A. How well can theoretical calculations predict properties of new materials?

B. The effect of the quantum mechanical nature of hydrogen:
   - release temperature of hydrogen gas,
   - rate of diffusion/desorption of hydrogen
Solid State Calculations - the ‘industry standard’

Step 1:  Electronic degrees of freedom (fixed atom coordinates)

- **Density Functional Theory** calculations (DFT)
  - Using some gradient dependent functional, PW91 or PBE or RPBE
  - Only treat valence electrons
  - Pseudopotentials or PAW to treat core electrons
  - Plane wave basis

- VASP or CASTEP or SIESTA or Ab Init codes

Step 2:  Atomic degrees of freedom (changes in nuclear positions)

- Classical dynamics with simulated annealing to find optimal structure
- Harmonic approximation to describe vibration (phonons)
- Harmonic transition state theory to estimate transition rates
- Feynman Path Integral representation of quantum delocalization
‘Accurate, first principles calculations using DFT with PBE functional’
A. Reaction and activation energy

Example: Extraction of H$_2$ from silane and disilane, reaction energy and saddle point energy

<table>
<thead>
<tr>
<th></th>
<th>SiH$_4$ → SiH$_2$ + H$_2$</th>
<th>Si$_2$H$_4$ → 2SiH$_2$</th>
<th>Si$_3$H$_6$ → SiH$_4$ + SiH$_3$</th>
<th>Si$_2$H$_6$ → Si$_2$H$_4$ + H$_2$</th>
<th>ΔΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{rxn}$</td>
<td>$E_{ts}$</td>
<td>$E_{rxn}$</td>
<td>$E_{rxn}$</td>
<td>$E_{ts1}$</td>
</tr>
<tr>
<td>Plane-Wave</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDA</td>
<td>-2.89</td>
<td>2.06</td>
<td>-3.49</td>
<td>-2.86</td>
<td>-2.26</td>
</tr>
<tr>
<td>PBE</td>
<td>-2.56</td>
<td>2.21</td>
<td>-3.06</td>
<td>-2.58</td>
<td>-2.09</td>
</tr>
<tr>
<td>PBE-PZSI</td>
<td>-2.87</td>
<td>3.35</td>
<td>-2.68</td>
<td>-2.73</td>
<td>-2.92</td>
</tr>
<tr>
<td>PBE-OSI/2</td>
<td>-2.70</td>
<td>2.69</td>
<td>-2.90</td>
<td>-2.64</td>
<td>-2.43</td>
</tr>
<tr>
<td>HF</td>
<td>-2.63</td>
<td>3.22</td>
<td>-2.17</td>
<td>-2.24</td>
<td>-2.70</td>
</tr>
<tr>
<td>B3LYP$^*$</td>
<td>-2.51</td>
<td>2.44</td>
<td>-2.65</td>
<td>-2.38</td>
<td>-2.24</td>
</tr>
<tr>
<td>QCISD(T)$^*$</td>
<td>-2.60</td>
<td>2.60</td>
<td>-2.70</td>
<td>-2.40</td>
<td>-2.30</td>
</tr>
</tbody>
</table>

DFT/GGA calculations underestimate activation energy, often by half an eV. B3LYP is quite good for molecules (but fitted to molecular properties) - solids?
B. Localization of the vacancy state at the rutile TiO$_2$ (110) surface

DFT (PBE)

Conduction band

Vacancy state

Valence band top

1.8 eV

Experiment

Conduction band

0.8 eV

Valence band top

3.0 eV

Vacancy state

PBE-OSI/2

Conduction band

0.9 eV

Valence band top

3.3 eV

DFT/GGA calculations often delocalize the electrons too much
How should the atoms be arranged?
Search for optimal structure using simulated annealing

Simulate classical dynamics of the system coupled to a heat bath. Use DFT to find force on atoms.

Can be applied to clusters but of limited use for crystals
Calculate structure and $\text{H}_2$ desorption temperature for free $(\text{MgH}_2)_n$ clusters

For example, a cluster with 15 Mg atoms:

Do simulated annealing for each cluster composition

Release of hydrogen gas at 1 bar from $\text{MgH}_2$ predicted at 620 K (90 deg. higher than calculated for $\text{MgH}_2$ crystal at the same level of theory)

If going to clusters can increase $T_d$, why not look at a metal where the release temperature for the crystal is too low?
H adsorption in (or rather on) Al cluster

$\text{Al}_{13} Icosahedron$

$\text{Al}_{13}\text{H}_{13}$ central atom pulled out

$\text{Al}_{13}\text{H}_{20}$ cluster elongates

$\text{Al}_{13}\text{H}_{27}$ cluster opens up, Al-H-Al bonds

$\text{Al}_{13}\text{H}_{37}$ No interior H-atom

10% H by weight
The release of hydrogen gas at 1 bar is predicted to occur at 270 K within quantum, harmonic approximation. At 80 °C the hydrogen gas pressure is predicted to be 60 bars.
Calculations of the desorption temperature

How should the quantum mechanics of hydrogen atoms be included?

Use *quantum mechanical partition functions* within the harmonic approximation to evaluate the chemical potential of hydrogen and equate the solid and gas phase to get thermodynamic desorption temperature of H\(_2\) at a given gas pressure.

**Example:** DFT desorption temperature of H\(_2\) from MgH\(_2\)

<table>
<thead>
<tr>
<th>T(_d)/deg.C</th>
<th>harmonic-quantum</th>
<th>Cl. with ZPE</th>
<th>Classical</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>140</td>
<td>200</td>
<td></td>
</tr>
</tbody>
</table>

As close to exp. as one can hope with DFT!

**Note:** A simple zero point energy ‘correction’, i.e. simply replacing

\[
E_{\text{min}} \quad \text{with} \quad \left( E_{\text{min}} + \sum_{i}^{D} \frac{\hbar \nu_{R,i}}{2} \right)
\]

in a otherwise classical mechanical treatment can be a worse approximation for thermally activated transitions than purely classical calculation!
Conventional approach to the modeling of solids

Born-Oppenheimer (adiabatic) approximation

1. Solve for the electronic degrees of freedom, $r$, while keeping the nuclei fixed at $R$.
   Usually done with density functional theory (DFT) using approximate functionals such as PW91 or PBE.
   Get energy surface, $E(R)$.

2. Solve for the motion of the nuclei. Usually with the classical approximation, $F=ma$, and within a harmonic approximation (----)
   $E(R) \sim \frac{1}{2} k_{sp} (R-R_{min})^2$. 

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perfect crystal, global minimum

defect configuration
Atoms should be described quantum mechanically

The classical approximation can, in particular, be poor when hydrogen atoms are present.

*Quantum delocalization* - cannot fix the position of the atoms at \( \mathbf{R} \), rather use probability distribution.

The minimum energy of the solid is higher than the classical minimum energy \( (\cdot) \),

\[
E_{\text{ZPE}} = E_{\text{min}}^{\text{QM}} - E_{\text{min}}^{\text{CM}}
\]

A commonly used first order approximation is to add the zero point energy but otherwise treat the system classically.
Simple example: Photoreaction

Assume the system is in the ground state. Photon energy required to induce reaction is

$$h\nu = \Delta E - E_{ZPE}$$

Zero point energy correction works well.
What about thermally activated transitions?

For example: Thermal desorption of hydrogen gas from a hydride, want to estimate desorption temperature. 

*Can we simply add zero point energy correction to include the quantum mechanical effects?*

The system is in this case necessarily not just sitting in the ground vibrational state before escaping the energy well. Relatively high temperature for some of the vibrational modes. Need to apply statistical mechanics to include thermal effects.
Calculate H₂ desorption temperature w/harmonic approx.

Use statistical mechanical methods to find temperature at which 1 bar H₂(g) desorbs.

Desorption occurs when \( \mu_{\text{H(in solid)}} = \mu_{\text{H₂(g)}}/2 \) where

\[
\mu_i = -kT \left( \frac{\partial \ln Q}{\partial N_i} \right)_{T,V,N_j}
\]

For hydrogen gas, \( Q_g \) depends on the single molecule partition function, where

\[
q_{H₂(g)} = q_{tr}q_{rot}q_{vib}q_{nuc}q_{el}
\]

and

\[
q_{tr} = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{NkT}{p}
\]

\[
q_{rot,nu} = \sum_{J, \text{even}} (2J+1) e^{-J(J+1)T_{rot}/T} + 3 \cdot \sum_{J, \text{odd}} (2J+1) e^{-J(J+1)T_{rot}/T}
\]

\[
q_{vib} = \sum_{n=0}^{\infty} e^{-\varepsilon_n/kT} = e^{-T_{vib}/2T} \sum_{n=0}^{\infty} e^{-nT_{vib}/T} = \frac{e^{-T_{vib}/2T}}{1 - e^{-T_{vib}/T}}
\]

For crystals, exclude translation or rotation and only include vibrational modes

- \( Q_s \) is a product of partition functions corresponding to all vibrational modes of hydrogen in the crystals (OK to leave the metal atoms frozen to within 20 degrees in \( T_d \))

\[
Q_s = \prod_{i=1}^{N_{vib}} q_{vib,i} = q_s^{N_{vib}}
\]

where

\[
q_{vib,i} = \frac{e^{-T_{vib,i}/2T}}{1 - e^{-T_{vib,i}/T}}
\]
But, is the harmonic approximation good enough?

The fact that the Al$_{13}$H$_{37}$ cluster is floppy and changes easily configuration on psec time scale at 400 K means that there are many local minima with small energy barriers in between. Need to go beyond harmonic approximation to evaluate thermodynamic properties, such as release temperature.

This can also be the case with crystals (not just clusters)
The energy surface for crystals can be rough!

Example: $\text{Mg}_7\text{TiH}_{16}$

Initially, place H-atoms in center of each Td hole.
After relaxation, H-atoms have moved near the face between Td and Oh holes.

The structure is complex, multiple local minima on the energy surface,
see minimum energy path from regular calcite structure to lowest energy str.

At room temperature, H-atoms can quantum mechanically delocalize over more than one local minimum (harmonic approximation not valid).
Need to go beyond harmonic approximation, can calculate quantum statistical mechanics using Feynman Path Integrals

* Statistical mechanics of a quantum particle is mathematically equivalent (isomorphic) to classical statistical mechanics of a distribution of images of the particle connected with springs with stiffness proportional to $T^2$

\[ k_{sp} = mP \left(2\pi k_B T/h\right)^2 \]

* Instead of the potential surface, work with an effective potential

\[
V(r) \quad \rightarrow \quad V_{\text{eff}}(r_1, r_2, \ldots, r_p) = \sum_{i=1}^{P} \left( \frac{1}{2} k_{sp}(x_{i+1} - x_i)^2 + V(x_i)/P \right)
\]
The tunneling mechanism will dominate the rate of atomic rearrangements (chemical reactions, diffusion) at low enough temperature.

Typical temperature dependence of a rate constant

How can the cross over temperature, $T_c$, be estimated and the contribution of tunneling to the transition rate evaluated?
Analogy between HTST and HQTST

HTST (N dimensions)

Spreading of replicas lowers effective activation energy - Accounts for tunneling

HQTST (NP dimensions)

\[ Q^R k_{\text{HTST}} = \frac{k_B T}{h} \frac{1}{\prod_j \nu_j} e^{-\Delta E/k_B T} \]

\[ Q^R k_{\text{HQTST}} = \sqrt{\frac{S_0}{2\pi \hbar}} \frac{1}{\Delta \tau |\prod_j' \nu_j|} e^{-V_{\text{eff}}/k_B T} \]

1st order saddle point of \( V \)

1st order saddle point of \( V_{\text{eff}} \)
Hydrogen diffusion in a bcc metal, Ta

DFT calculations using PAW, PW91
16 Ta atoms, 1 H atom
Hops between adjacent tetrahedral holes
Up to 58 images used to represent the Feynman paths

Excellent agreement with experiments at low temperature.
Tunneling dominates at temperature below ca. 200 K.
Ammoniaborane, a candidate for hydrogen storage (Schenter, Gutowski, …)

Calculate desorption of hydrogen, use the semi-empirical AM1 to evaluate atomic forces and up to 96 replicas at the lowest temperature.

\[
H_3BNH_3(g) \rightarrow H_2BNH_2(g) + H_2(g)
\]

- Dominated by tunneling at room temperature.
- About 300 fold increase in rate at 370 K
- SCT overestimates the rate at low temperatures.
Summary

- **Nano-scale Al-H clusters** seem interesting for H-storage. They deform to bind H-atoms in bridging configuration at surface. The overall binding energy is 0.20 eV per H-atom and calculated release temperature of gas at 1 bar is around room temperature.

- Don´t use a zero point energy ‘correction’ when calculating release temperature of hydrogen gas from hydrides!

- In **floppy systems** where the energy surface for the motion of the atoms has many local minima with small barriers in between, the harmonic approximation is likely not valid. Then need full quantum simulation which can be done with Feynman path integrals.

- Quantum mechanical description of hydrogen atoms can be important, especially when **tunneling** is the dominant mechanism for transitions, such as diffusion hops and desorption.