Optimising Chemistry Sets

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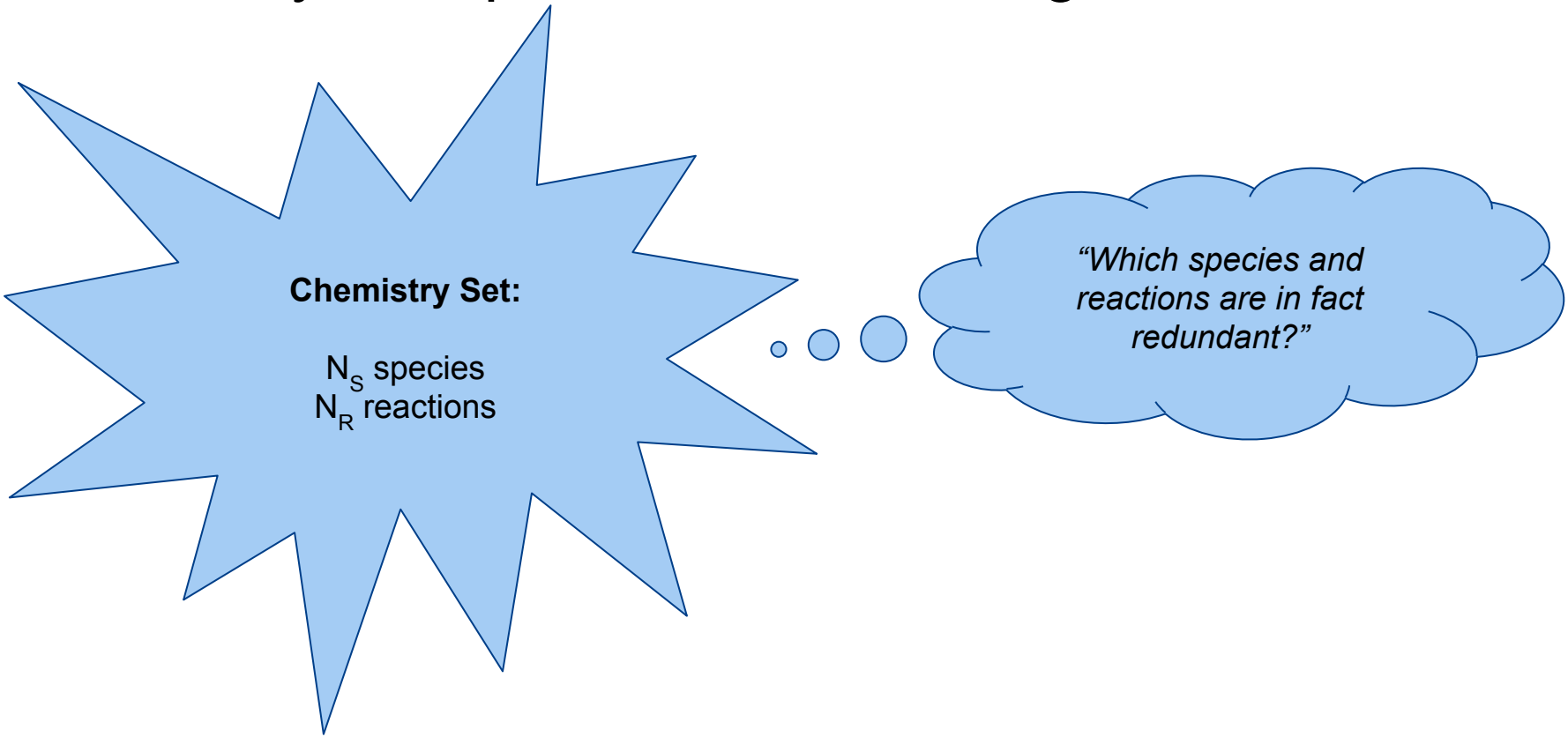
Motivation

- *Chemistry set* (a.k.a. *kinetic scheme*, *reaction set*, *kinetic mechanism*, ...) is in the centre of *every plasma numerical model*.
- Large published chemistry sets for plasma modeling might contain up to a hundred species and many thousand reactions [1]. This can pose some challenges with computational cost.
- Almost all published chemistry sets contain *redundant species and reactions* [2].

[1] Koelman P, *et al* 2017 *Plasma Processes and Polymers* **14** 1600155
[2] Tomlin A S, *et al* 1992 *Combustion and Flame* **91** 107-130

Chemistry set optimisation and insights



Chemistry set optimisation and insights

- Redundant species/reactions ...
  - ... related to which model outputs? *Species of interest.*
  - … related to which set of plasma parameters or process conditions? *Reduction conditions.*

Chemistry reduction example - N_2/H_2

- Starting with the detailed reduction set for N_2/H_2 plasmas (published [3])
  - 42 species
  - 408 reactions

Neutrals	$H\ H_2\ N\ N_2\ NH\ NH_2\ NH_3$
Excited States	$H_2(b\,^3\Sigma_u^+)\ H_2(B\,^1\Sigma_u^+)\ H_2(c\,^3\Pi_u)\ H_2(a\,^3\Sigma_g^+)\ H_2(\nu_1) - H_2(\nu_3)$ $N(^2D)\ N(^2P)\ N_2(A\,^3\Sigma_u^+)\ N_2(B\,^3\Pi_g)\ N_2(a'\,^1\Sigma_u^-)\ N_2(C\,^3\Pi_u)$ $N_2(\nu_1) - N_2(\nu_8)$
Positive Ions	$H^+\ H_2^+\ H_3^+\ N^+\ N_2^+\ N_3^+\ N_4^+\ NH^+\ NH_2^+\ NH_3^+\ NH_4^+\ N_2H^+$
Negative Species	$e\ H^-$

[3] Hong J, *et al* 2017 *Journal of Physics D: Applied Physics* **50** 154005

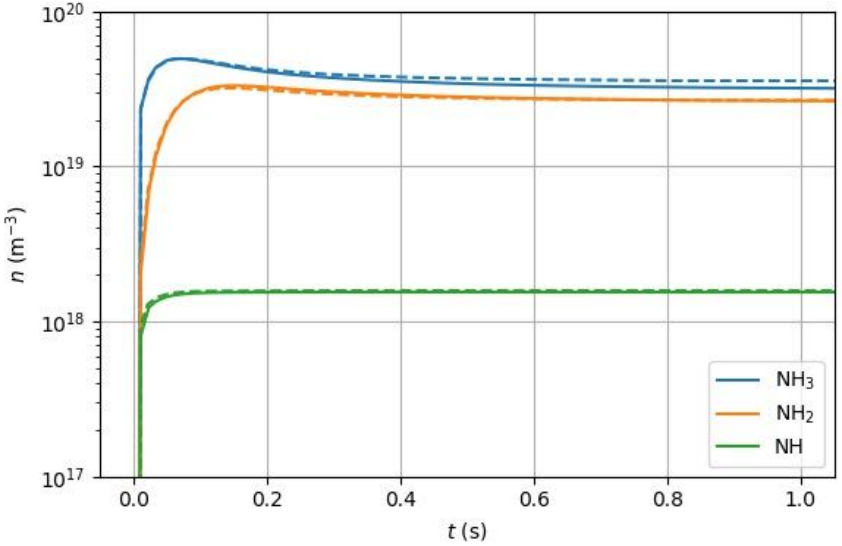
Chemistry reduction example - N_2/H_2

- Species of interest:
  - NH, NH_2, NH_3
- Reduction conditions:
  - Pressure: 9 Pa
  - Temperature: 300 K
  - N_2/H_2 ratio: 1:9

Chemistry reduction example - N_2/H_2

23 species identified as redundant:

N_3^+, N_4^+, N(2D), N(2P), N^+,
H_2(B), N_2(a'), NH^+, H_2(a), N_2(C),
H^+, N_2(B), N_2(A), H_2(v3), N_2(v8),
N_2(v7), N_2(v6), N_2H^+, N_2(v5),
N_2^+, N_2(v4), N_2(v3), N_2(v2)



Species: 42 ⟶ 19

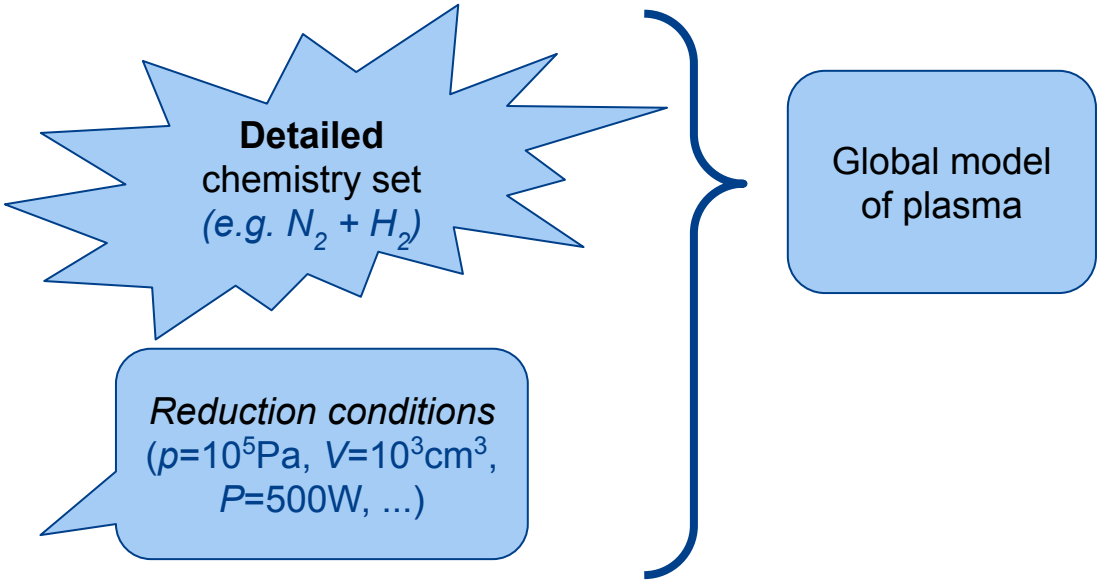
Reactions: 408 ⟶ 91

Species ranking

Detailed
chemistry set
(e.g. N_2 + H_2)

Reduction conditions
(p=10^5Pa, V=10^3cm^3,
P=500W, ...)

Species ranking



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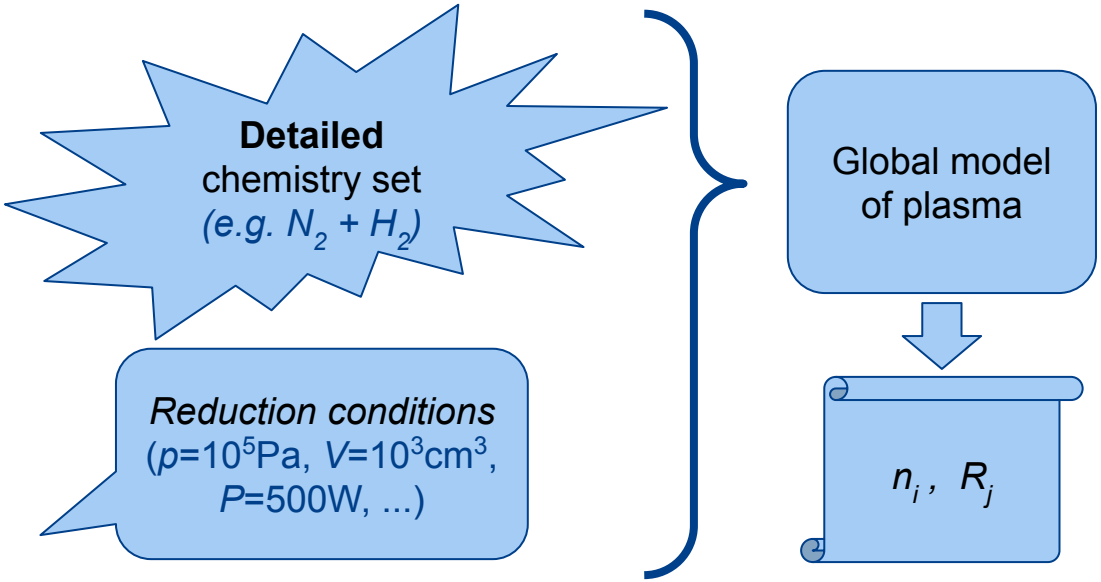

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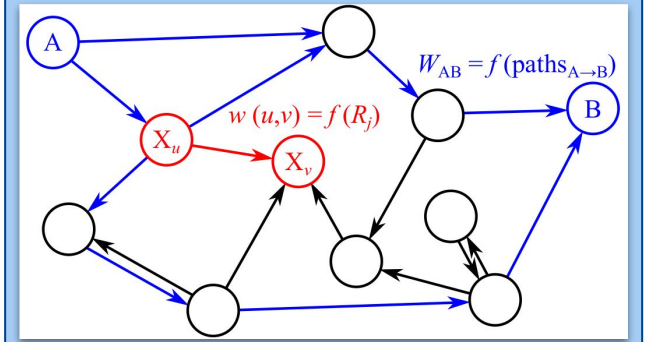
Global model of plasma

n_i , R_j

Chemistry graph
Species: A, B, …
Direct interaction coefficients: *w*
Indirect coupling coefficients: *W*



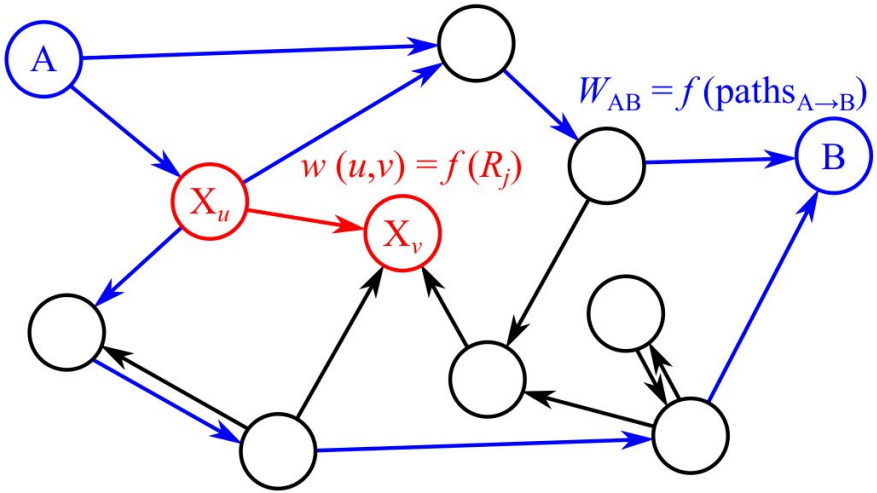
Species ranking

Direct interaction coefficients *w*

- Based on the DRG theory [4]
- $$w(u,v) = \frac{\sum_{j=1}^{N_R} |a_{vj} R_j \delta_u^j|}{\sum_{j=1}^{N_R} |a_{vj} R_j|}$$

Indirect coupling coefficients *W*

- Based on Dijkstra's "shortest path" graph search algorithm [5]
- Searching for the path minimizing $\sum(1/w)$
- $W = \sum w$



[4] Lu T and Law C K 2005 *Proceedings of the Combustion Institute* **30** 1333-1341
[5] Dijkstra E W 1959 *Numerische Mathematik* **1** 269-271

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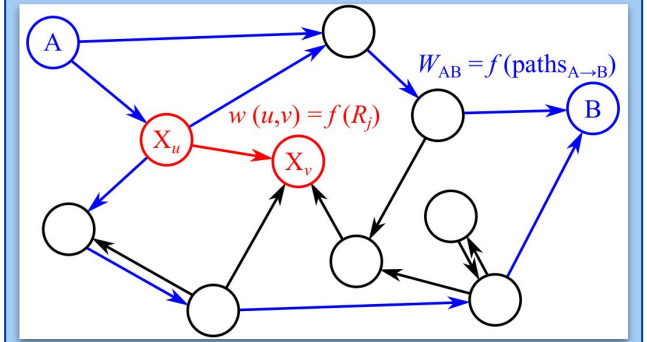

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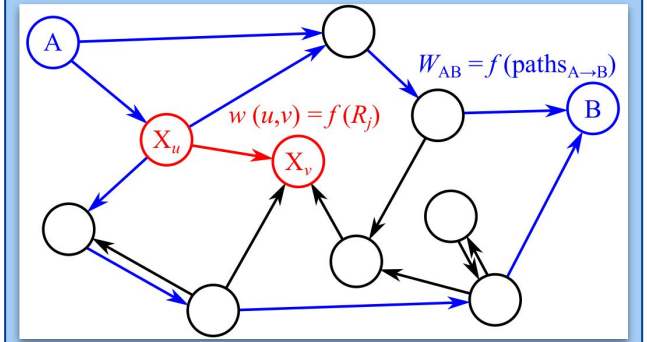
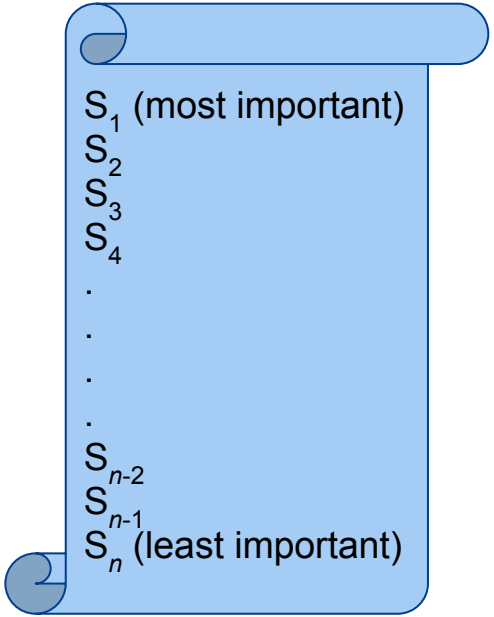


Species ranking scores

$$C_i = \max_k W_{X_i X_k}, \quad \text{species of interest } \{X_k\}.$$

Species ranking

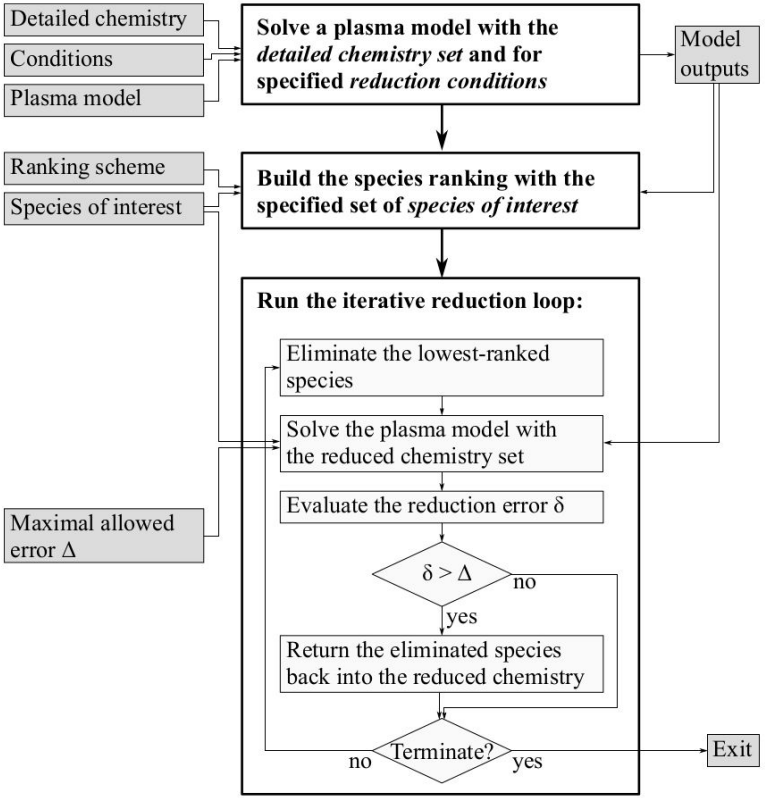
Resulting species hierarchy reflects how each species is important to model the collective set of *species of interest*



Likely to be essential species

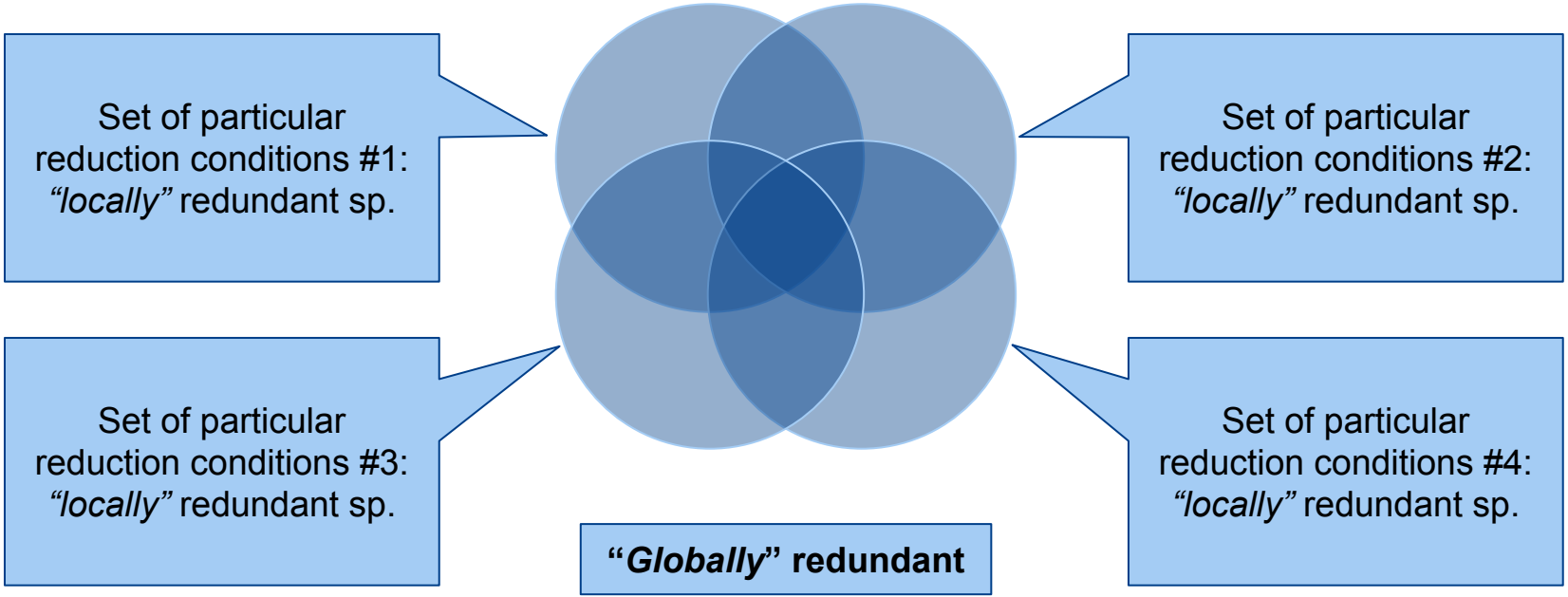
Likely to be redundant

Species-oriented ranking-based reduction method



Reduction conditions

It is important to capture *a range* of conditions in the chemistry set reduction



Thank you for your attention.

For people interested in details, check out the paper accepted in PSST:

Fast species ranking for iterative species–oriented skeletal reduction of chemistry sets

https://doi.org/10.1088/1361-6595/abcd53