ML-Assisted Plasma Kinetics Reduction in N_2-H_2 Discharges

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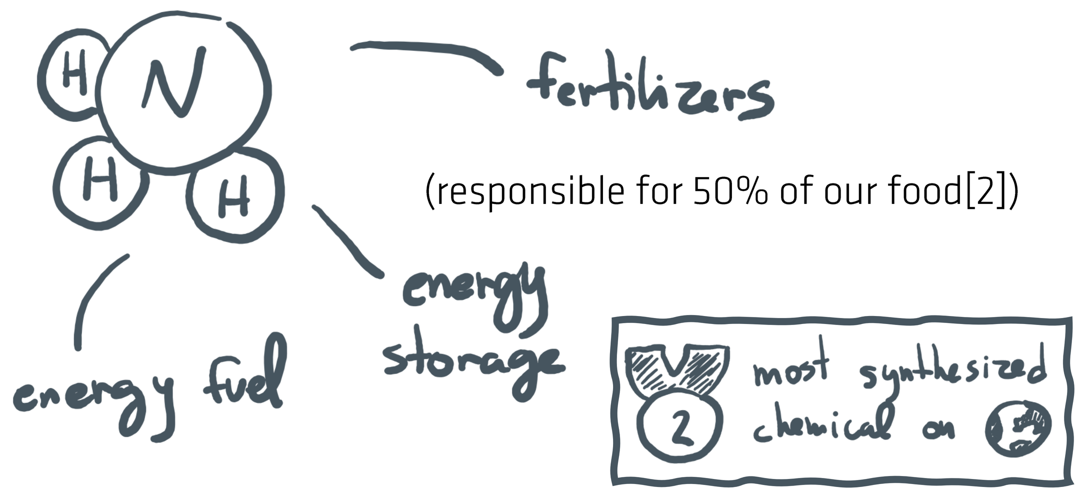
Abstract

We investigate a Machine Learning (ML) framework to infer reaction pathway importance in plasma chemistry with explicit plasma-surface coupling. Chemical schemes are represented as Petri nets. Given initial and final species densities (b, y), we estimate reaction weights x in Ax + b ≈ y by optimizing a KL-divergence objective with partition-wise normalization (volume/surface plasma species). Future work outlines, namely a KKT approach to enforce physics while keeping fit quality, are discussed.

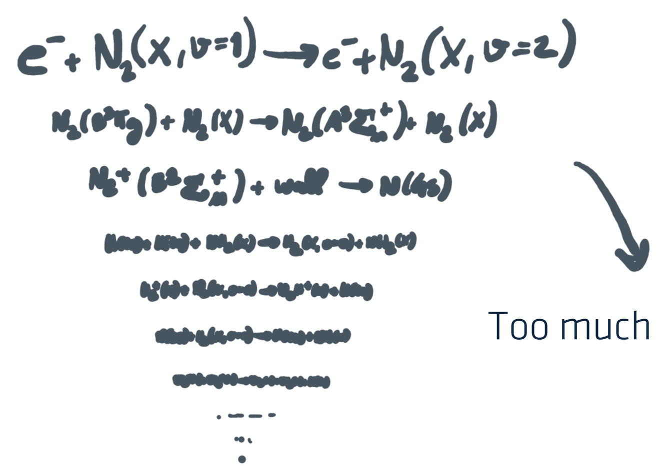
PSI.COM – Project Overview

PSI.COM advances modelling of N_2–H_2 plasma-surface chemistry to enable greener NH_3 synthesis. The project links volume and surface reactivity, supports experiments with kinetic simulations, and uses Petri-net and ML methods to identify key reactions and reduce chemical schemes. It also contributes curated data and methodology to the LXCat ecosystem[1]. PSI.COM is hosted by Instituto de Plasmas e Fusão Nuclear of Instituto Superior Técnico, Centro de Física das Universidades do Minho e do Porto, and Laboratoire de Physique des Plasmas (École Polytechnique, Palaiseau, France).

Motivation



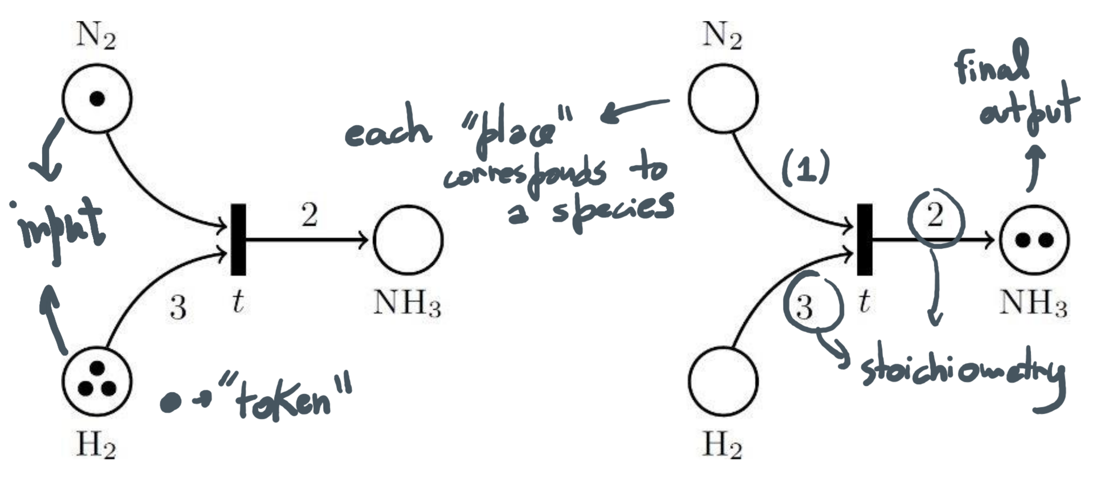
Green NH_3 synthesis via Low-Temperature Plasmas (LTPs) represents a promising alternative to the energy-intensive **Haber-Bosch** process. Understanding and modeling these plasma systems is critical for advancing this technology. Yet, accurate plasma-surface coupling remains essential but computationally expensive when using full kinetic models.



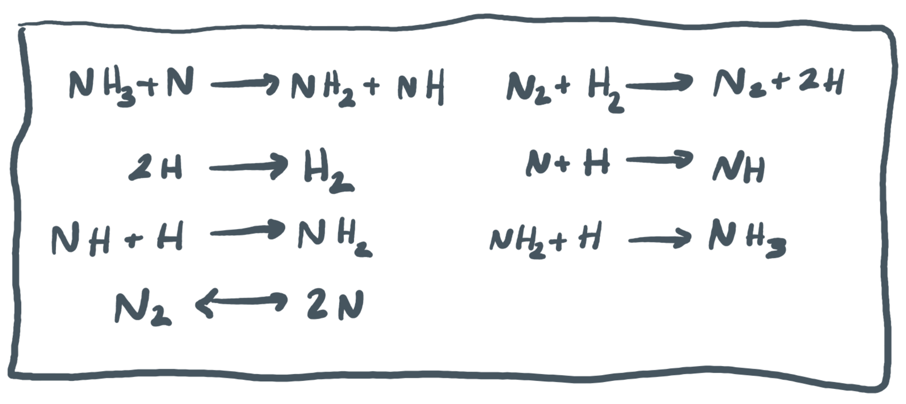
Too much complex!

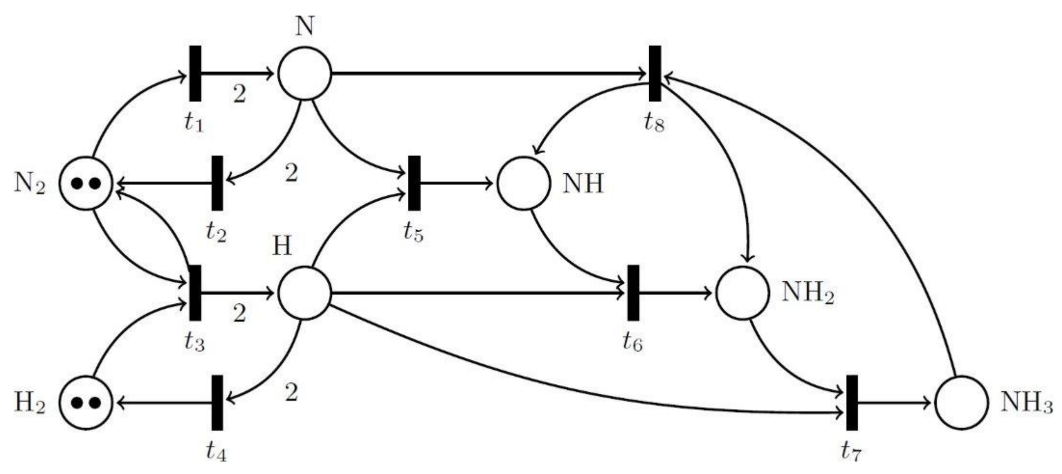
Approach

We use **ML** to identify the most important reactions in the full kinetic scheme by representing the chemical network as a **Petri net**[3].



A "transition" only happens if we place the correct number of tokens. We illustrate the definition of the transition matrix A, the "firing" vector x, the initial vector b, and the final vector y, with the following (simpler) chemical reaction network:





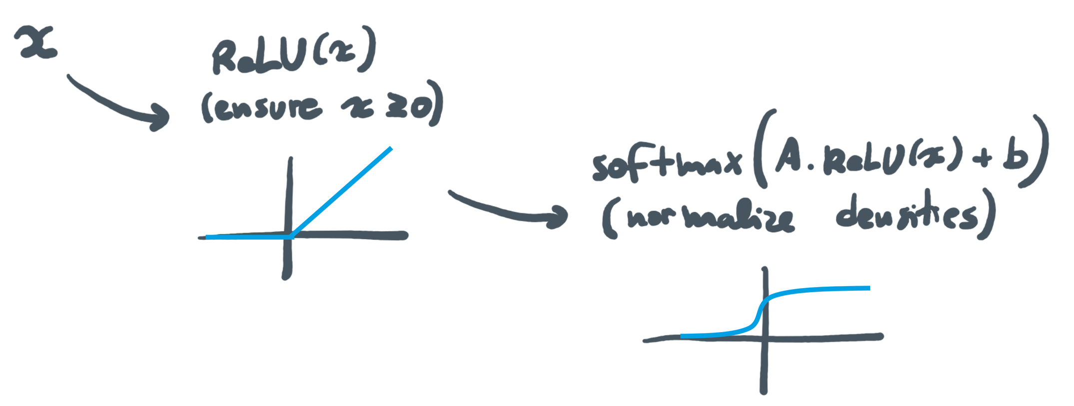
$$\underbrace{\begin{array}{c} A \\ \left[\begin{array}{rrrrrrrr} 0 & 0 & 2 & -2 & -1 & -1 & -1 & 0 \\ 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 \\ 2 & -2 & 0 & 0 & -1 & 0 & 0 & -1 \\ -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & -1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 \end{array}\right] \begin{array}{l} H \\ H_2 \\ N \\ N_2 \\ NH \\ NH_2 \\ NH_3 \end{array} \\ \begin{array}{cccccccc} t_1 & t_2 & t_3 & t_4 & t_5 & t_6 & t_7 & t_8 \end{array} \end{array}}_{\text{net stoichiometry}} \times \underbrace{\begin{array}{c} x \\ \begin{bmatrix} 1 \\ 0 \\ 2 \\ 0 \\ 1 \\ 1 \\ 1 \\ 0 \end{bmatrix} \begin{array}{l} t_1 \\ t_2 \\ t_3 \\ t_4 \\ t_5 \\ t_6 \\ t_7 \\ t_8 \end{array} \end{array}}_{\text{how much } t_i \text{ occurred}} + \underbrace{\begin{array}{c} b \\ \begin{bmatrix} 0 \\ 2 \\ 0 \\ 2 \\ 0 \\ 0 \\ 0 \end{bmatrix} \begin{array}{l} H \\ H_2 \\ N \\ N_2 \\ NH \\ NH_2 \\ NH_3 \end{array} \end{array}}_{\text{initial densities}} = \underbrace{\begin{array}{c} y \\ \begin{bmatrix} 1 \\ 0 \\ 1 \\ 1 \\ 0 \\ 0 \\ 1 \end{bmatrix} \begin{array}{l} H \\ H_2 \\ N \\ N_2 \\ NH \\ NH_2 \\ NH_3 \end{array} \end{array}}_{\text{final densities}}$$

(−) → reagents
(+) → products

With the linear approximation Ax+b=y we consider the global transformation of the initial state densities **b** to the steady-state densities **y**. This final density **y** is compared with reference data from LoKI-B software[4], an electron Boltzmann equation solver for LTPs. Our goal is then to find the weights **x** that minimize this difference. Since these reaction weights represent pathway importance, we effectively reduce our original kinetic scheme by removing low-weight reactions.

Model

The system is undetermined, meaning there are many solutions for **x**. It starts by guessing a solution for it, exponentiating random values of a normal distribution.



ReLu(x) is used since we are interested in **positive** reaction weights only. After the last stage, where final densities **y** = **softmax**[A·ReLU(x) + b] are normalized, we minimize a loss function (Kullback-Leibler (KL) divergence[3]):

$$L(x) = || y - y_{reference} ||$$

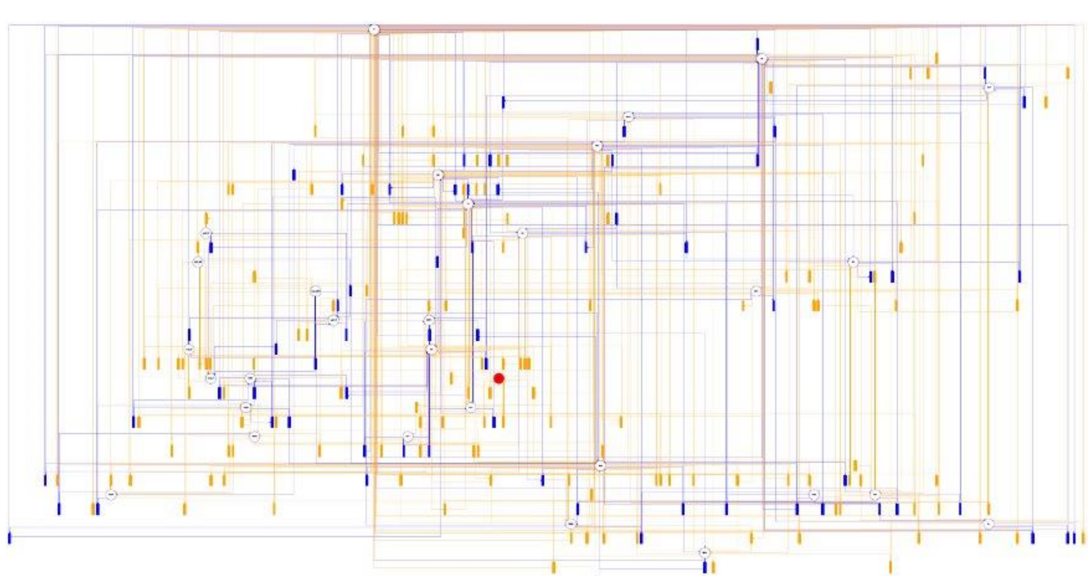
by **Adaptive Moment Estimation (Adam)** algorithm, a more sophisticated version of the classic gradient descent[5]

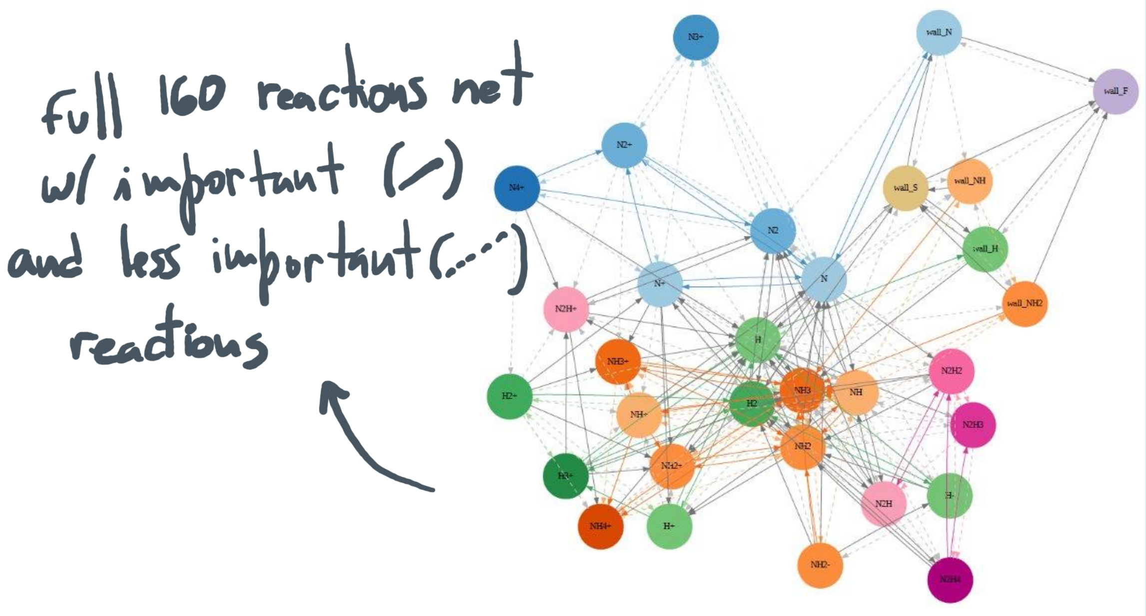
$$x^{(k+1)} = x^{(k)} - \eta \nabla L(x^{(k)})$$

The cycle runs until an error of less than 10^{-6} is achieved or 200.000 iterations are reached, whichever occurs first. Missing sink terms are manually incorporated in the chemical scheme to ensure mass conservation (e.g., $2e^- \rightarrow e^-$) and charge neutrality is ensured by setting electron's density equal to ions' density.

Results

Preliminary results on a 160-equation N_2–H_2 scheme show blue reactions as important. At this early stage, the algorithm still produced some negative values in **x** before the final ReLU, which were identified as less important reactions.



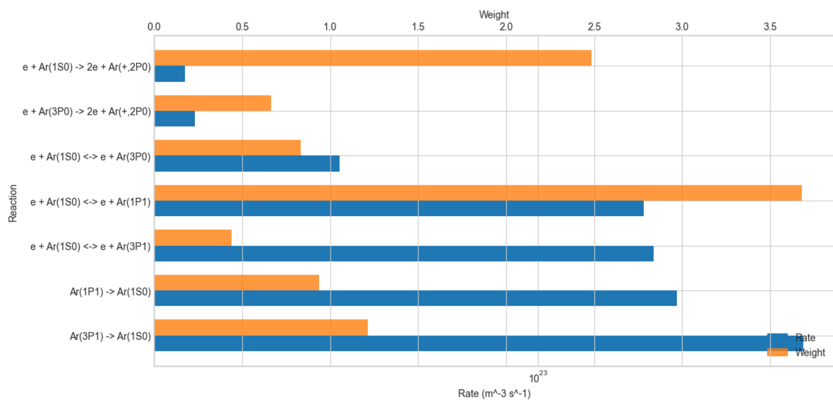


A penalty was added to the loss function to impose further positive values for **x**.

```python
# (...)
penalty_weight = 1e-1

# Add penalty for negative values in X
penalty = tf.reduce_sum(tf.square(tf.minimum(X, 0.0)))
total_loss = loss + penalty_weight * penalty
```

This simple penalty was sufficient to turn all weights positive in a simpler 26 reactions Argon-system, used as testbed. Below, a comparison between the normalized weights and chemical rates obtained with LoKI-B for some selected reactions.



Future Work and Final Remarks

Future work will focus on implementing **Karush-Kuhn-Tucker (KKT) conditions** for non-negativity constraints and integrating reaction **rate coefficients** through data assimilation methodologies. KKT conditions are a generalization of Lagrange multipliers that handle both equality and inequality constraints, and instead of "forcing" positive weights after the event, they solve the constrained optimization directly[6]. On the other hand, reaction weights **x** should be physically informed through rate coefficients (k), since these encapsulate the different probability of reactions, information that is currently missing. Instead of random initialization, weights should be initialized with known rate coefficient values, resulting in a physically consistent and interpretable model.

References

[1] LXCat project. URL: https://lxcat.net
[2] H. Ritchie and M. Roser, "Half of the world's habitable land is used for agriculture", *Our World in Data*, 2019
[3] D. Ferreira et al. "Machine Learning for Chemistry Reduction in N2-H2 Low-Temperature Plasmas". In: Proceedings of the International Conference on Plasma Physics. Lisbon, Portugal: Instituto Superior Técnico, Universidade de Lisboa, 2023
[4] A. Tejero del-Caz et al. "The LisbOn KInetics Boltzmann solver". In: Plasma Sources Science and Technology 28.4 (2019), 043001–043001
[5] S. Ruder, "An overview of gradient descent optimization algorithms." arXiv preprint arXiv:1609.04747 (2016)
[6] M. Li, "Generalized Lagrange Multiplier Method and KKT Conditions With an Application to Distributed Optimization," in IEEE Transactions on Circuits and Systems II: Express Briefs, vol. 66, no. 2, pp. 252-256, Feb. 2019

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