CONNECT THE DOTS: *IN SILICO* PREDICTION OF HETEROGENEOUS REACTION MECHANISMS

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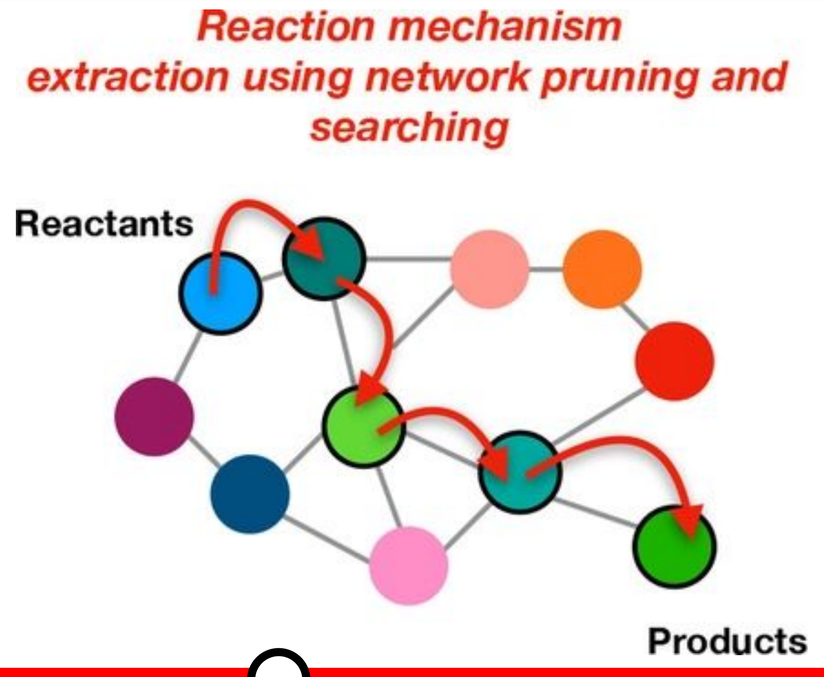
TOWARDS RATIONAL DESIGN…

The core aims of our study are to:

- Accelerate the discovery of novel, complex multi-step reaction mechanisms.
- Enhance our understanding of the underlying chemical and physical processes that govern their behaviour.
- Propose new computational schemes towards optimising heterogeneous, nanoparticle catalysts.
- Use rational design approaches to rapidly explore complex, multidimensional chemical space and leverage AI-driven platforms to execute such processes.



THE *"VIRTUAL FLASK"* PARADIGM…

(1) The graph driven sampling (**GDS**) algorithm is used to sample chemical space in a stochastic graph based fashion using **matrix transformations** to guide exploration. In this context, chemical reactions are defined as matrix addition or subtraction operations. **NEB** calculations were used to optimise the geometry of reaction end points using the **ReaxFF-PES**.

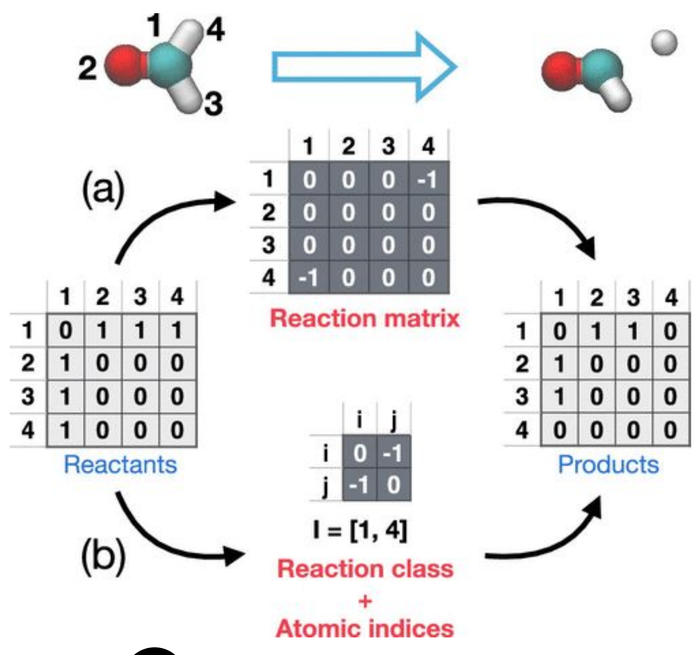
(2) We use simple chemical heuristics to generate a flexible library of chemical reaction operations for any given molecular system and use a constraint term called the **graph restraining potential** (GRP) to constrain our search, which takes on the following functional form:

$$W(\mathbf{r},\mathbf{G}) = \sum_{j>i}\Big[\delta(G_{ij}-1)\left[H(r_{ij}^{min}-r_{ij})\sigma_1(r_{ij}^{min}-r_{ij})^2 + H(r_{ij}-r_{ij}^{max})\sigma_1(r_{ij}^{max}-r_{ij})^2\right] + \delta(G_{ij})\sigma_2 e^{-r_{ij}^2/(2\sigma_3^2)}\Big] + V_{mol}(\mathbf{r},\mathbf{G}).$$

DISCRETISING CHEMICAL SPACE USING CONNECTIVITY MATRICES…

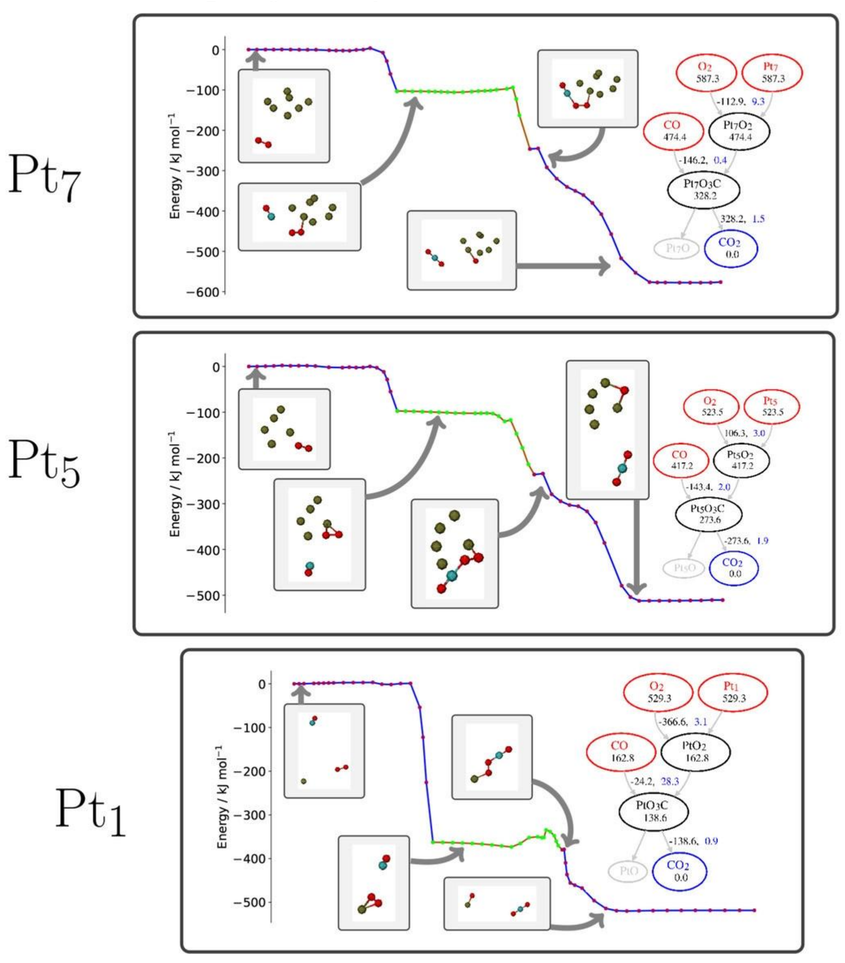
$$H(x)=\begin{cases}0 & \text{if } x<0,\\ 1 & \text{if } x>0.\end{cases}$$

$$\delta(x)=\begin{cases}1 & \text{if } x=0,\\ 0 & \text{otherwise,}\end{cases}$$

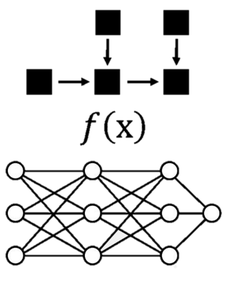


REACTION NETWORK GENERATION…

(4) Relevant intermediate molecules can be reduced to a single chemical reaction network (CRN) deemed the **'most likely'** reaction-mechanism using **DFS-based algorithms** coupled to sensible search-restriction criteria. We conduct our search for systems of **Pt_1** , **Pt_5**and **Pt_7**



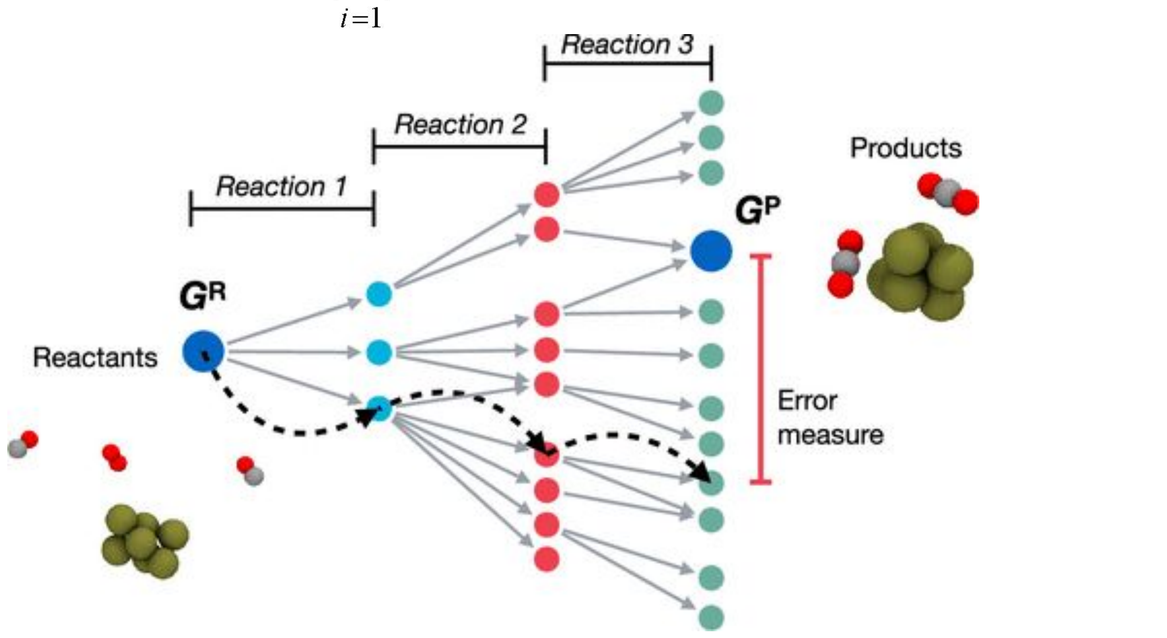
(5) We are now looking towards moving to using **machine learning** methods to further accelerate the prediction and optimisation of heterogeneous catalysts using a combination of geometric descriptors that accurately describe our chemical system.



CONNECT THE DOTS…

(3) The goal is to then find a sequence of elementary reactions for **CO** oxidation over a **Pt_7** catalyst that connect $\mathbf{G}^R$ and $\mathbf{G}^P$, such that:

$$\mathbf{G}^P = \mathbf{G}^R + \sum_{i=1}^{n_r}\mathbf{R}^{k(i)}(\mathbf{I}_i).$$



The error measure ***F*** describes the distance from the target connectivity matrix and is calculated using the simulated annealing algorithm, taking the following functional form:

$$F=\sum_{i<j}^{n}\left(\tilde{G}_{ij}^{P}-G_{ij}^{P}\right)^2,$$

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