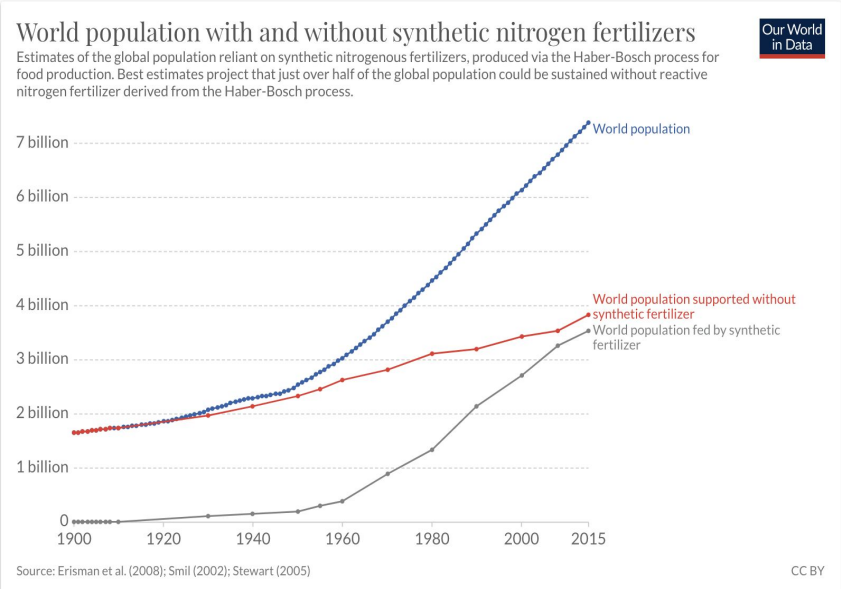
Nitrogen Fixation via Photo-Driven Gallium Nitride Electrocatalysis

Richard Bao

Background

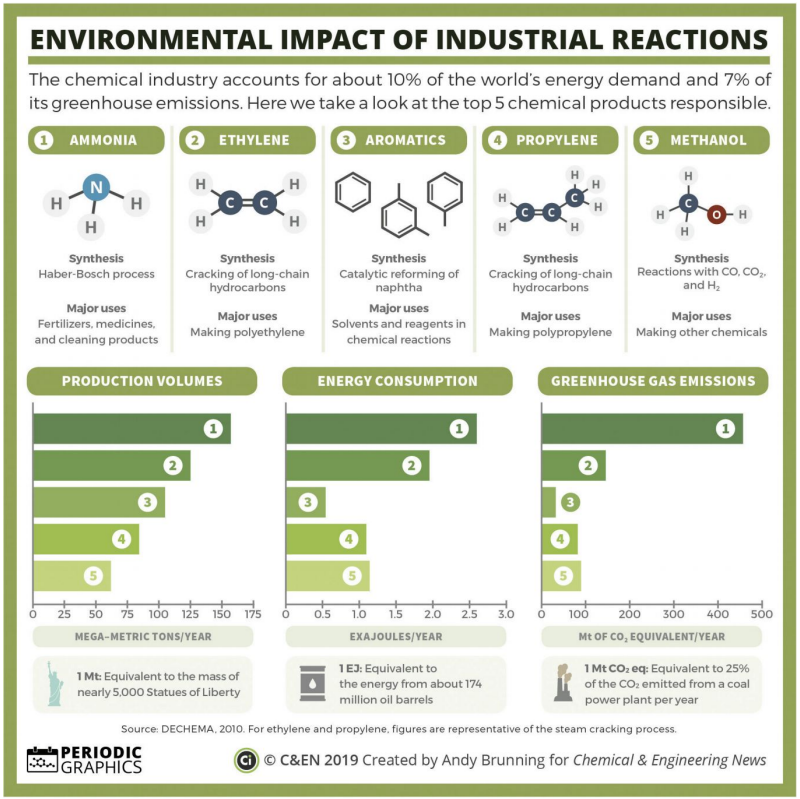
Nitrogen Fixation

- Conversion of molecular nitrogen from the air into ammonia
- More than 80% of ammonia produced by industry is used in agriculture as fertilizer
  - Global agriculture consumes more than 200 million tons of ammonia per year
- Supports the global population.
  - Along with pesticides, helped to eliminate widespread famines in industrialized countries.



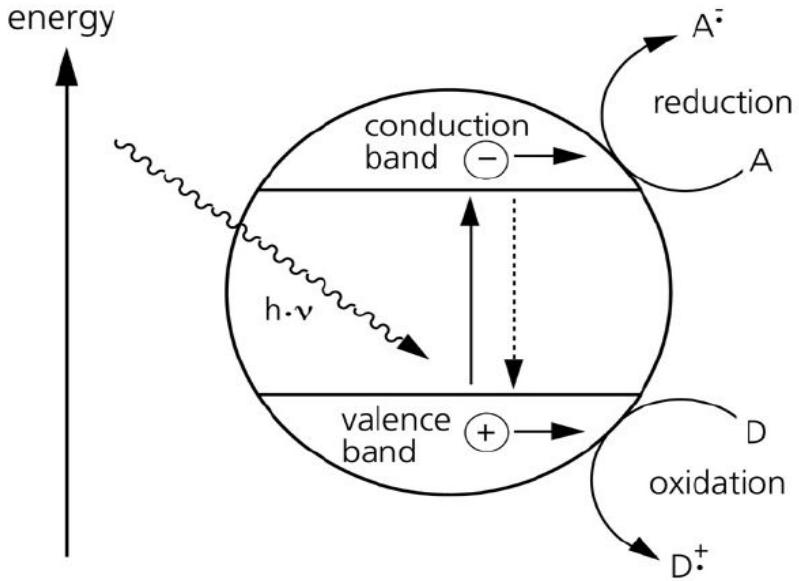
Haber Process

- Requires high temperatures and pressures
  - 400-500 degrees celsius and 150-300 atmospheres.
  - Triple bond in nitrogen is very stable
- Directly consumes around 2% of the world's energy production.
- Responsible for 1.44% of global carbon emissions.
  - More than any other industrial chemical
  - Emissions also come from producing the required hydrogen gas through steam reforming of methane



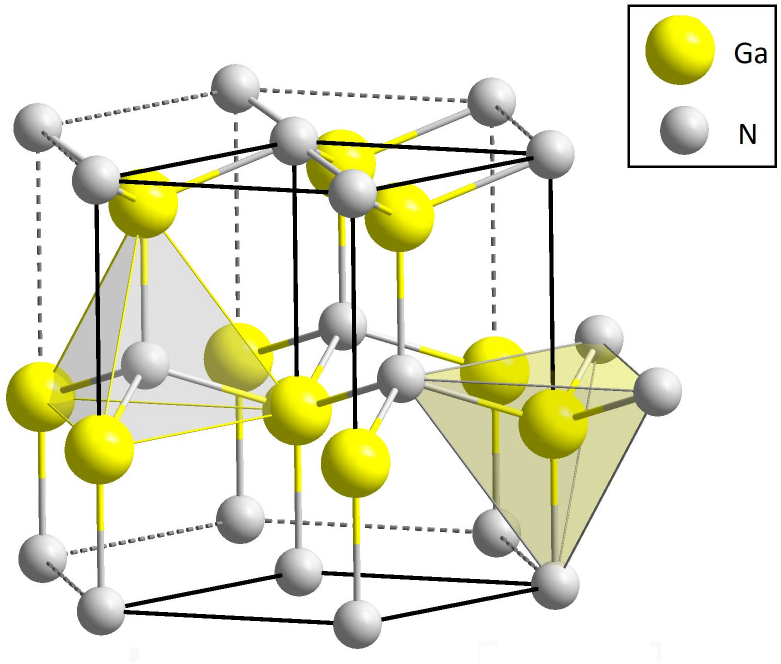
Solution: Solar Fuels Approach

- Electrochemical reaction
  - H is obtained from water, not H_2 gas
  - Finer control of reaction mechanisms
- Electrochemical processes are less energy intensive, more environmentally friendly
  - Use photo/electrocatalytic materials to expedite this process
- Initial electron donation to ground-state N_2 ($N_2+e^- \rightarrow N_2^-$) is rate-limiting step due to large reduction potential of -4.2 V.
  - Reduce energy barrier with materials that absorb N_2 onto surface, donate an electron, and stabilize the N_2^- intermediate
  - Photo-excited electrons enable further reduction and subsequent hydrogenation



Why Gallium Nitride?

- High surface activity and stability
  - High energy of elections at the conduction band edge energy
  - Wide band gap
- Prior research suggests GaN is good for hydrogen evolution reaction (HER)
- N2 physisorption onto GaN demonstrated
- Nitrogen vacancies in GaN can enable strong chemisorption as well
- Wurtzite structure (vs sphalerite) lacks inversion symmetry, has polarization.
  - Labs are growing nanowires



Fall Term Research Scope

- First, we want to see how well GaN supports the hydrogen evolution reaction (HER).
  - Water splitting supplies the hydrogens for hydrogenation of intermediaries
  - How does hydrogen bind to the GaN surface?
  - How does water dissociate on the GaN surface?
- How does p-type Magnesium doping change chemical properties and influence reaction mechanisms?
  - We suspect that Mg doping might help with HER, especially with the first water oxidation step
- Later, we will look at nitrogen absorption and reduction, and photo driving. We will also explore different solvents.

Experimental Methods

VASP

- VASP computes an approximate solution to the many-body Schrödinger equation, either within density functional theory (DFT), solving the Kohn-Sham equations, or within the Hartree-Fock (HF) approximation, solving the Roothaan equations
- Using Density Functional Theory (DFT), the properties of a many-electron system can be determined by using functionals of the spatially dependent electron density.
- However, normal DFT is not accurate because it uses the same density for all electrons. It is classically correct but not quantum mechanically correct because it does not account for the self interaction term, which causes more delocalization.
- VASP improves upon this by using the projector augmented wave method, a generalization of Vanderbilt-type pseudopotentials, with a plane wave basis set, which depends on angular momentum.

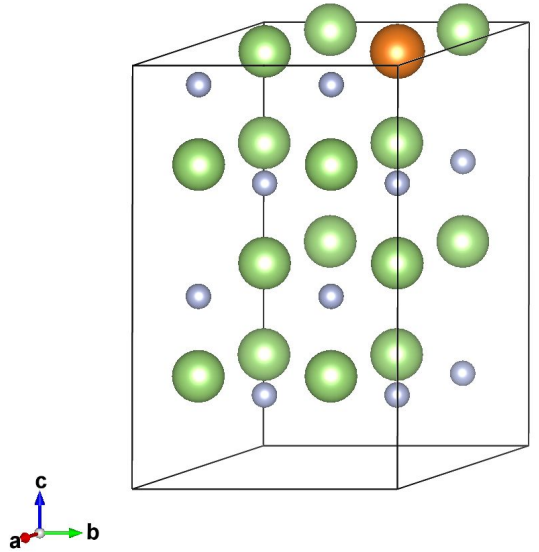
Why Can We Trust This?

- We further improve upon this by accounting for D3 dispersion corrections (Van Der Waals forces) using the Hubbard U parameters, which introduces a strong intra-atomic interaction in a (screened) Hartree-Fock like manner, as an on-site replacement.
    - Ideally, we would use hybrid functionals, or range-separated functionals, but these are hard to do in periodic systems, and computationally expensive
- We optimized the Hubbard U parameters so that the calculated lattice constants and band gap converge with what is measured in real life experimentation.
- We use the U parameters for other calculations as well because they should be good for chemical properties too.

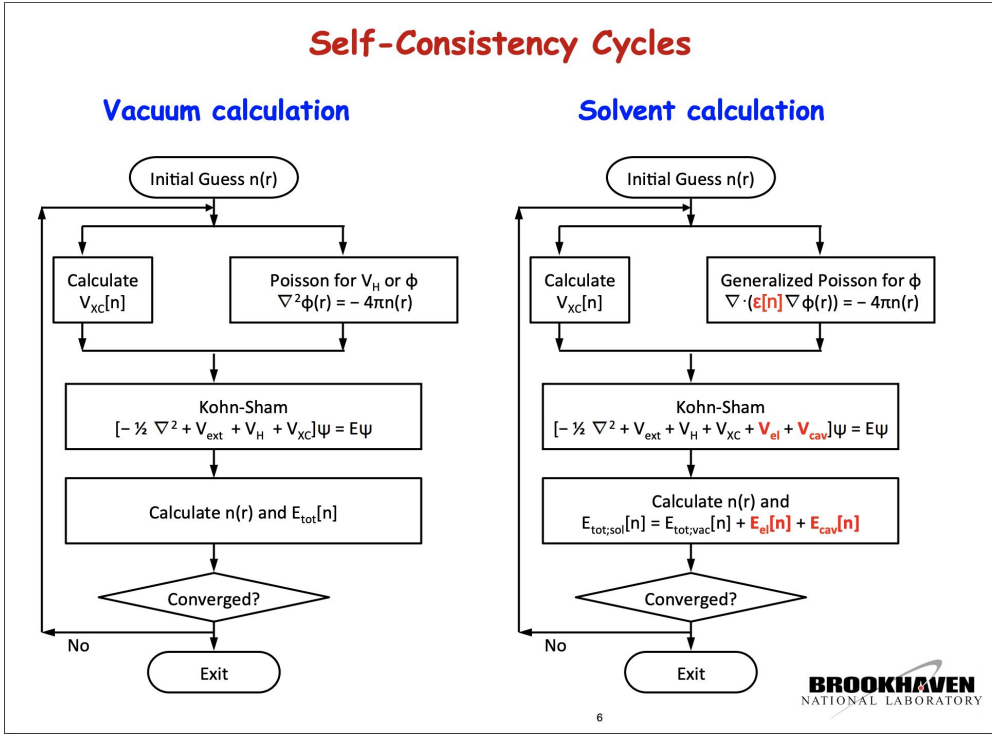
Bulk Model

Structure

- Periodic unit cell in vacuum
- Wurtzite structure with lattice constants a = 3.186 Å, c = 5.186 Å
- 2x2x2 extension of the unit cell, 32 atoms
  - 15 Ga, 1 Mg, 16 N
- KPOINTS sampling
  - 5x5x3 gamma centered mesh



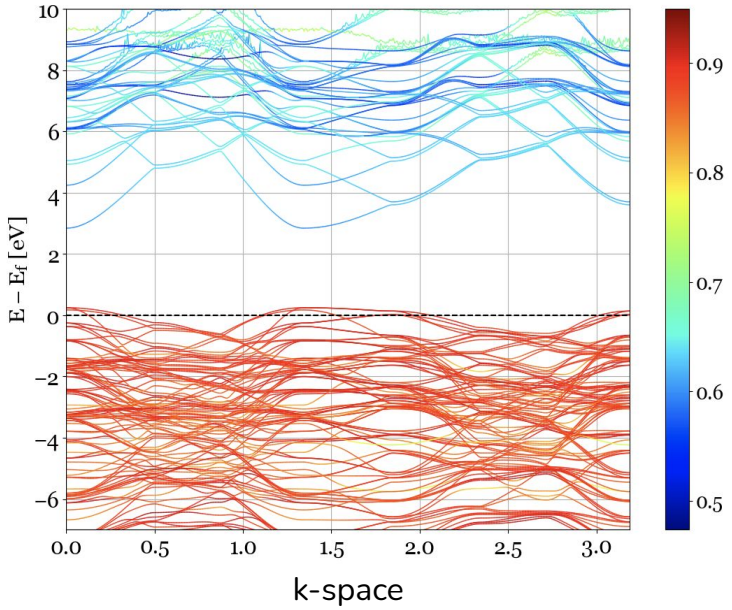
Bandgap Calculations

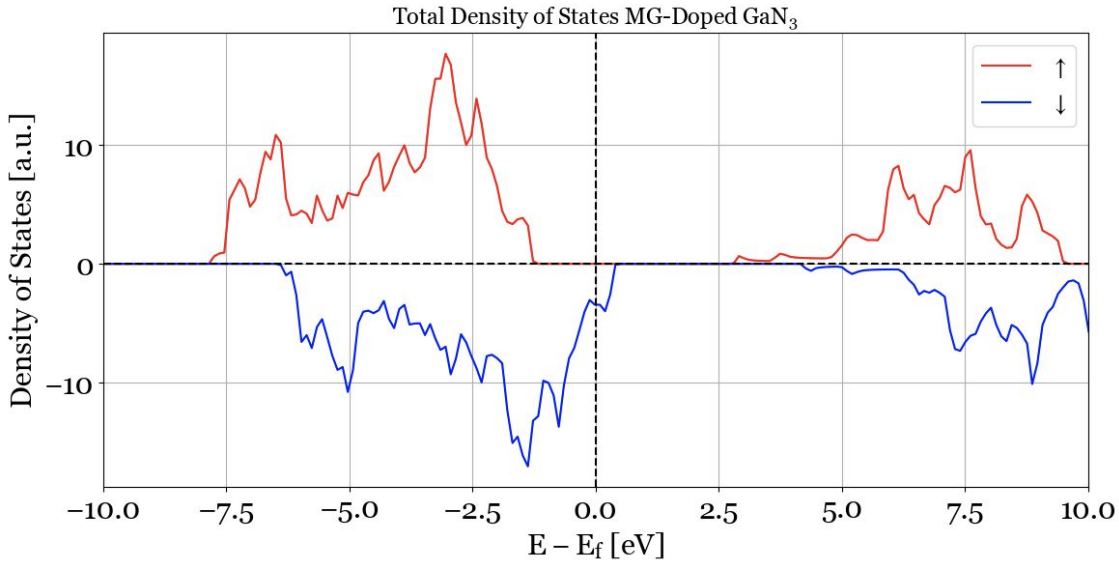


- Self-consistent run
  - Hartree Fock method
  - Stationary state
  - Finds lowest-energy arrangement of atoms
- Non-self consistent run

Results

- One more occupied spin up than spin down (integrate down spins from E=0 to E=0.5)
- Mg is a shallow acceptor, adds hole with energy levels just above valence band edge
- Band gap energy around 3 eV, slightly less than undoped. Fermi energy of 2.0208 eV

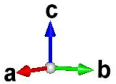


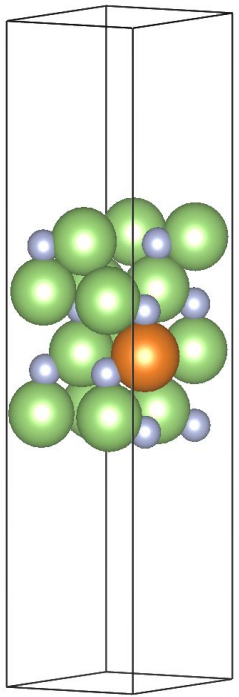


Slab Model

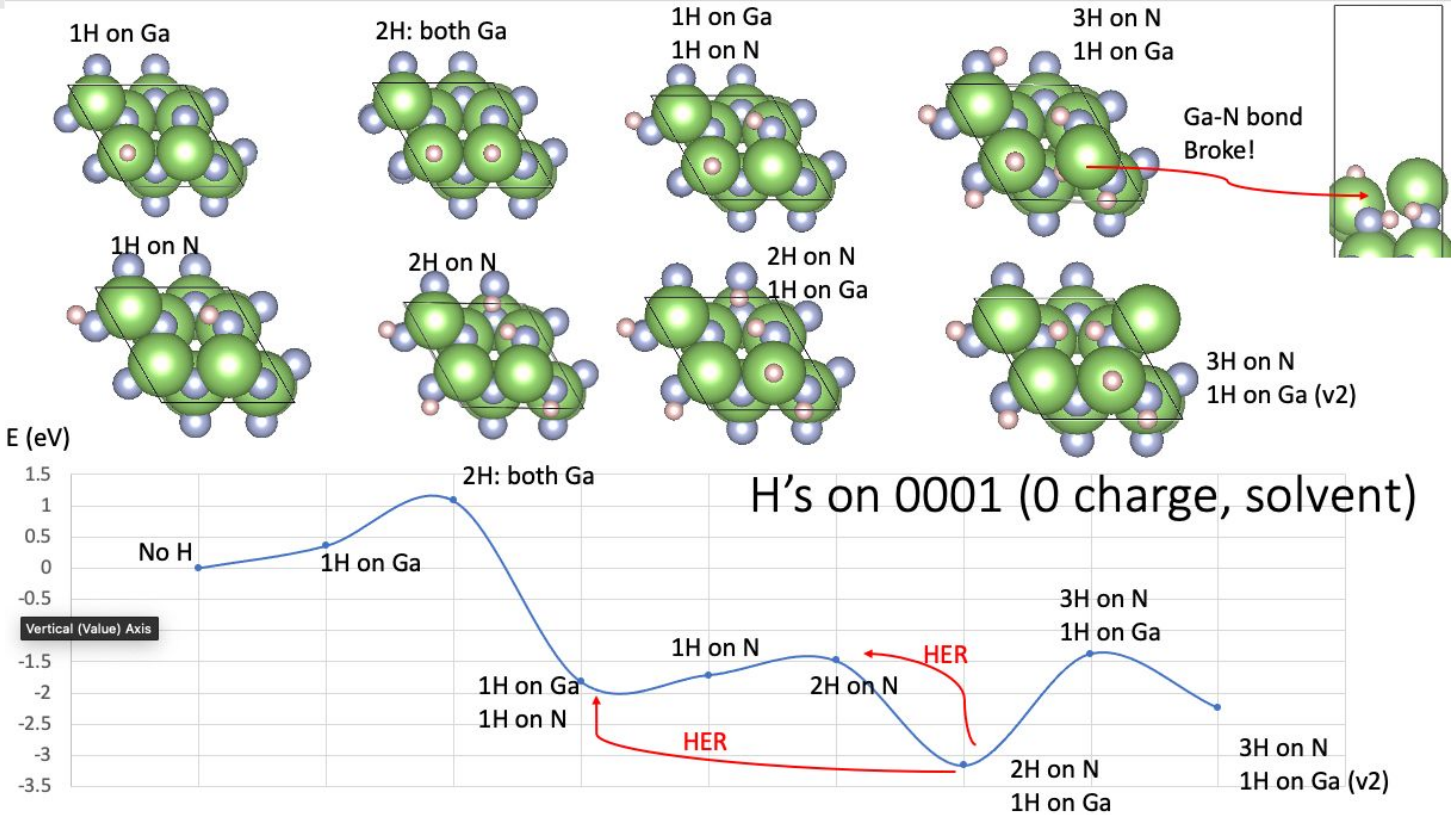
Structure

- 0001 and 0001 bar surfaces
  - Exposed Ga vs exposed N
  - Vacuum of around 10 Angstroms on either side, can be filled with solvent
- Construction of polar surface
  - Remove 1 Ga and 1 N from the top
  - Remove 1 N from the bottom
- KPOINTS sampling
  - 5x5x3 gamma centered mesh
- Minimization
  - Fix two middle double layers (7 Ga, 1 Mg, 8 N), relax everything else. Then relax everything





Hydrogen Binding



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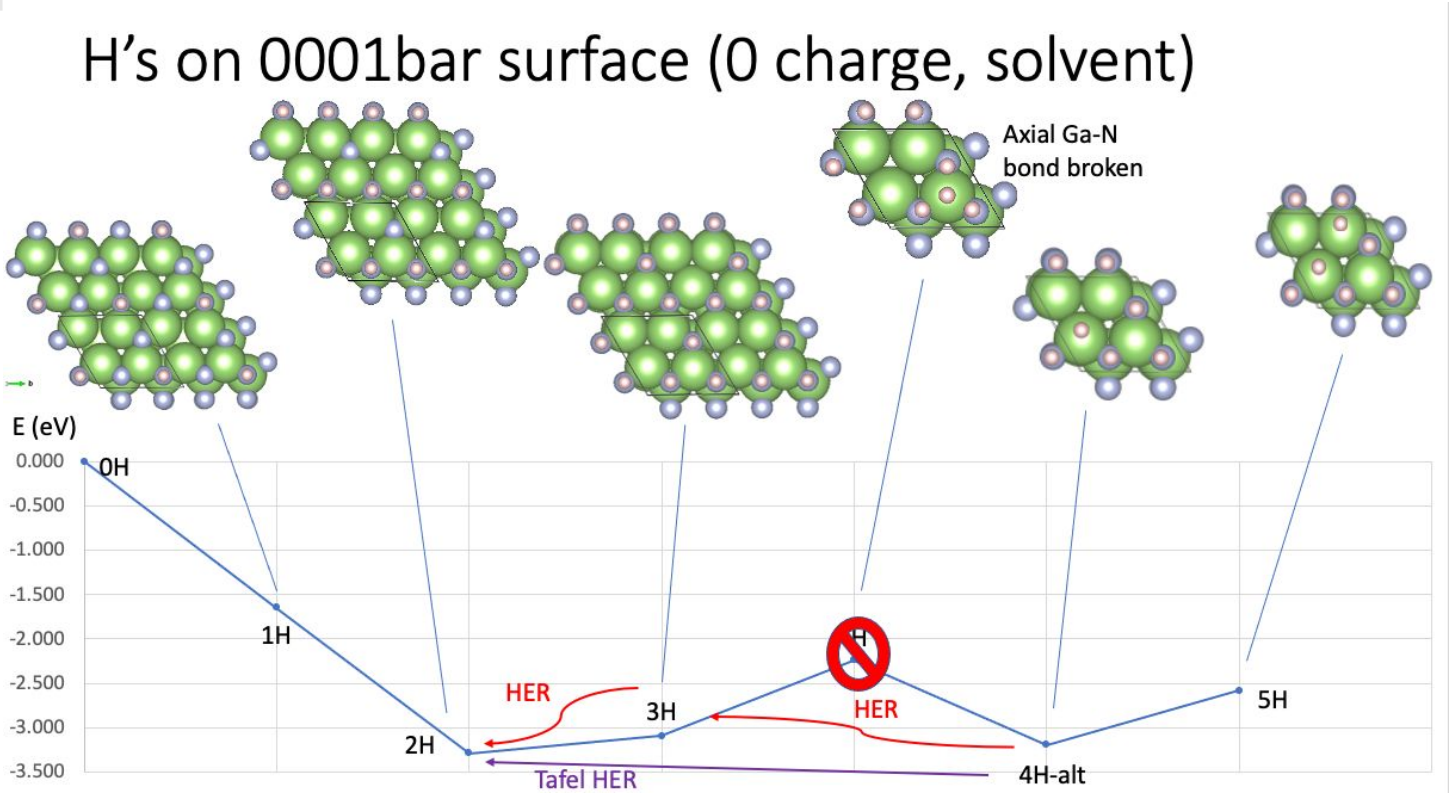
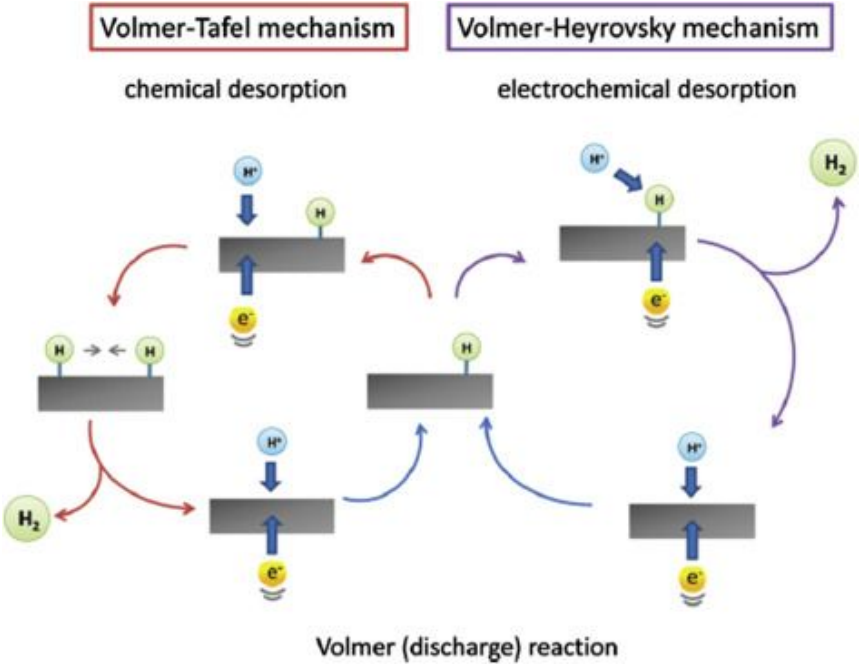
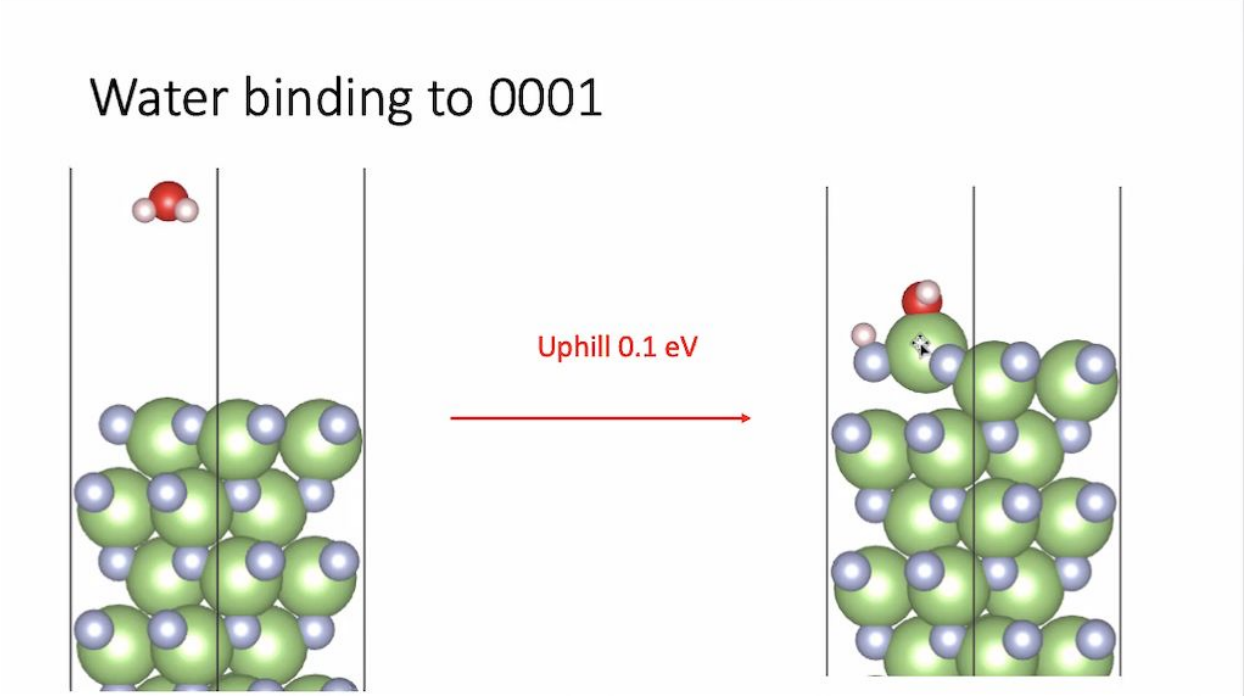


Hydrogen Evolution Reaction

1. Volmer or discharge reaction
    a. An electron transfer to the electrode is coupled with a proton adsorption on an empty active site of the electrode to yield an absorbed hydrogen atom
2. Heyrovsky reaction
    a. The transfer of a second electron to the absorbed hydrogen atom is coupled with the transfer of another proton from the solution to evolve H2



Water Binding



Future

Calculate the potential from the middle of the slab to the vacuum to get the ionization potential as a function of space, approximating the work function.

Simulate nitrogen absorption to determine how well the surface can capture nitrogen and donate an electron

Run both HER and Nitrogen absorption in basic and acidic solvents

Run excited state calculations (photo-excited)

Replace Ga with Indium or Boron to shift band gap, make it narrower to yield more electrons from photo driving, or include a photocatalyst, such as a Ruthenium complex, and see if this speeds up either hydrogen evolution or nitrogen fixation