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## **Project 1**

### **Introduction**

The Haber-Bosch process is one of the most relevant chemical processes to modern society. Throughout this report, we aim to focus on the crucial step of absorption onto the catalyst using a grand-canonical Monte-Carlo simulation and parlaying this with a host of different parameters to effectively model how Hydrogen and Nitrogen will compete for sites. It is well documented that the rate limiting step of the Haber-Bosch process is the dissociation of Nitrogen on the catalyst surface (acs.org) that requires proximal co-absorption of Hydrogen which will allow us to understand what lattice arrangements will be physically relevant. Further discussion of the parameterization of relevant variables and other methods will follow below.

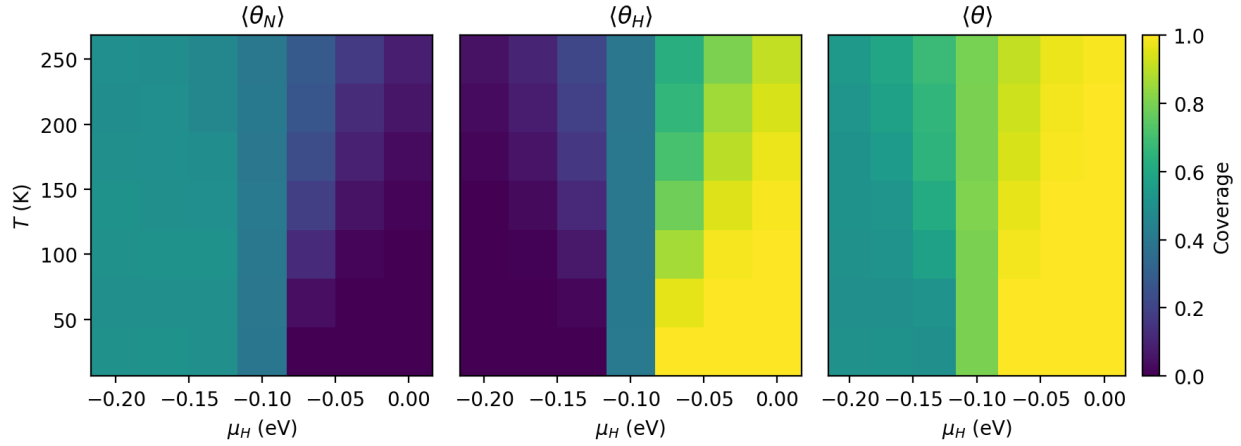
### **Methodology**

To conduct the relevant simulations, we initialized a square lattice with periodic boundary conditions in python. Each site was considered to have 4 adjacent neighbors whose states were considered in the computation, and all sites can be in 3 possible states: occupied by nitrogen, occupied by hydrogen, or occupied by nothing. In the main script, there are 5 listed epsilon variables for the relevant interactions where Epsilon\_A is for the absorption energy of Nitrogen, Epsilon\_B is for the absorption energy of Hydrogen, Epsilon\_AB is the absorption energy of Hydrogen and Nitrogen neighbors, Epsilon\_AA is the absorption energy of Nitrogen

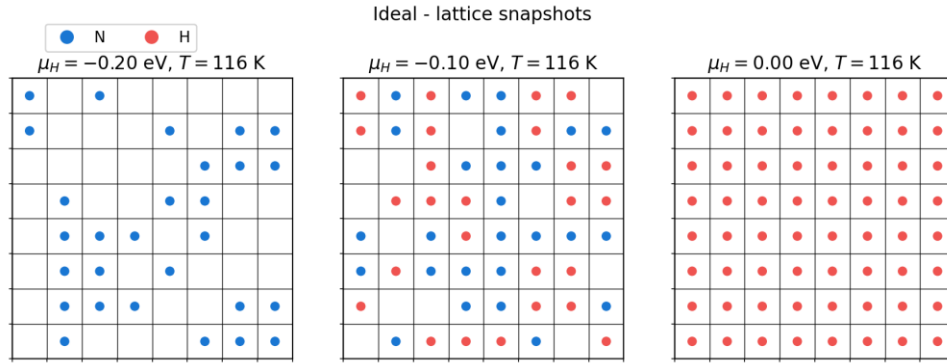
neighboring Nitrogen, and  $\epsilon_{BB}$  is the absorption energy of Hydrogen neighboring Hydrogen. The addition or removal of particles to our lattice is dictated by the calculations done in `calculate_interaction_energy` that utilizes the interaction values to find the value of  $e_{\text{pairs}}$  for each site that will be combined with the energy of absorption for the site itself to yield a final change in energy. The calculation of the energy of the move will allow us to proceed into our `attempt_move` function which utilizes the Metropolis Hastings factors, the temperature and this energy difference to sample the grand-canonical correctly. This is stored in the variable `acc` that is then compared to our randomly sampled number to see whether the proposed addition or removal is accepted or not. All visualizations are conducted in the `run_all.py` script that show how we utilize a range of temperatures and chemical potentials of H to observe phase transitions across our sets of parameters. Sampling across different values of temperature and chemical potential will change the value of our “acc” variable and will allow different trends of particle addition or subtraction to take place.

## **Results:**

The first heat map and lattice configurations are for the ideal absorption case of Nitrogen and Hydrogen where the Epsilon of absorption are both  $-0.10$  eV and the neighboring interactions are all set to 0.



**Figure 1:** Scans across varying chemical potentials and temperatures for Ideal absorption.

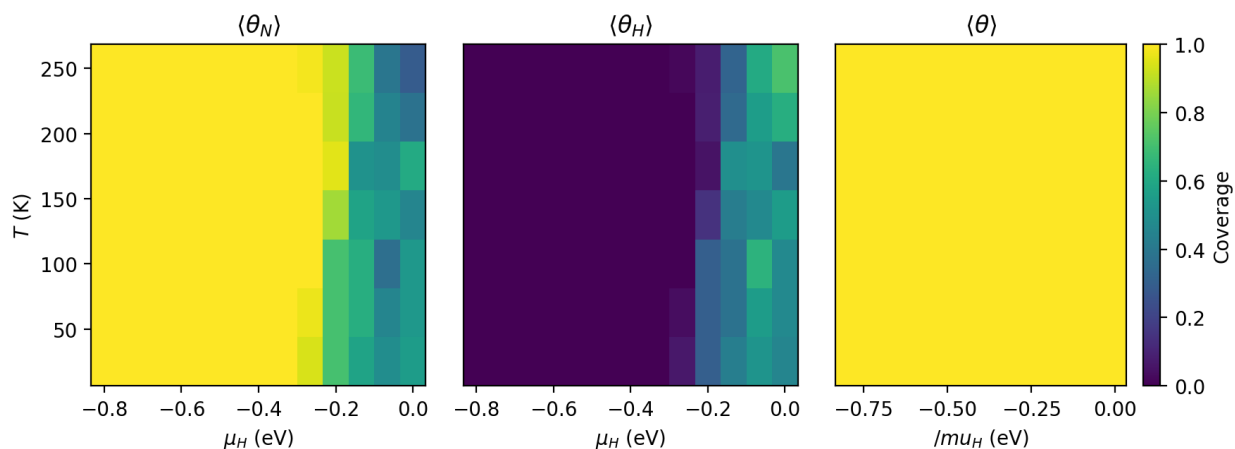


**Figure 2:** Lattice configurations of Nitrogen and Hydrogen at constant temperature but varying potential for Ideal absorption.

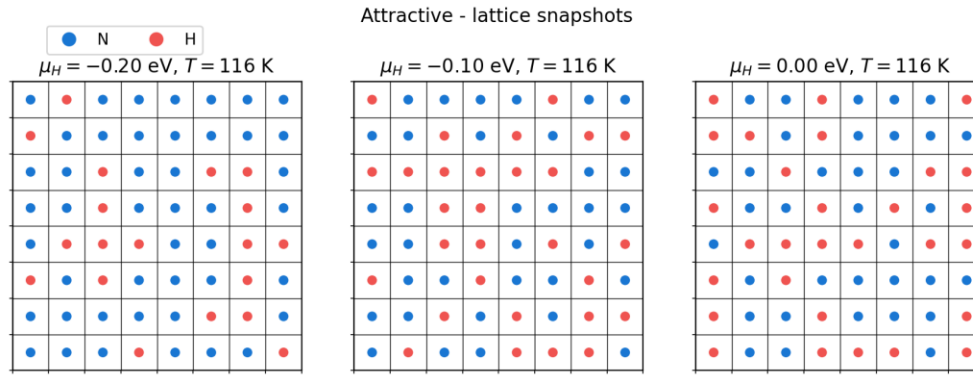
The ideal lattice shows very little trend to the patterns observed, which is exactly what we would expect given that neighbor interactions are set to 0. The Nitrogen is present throughout the first panel and hydrogen's chemical potential is low enough to be a non-factor in the lattice. The middle panel where the chemical potential is -0.10 eV for hydrogen shows the case where the Nitrogen and Hydrogen are just about equally likely to occupy any given site and this shows as a completely disordered lattice with no distinct patterns emerging. The Hydrogen at 0.0 eV is high

enough to be completely favorable over the Nitrogen at the given temperature, which is roughly in the middle of our sampled range. This matches what is seen in the heat maps in figure 1 where the temperature softens the changing of potentials, and at high ranges is enough to overcome the total preference of hydrogen and allows some nitrogen to persist. This can be rationalized through our code because when the temperature term is relatively big, the energy weighted term is not as important to whether our attempted move may occur.

The next set of figures are for the Attractive case where the Epsilons of absorption for the Hydrogen and Nitrogen were both  $-0.10$  eV and the Epsilons of interaction were  $-0.05$  eV across all neighbor cases.



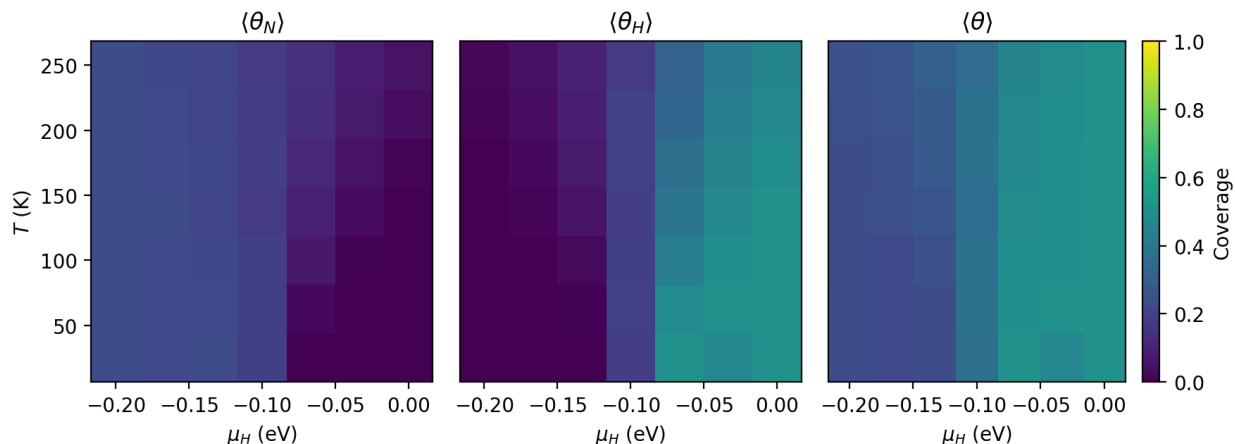
**Figure 3:** Scans across varying chemical potentials and temperatures for Attractive absorption.



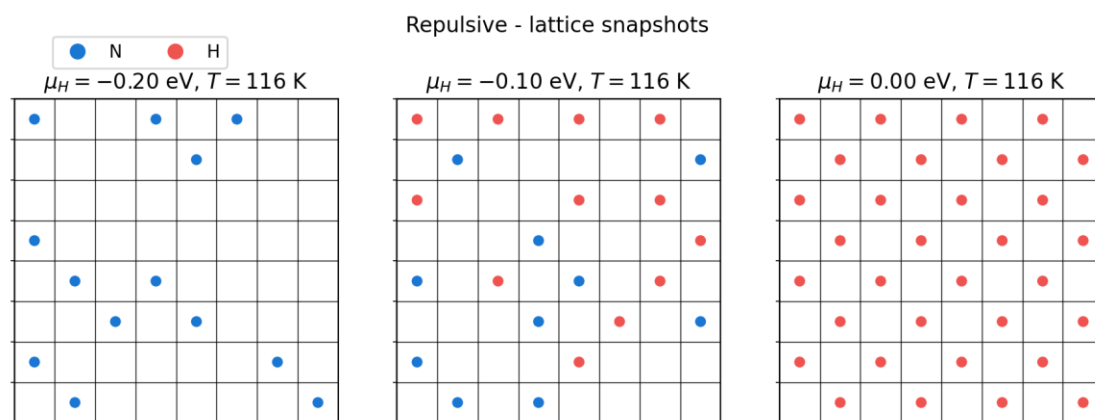
**Figure 4:** Lattice configurations of Nitrogen and Hydrogen at constant temperature but varying potential for Attractive absorption.

We can see in the attractive case the lattices are all filled, and the neighboring effects allow even the chemical potential of hydrogen at  $-0.20 \text{ eV}$  to persist throughout the lattice. The Nitrogen and Hydrogen species are both present throughout, and the Hydrogen is slightly more prevalent at the  $0.0 \text{ eV}$ , but the attractive effects mean that both species remain relatively ubiquitous. The heat maps were expanded out to  $-0.8 \text{ eV}$  so that we can better observe the places where there's a distinct change from Nitrogen to H coverage. The temperature has an important effect on the prevalence of H on the lattice because when temperatures are low, the energetic favorability of the attractive neighbor arrangement can be enough to overcome the unfavorable chemical potential of the hydrogen and make adding it to the lattice more probable. This effect starts to go away at higher temperatures as we can see that as temperature rises, the chemical potential of H must become more favorable for it to have a chance to be added to the lattice.

The next set of figures are for the Repulsive case where the Epsilons of absorption for Nitrogen and Hydrogen are both  $-0.10 \text{ eV}$  and the Epsilons of interactions were all  $.05 \text{ eV}$ .



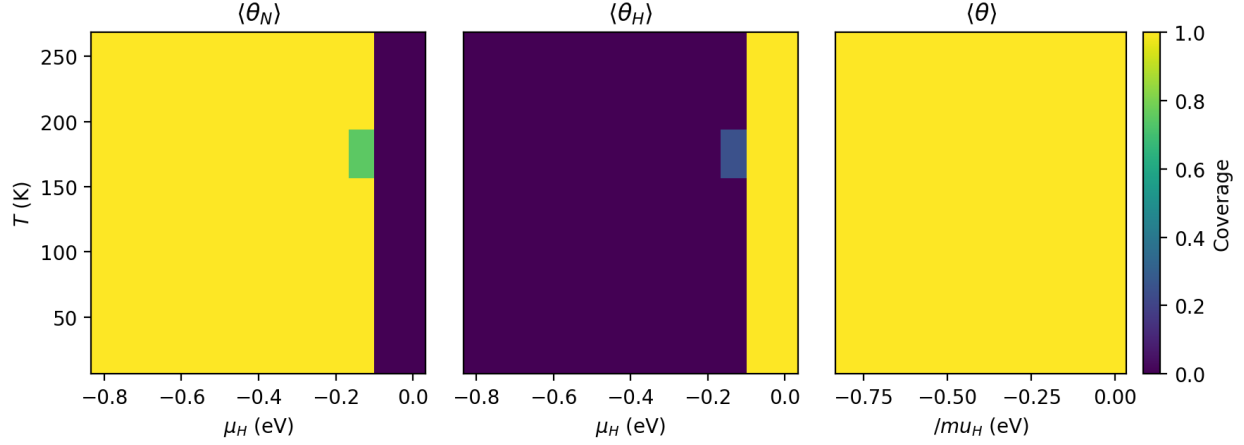
**Figure 5:** Scans across varying chemical potentials and temperatures for Repulsive absorption.



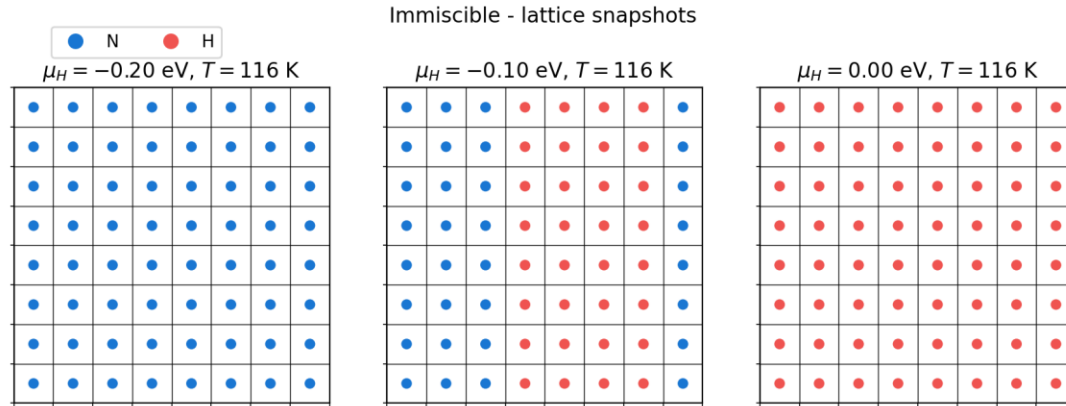
**Figure 6:** Lattice configurations of Nitrogen and Hydrogen at constant temperature but varying potential for Repulsive absorption.

Throughout both the lattice configurations and the heat maps, there is a distinct lack of site occupancy as we never see anything close to the max coverage. There are no neighbors for any of the lattice configuration panels, proving that the interaction terms are significant enough to overcome any probability of adjacent site absorption. The total coverage heat map shows a temperature trend that results in the highest coverage at less negative chemical potential and

more importantly high temperature. When temperature is sufficiently high, the beta term in our calculation will work against the energy penalty incurred by the local interactions and make it more probable that we accept a placement in an already crowded area.



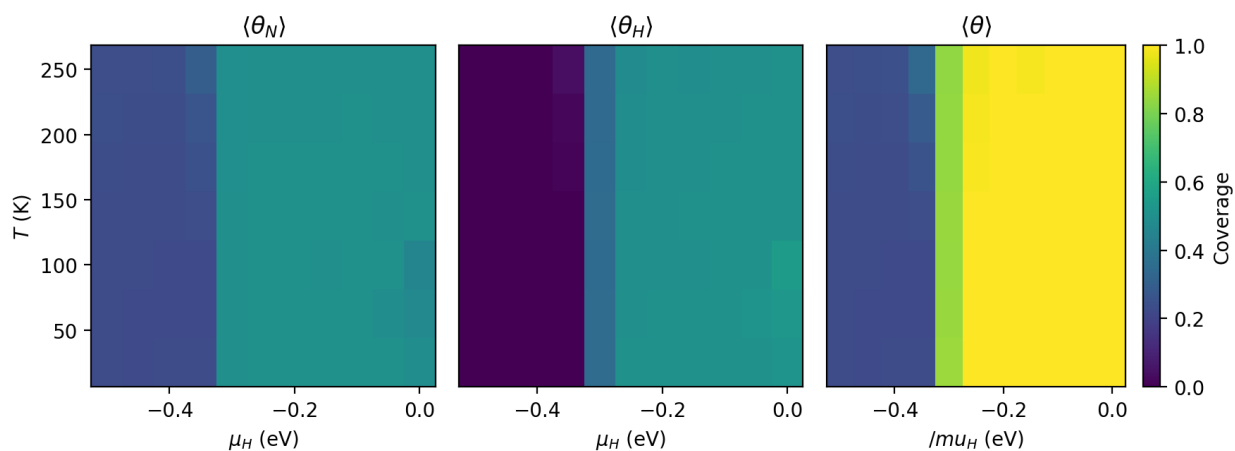
**Figure 7:** Scans across varying chemical potentials and temperatures for Immiscible absorption.



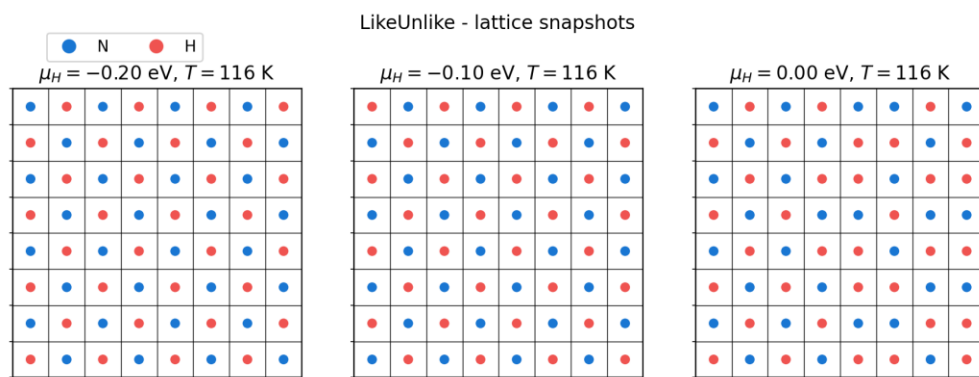
**Figure 8:** Lattice configurations of Nitrogen and Hydrogen at constant temperature but varying potential for Like-Unlike absorption.

Throughout the lattice configuration panels and the heat maps, we can see incredibly abrupt transitions between Hydrogen and Nitrogen because like-like neighbors are favored which

leads to highly ordered homogenous clusters. This is best visualized when the chemical potential of Hydrogen is at an intermediate value of  $-0.10$  eV where both species are present, but they are in highly ordered blocks that try to maximize the local like-like interactions. The temperature range actually doesn't show distinct trends like other sets of parameters. This can be rationalized because of the massive difference between having a like versus unlike neighbor which effectively blocks the probability of removing a like particle neighbor and replacing it with an unlike particle. The temperature term being unable to affect the massive energy difference between neighboring cases is observed as our heat maps showcase a complete flip around  $-0.10$  eV that leads to total domination by one species.



**Figure 9:** Scans across varying chemical potentials and temperatures for Like-Unlike absorption.



**Figure 10:** Lattice configurations of Nitrogen and Hydrogen at constant temperature but varying potential for Like-Unlike absorption.

The lattice configurations and the heat maps of the Nitrogen and Hydrogen absorption for the Like-Unlike case show remarkable order throughout the different chemical potentials. The potential window was expanded to better understand the transitions in Hydrogen and Nitrogen coverage which went against many of the other trends that make the hydrogen and nitrogen somewhat mirror each other. Instead, there is a distinct symbiotic relationship where the chemical potential of H being made more favorable and leading to more absorption makes the absorption of Nitrogen more favorable and leading to more absorption. As we can see when looking at very unfavorable chemical potentials of H, the nitrogen is effectively limited in their coverage of the lattice due to not having any nearby Hydrogens to interact with. The temperature change doesn't have a distinct effect on the coverage and persistence of certain species. This is because the energy difference between the ground state where the lattice is perfectly ordered with opposite neighbors is so much more favorable, that the temperature component of the beta term cannot compete with this unfavorable energy difference. From this, the probability of an unfavorable placement of a like neighbor or removal of an unlike neighbor are remarkably small.

### **Analysis**

The parameter sets above give important insight into the optimal way to conduct ammonia synthesis and what we should aim to manipulate to achieve this. As we see at low temperatures, the particles become far more fixed due to unfavorable moves being much more unlikely because the beta term is larger which when combined with the energy difference term for potential moves make the related probabilities exceedingly low. These low temperatures resulting in a static lattice aren't ideal for a process like Ammonia synthesis because we need

both species to comfortably absorb and to absorb near one another. This leads to the problem with many of our tested parameters, where Nitrogen and Hydrogen don't work cooperatively to bind adjacently. The synthesis of ammonia will require a relatively efficient co-absorption of Hydrogen and Nitrogen. In the Like-Unlike interactions where the energetic favorability of having heterogeneous neighbors is so great; the system will aim to achieve this across a comfortable range of chemical potentials and temperatures. The other cases are less ideal for ammonia synthesis because they all essentially create competition for absorption to sites, and a lattice that is completely overflowing with hydrogen or nitrogen isn't ideal for catalysis. The case of Like- Unlike gives us a roughly equal mixture of species with close proximity to one another that would be best.

To best maximize favorability, it is important to consider how some of our variables must be managed. In the case of Like- Unlike interactions, the hydrogen chemical potential can't be too unfavorable (negative), or even the favorable stabilization of heterogeneous neighbors won't be enough to coerce binding. By managing the partial pressure of hydrogen and maintaining a sufficiently high value, we can create conditions that maximize binding for both Nitrogen and Hydrogen. Building on this, it is important to consider adding materials to the lattice that could help penalize the interactions of neighboring Nitrogen with Nitrogen and Hydrogen with Hydrogen and would favor the addition of heterogeneous neighbors. Combined with a temperature that maintains some order to the system but also prevents local clustering will hopefully lead to an efficient set of conditions for ammonia synthesis.

## **Sources**

ACS

[https://acs.figshare.com/collections/How\\_Poisoning\\_Is\\_Avoided\\_in\\_a\\_Step\\_of\\_Relevance\\_to\\_the\\_Haber\\_Bosch\\_Catalysis/7126728](https://acs.figshare.com/collections/How_Poisoning_Is_Avoided_in_a_Step_of_Relevance_to_the_Haber_Bosch_Catalysis/7126728)

Computational Problem Solving Course GitHub

<https://wexlergroup.github.io/comp-prob-solv/lecture-19-project-1/>