Off-lattice kinetic Monte Carlo

and hydrogen vacancy-cluster interactions in α–Fe

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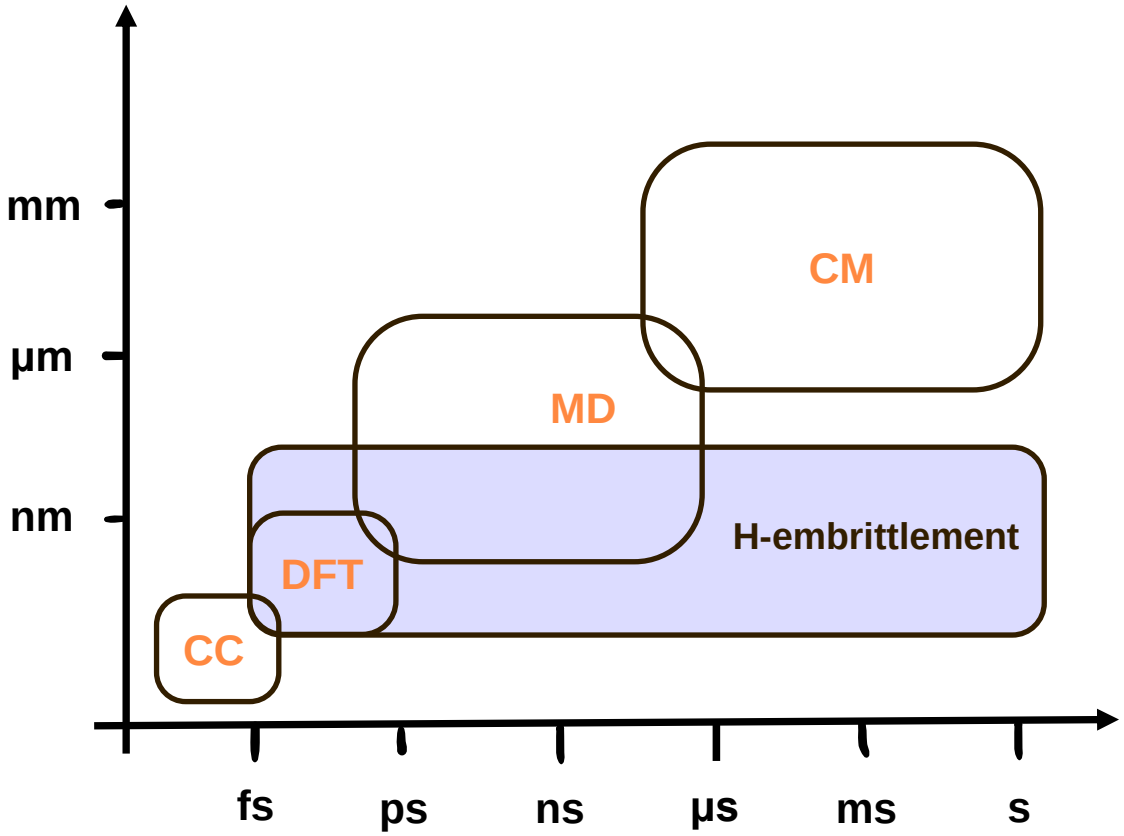
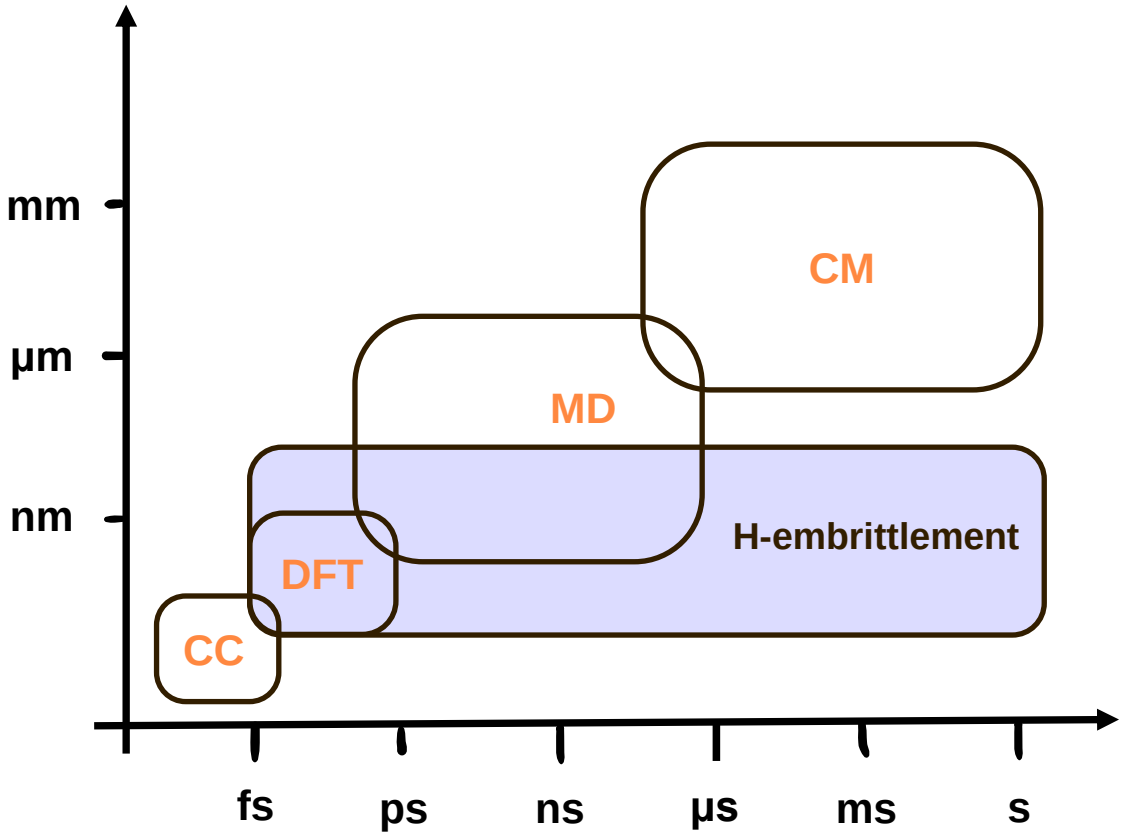
Outline

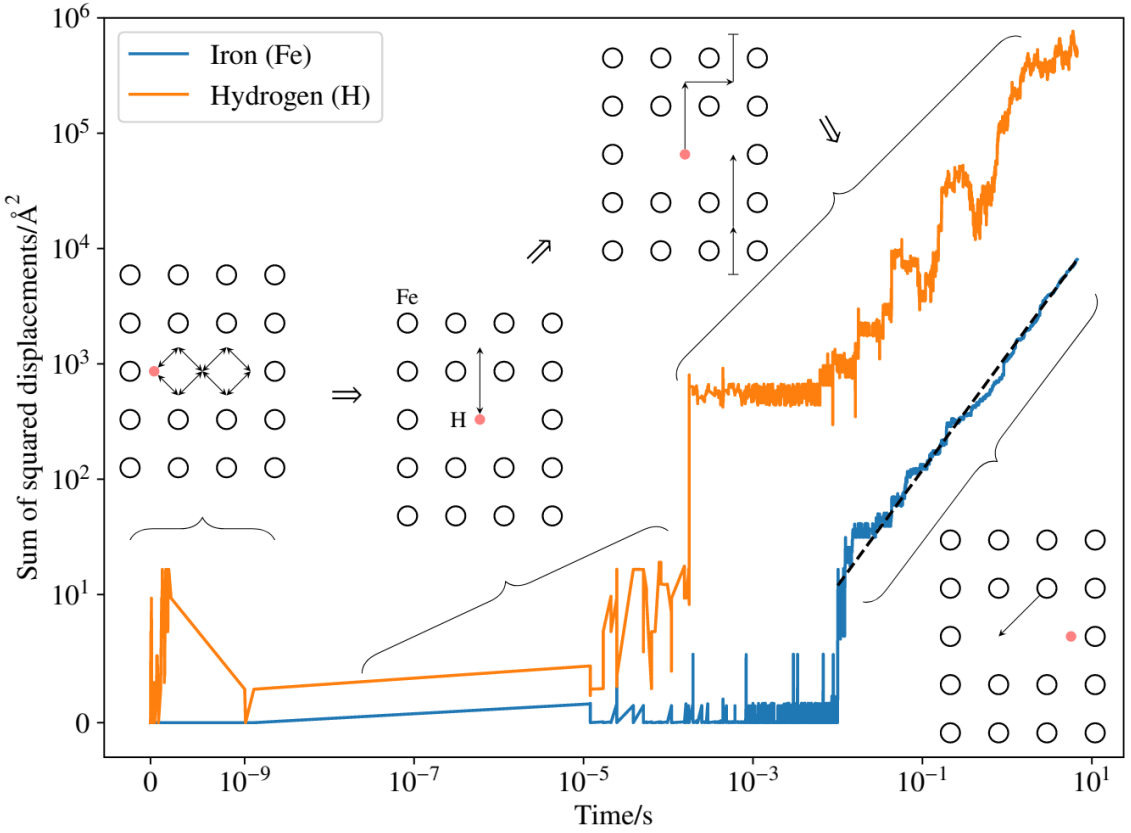
- Motivation & intro to off-lattice KMC (OLKMC)
- **Accelerating OLKMC**
  - **Local environments, tolerant classification.**
  - **Self symmetries.**
  - **An adaptive catalogue.**
- **Results**
  - **Vacancy clusters, H-complexes and lifetimes**

H-embrittlement

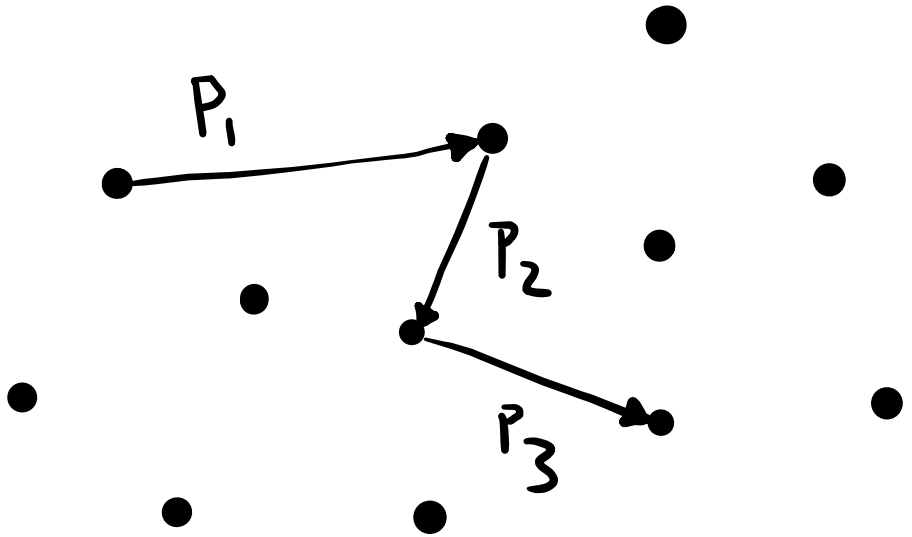


H-embrittlement



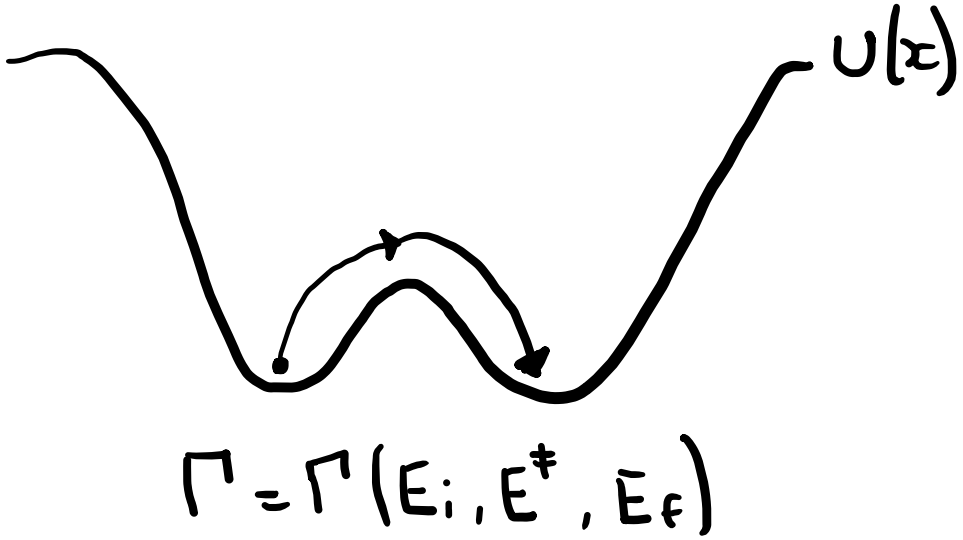


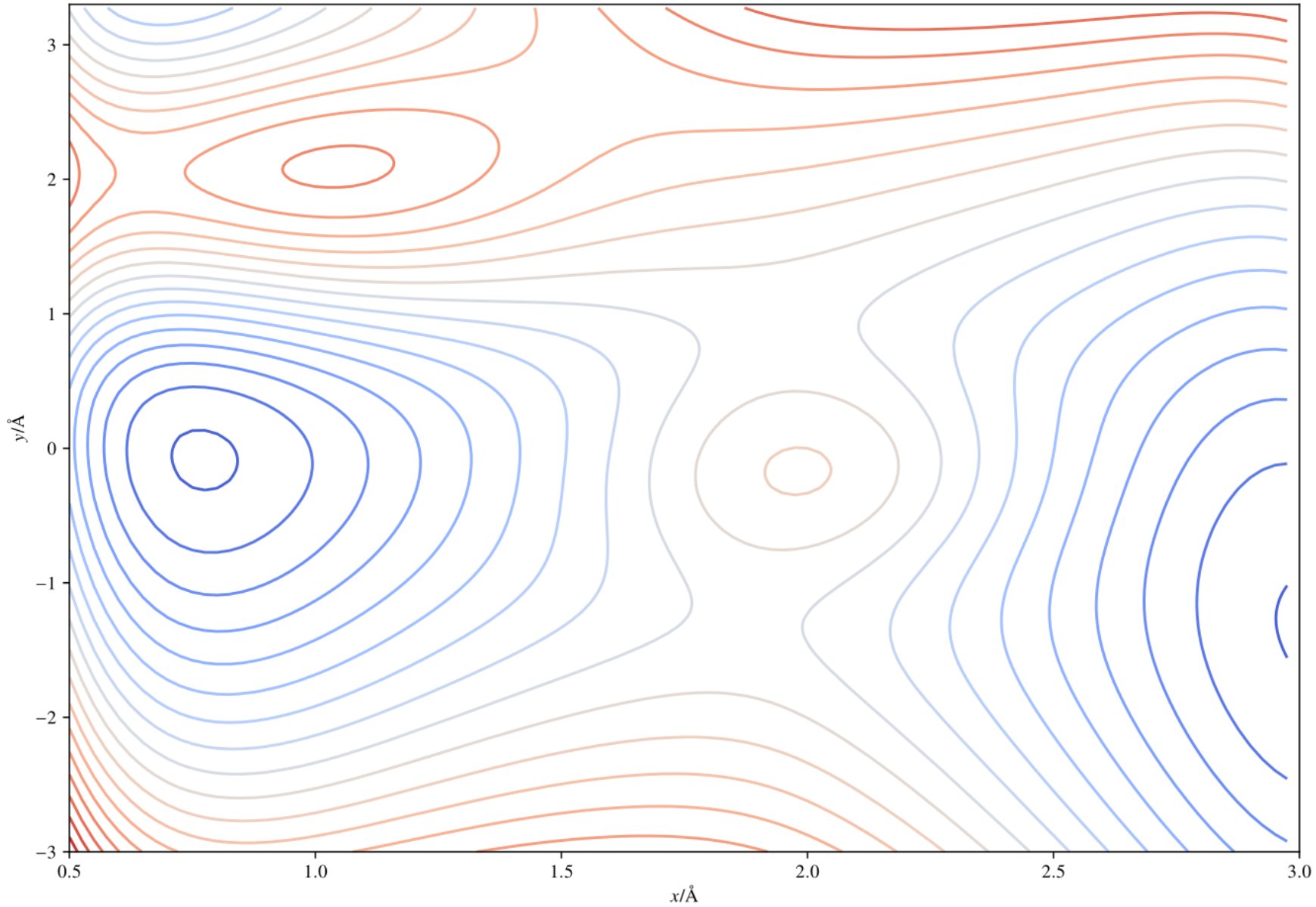
(Kinetic) Monte Carlo

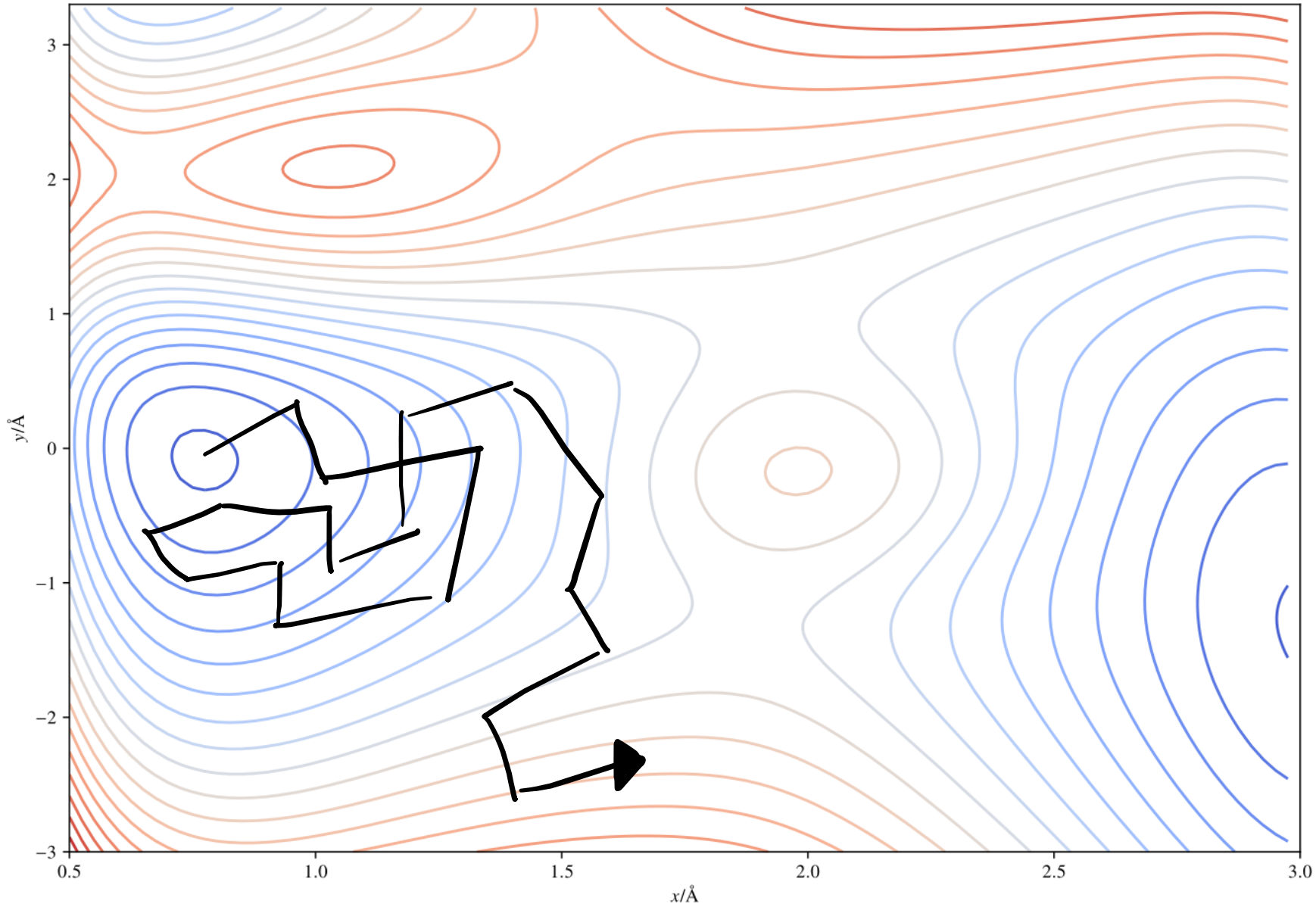


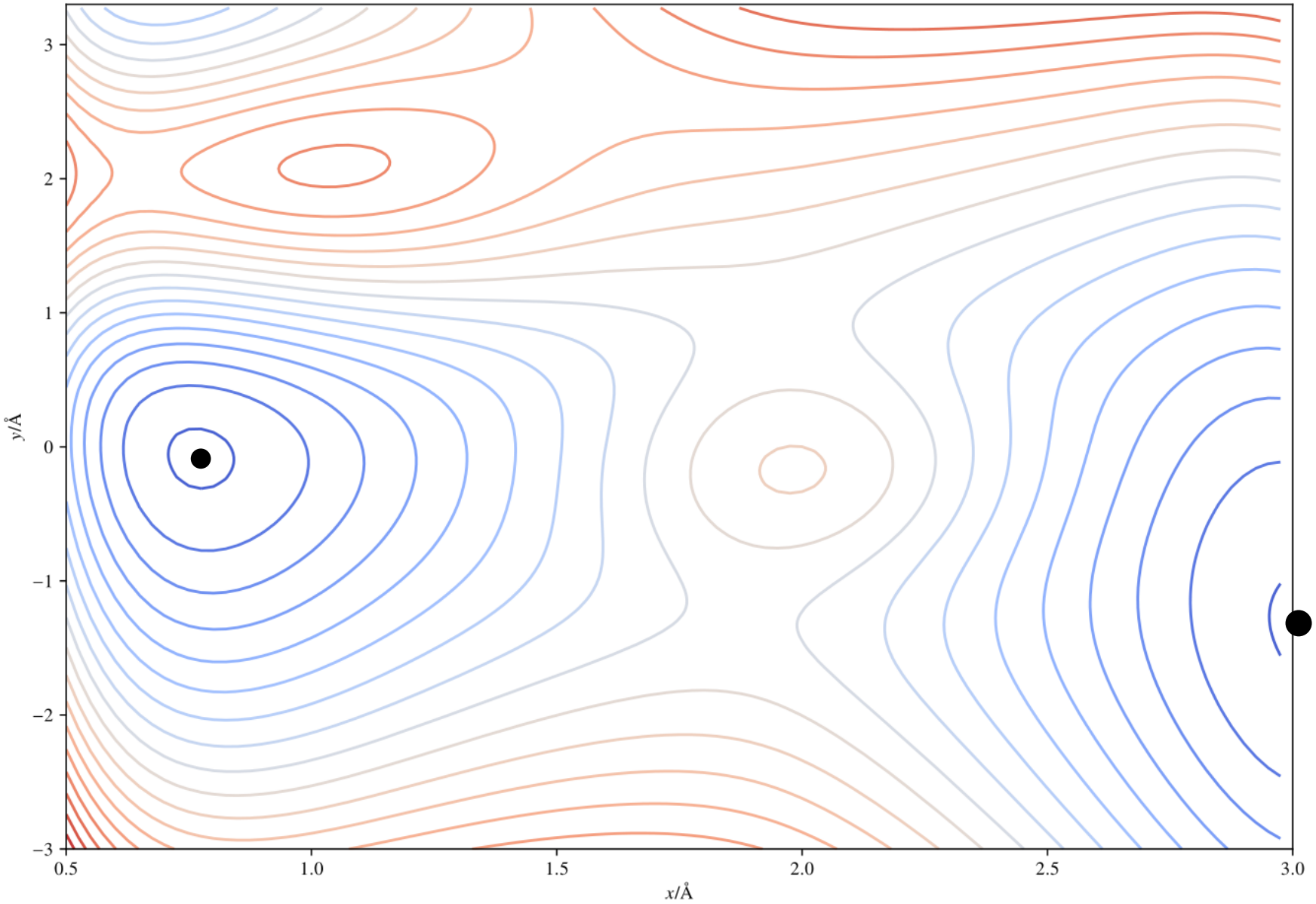
- Markov chain through state-space
- Compete set of mechanisms

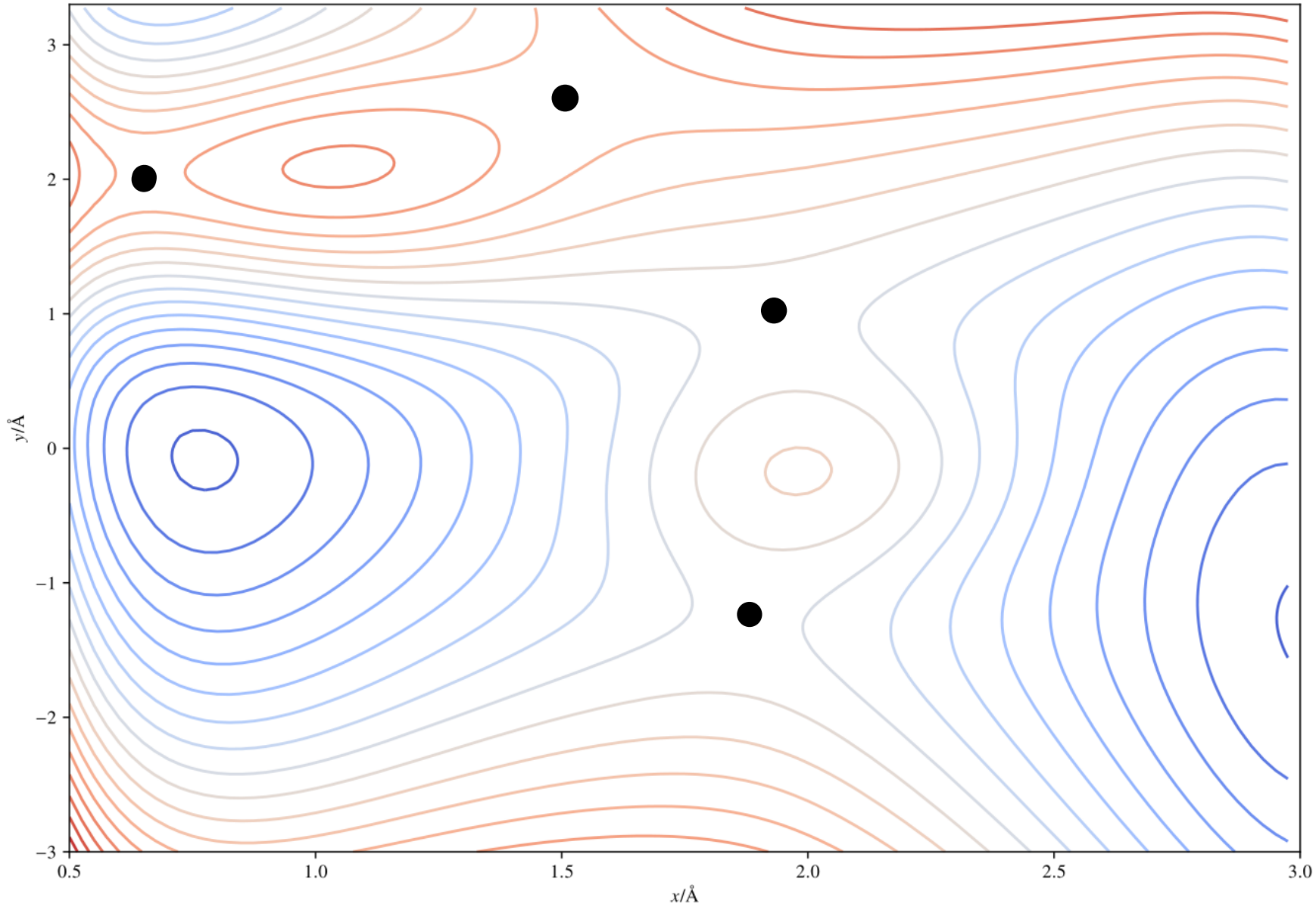
- Harmonic approximation to TST:

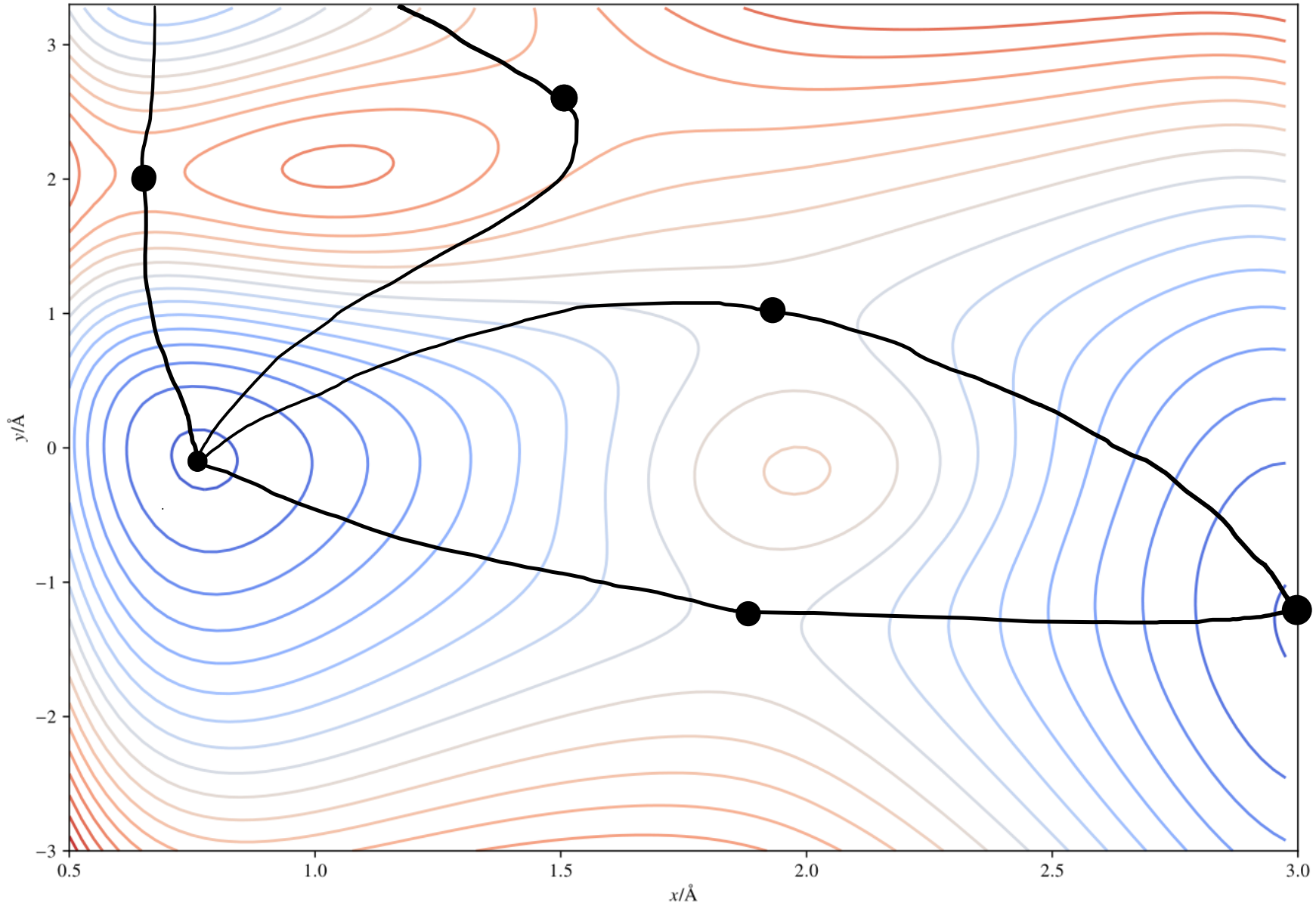



3
2
1
0
−1
−2
−3
y/Å
0.5
1.0
1.5
2.0
2.5
3.0
x/Å

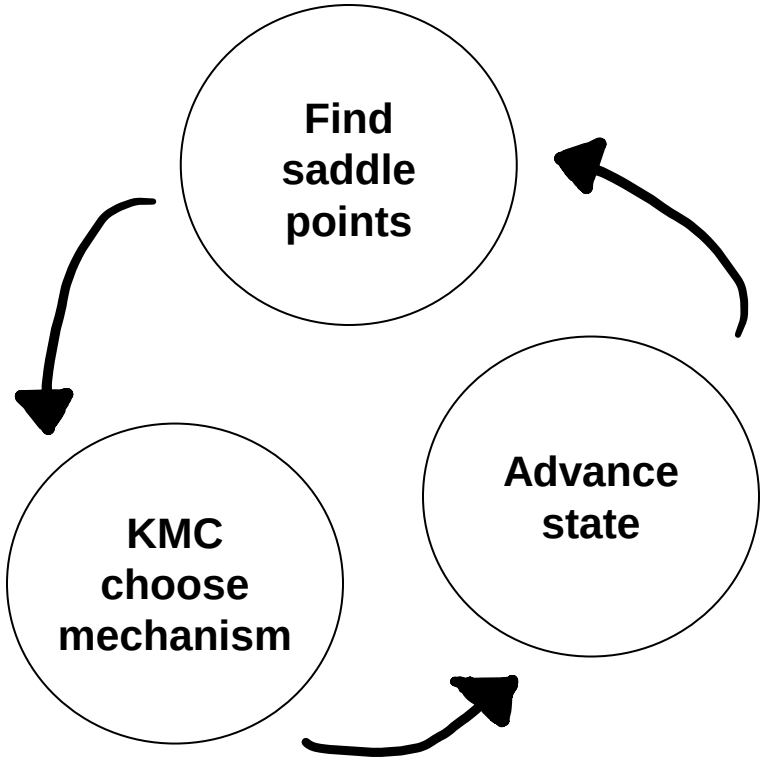

3
2
1
0
−1
−2
−3
y/Å
0.5
1.0
1.5
2.0
2.5
3.0
x/Å


3
2
1
0
−1
−2
−3
y/Å
0.5
1.0
1.5
2.0
2.5
3.0
x/Å


3
2
1
0
−1
−2
−3
y/Å
0.5
1.0
1.5
2.0
2.5
3.0
x/Å


3
2
1
0
−1
−2
−3
y/Å
0.5
1.0
1.5
2.0
2.5
3.0
x/Å

Off-lattice KMC



Outline

- **Motivation & intro to off-lattice KMC (OLKMC)**
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  - **Self symmetries.**
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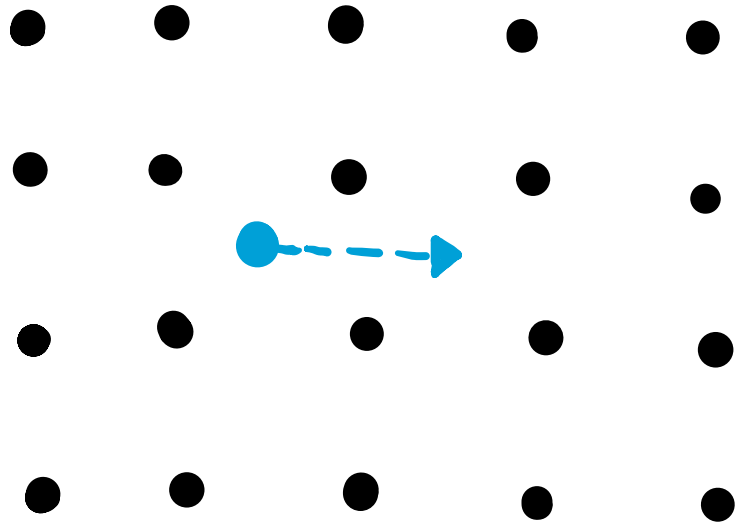
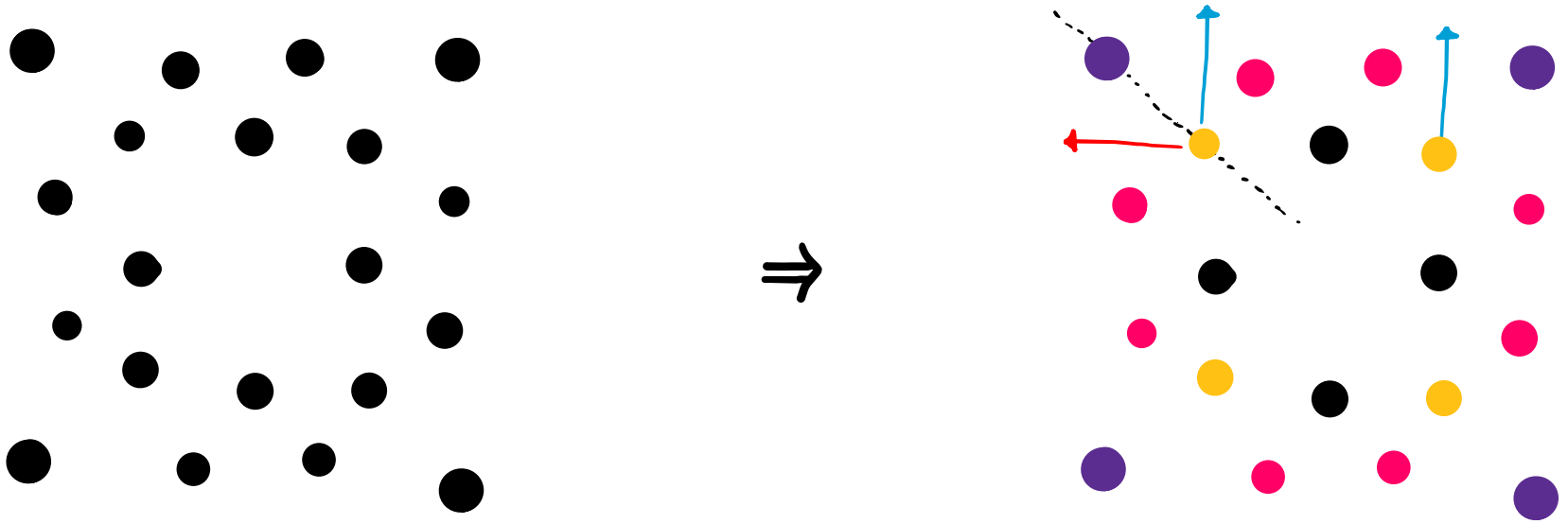
Locality

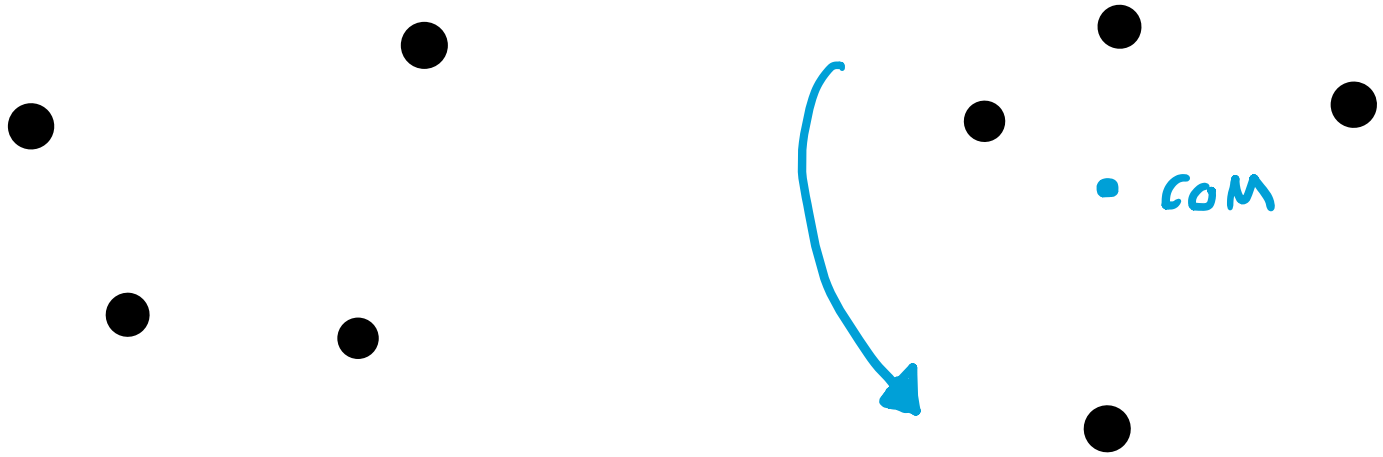


Local environments



Equivalence?

Invariant and tolerant equivalence



Invariant and tolerant equivalence

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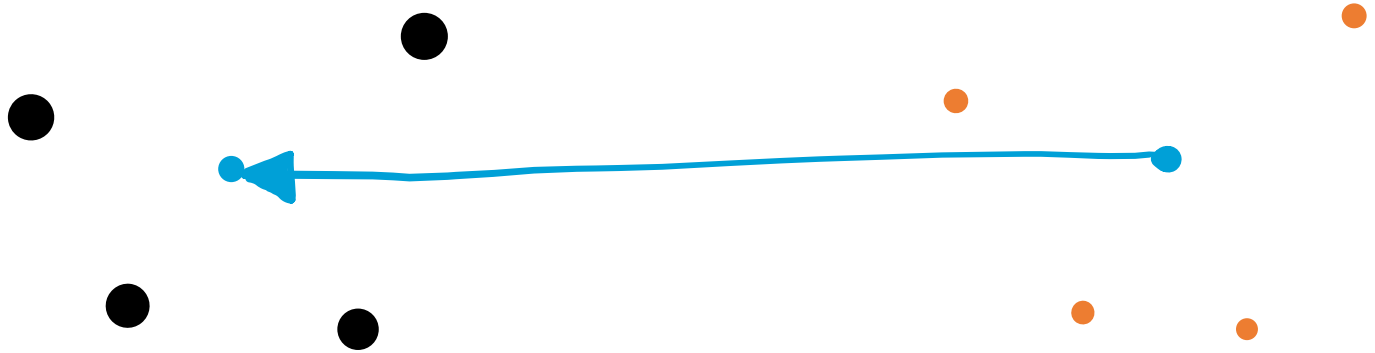
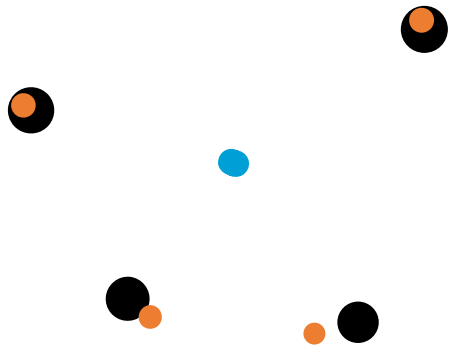
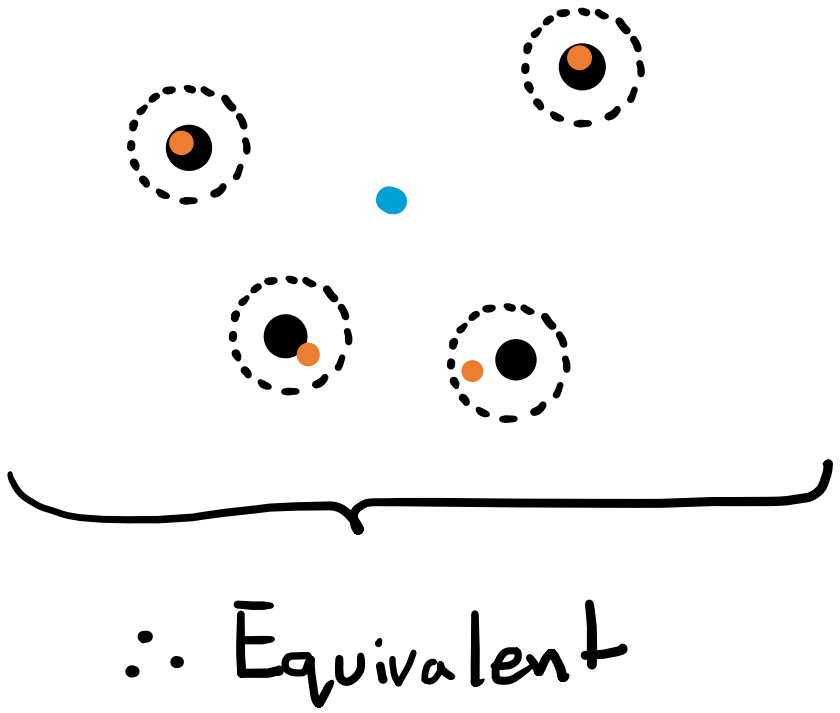
Invariant and tolerant equivalence



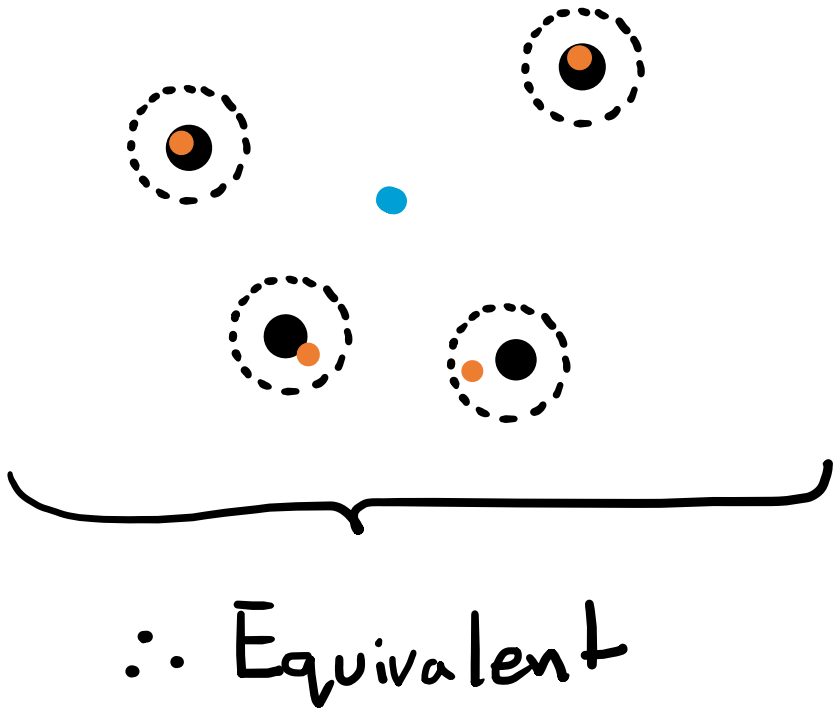
Invariant and tolerant equivalence



Invariant and tolerant equivalence

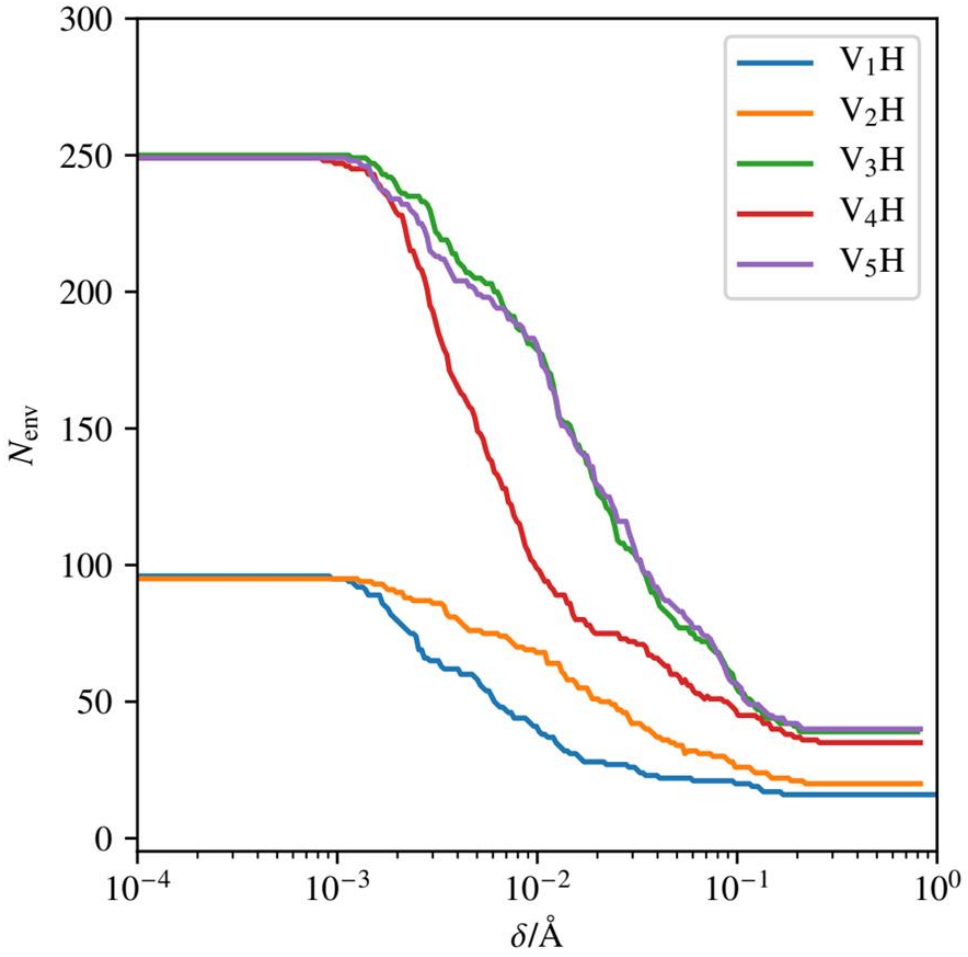


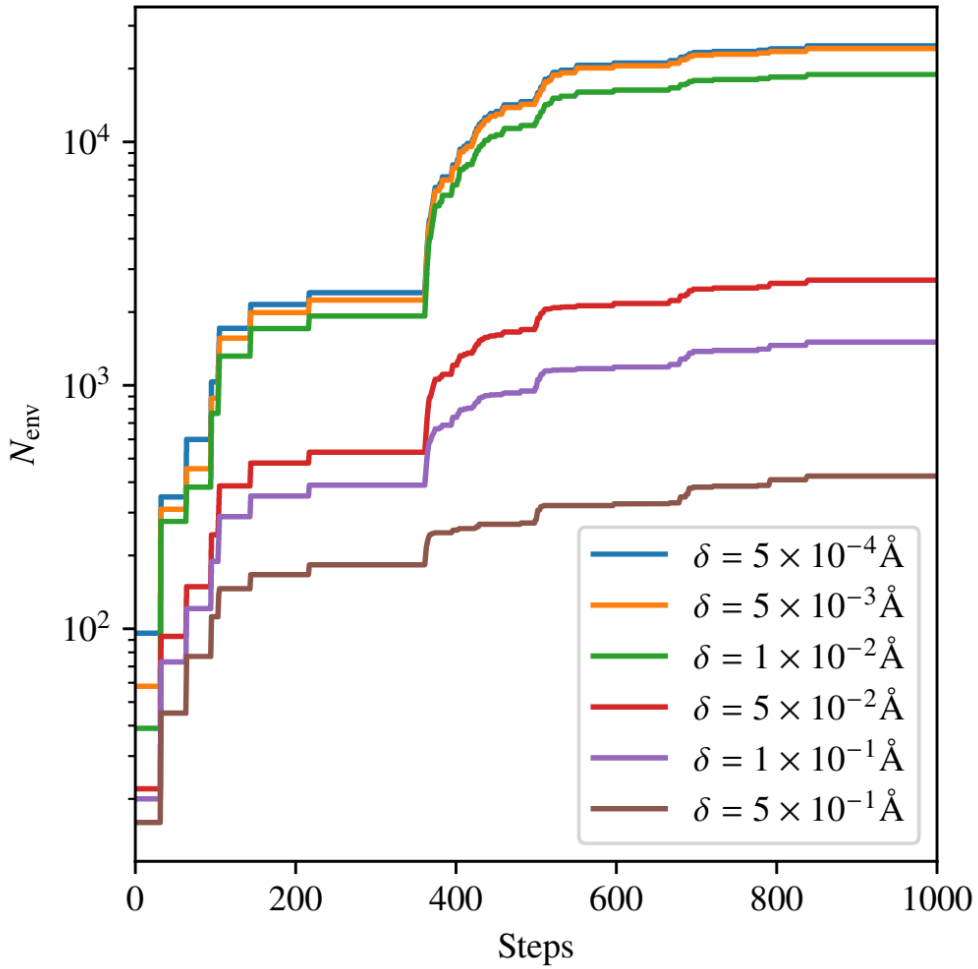
Invariant and tolerant equivalence



$$\sum_{i=0}^{n} \left\| p_i - O q_{\pi(i)} \right\|^2 \leq \delta^2$$

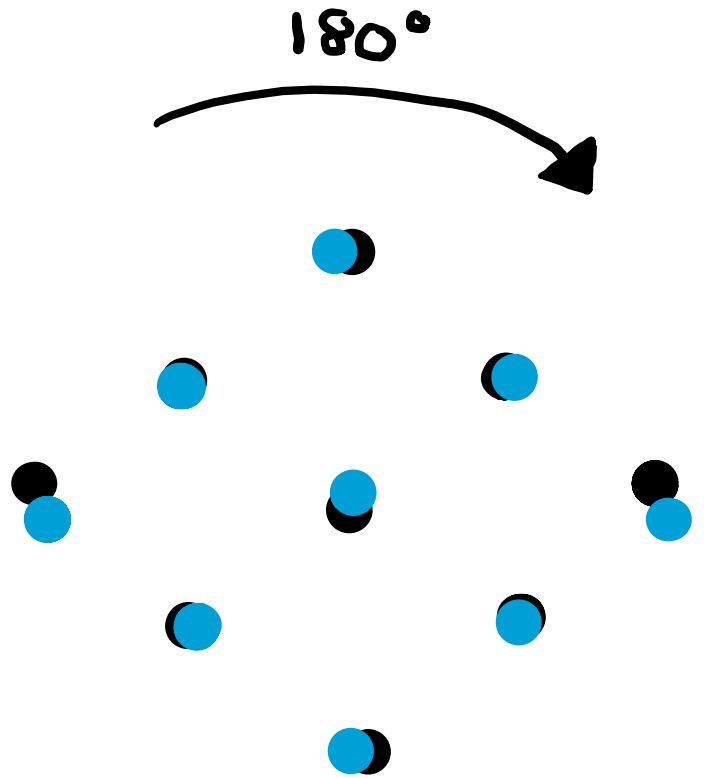
Efficiency


300
250
200
150
100
50
0
N_{env}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
δ/Å
V_1H
V_2H
V_3H
V_4H
V_5H

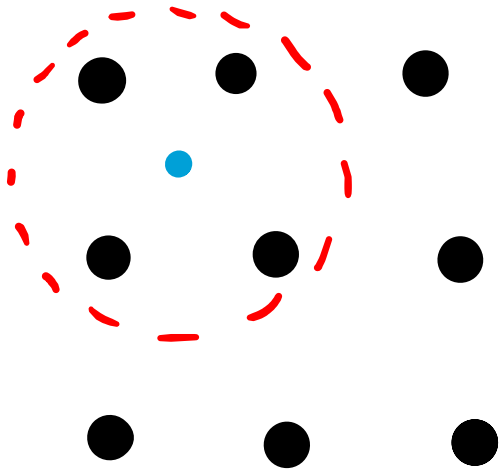

10^4
10^3
10^2
N_{env}
0
200
400
600
800
1000
Steps
$\delta = 5 \times 10^{-4}$ Å
$\delta = 5 \times 10^{-3}$ Å
$\delta = 1 \times 10^{-2}$ Å
$\delta = 5 \times 10^{-2}$ Å
$\delta = 1 \times 10^{-1}$ Å
$\delta = 5 \times 10^{-1}$ Å

Internal symmetries

- equiv : $P, Q, \delta \rightarrow$ bool $O(n)$*
- Let Q $\leftarrow P$

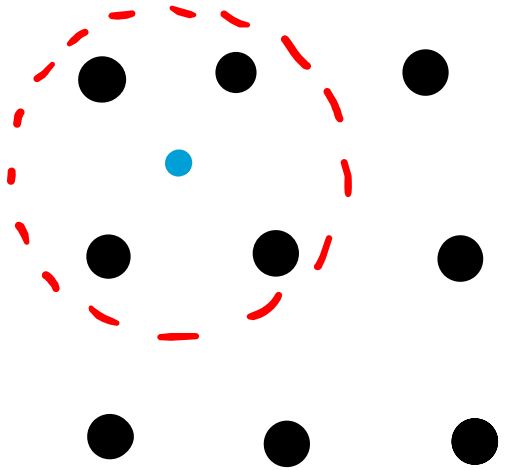


Adaptive δ



Adaptive δ

$$\{(\pi_i, R_i), \ldots\} \Leftarrow$$

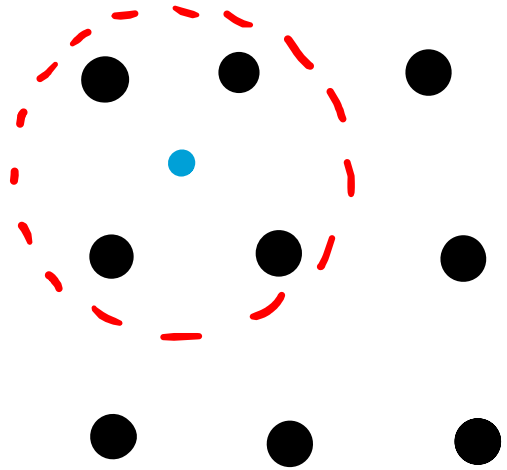


Adaptive δ

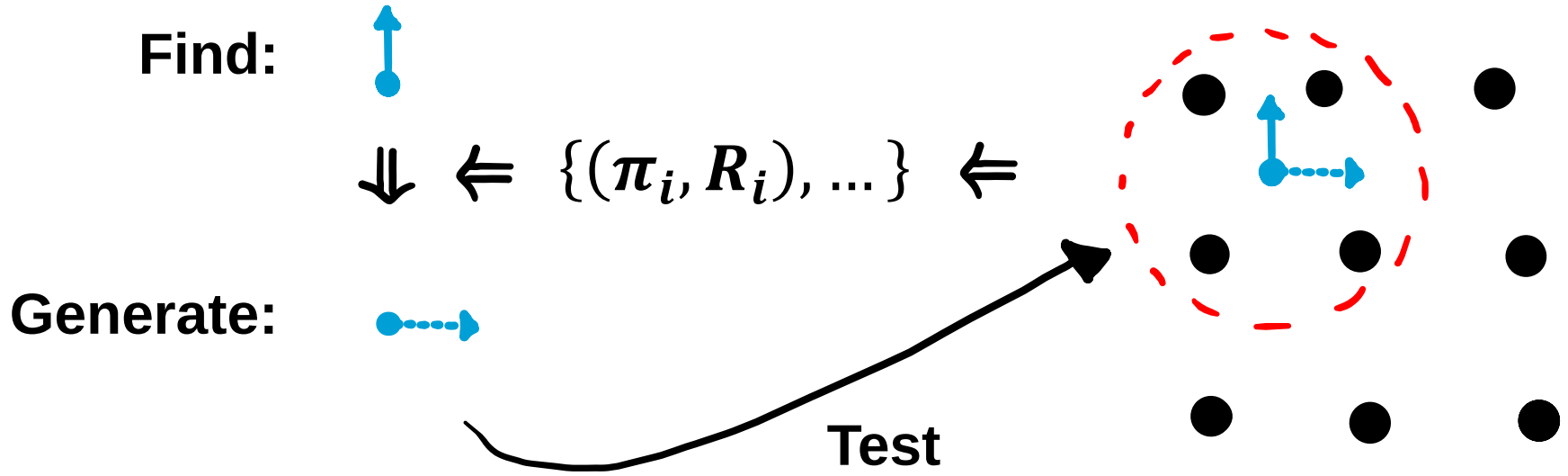
Find:

$\Downarrow \Leftarrow \{(\pi_i, R_i), \ldots\} \Leftarrow$

Generate:



Adaptive δ



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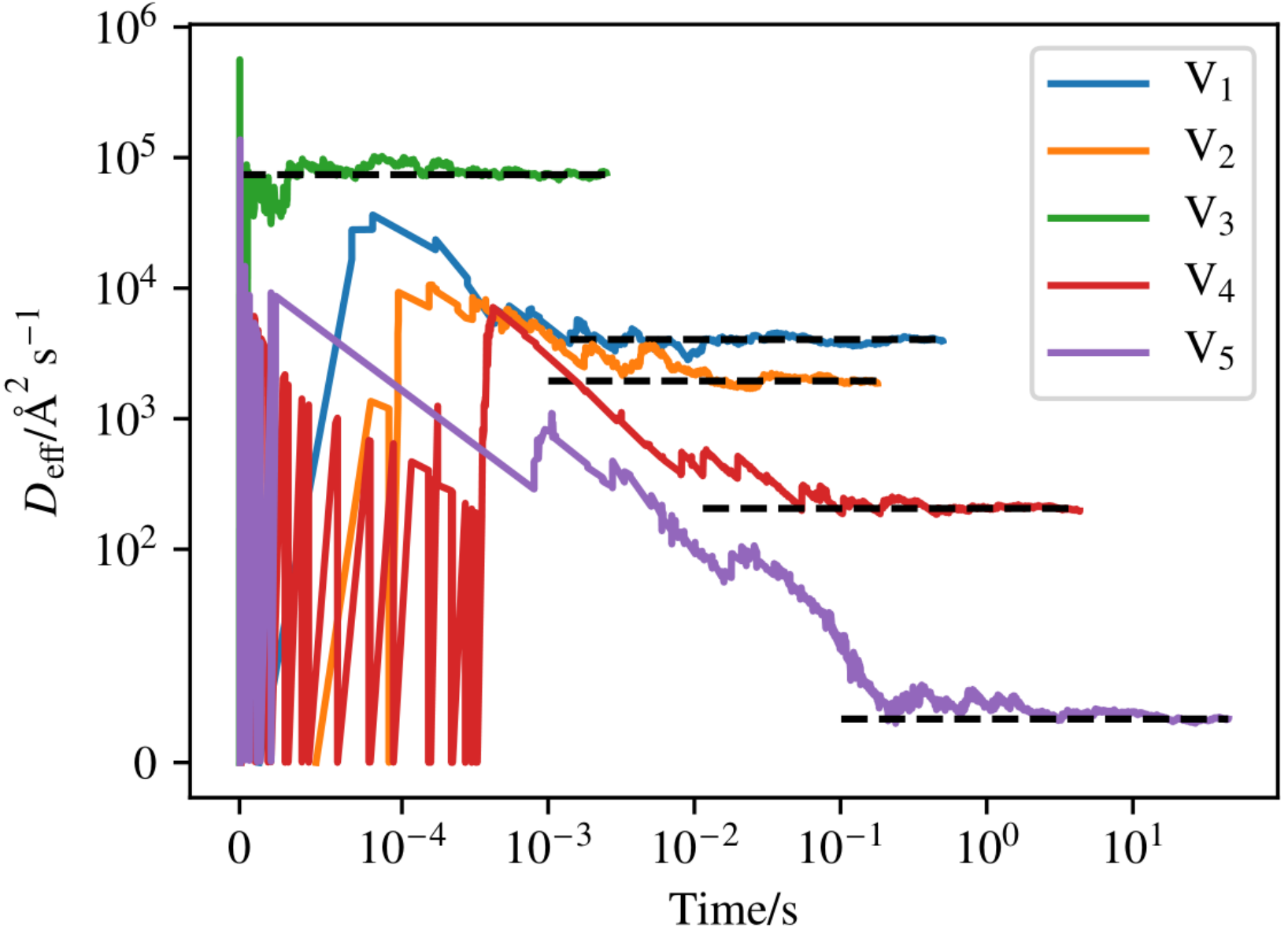
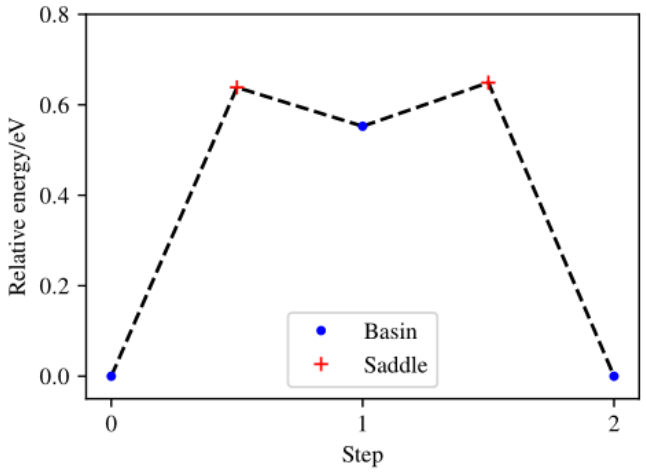
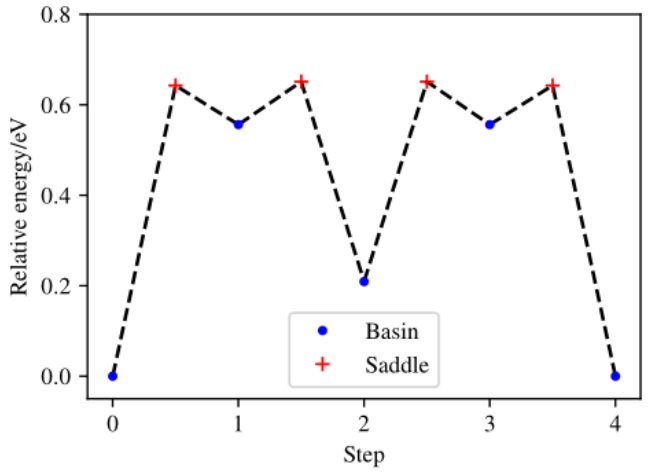
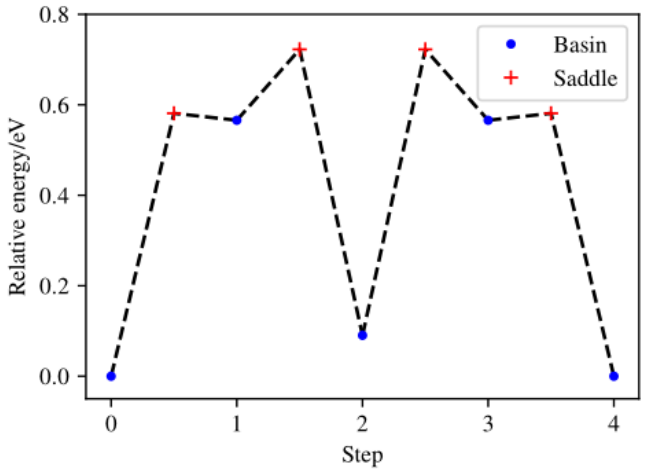

10^6
10^5
10^4
10^3
10^2
0
$D_{\mathrm{eff}}/\mathrm{Å}^2\ \mathrm{s}^{-1}$
0
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
Time/s
V_1
V_2
V_3
V_4
V_5



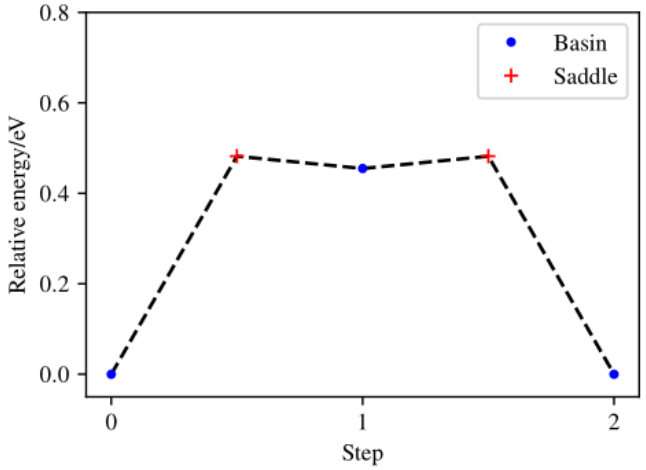
(a) V_1



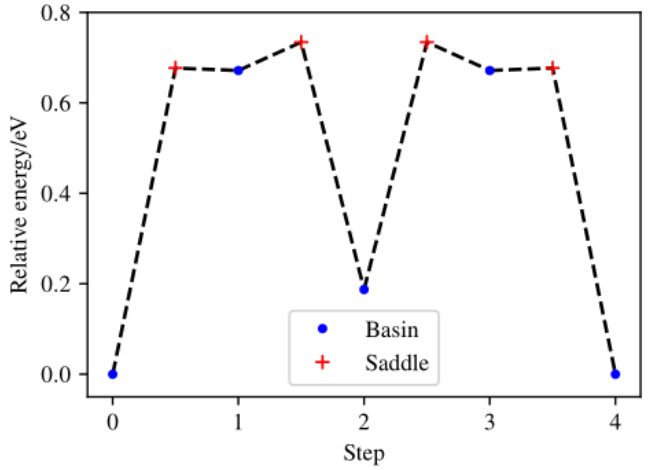
(b) V_2 via 4^{th} NN



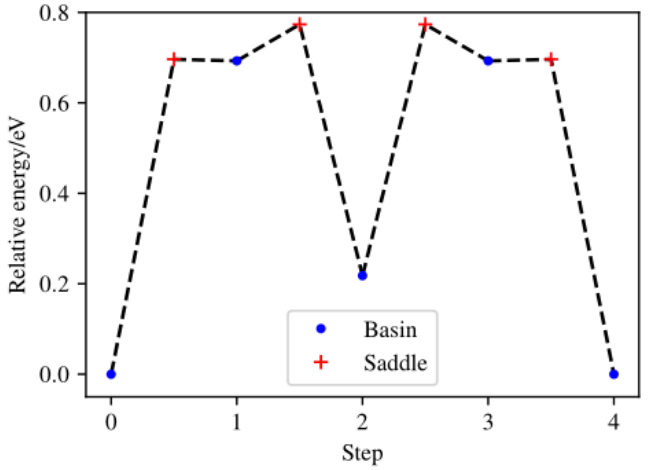
(c) V_2 via 1^{st} NN



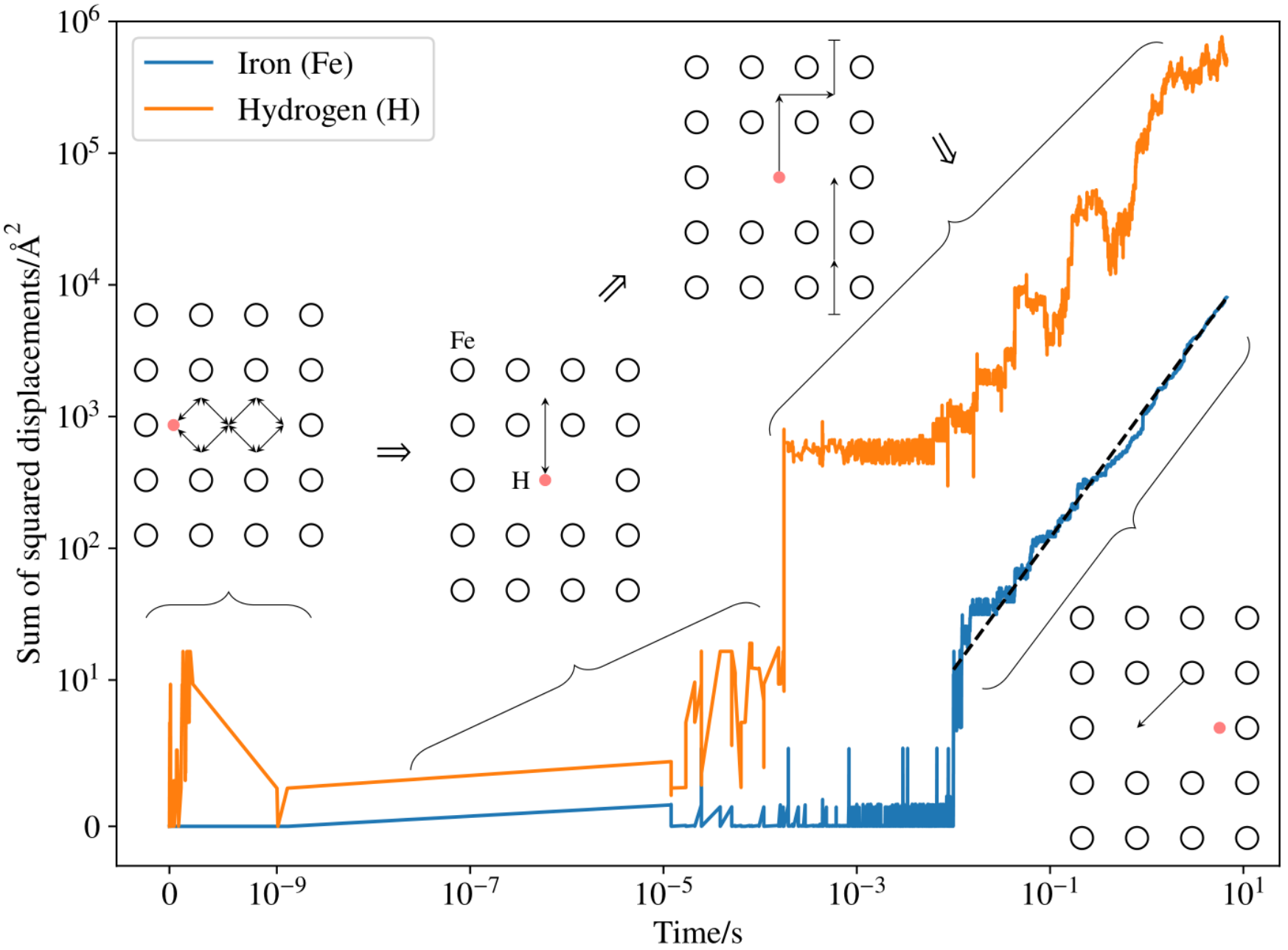
(d) V_3

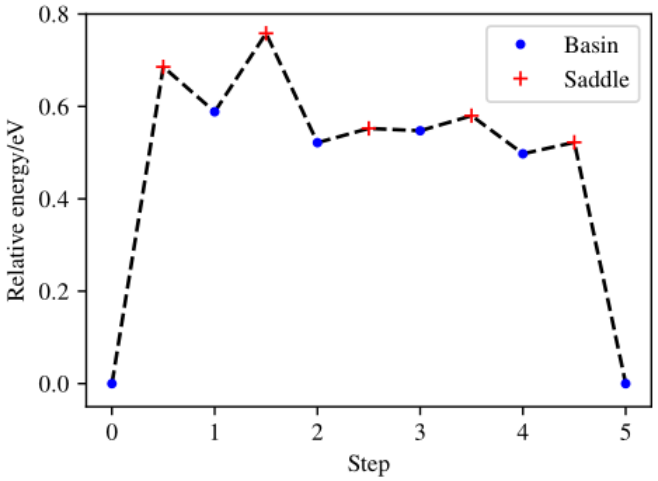


(e) V_4

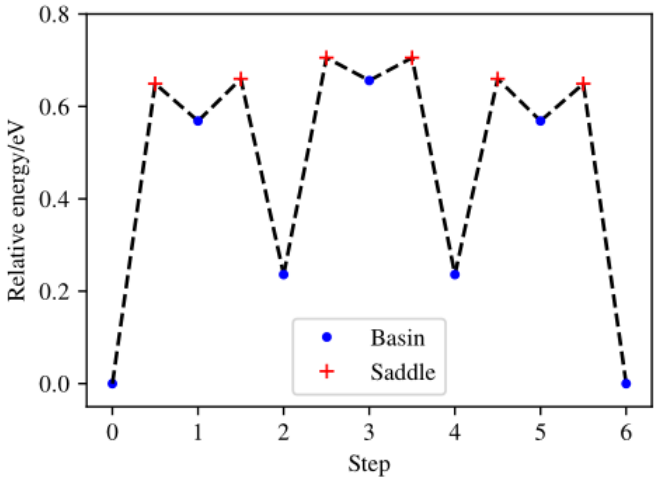


(f) V_5

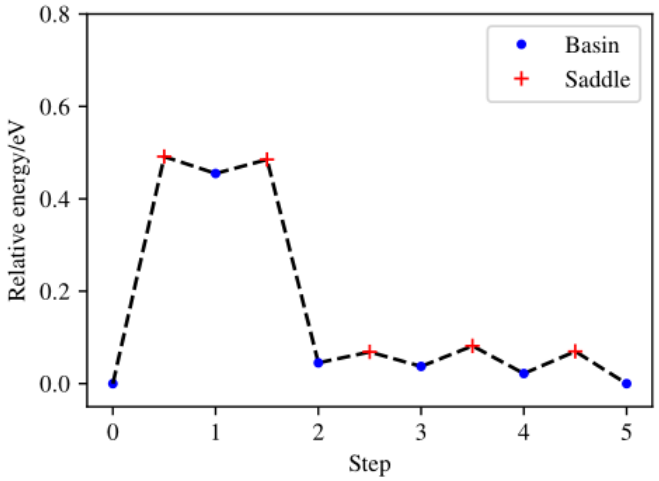

Iron (Fe)
Hydrogen (H)
Sum of squared displacements/Å^2
10^6
10^5
10^4
10^3
10^2
10^1
0
Fe
H
0
10^{-9}
10^{-7}
10^{-5}
10^{-3}
10^{-1}
10^1
Time/s



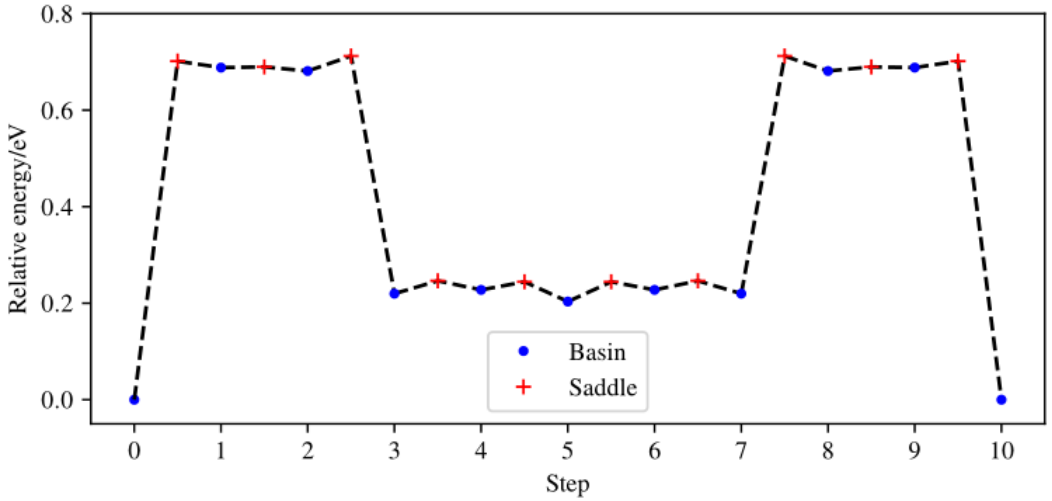
(g) V_1H



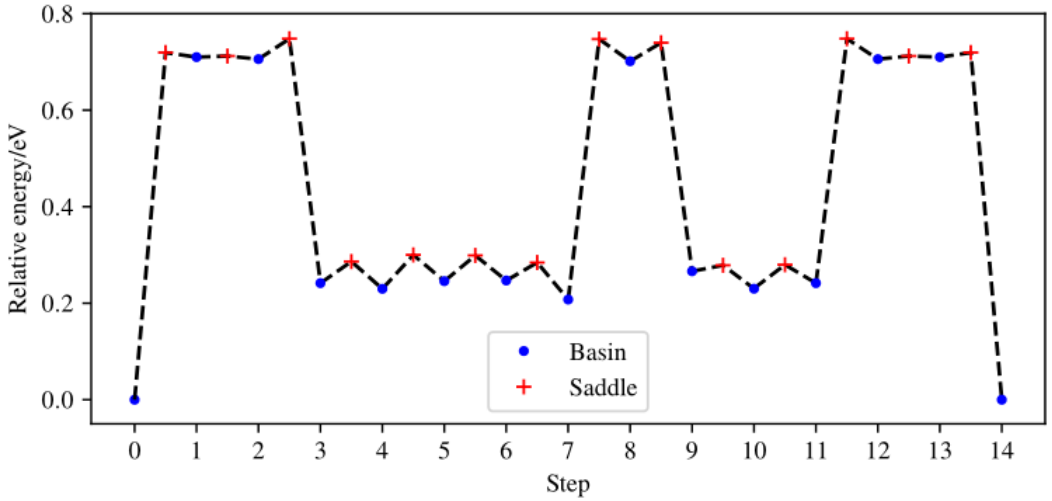
(h) V_2H



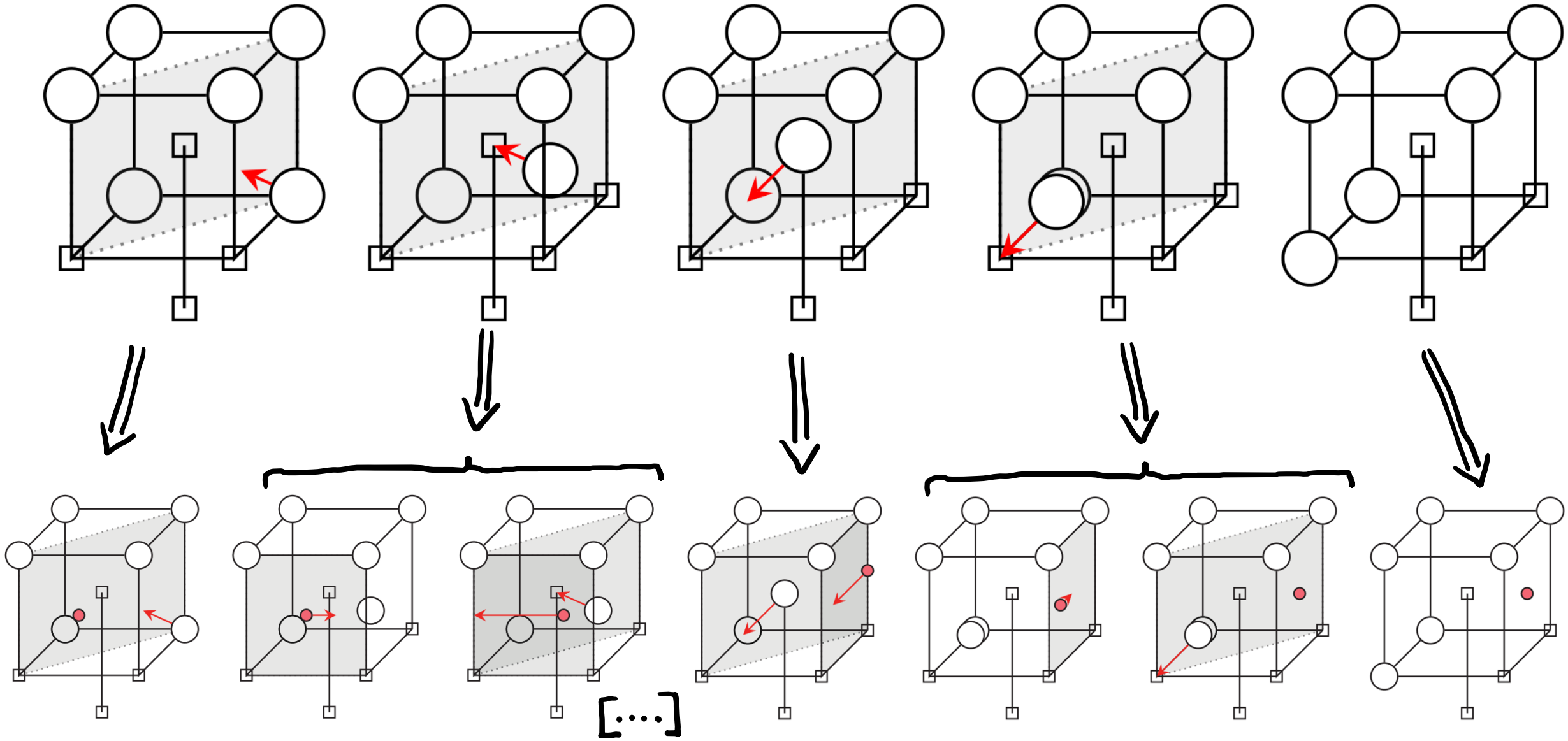
(i) V_3H

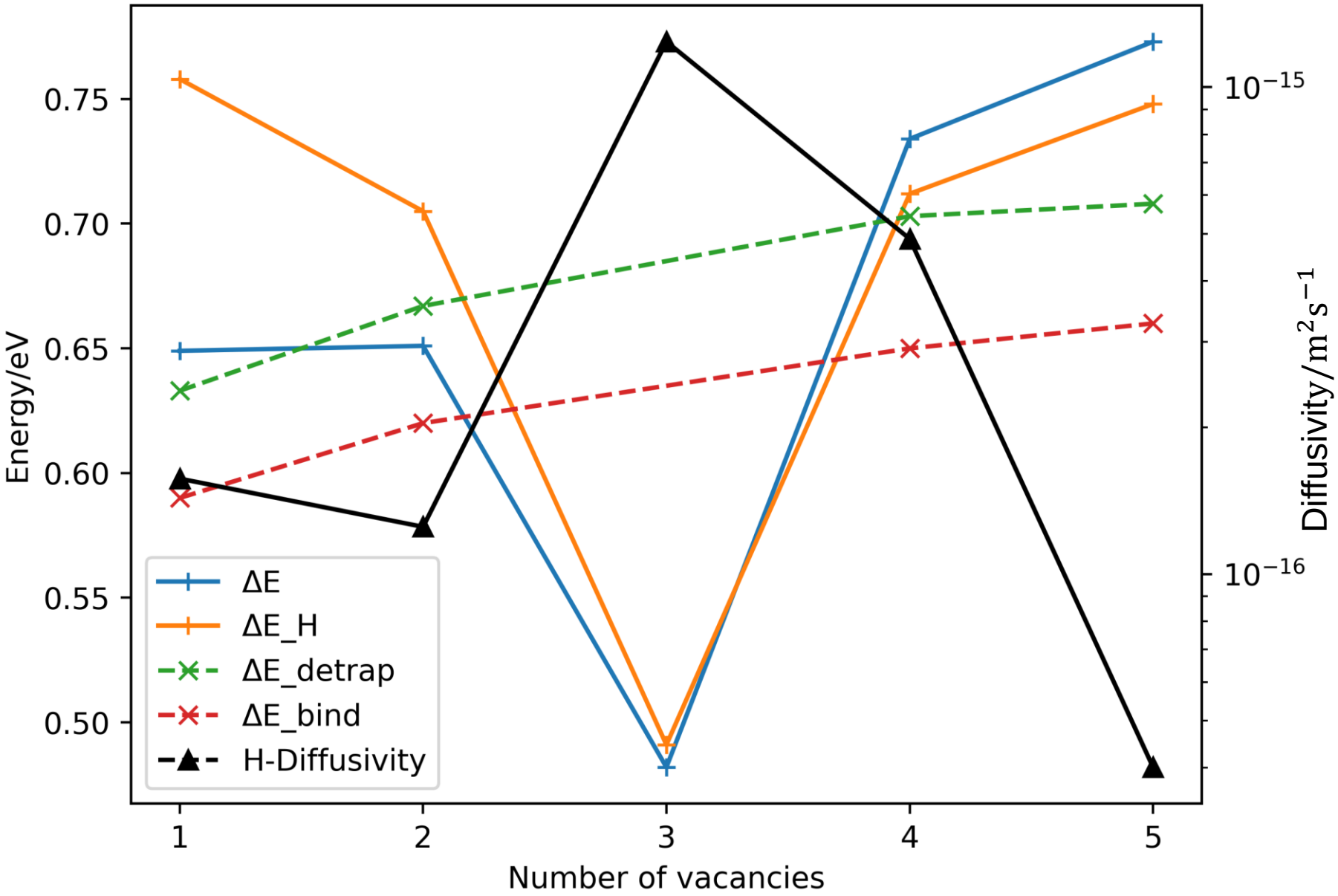


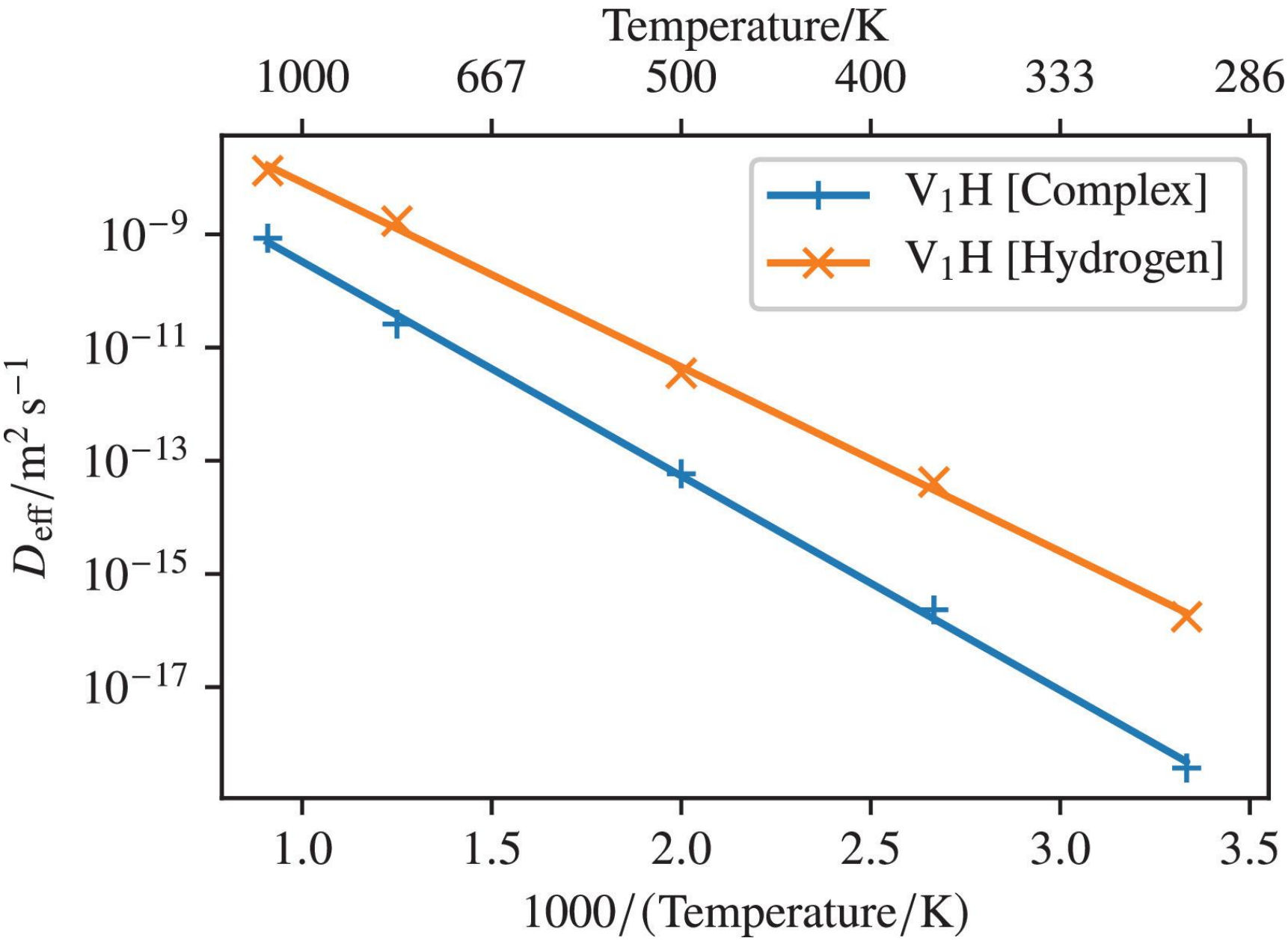
(j) V_4H



(k) V_5H




0.75
0.70
0.65
0.60
0.55
0.50
Energy/eV
10^{-15}
10^{-16}
Diffusivity/m^2s^{-1}
ΔE
ΔE_H
ΔE_detrap
ΔE_bind
H-Diffusivity
1
2
3
4
5
Number of vacancies


Temperature/K
1000
667
500
400
333
286
10^{-9}
10^{-11}
10^{-13}
10^{-15}
10^{-17}
$D_{\mathrm{eff}}/\mathrm{m}^2\,\mathrm{s}^{-1}$
V_1H [Complex]
V_1H [Hydrogen]
1.0
1.5
2.0
2.5
3.0
3.5
1000/(Temperature/K)

*preliminary

Complex	ΔE_{dis}/eV	ΔE_{dis}/eV with H	τ/s	τ/s with H
V_2H	$0.82(3)$	$0.87(0)$	4×10^{-2}	7×10^{-1}
V_3H	$0.68(5)$	$0.74(8)$	9×10^{-4}	9×10^{-3}

Summary

- Tolerant, invariant and continuous equivalence
- Adaptive catalogue
- Classified complexes' diffusion pathways
- Hydrogen can lower diffusion barrier
- H de-trapping barrier(s) from clusters
- H effective diffusivity
- Quantified the trapping atmospheres surrounding vacancy clusters
- Cluster lifetimes

Try openFLY - github.com/ConorWilliams/openFLY

- **Fully documented**
- **Parallelised**
- **Open source**
- **Implements all discussed and more (graph based methods, etc)**
- **Supports the GSD format**
- **Supports openKIM (EAM, DUNN, EMT, EDIP, MEAM, hNN, LJ_*, Tersoff, …)**

Acknowledgements

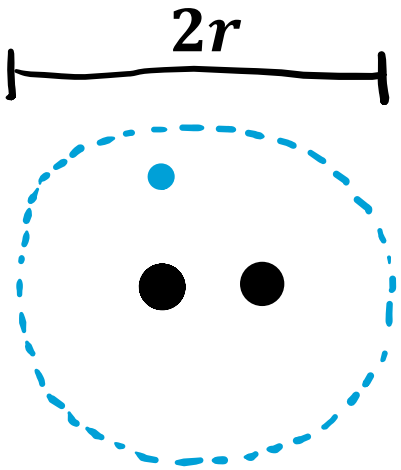
- We gratefully acknowledge the funding received from the EP-SRC via the CDT in Computational Methods for Materials Science (Grant number EP/L015552/1) and grant EP/T008687/2.
- E. I. Galindo-Nava acknowledges the Royal Academy of Engineering for his research fellowship funding.
- We also acknowledge Rolls-Royce PLC for the provision of funding. All information and foreground intellectual property generated by this research work is the property of Rolls-Royce PLC.

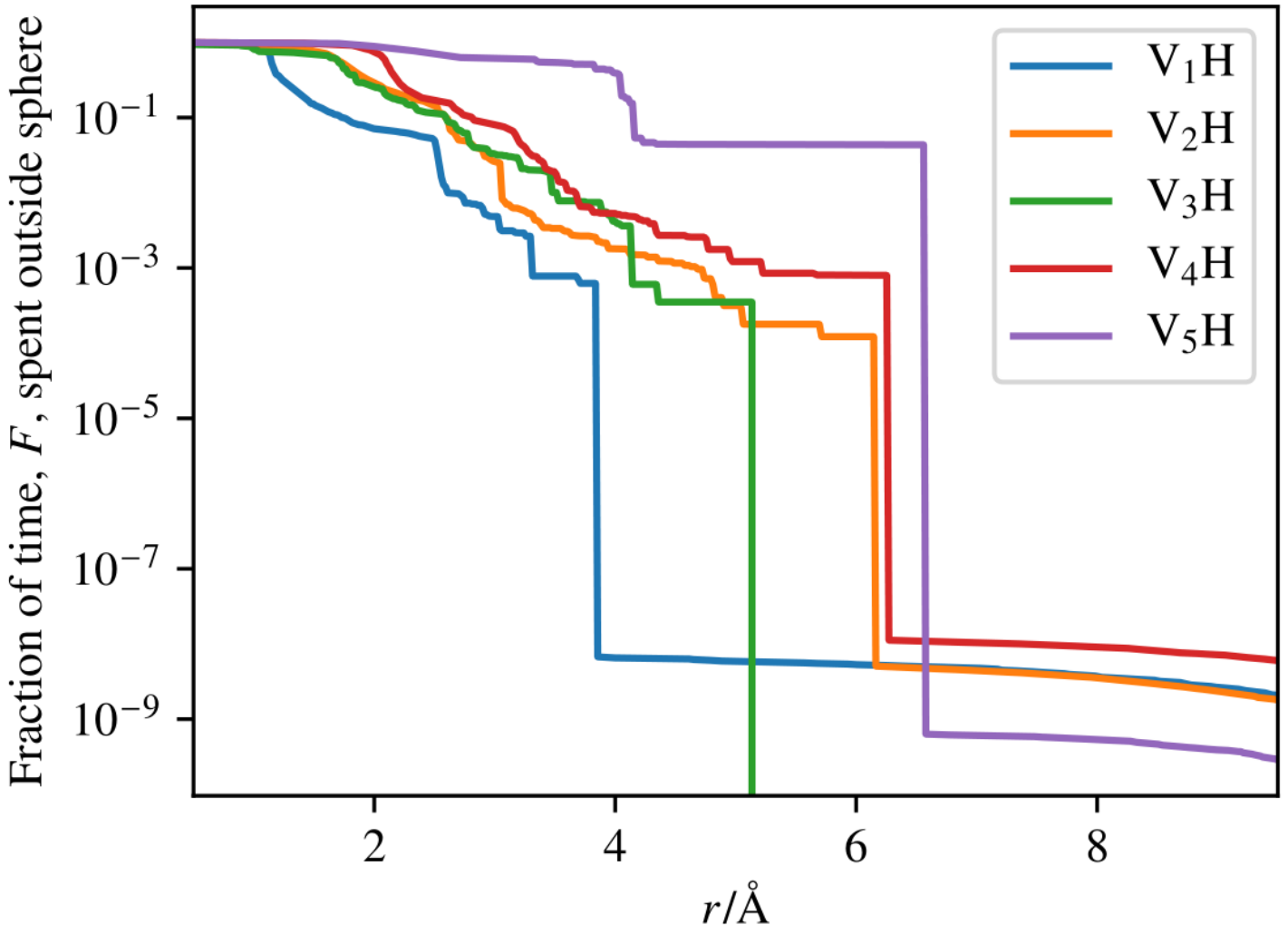
Complex diffusion

Cluster	ΔE/eV sans H	ΔE/eV with H	$D_{\text{eff}}/\text{m}^2\,\text{s}^{-1}$ sans H	$D_{\text{eff}}/\text{m}^2\,\text{s}^{-1}$ with H
V_1	0.64(9)	0.75(8)	4.05×10^{-17}	3.72×10^{-19}
V_2	0.65(1)	0.70(5)	2.07×10^{-17}	1.00×10^{-18}
V_3	0.48(2)	0.49(1)	7.40×10^{-16}	7.50×10^{-16}
V_4	0.73(4)	0.71(2)	2.05×10^{-18}	3.95×10^{-18}
V_5	0.77(3)	0.74(8)	9.01×10^{-20}	5.16×10^{-20}

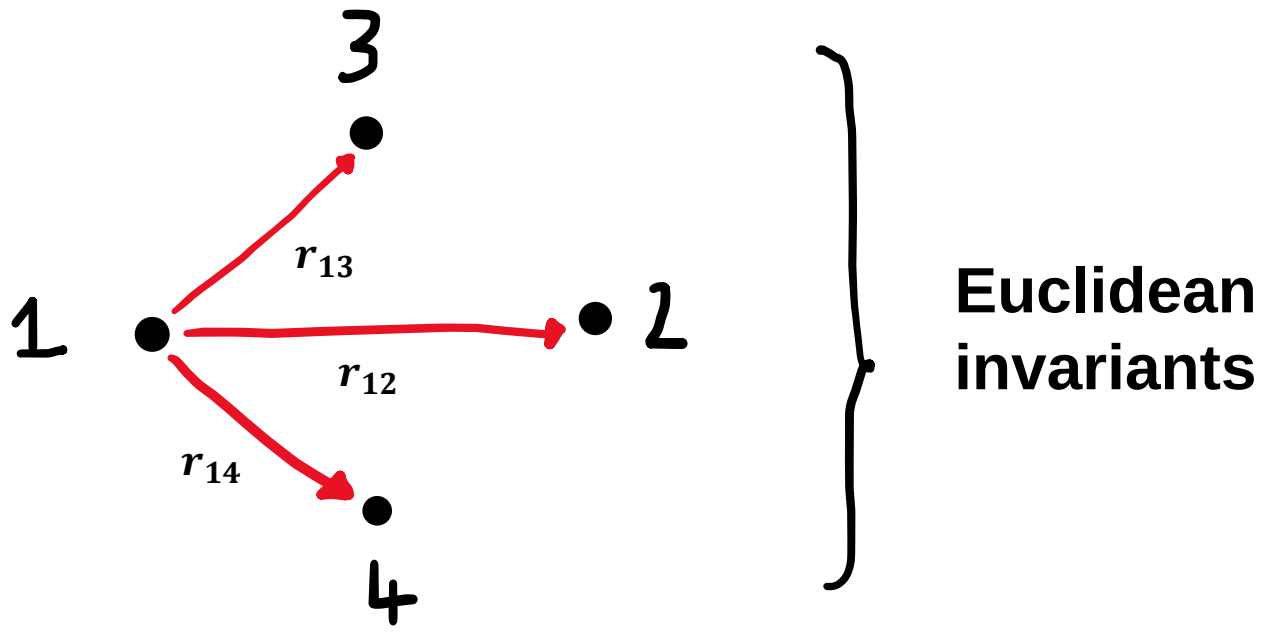
H parameters

Complex	r_x/Å	ΔE_{detrap}/eV	Δ/eV	E_B/eV	D_{H}/m^2 s^{-1}	D_{Or}/m^2 s^{-1}
V_1H	3.9	0.63(3)	0.13	0.59	1.57×10^{-16}	8.47×10^{-17}
V_2H	6.2	0.66(7)	0.04	0.62	1.25×10^{-16}	5.69×10^{-17}
V_3H	5.2	-	-	-	1.24×10^{-15}	-
V_4H	6.3	0.70(3)	0.01	0.65	4.88×10^{-16}	1.22×10^{-16}
V_5H	6.6	0.70(8)	0.04	0.66	4.01×10^{-17}	6.84×10^{-18}

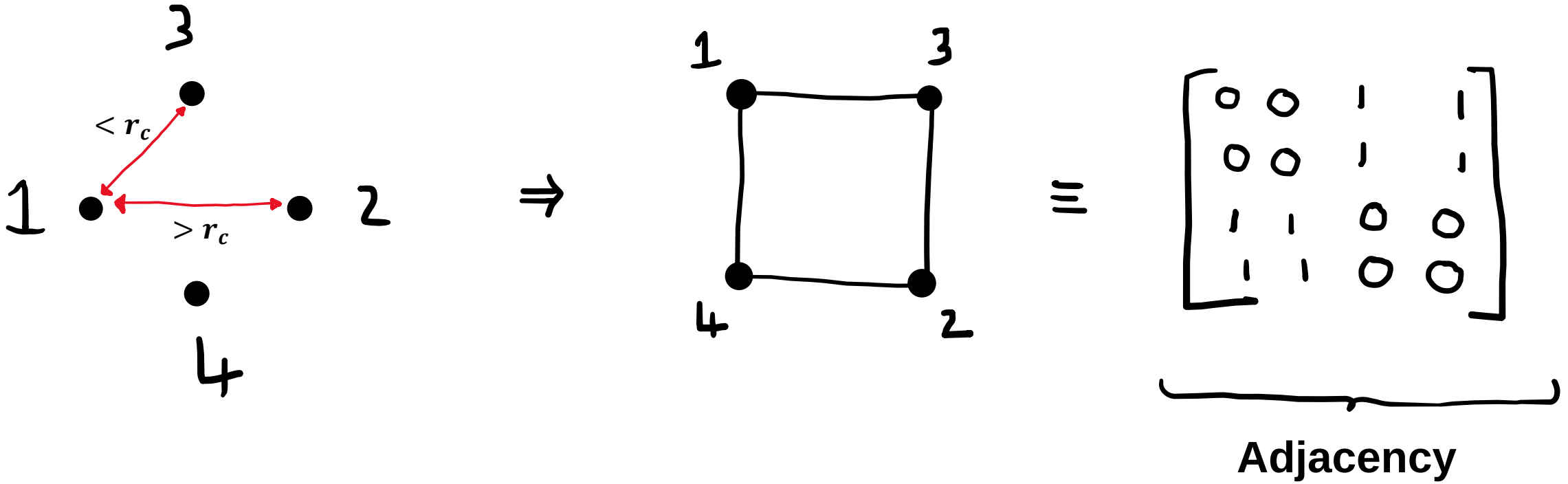

2r


Fraction of time, F, spent outside sphere
10^-1
10^-3
10^-5
10^-7
10^-9
2
4
6
8
r/Å
V1H
V2H
V3H
V4H
V5H

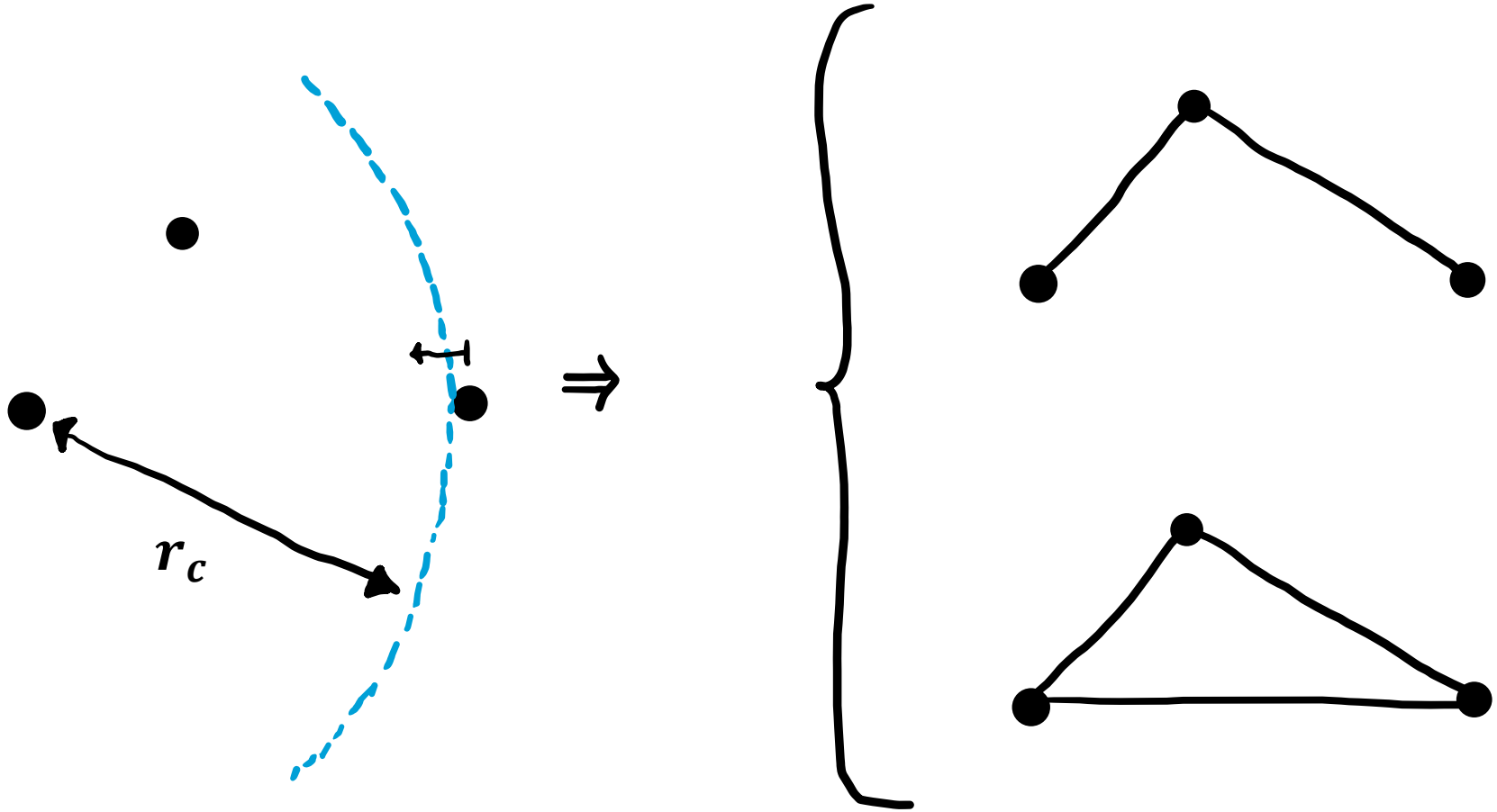
Symmetries and local environments



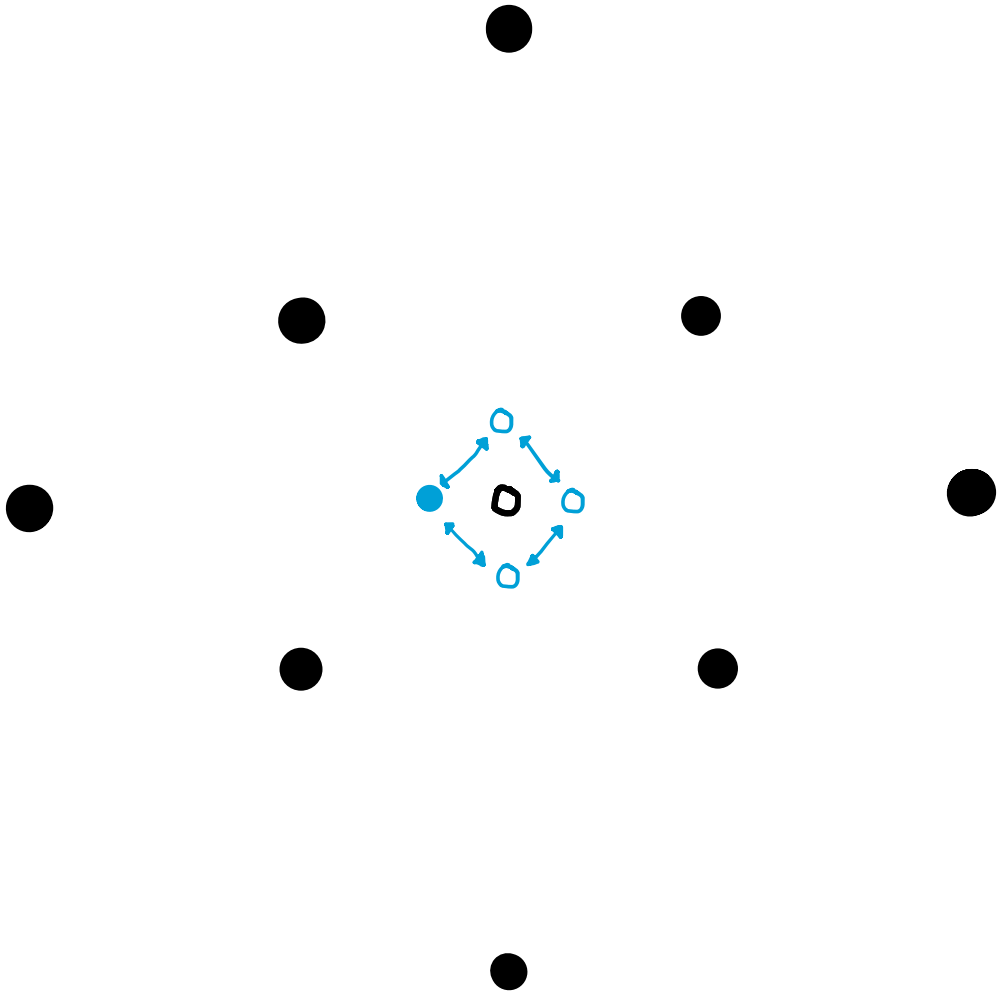
Topological representation



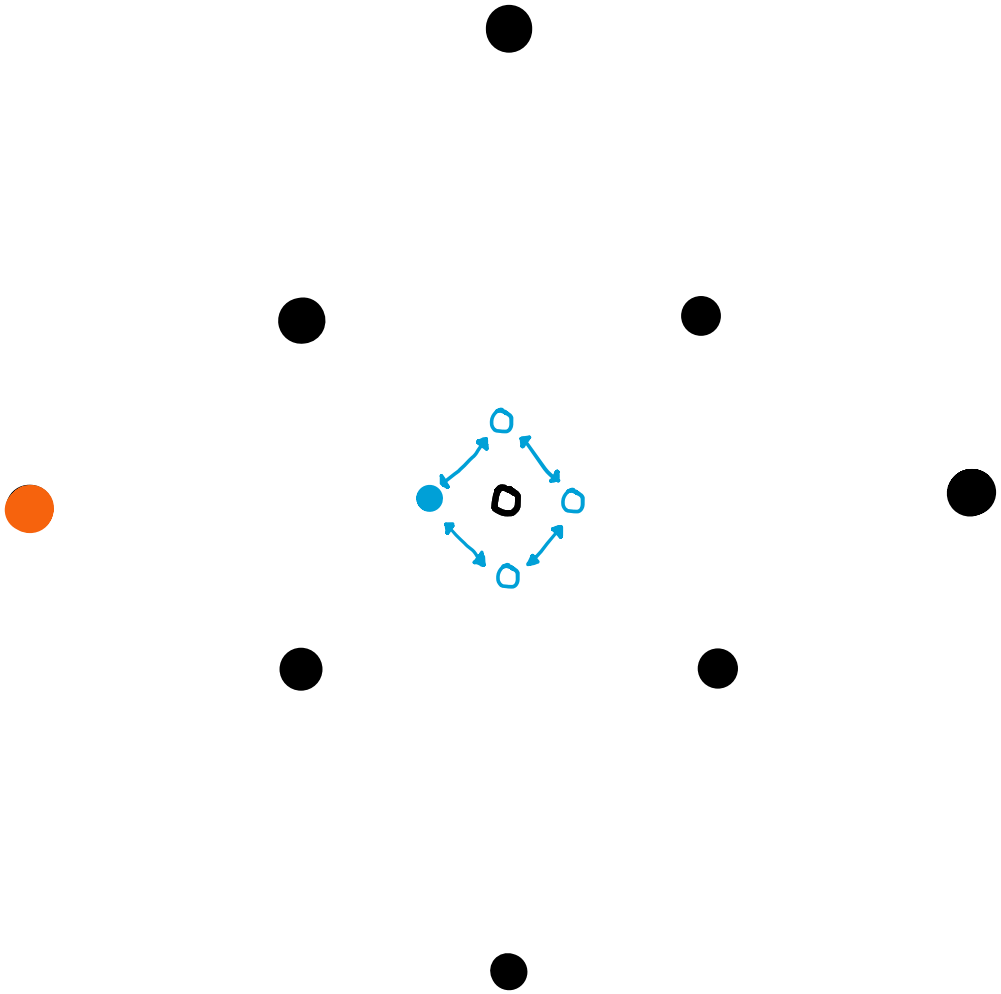
Topological representation - problems



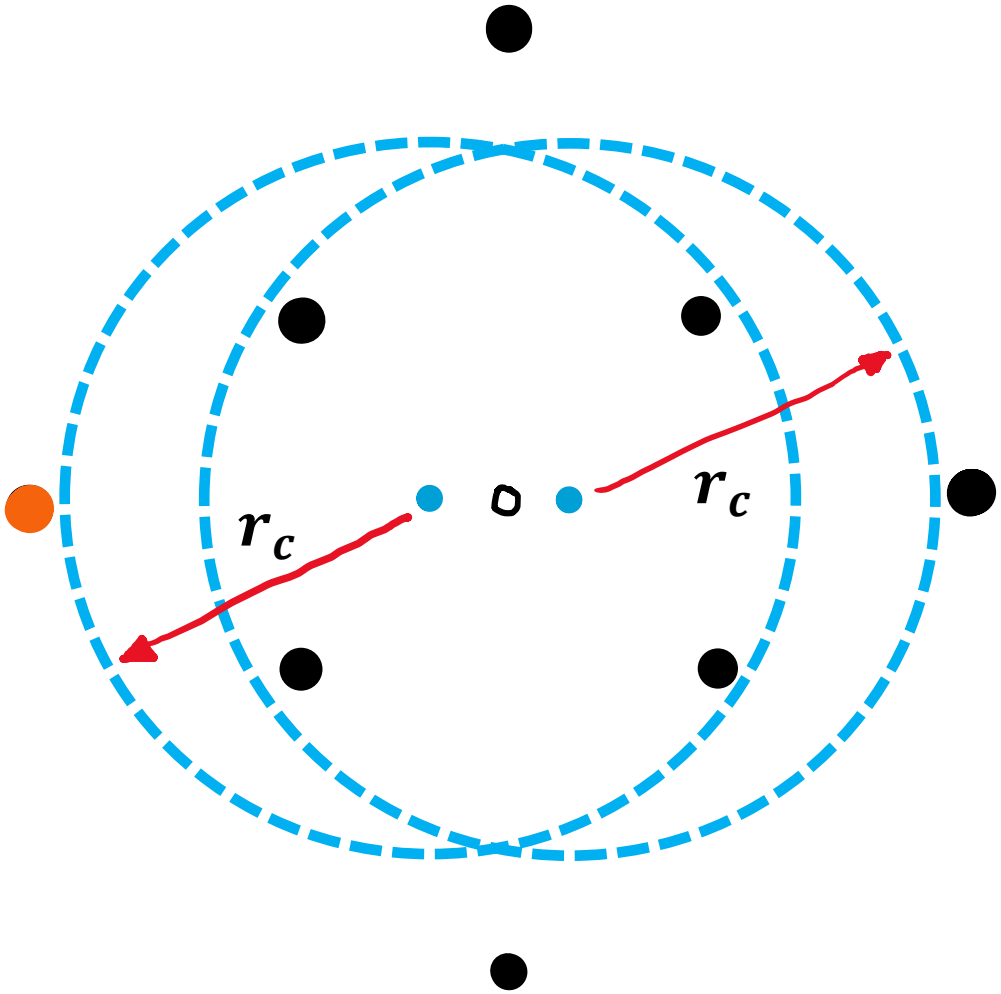
Topological representation - problems



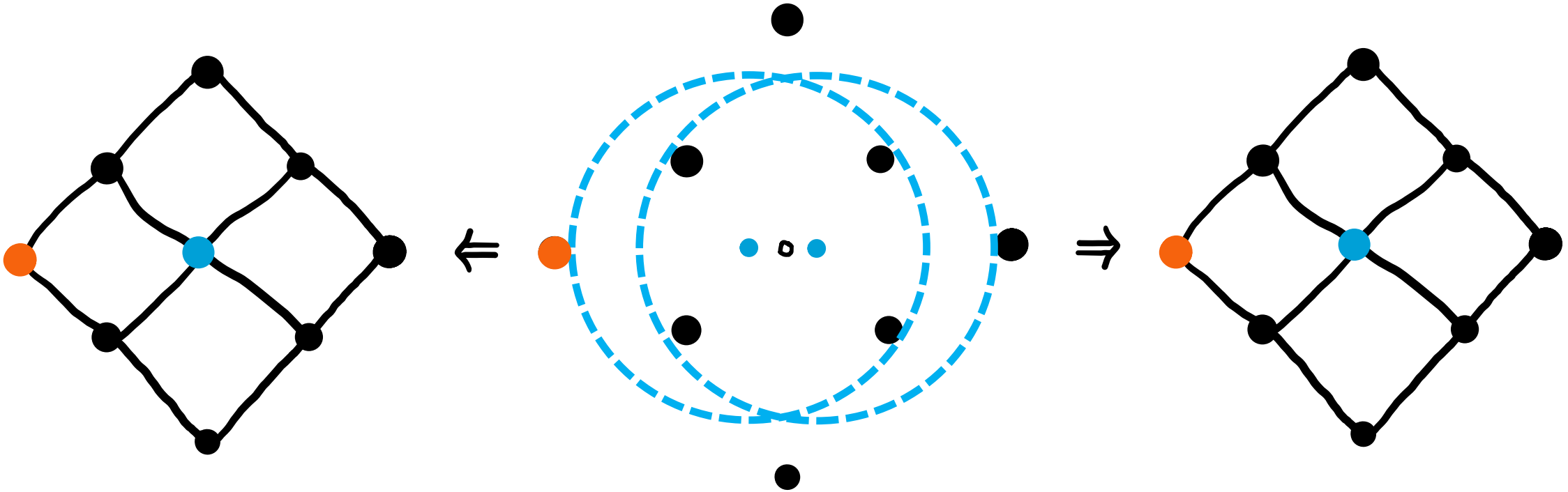
Topological representation - problems

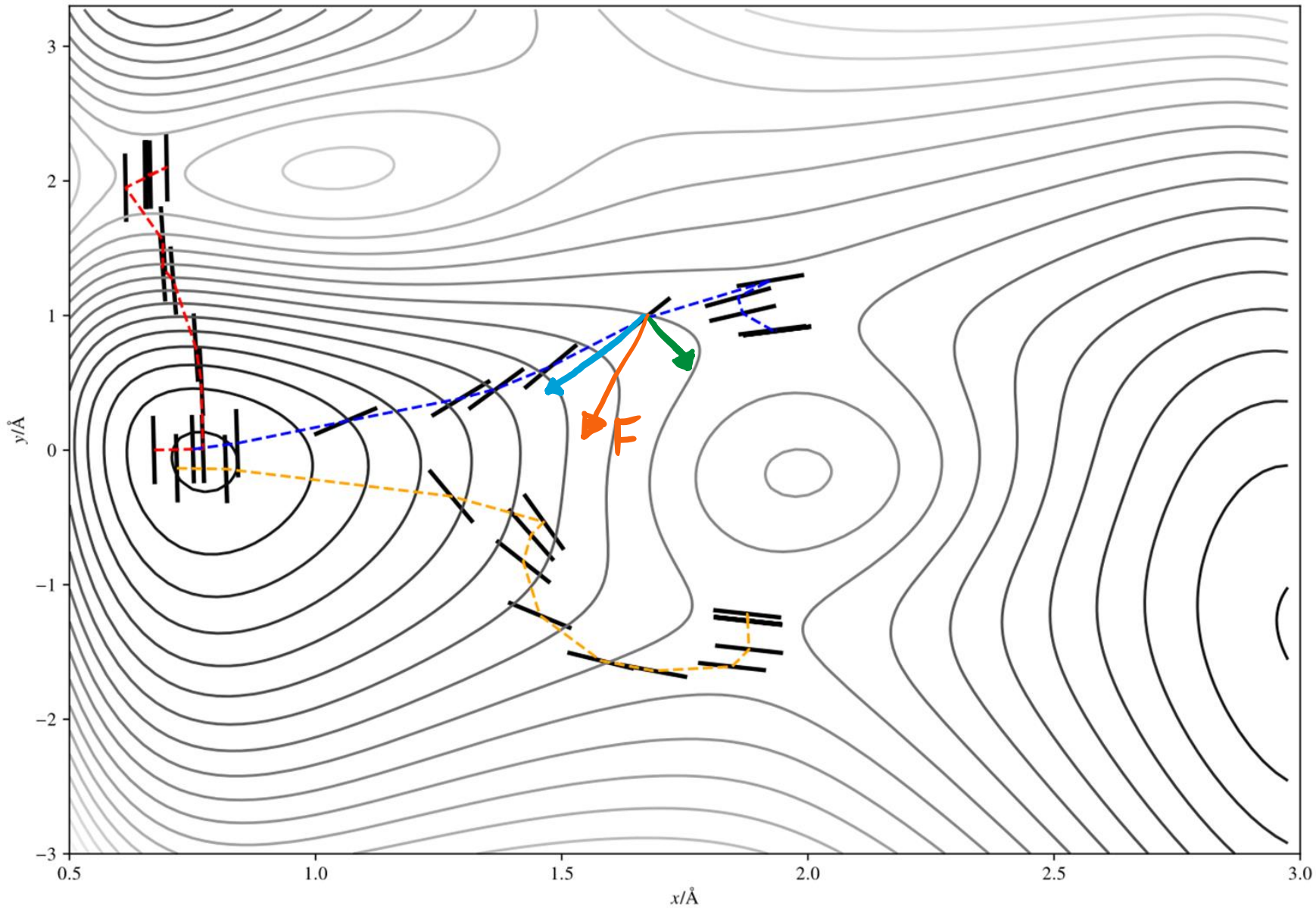


Topological representation - problems

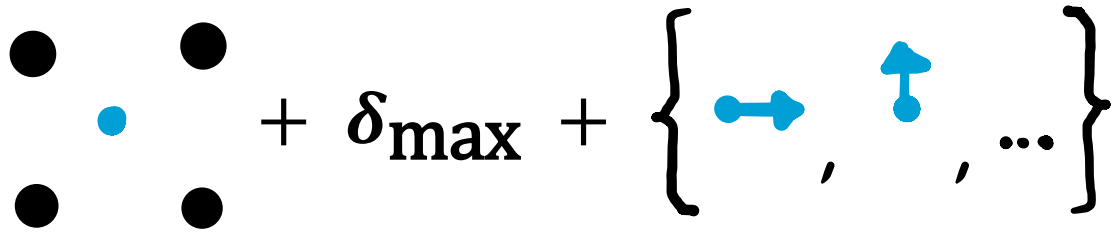


Topological representation - problems

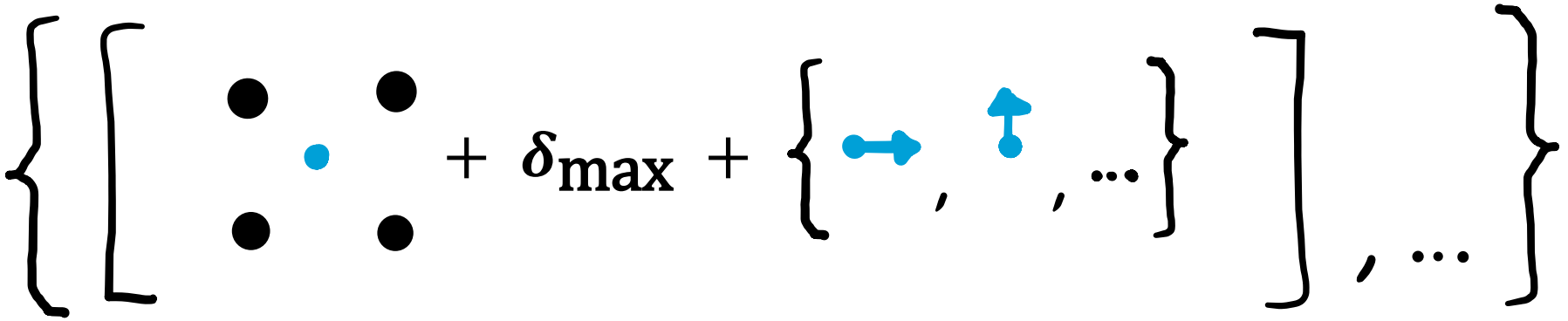



3
2
1
0
−1
−2
−3
y/Å
0.5
1.0
1.5
2.0
2.5
3.0
x/Å
F

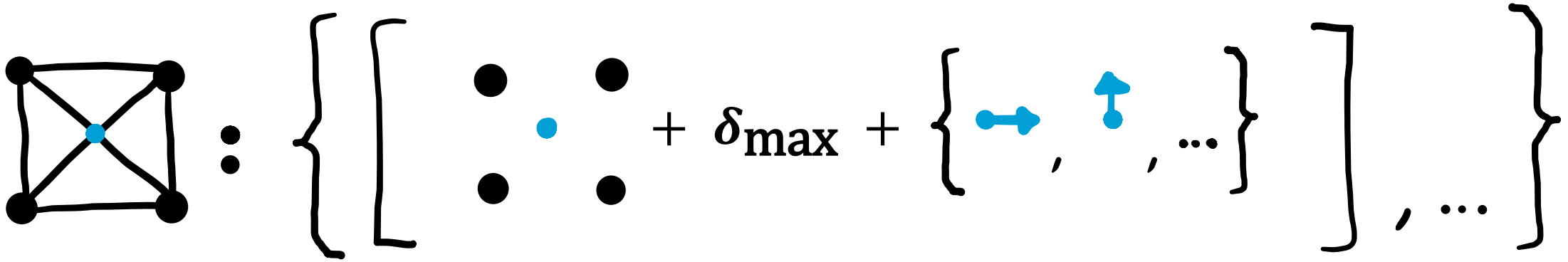
Hierarchical catalogue



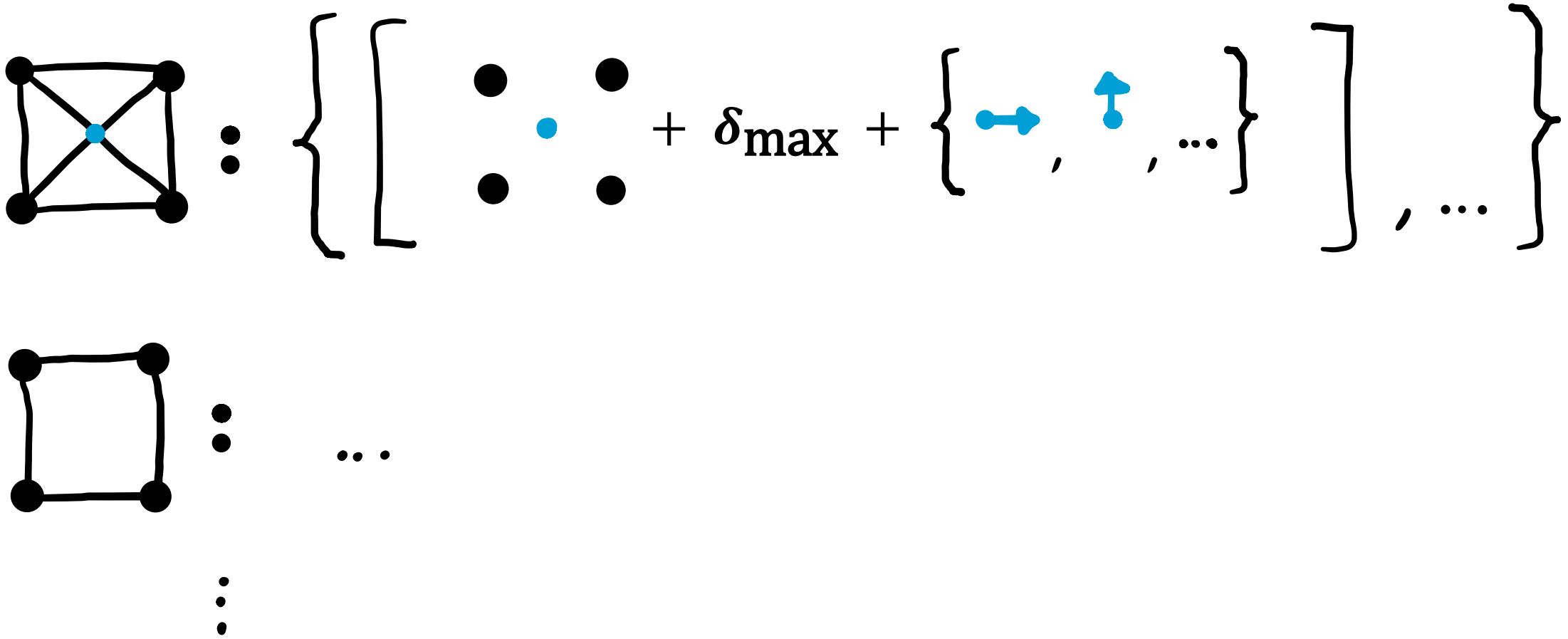
Hierarchical catalogue



Hierarchical catalogue



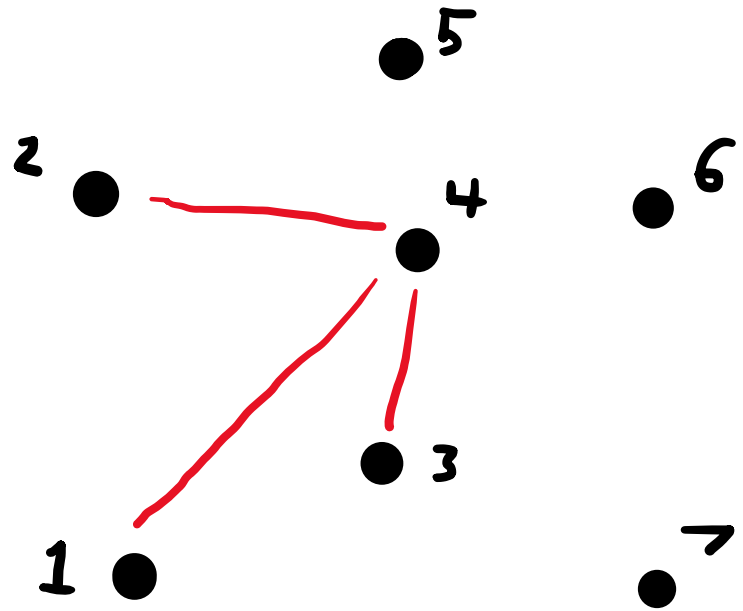
Hierarchical catalogue

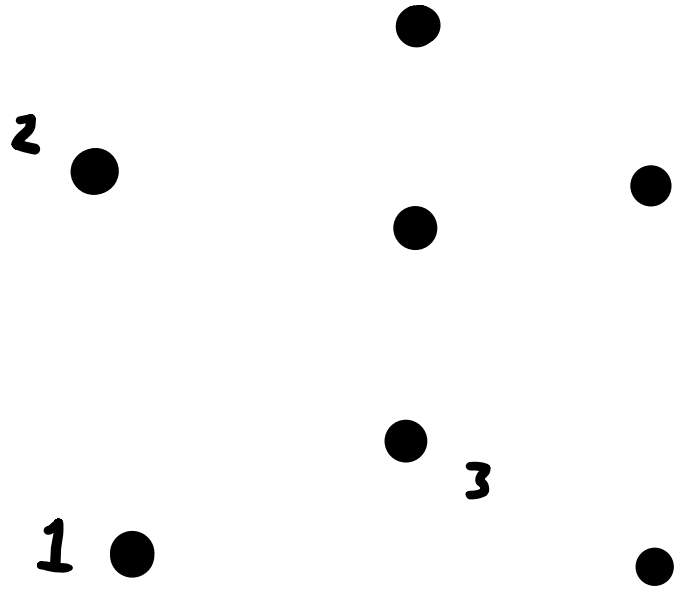


Invariant and tolerant equivalence

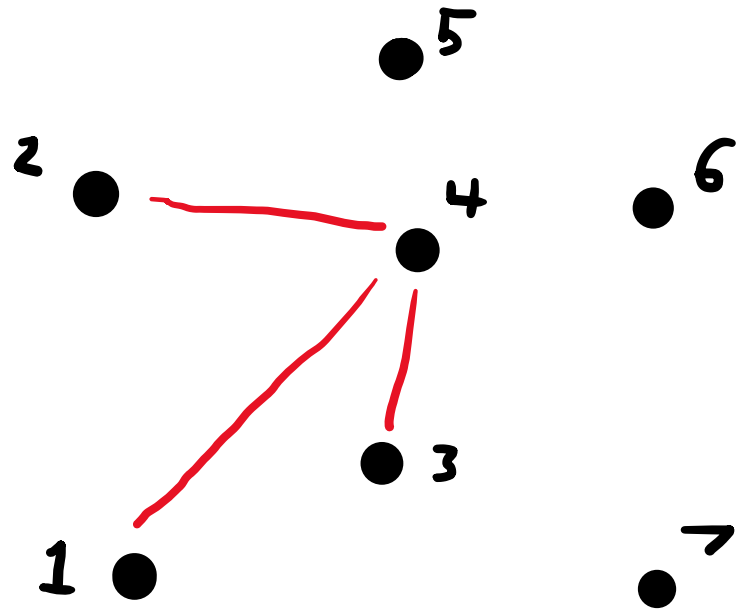
$$\sum_{i=0}^{n} \left\| p_i - O q_{\pi(i)} \right\|^2 \leq \delta^2 \quad \Rightarrow \quad \boxed{\left| p_{ij} - q_{ij} \right| \leq \sqrt{2}\delta}$$

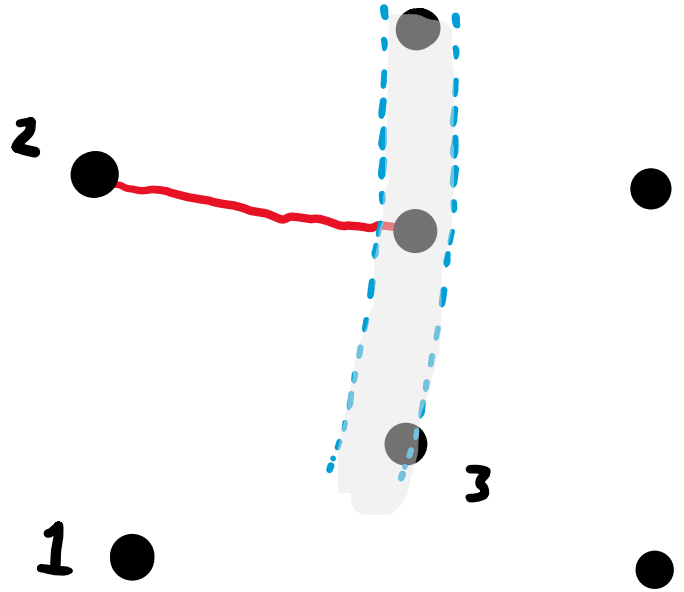
Greedy algorithm



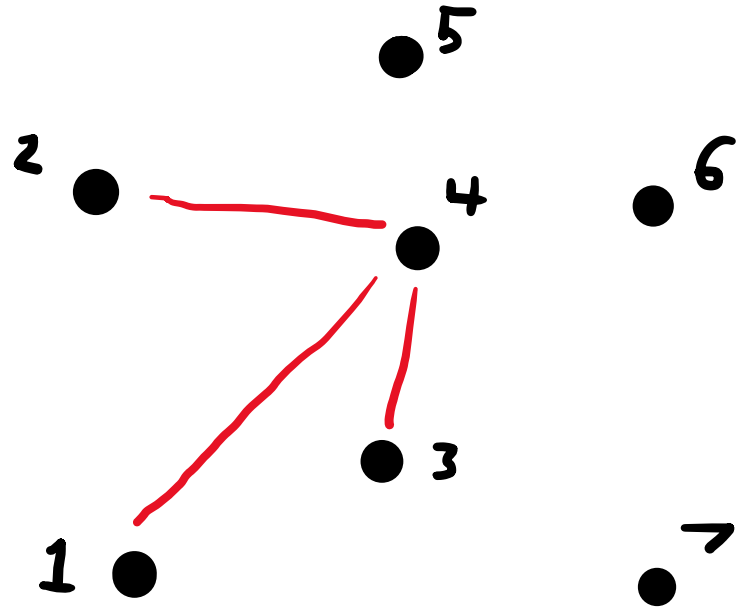


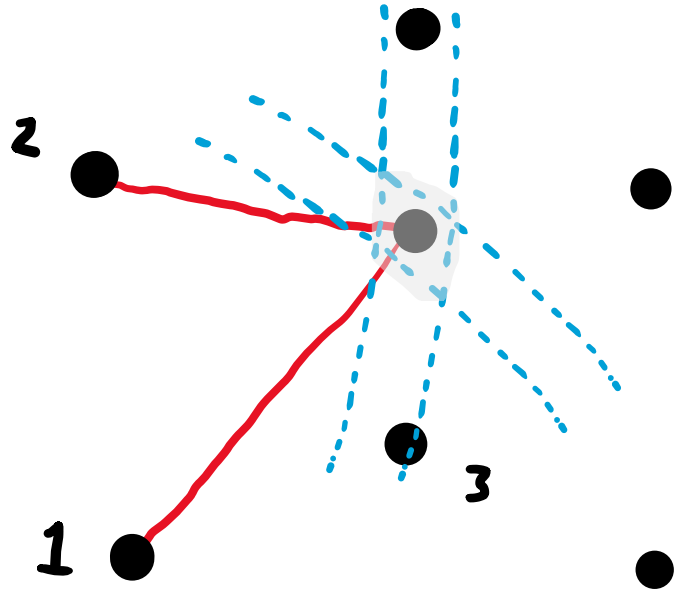
Greedy algorithm



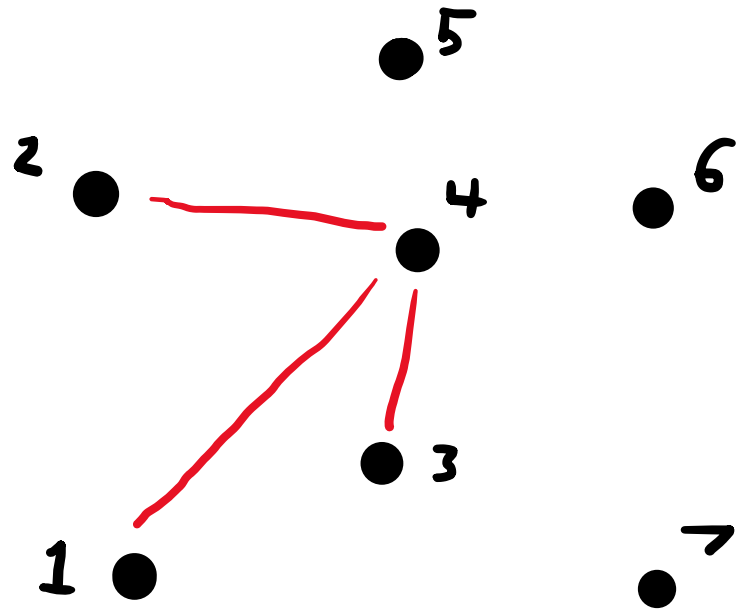


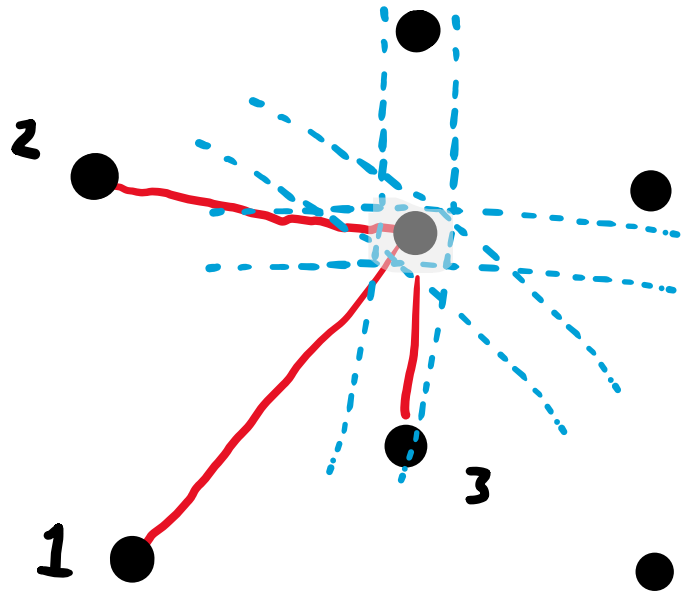
Greedy algorithm



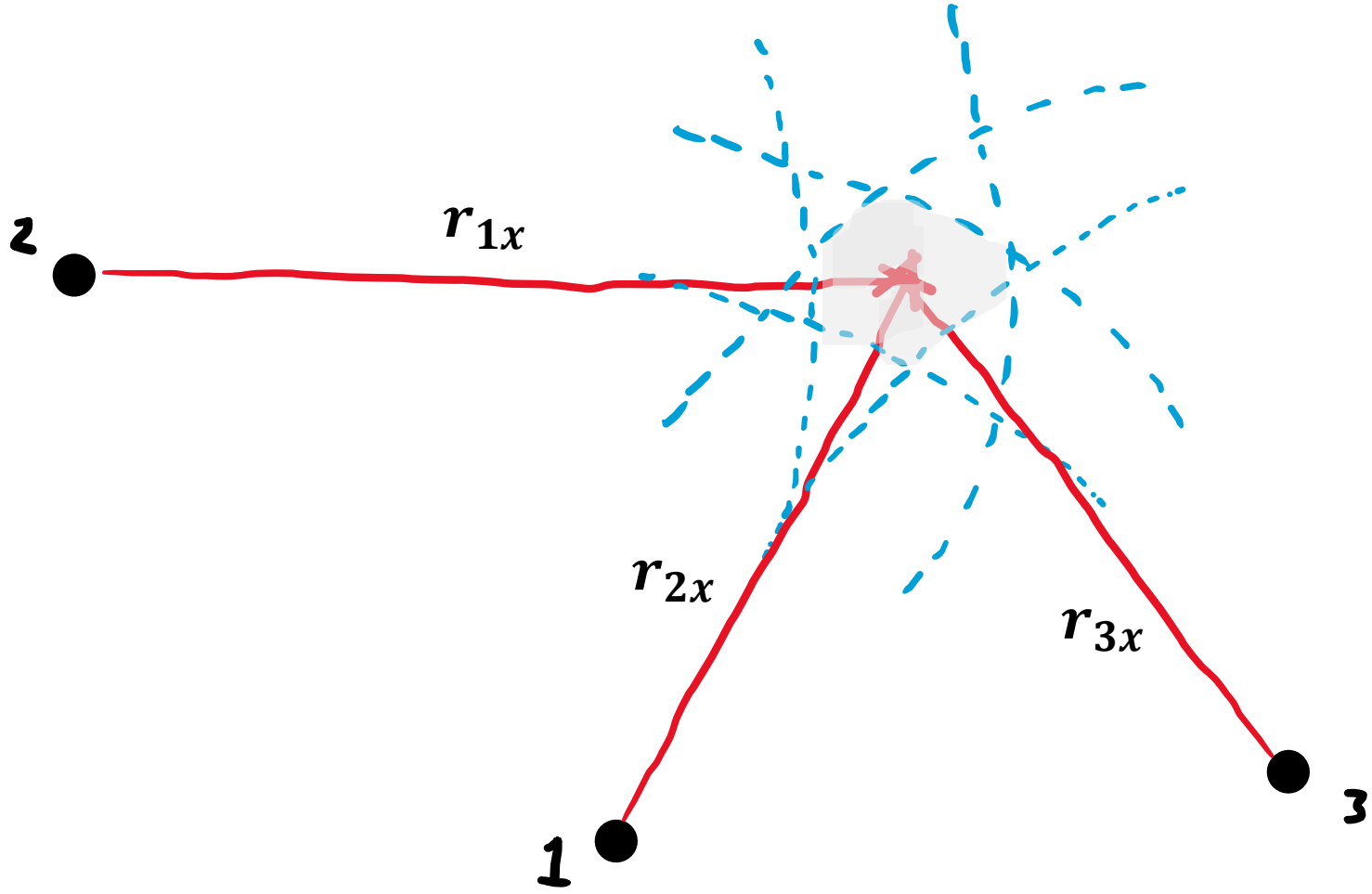


Greedy algorithm

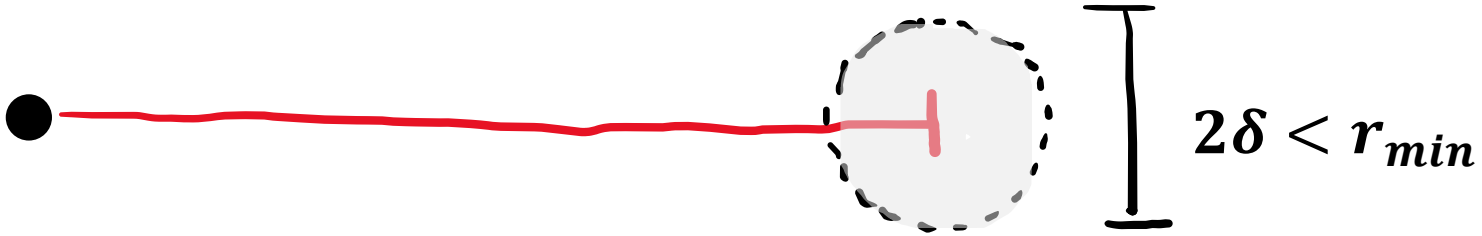




Exponential?



Exponential?



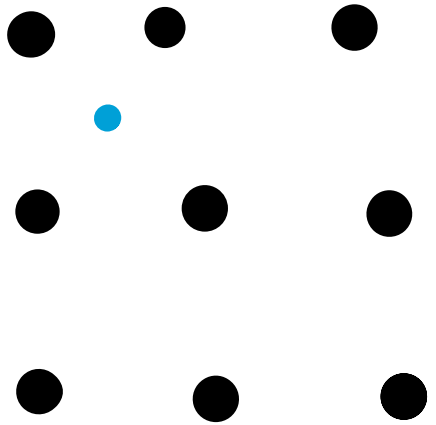
Rotation

- **Given permutation that satisfies equivalence**
- **Orthogonal Procrustes problem:**

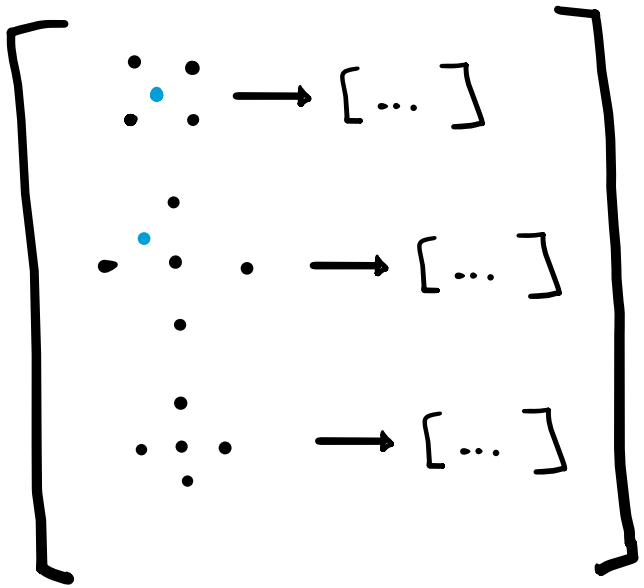
$$\boldsymbol{R} = \min_{\boldsymbol{O}} \|\boldsymbol{OA} - \boldsymbol{B}\|_{\boldsymbol{F}} \text{ s.t. } \boldsymbol{OO}^{T} = I$$

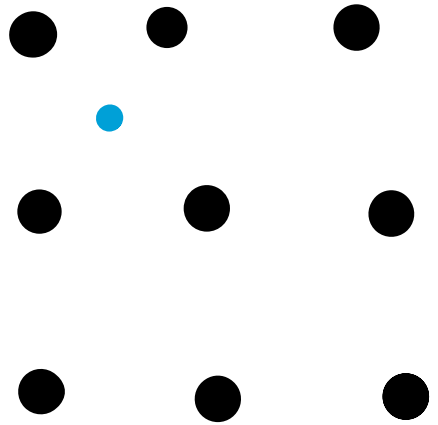
- **Solution via SVD**

Adaptive catalogue

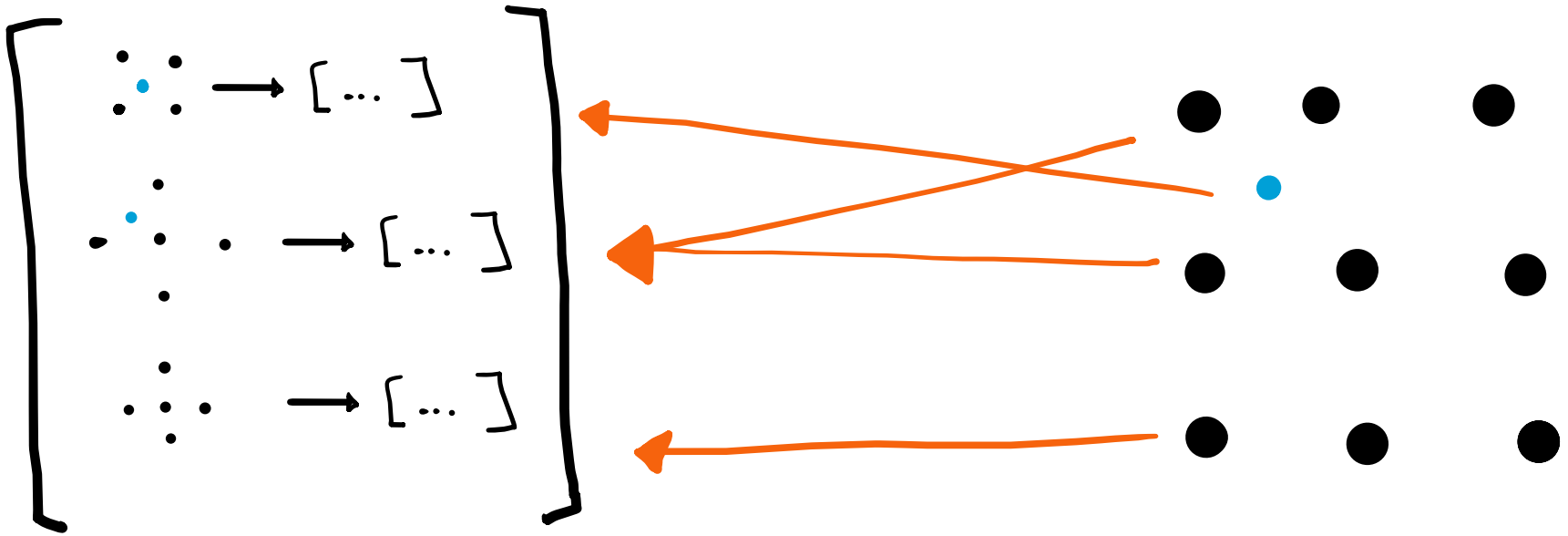


Adaptive catalogue

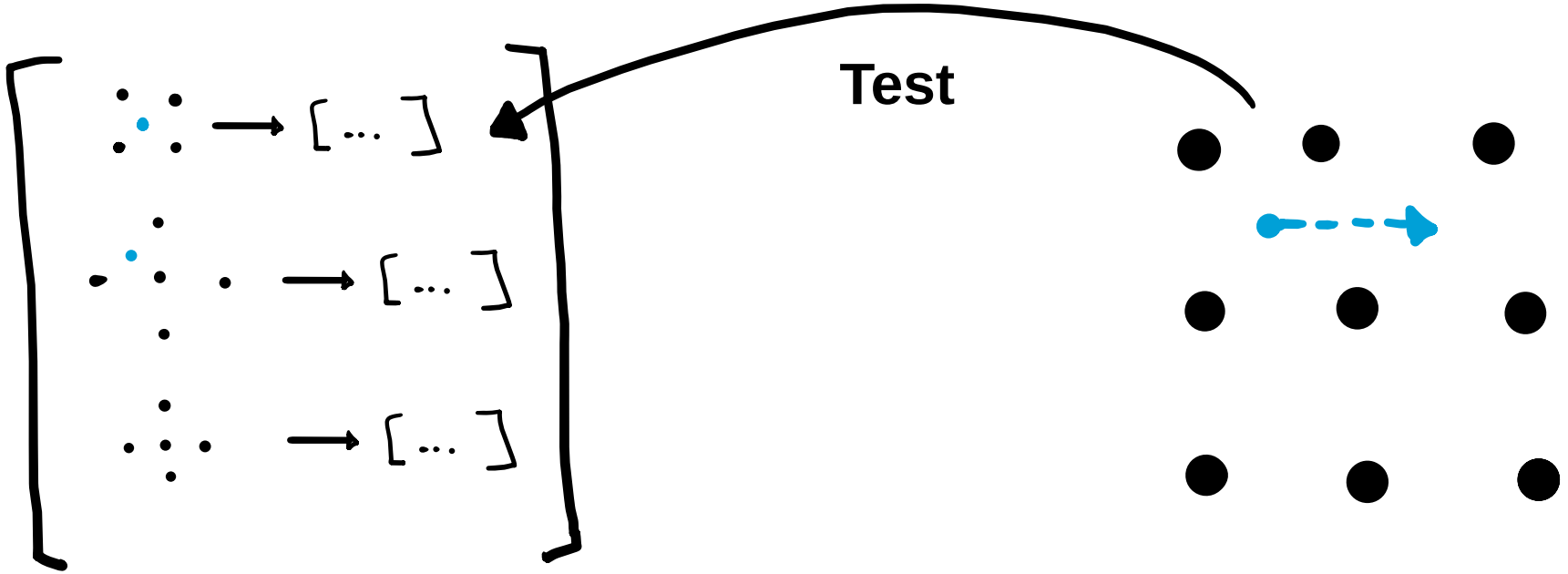




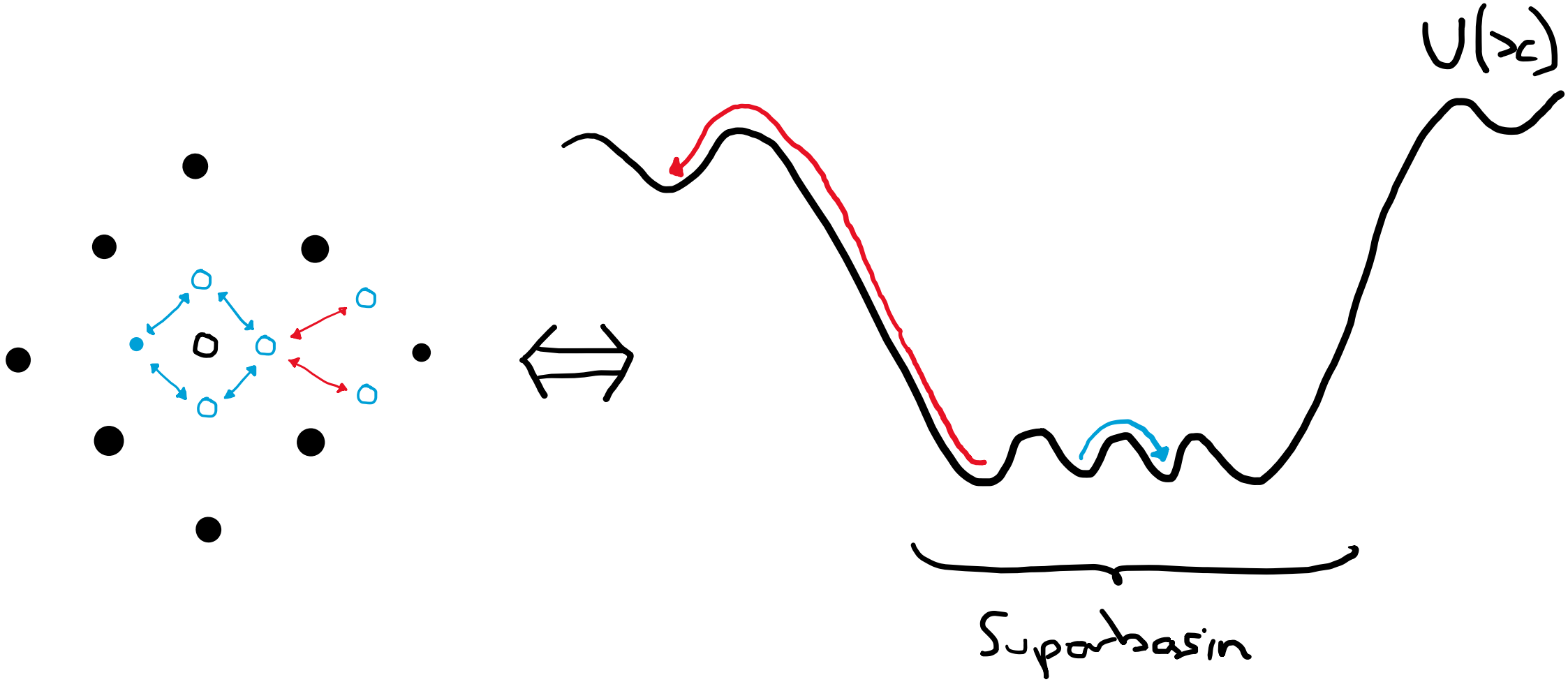
Adaptive catalogue



Adaptive catalogue



The *flickering problem*



Superbasins

- **Partition mechanisms into transient and absorbing:**