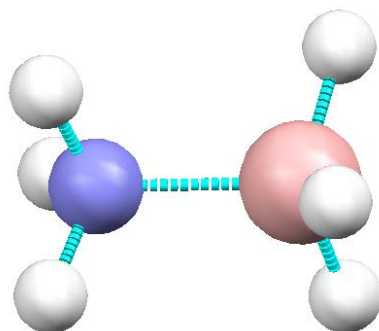
So why does AB exist at room T?



# 3: H<sub>2</sub> dissociation barrier (NH<sub>3</sub>BH<sub>3</sub>)



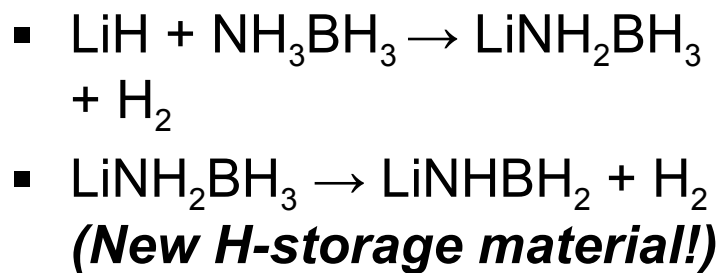
**B3LYP**



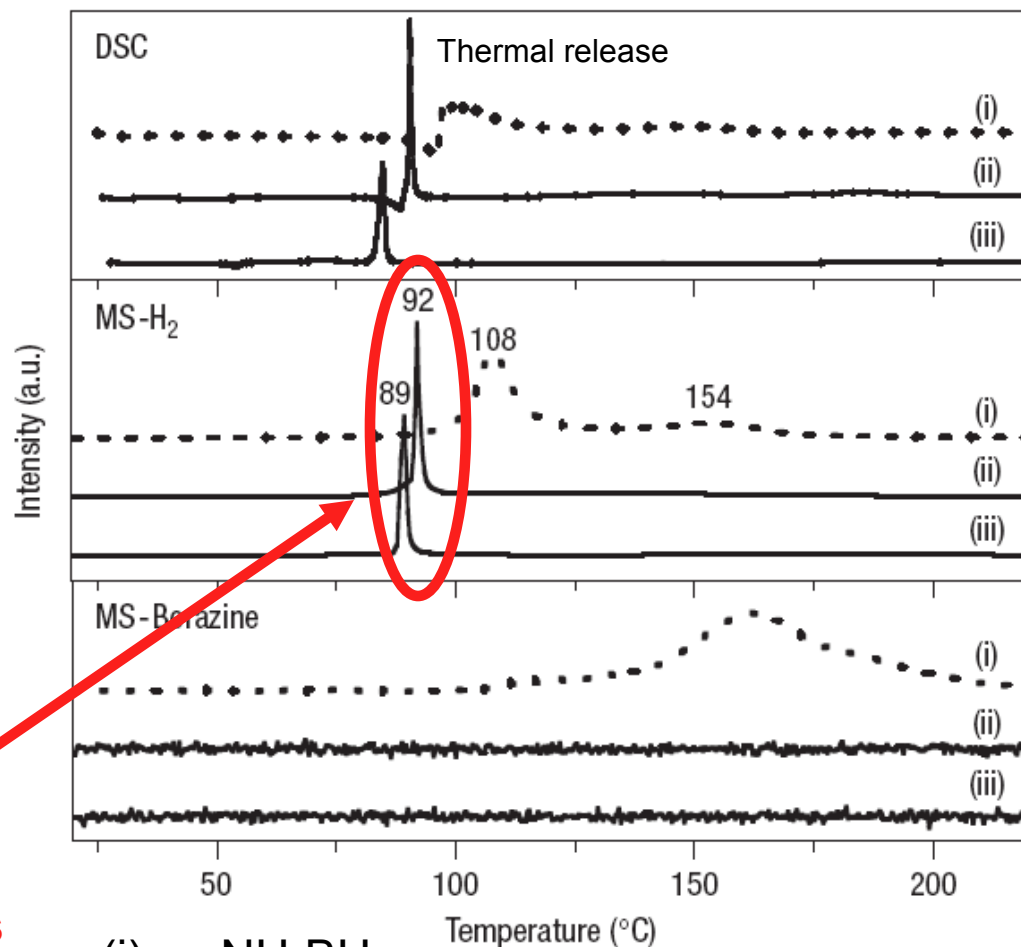
Not an ideal material for hydrogen storage

# 4: Metal-doped amidoboranes

- A recent experiment <sup>[1]</sup> found H<sub>2</sub> release from the interaction of Group I hydrides (LiH, Na) with **AB**



- These new materials have significantly improved hydrogen storage properties
- H<sub>2</sub> release at lower temperatures**



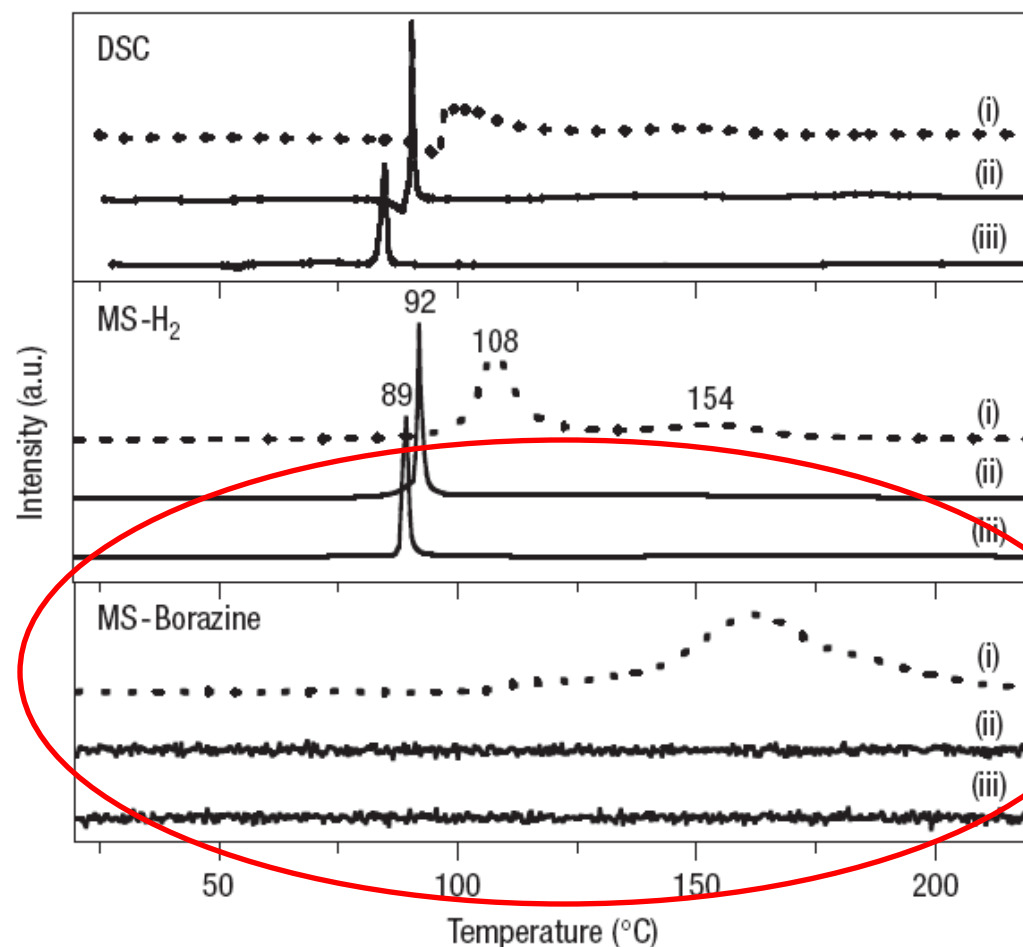
(i) = NH<sub>3</sub>BH<sub>3</sub>

(ii) = LiNH<sub>2</sub>BH<sub>3</sub>

(iii) = NaNH<sub>2</sub>BH<sub>3</sub>

# 4: Metal-doped amidoboranes

- Borazine ( $B_3N_3H_6$ ) is aromatic and toxic



2. No borazine release for the alkali-metal amidoboranes, which could be indicative of reversibility

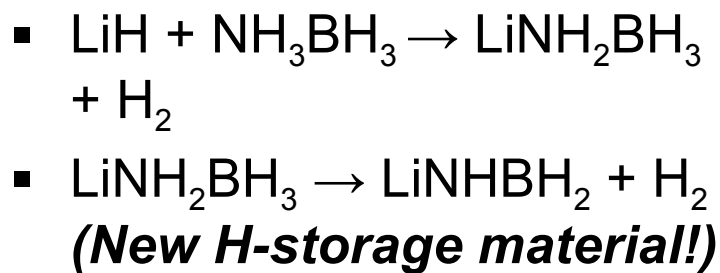
(i) =  $NH_3BH_3$

(ii) =  $LiNH_2BH_3$

(iii) =  $NaNH_2BH_3$

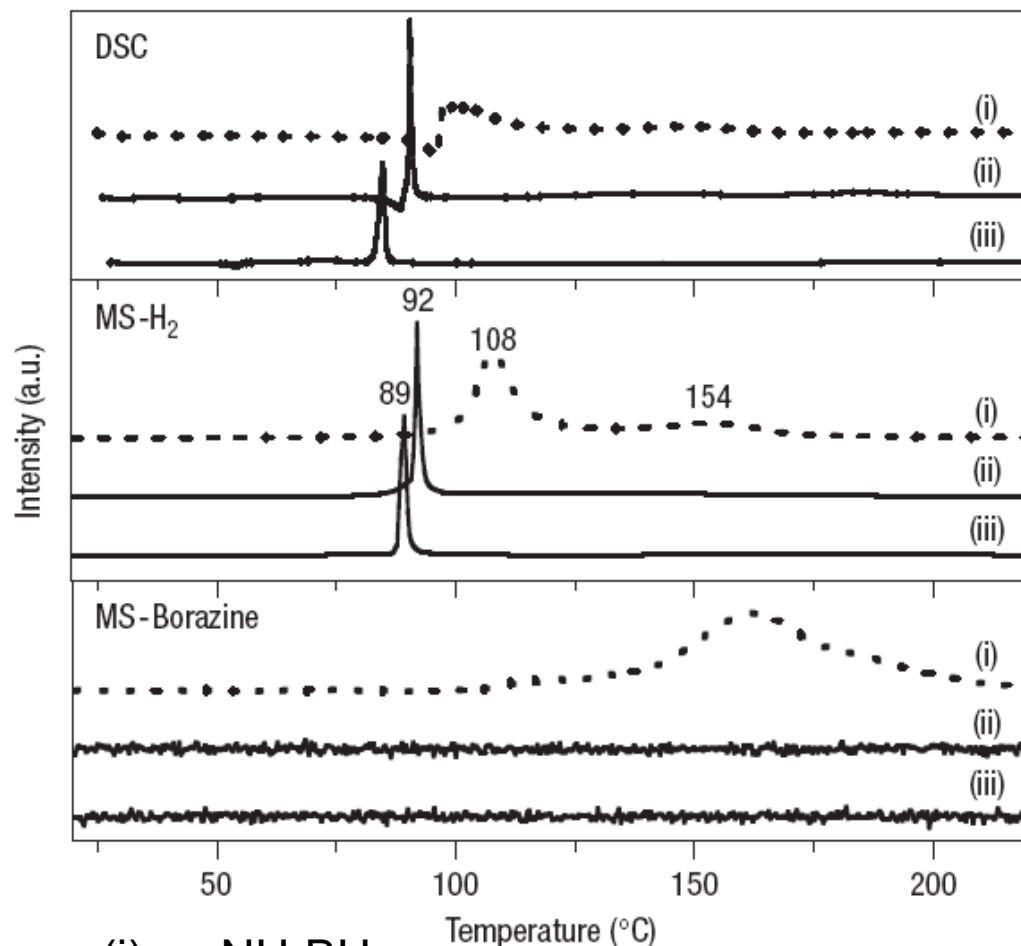
# 4: Metal-doped amidoboranes

- A recent experiment <sup>[1]</sup> found H<sub>2</sub> release from the interaction of Group I hydrides (LiH, NaH) with **AB** with **AB**



- These new materials have significantly improved hydrogen storage properties

- What are their structural, electronic, and thermodynamic properties?**



(i) = NH<sub>3</sub>BH<sub>3</sub>

(ii) = LiNH<sub>2</sub>BH<sub>3</sub>

(iii) = NaNH<sub>2</sub>BH<sub>3</sub>



# 4: Molecular properties

- In order to understand these reactions, we first need to consider gas-phase properties
- We calculate structure, energetics, and electronic properties of the following molecules:
  - $\text{LiNH}_2\text{BH}_3$
  - $\text{NaNH}_2\text{BH}_3$
  - $\text{NH}_3\text{BH}_3$
  - $\text{MgHNNH}_2\text{BH}_3$  (Mg needs to be twofold coordinated)
- Note, in order to include finite temperature effects we calculate the full Gibbs free energy:

$$G(T) = E_0 + U(T) - TS(T)$$

$$G(T) = E_0 + E_{\text{ZPE}} + U_{\text{vib}}(T) - T(S_{\text{vib}}(T) + S_{\text{rot}}(T) + S_{\text{trans}}(T))$$

$$G(T) \sim E_0 + E_{\text{ZPE}} + U_{\text{vib}}(T) - TS_{\text{vib}}(T)$$

# 4: Structure, energetics

- It was proposed that the metal atom replaces a H atom on the N-moiety
- This binding is energetically preferred w.r.t. bulk hydride (chosen as reference)

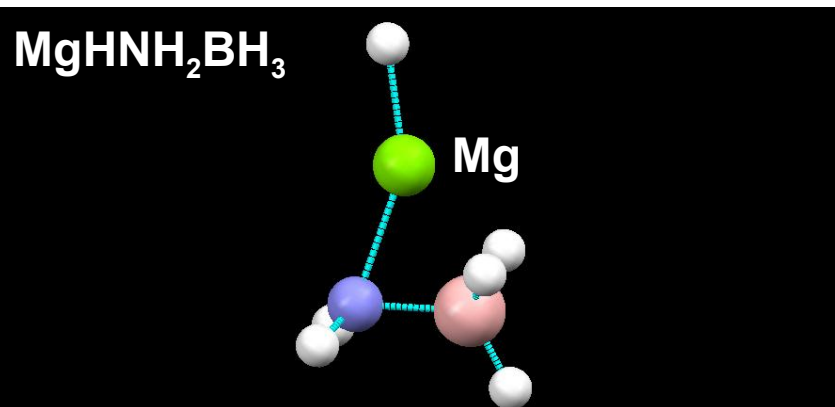
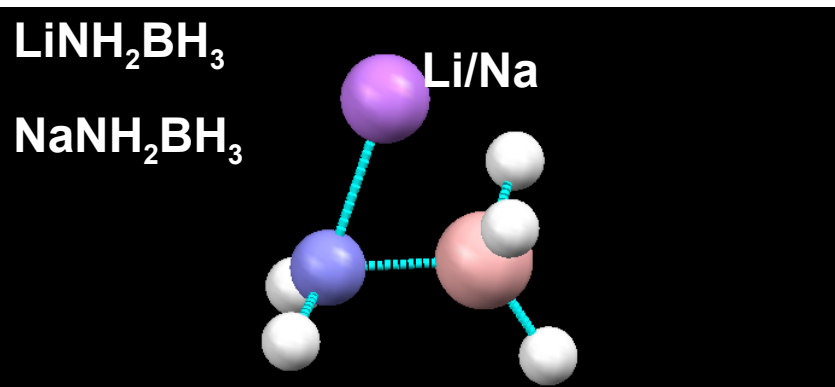
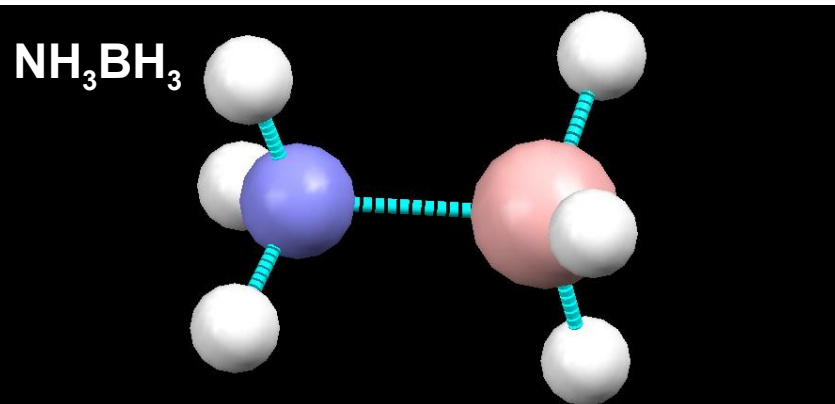
$$E_{\text{bind}}(\text{Li}) = \underline{0.85 \text{ eV/atom}}$$

$$E_{\text{bind}}(\text{Na}) = 0.42 \text{ eV/atom}$$

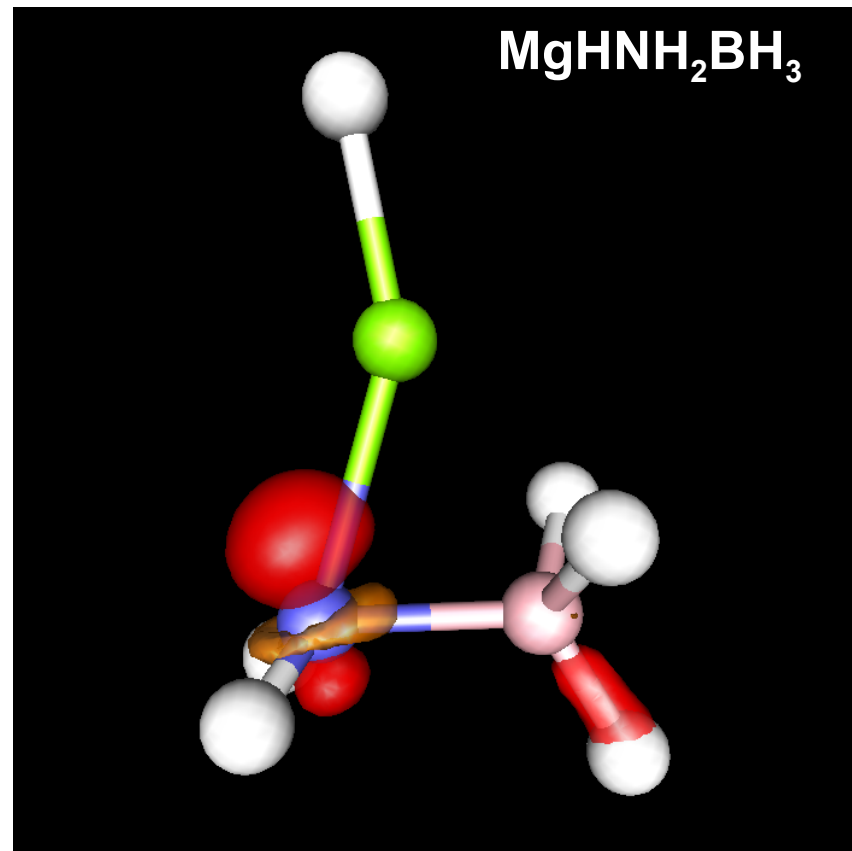
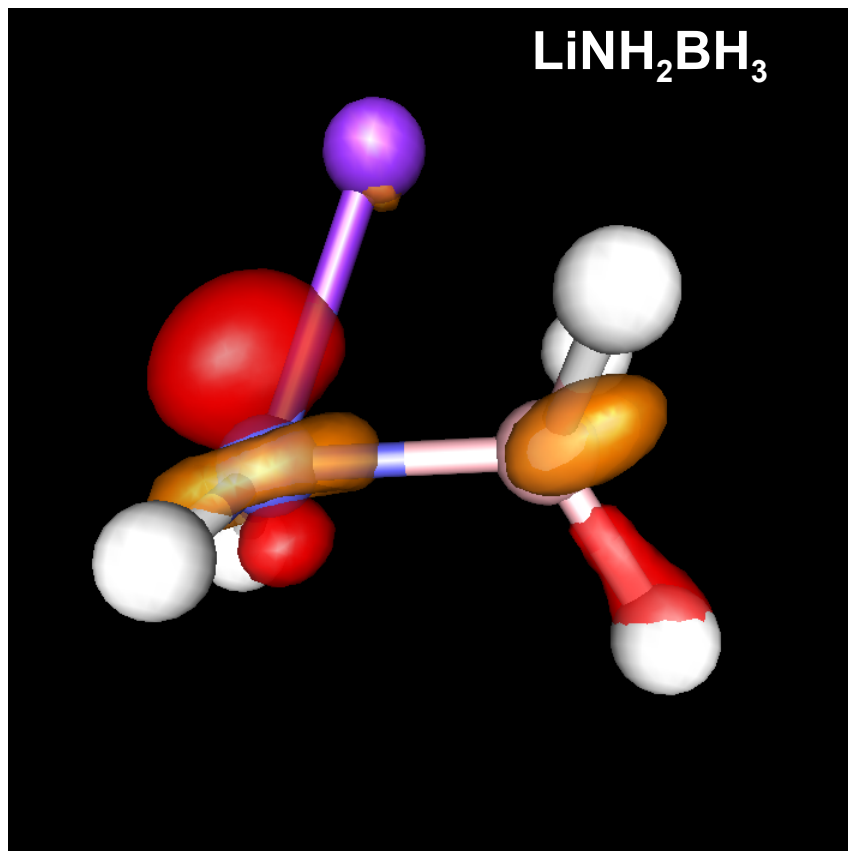
$$E_{\text{bind}}(\text{MgH}) = 0.43 \text{ eV/atom}$$

- All structures are stable

- The Li, Na, and MgH pair all “bridge” the BN bond, with metal-N distance  $\sim 0.1 \text{ \AA}$  smaller than metal-B distance

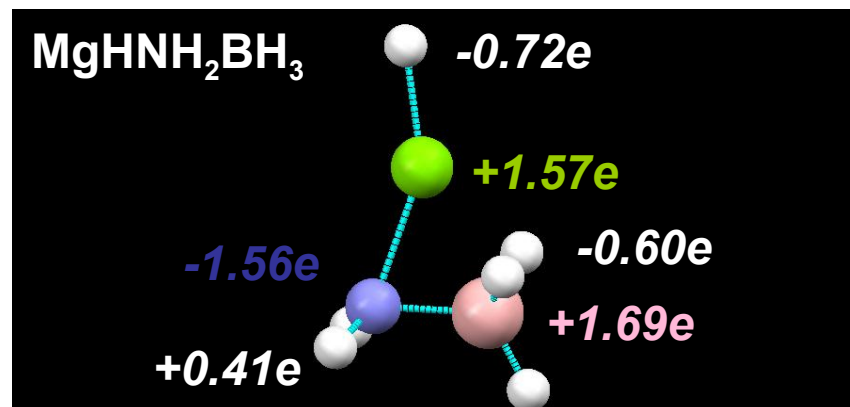
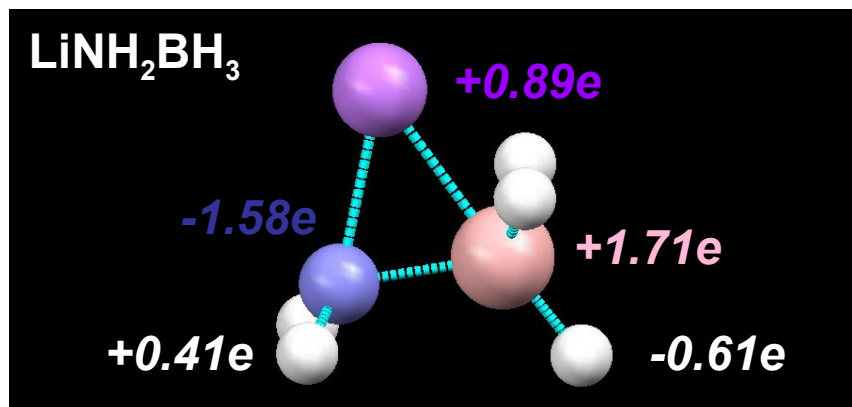
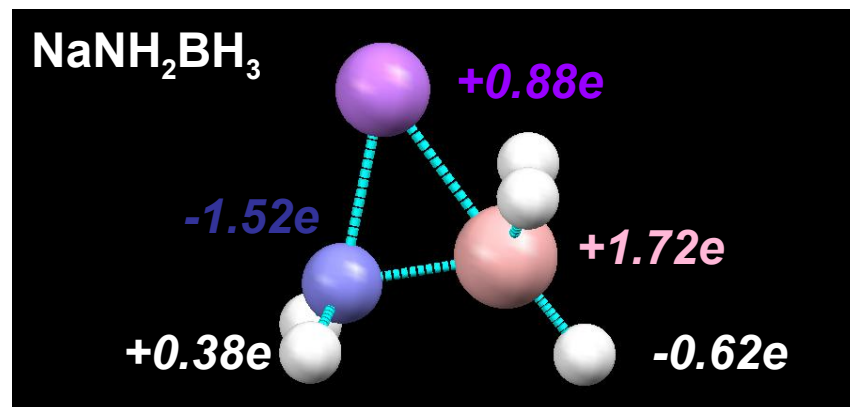
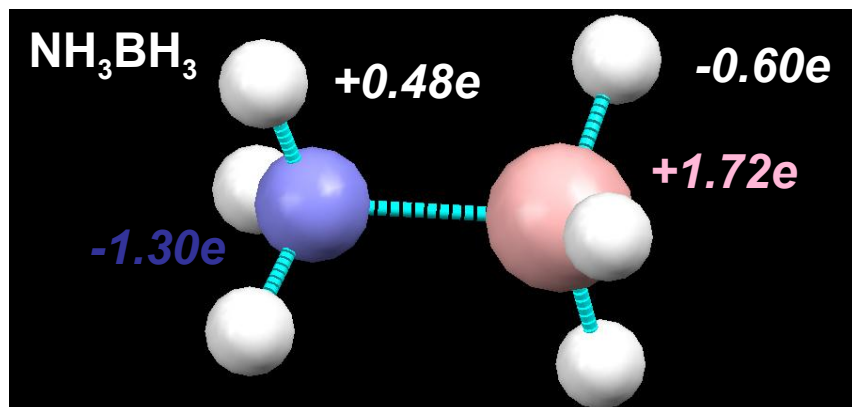


# 4: CDD analysis



- Charge density difference for the Li/MgH component can reveal nature of binding (**red** is electron accumulation, **orange** is electron depletion)
- We see that there is a **strong accumulation** of density on the N atom due to donation from Li/Na or MgH: **the bond is truly formed with N**

# 4: Bader charge analysis



- **H(N)** is positively charged and **H(B)** is negatively charged (Mulliken analysis agrees)
- Addition of Group I and II metal atoms increases the charging of N, but decreases the charging on H(N) atoms. We expect stronger H binding
- Note: The  $(\text{NH}_3)^+(\text{BH}_3)^-$  complex becomes more ionic with addition of I/II atom  
 Stronger dipole than AB, more stable amidoborane complex?



# 4: Complexation energy

- $(\text{NH}_2\text{X})^+(\text{BH}_3)^-$  complex becomes more ionic upon H substitution
- How does this affect energy of complexation?

$$E_{\text{Comp}} = E_{\text{Tot}}(\text{NH}_2\text{X}) + E_{\text{Tot}}(\text{BH}_3) - E_{\text{Tot}}(\text{NH}_2\text{XBH}_3)$$

	$E_{\text{Comp}} + \text{ZPE (eV)}$
$\text{NH}_3\text{BH}_3$	1.26
$\text{LiNH}_2\text{BH}_3$	2.69
$\text{NaNH}_2\text{BH}_3$	2.71
$\text{MgH}\text{NH}_2\text{BH}_3$	2.28

More strongly bound compounds

- Why is this important? For bare **AB**,  $E_{\text{Comp}}$  is less than activation barrier (1.48) for  $\text{H}_2$  release
  - Ammonia borane will disintegrate, not a reversible hydrogen store
- Is this true for metal amidoboranes? And what is  $E_{\text{Bind}}$ ?

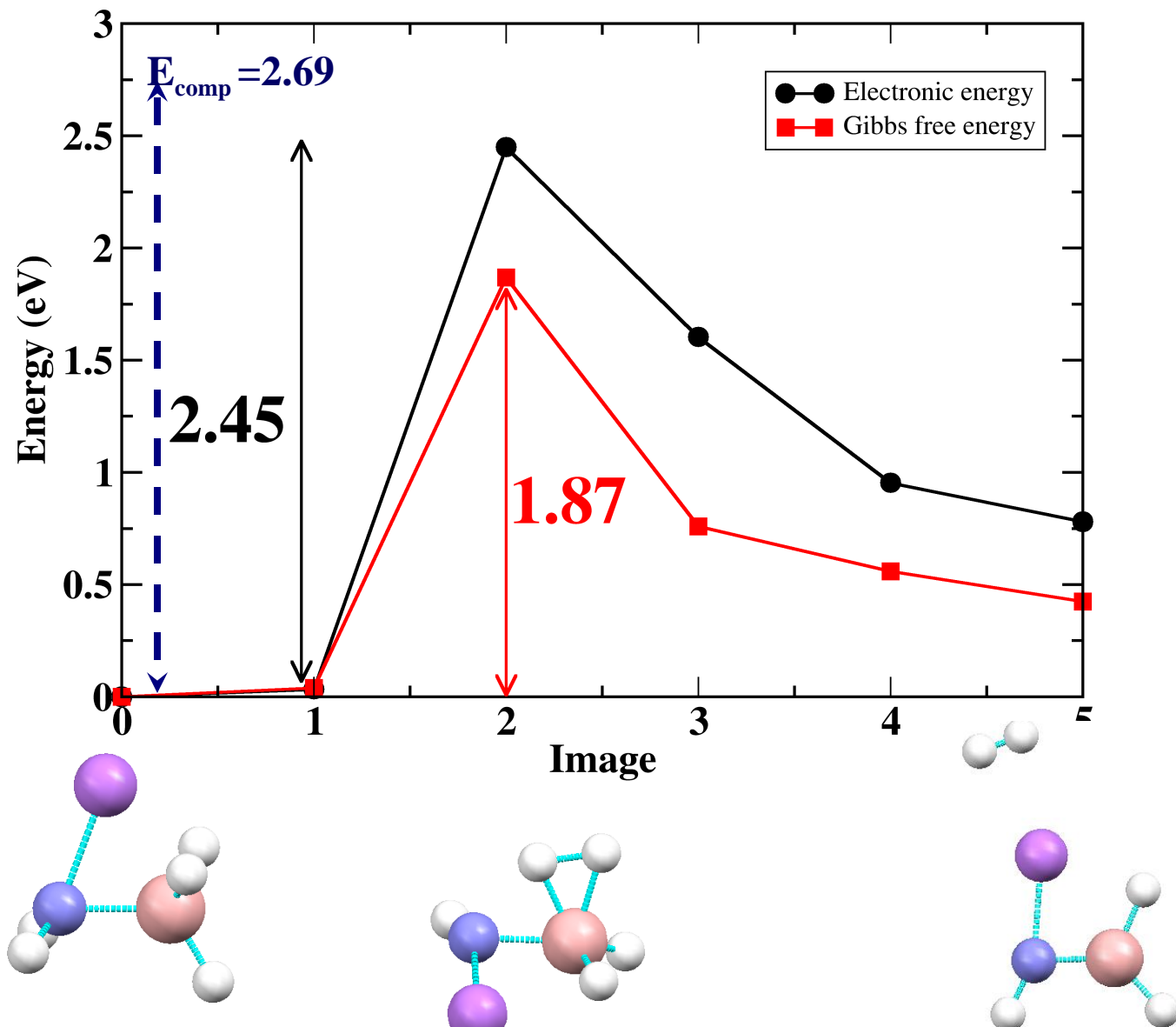
## 4: Thermodynamics of H<sub>2</sub> release

System	$E_{\text{bind}}(E_0)$	$E_{\text{bind}}(E_{0,\text{ZPE}})$	$G(T=300)$	$H(T=300)$
NH <sub>3</sub> BH <sub>3</sub>	0.08 eV	-0.23 eV	-0.53 eV	-0.15 eV
LiNH <sub>2</sub> BH <sub>3</sub>	0.91 eV	0.61 eV	0.30 eV	0.75 eV
NaNH <sub>2</sub> BH <sub>3</sub>	0.96 eV	0.66 eV	0.35 eV	0.74 eV
MgHNNH <sub>2</sub> BH <sub>3</sub>	0.86 eV	0.53 eV	0.22 eV	0.62 eV

- Similar ZPEs, the trend remains the same for the free energies
- Dehydrogenation of NH<sub>3</sub>BH<sub>3</sub> is exothermic at room temperature, others are endothermic
- All amidoboranes are more stable w.r.t. dehydrogenation than NH<sub>3</sub>BH<sub>3</sub>
  - ***This is contrary to experiment***
- Regarding functionals, B3LYP underbinds w.r.t. electronic binding energies and enthalpies, but no clear trend for free energies.
- MgHNNH<sub>2</sub>BH<sub>3</sub> is most unstable amidoborane at RT, **Addition of MgH is best for releasing H<sub>2</sub> at or near room temperature**

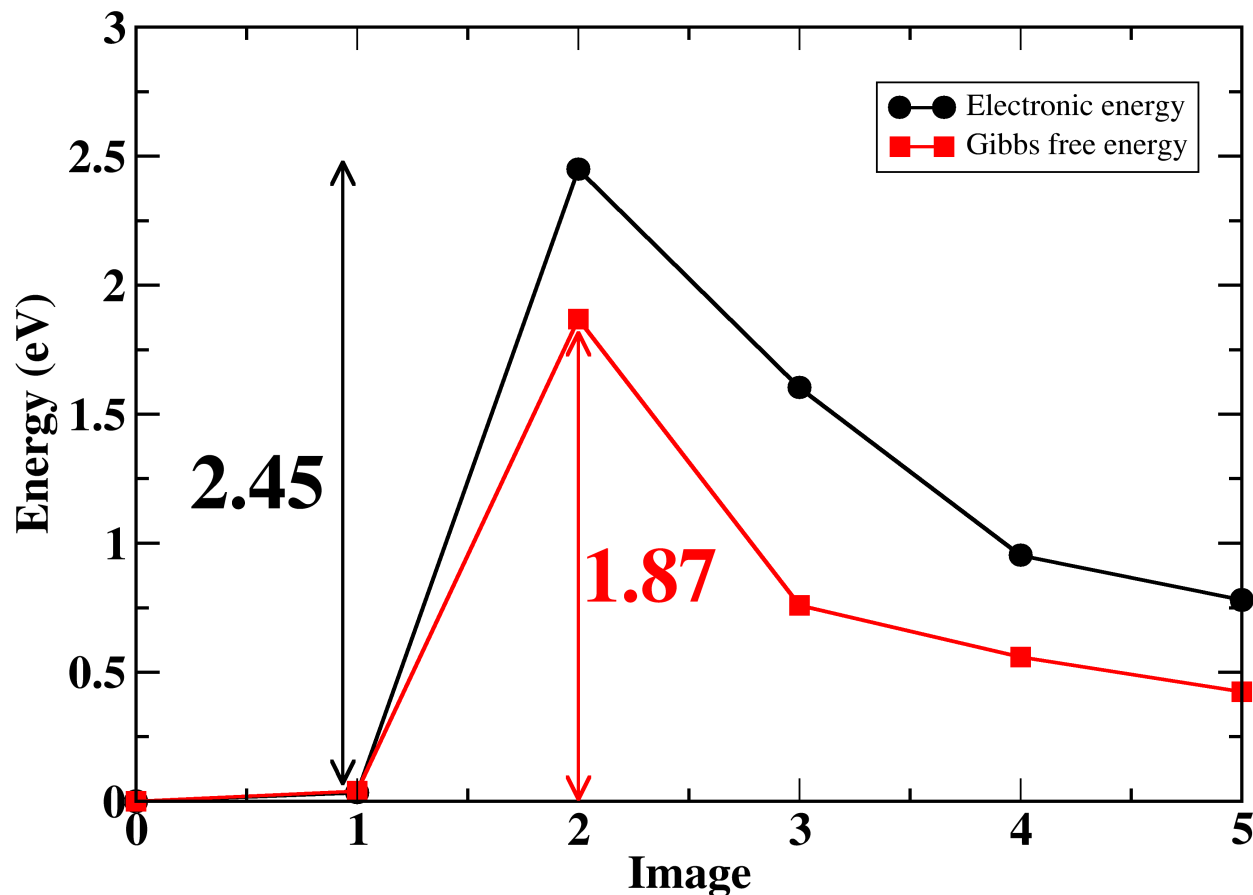
Same kind of fragmentation as seems likely for AB?

# 4: Activation barrier ( $\text{LiNH}_2\text{BH}_3$ )



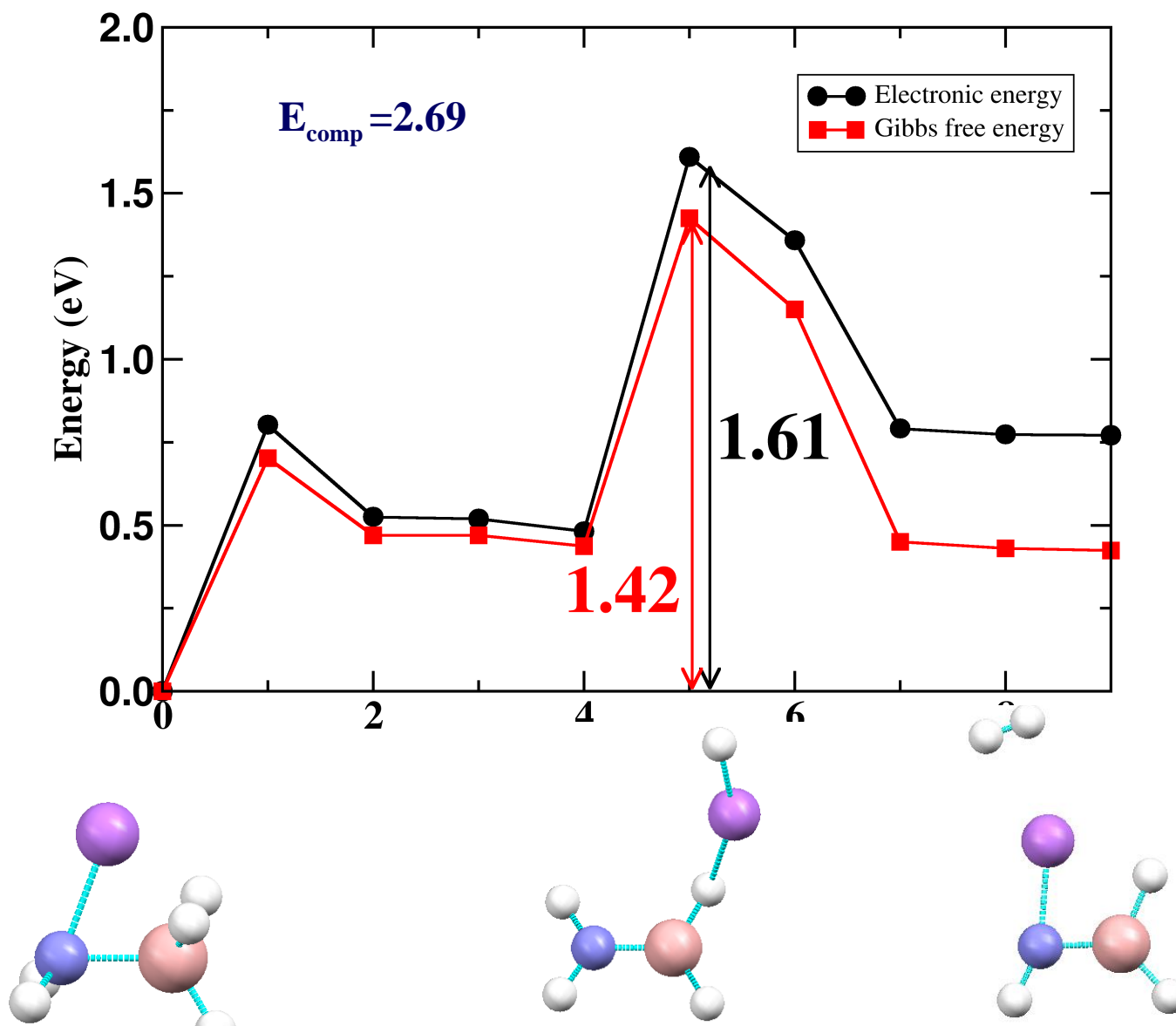
$\text{LiNH}_2\text{BH}_3$  is less likely to disintegrate before  $\text{H}_2$  release

## 4: Activation barrier ( $\text{LiNH}_2\text{BH}_3$ )



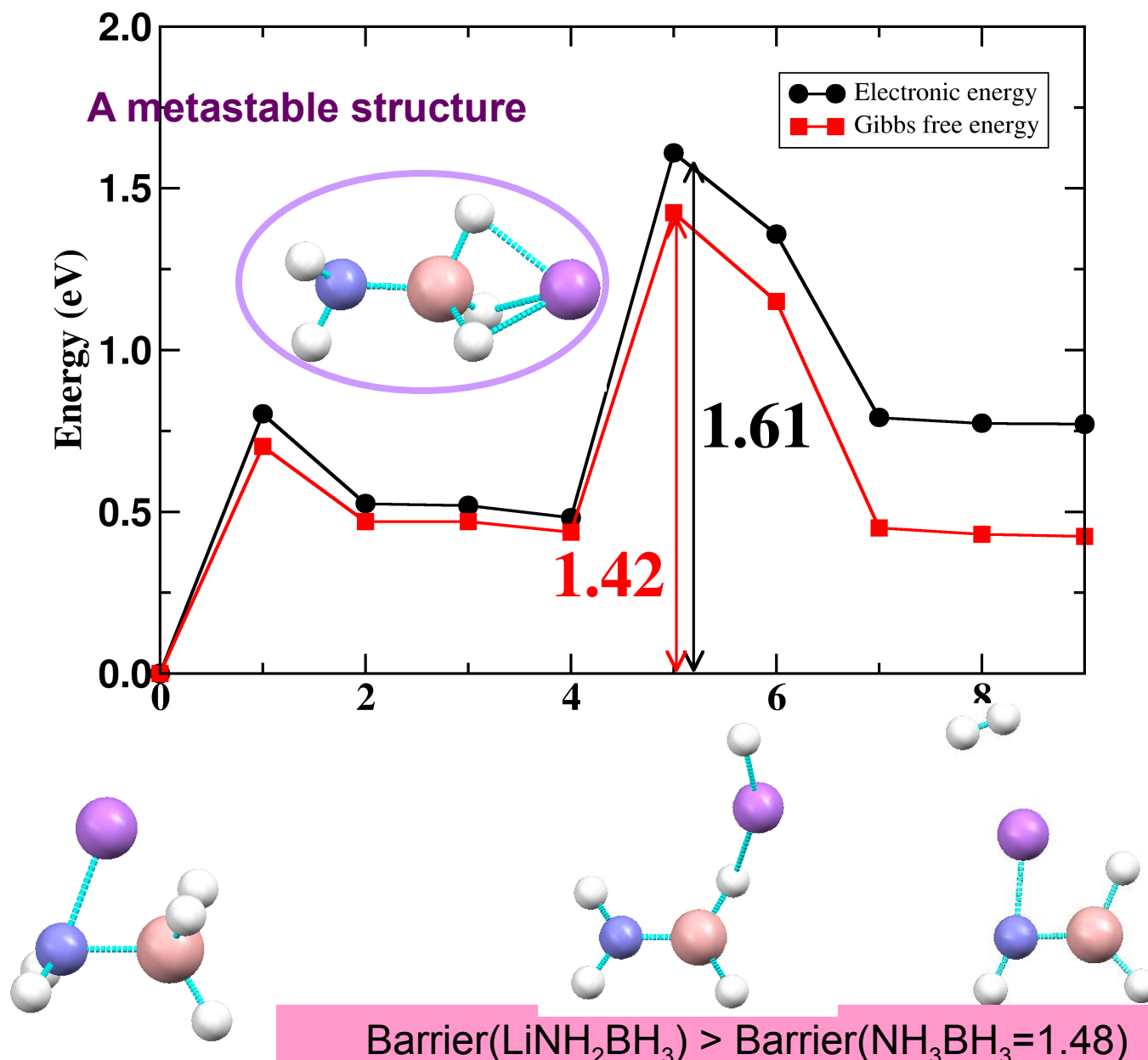
**Interesting but this is not minimum energy pathway!**

# 4: MEP of $\text{LiNH}_2\text{BH}_3$



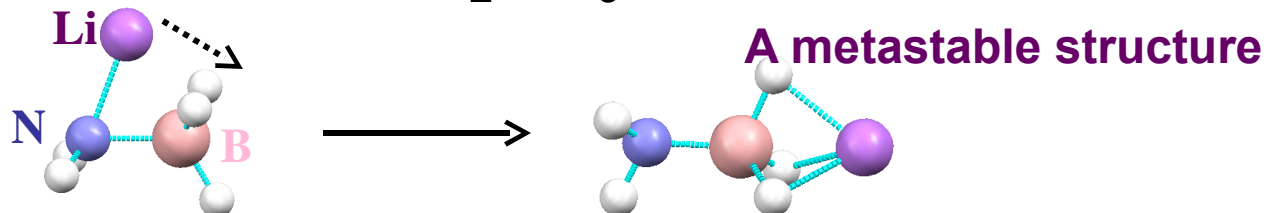
The molecule backbone is stable and the reaction more likely to be reversible

# 4: MEP of $\text{LiNH}_2\text{BH}_3$

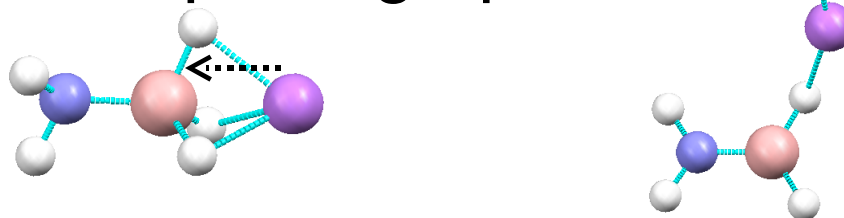


# 4: Li is a carrier!

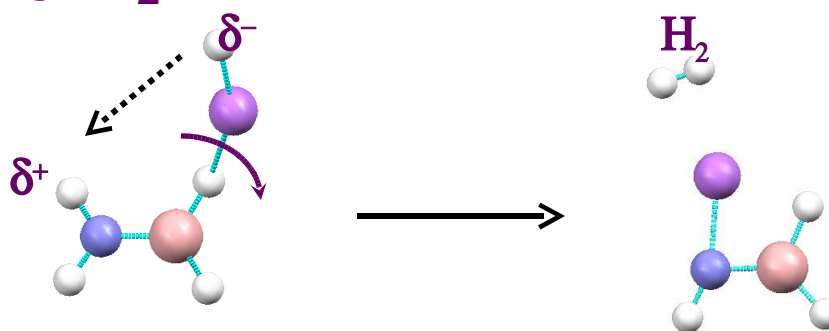
- Moves from one end of  $\text{LiNH}_2\text{BH}_3$  to the other



- Then moves back picking up a H



- Rotates around bond placing H atoms together, and facilitating  $\text{H}_2$  release



Hydrogen removal energy and the reaction barrier are > than AB

# 5: Conclusions

- Metal-coordinated amido-boranes are stable w.r.t. segregation to hydrides
- Metal atoms dump electron density into N atom, this acts to increase hydrogen binding, with concomitant modification of the chemical bonding between B and N
  - Consistent picture regardless of exchange-correlation functional used
- Pure **AB** will fragment, as **complexation** energy less than **activation barrier** for  $H_2$  release
- This is not the case for  $LiNH_2BH_3$  (and others)
  - This bodes well for potential reversibility



# 5: Conclusions

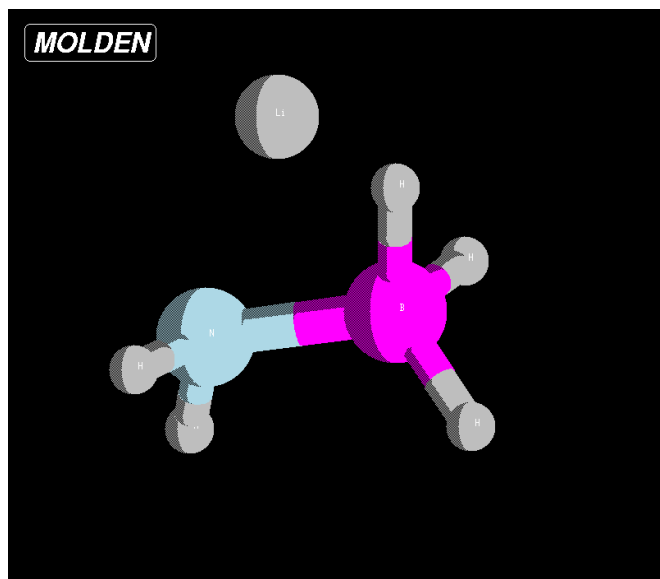
- Pure **AB** is unstable against dehydrogenation, but metal amidoboranes are not
- A cause for concern? Our calculated thermodynamics and activation barriers do not match experimental picture
  - Is this due to other reactions that occur in complexes?
  - **Picture is more complicated than assumed**
- These molecules can act as H-storage media, the low-T release of a large amount of hydrogen is significant and provides the potential to fulfil many of the principal criteria required for an on-board hydrogen store.  $\text{MgHNNH}_2\text{BH}_3$  has the best thermodynamics.

# Acknowledgements

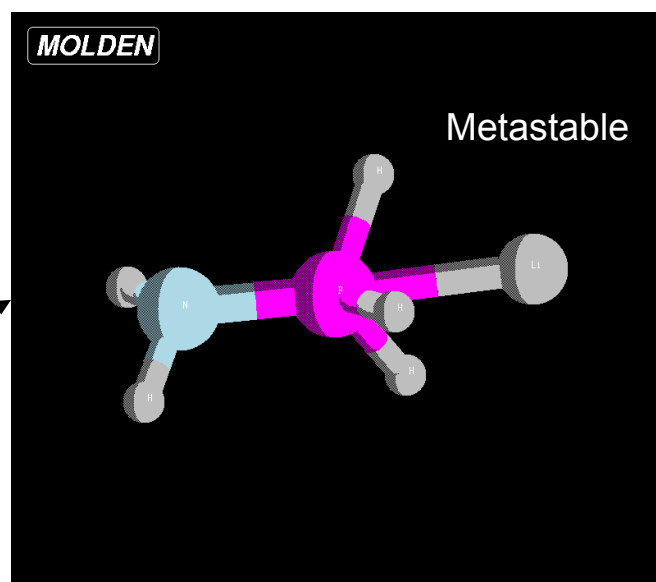
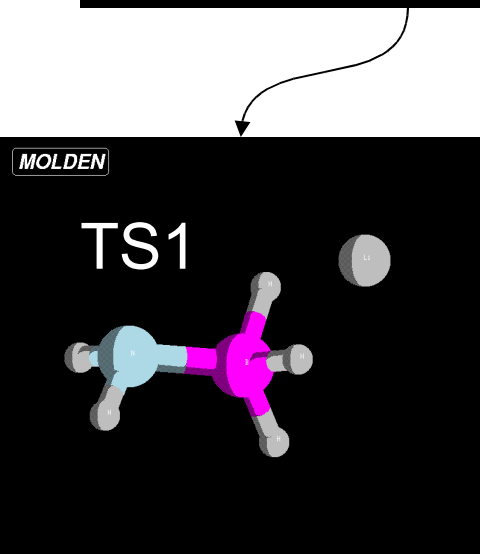
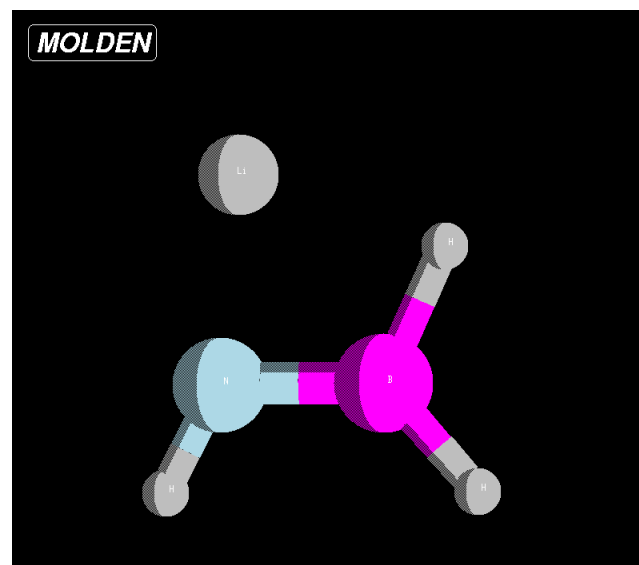
- EPSRC
  - UK-SHEC (GR/S26965/01, EP/E040071/1)
  - PLATFORM (GR/S52636/01, EP/E046193/1)
  - Grants for funding and access to HPCx and HECToR national computing facilities
- GDR organisers
- **The audience for paying attention!!!**

# Li NH<sub>2</sub>BH<sub>3</sub> : new

Reactants



Products



2 TSs

A state intermediate to the 2<sup>nd</sup> TS  
Li is shuttle/ carrier for catalysis

