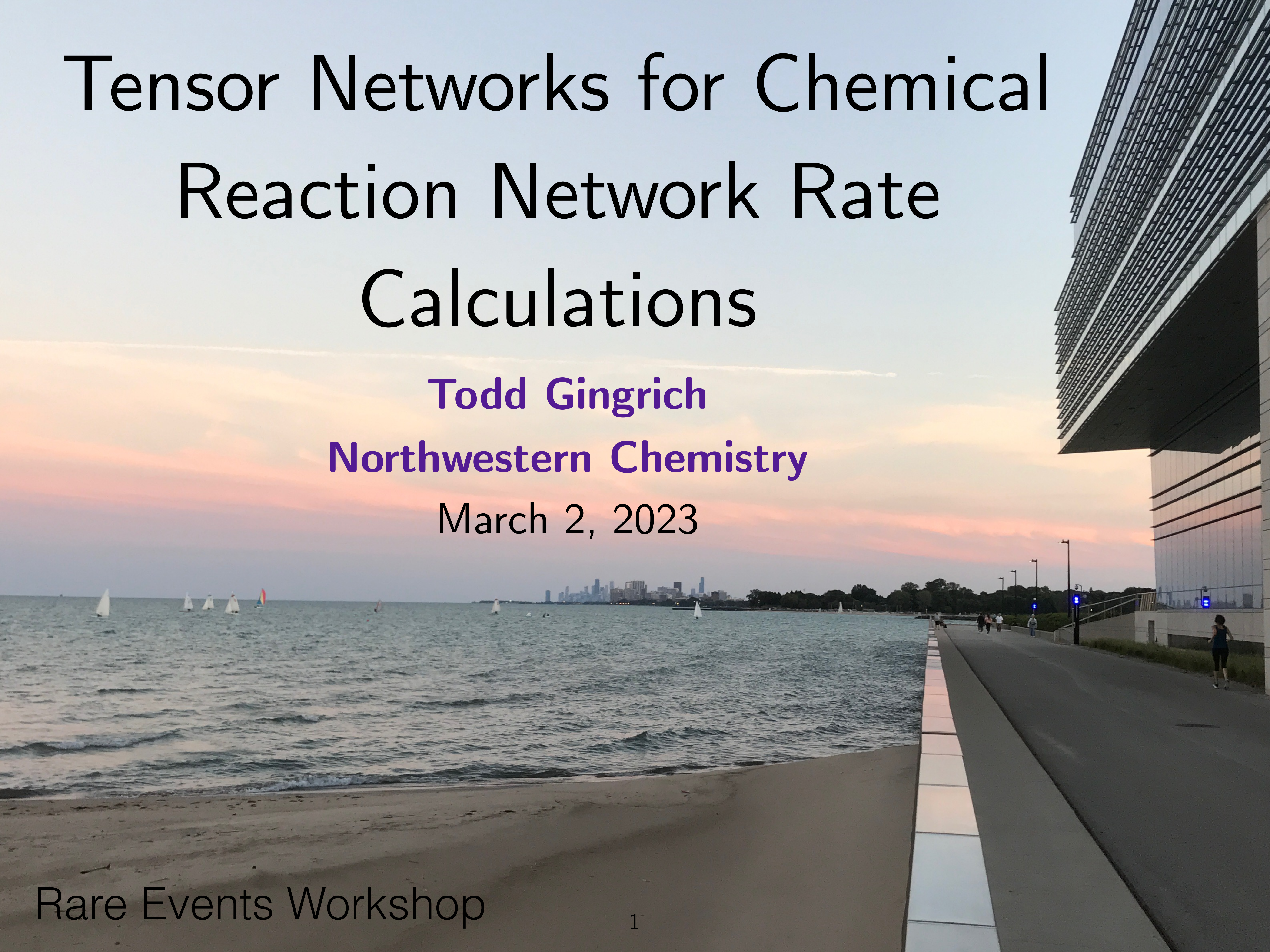
Tensor Networks for Chemical Reaction Network Rate Calculations

Todd Gingrich

Northwestern Chemistry

March 2, 2023



Rare Events Workshop

Overview

Doi-Peliti framework expresses Markov jump processes in a second quantized form.
[Doi, Peliti, Garrahan, van Wijland, Cardy, Tauber, others]

Given a Hamiltonian in second quantized form, tensor network numerical methods from quantum dynamics controllably find ground states (steady states here) and propagate dynamics.
[Fishman, White, Stoudenmire, Vanderstraeten, Haegeman, Verstraete, others]

Put the two together as a numerical method for calculating the rate of a rare event in a many-body discrete jump process.

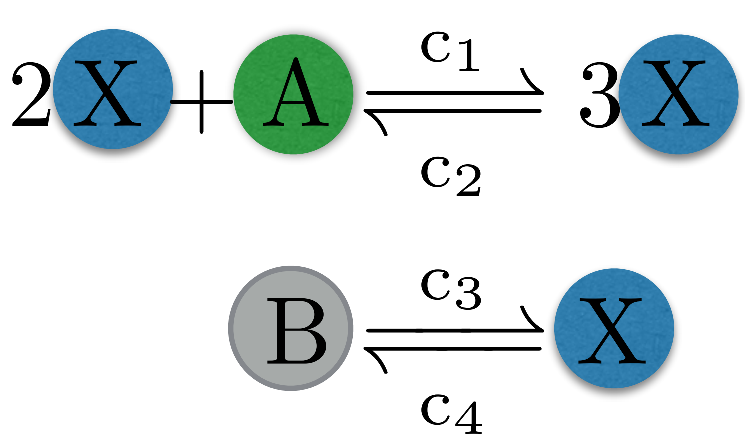
Act I:
Sick of Sampling

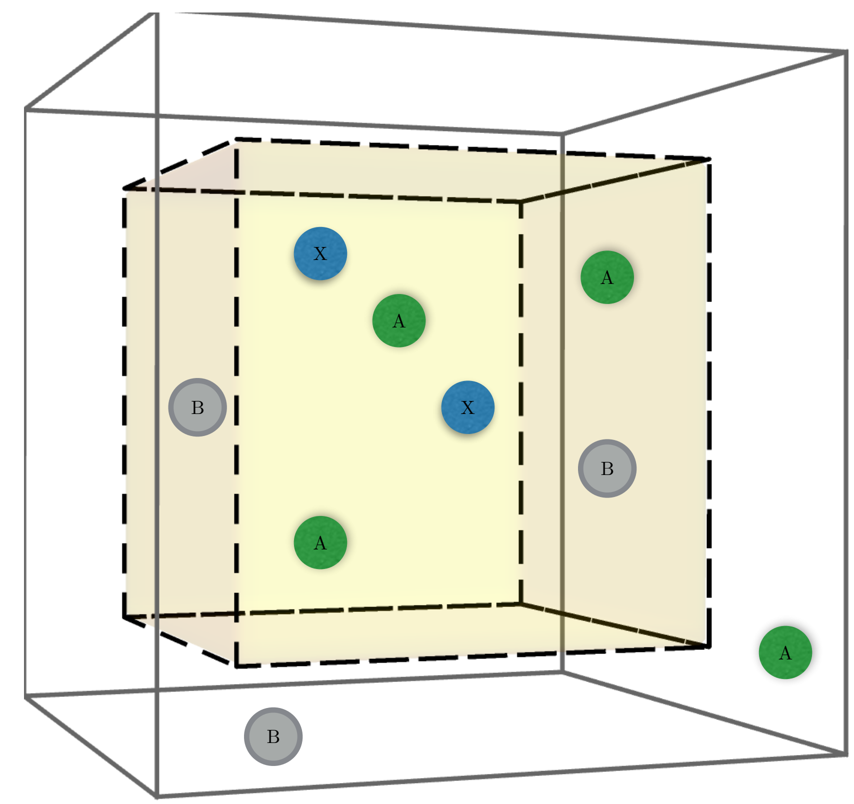
Schuyler
Nicholson
Postdoctoral Scholar

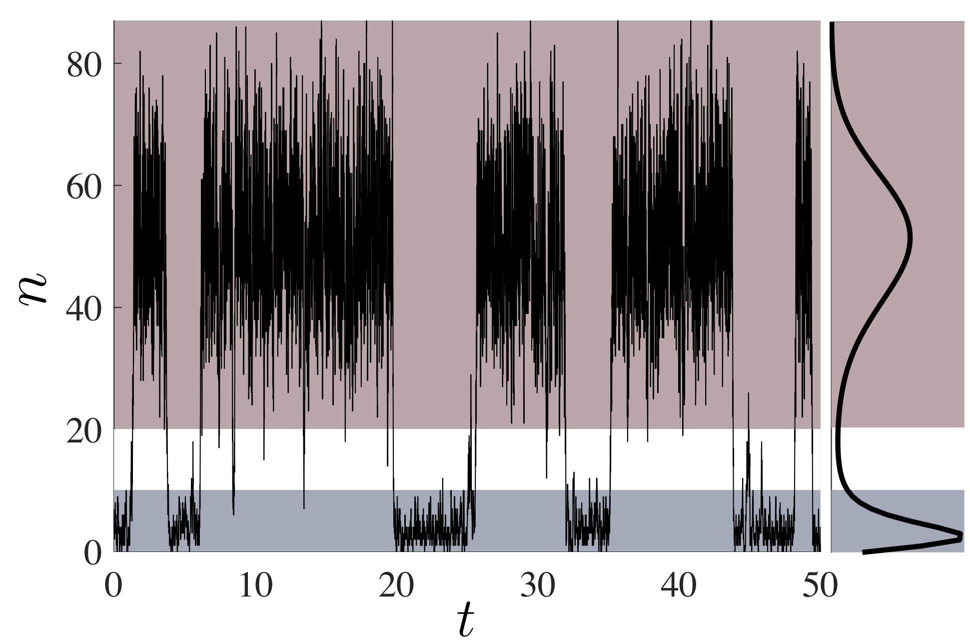
S.B. Nicholson and T.R. Gingrich, arXiv:2301.03717, 2023.

Well-mixed chemostated chemical kinetics

Schlögl (1972)

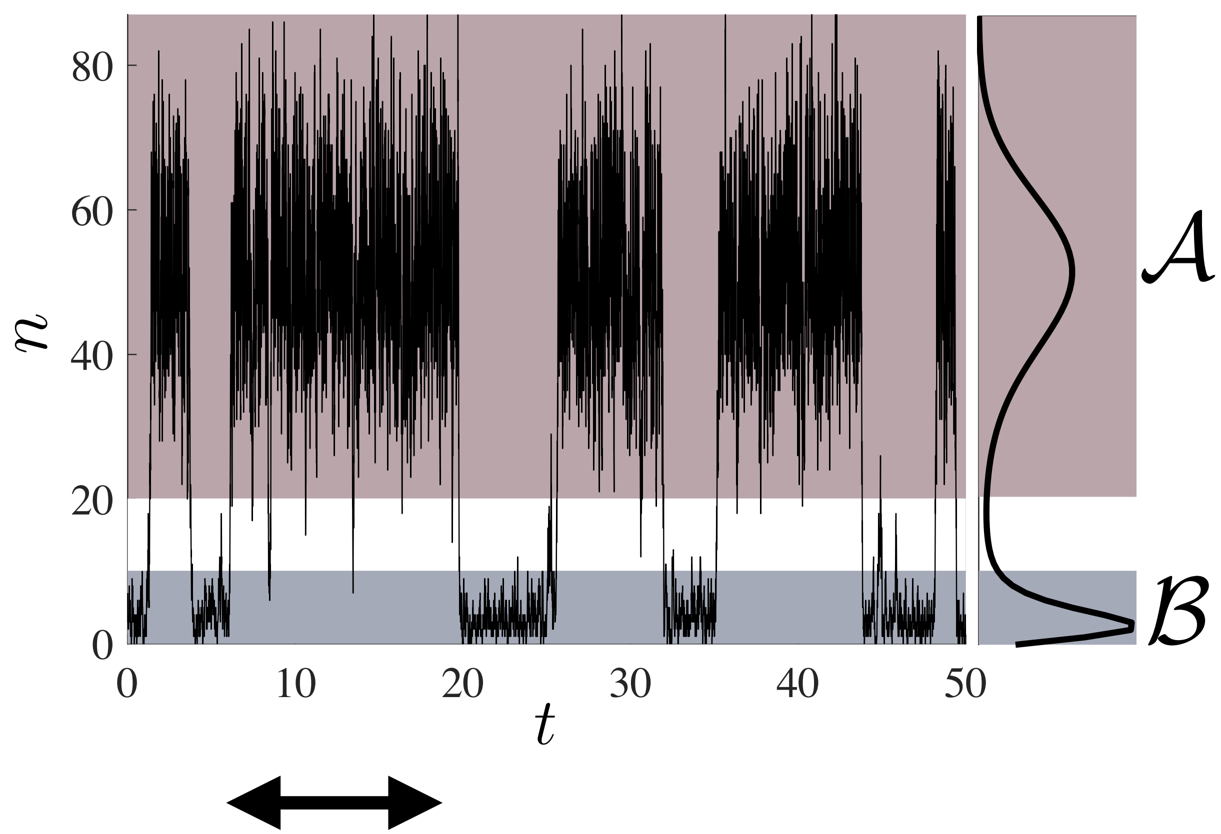






Stochastic switching with a rate characterizing switches between high and low concentration of X

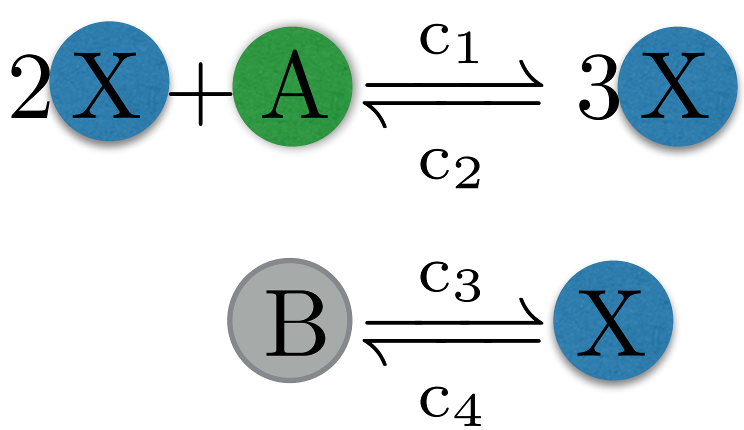
Rate calculations from realizations



$$\approx \frac{1}{k}$$

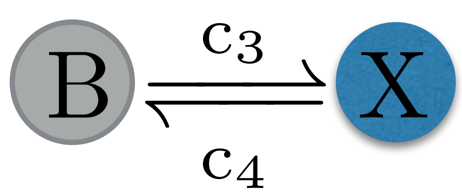
- Brute force Gillespie/SSA
- Milestoning
- TPS
- FFS
- Other Advanced Sampling

Realizations versus distributions



$$|p\rangle = \begin{pmatrix} p_{X=0} \\ p_{X=1} \\ p_{X=2} \\ p_{X=3} \\ \vdots \end{pmatrix}$$

Realizations versus distributions



$$|p\rangle = \begin{pmatrix} p_{X=0} \\ p_{X=1} \\ p_{X=2} \\ p_{X=3} \\ \vdots \end{pmatrix}$$

$$\mathbb{W}_B = \begin{pmatrix} -n_B c_3 & c_4 & 0 & 0 & \\ n_B c_3 & -n_B c_3 - c_4 & 2c_4 & 0 & \cdots \\ 0 & n_B c_3 & -n_B c_3 - 2c_4 & 3c_4 & \\ 0 & 0 & n_B c_3 & -n_B c_3 - 3c_4 & \\ & \vdots & & & \ddots \end{pmatrix}$$

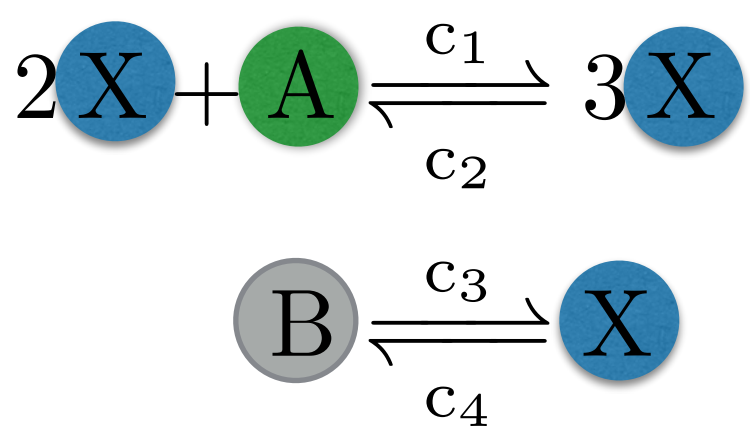
Evolution of the distribution

$$2\mathrm{X} + \mathrm{A} \underset{c_2}{\overset{c_1}{\rightleftharpoons}} 3\mathrm{X}$$

$$|p\rangle = \begin{pmatrix} p_{\mathrm{X}=0} \\ p_{\mathrm{X}=1} \\ p_{\mathrm{X}=2} \\ p_{\mathrm{X}=3} \\ \vdots \end{pmatrix}$$

$$\mathbb{W}_{\mathrm{A}} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & \\ 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & 0 & -n_{\mathrm{A}} c_1 & c_2 & 0 & \\ 0 & 0 & n_{\mathrm{A}} c_1 & -3 n_{\mathrm{A}} c_1 - c_2 & 4 c_2 & \\ 0 & 0 & 0 & 3 n_{\mathrm{A}} c_1 & -10 n_{\mathrm{A}} c_1 - 4 c_2 & \\ & \vdots & & & & \ddots \end{pmatrix}$$

Realizations versus distributions



$$\mathbb{W} = \mathbb{W}_{\mathrm{A}} + \mathbb{W}_{\mathrm{B}}$$

$$\frac{\partial \, |p\rangle}{\partial t} = \mathbb{W} |p\rangle$$ Master Equation

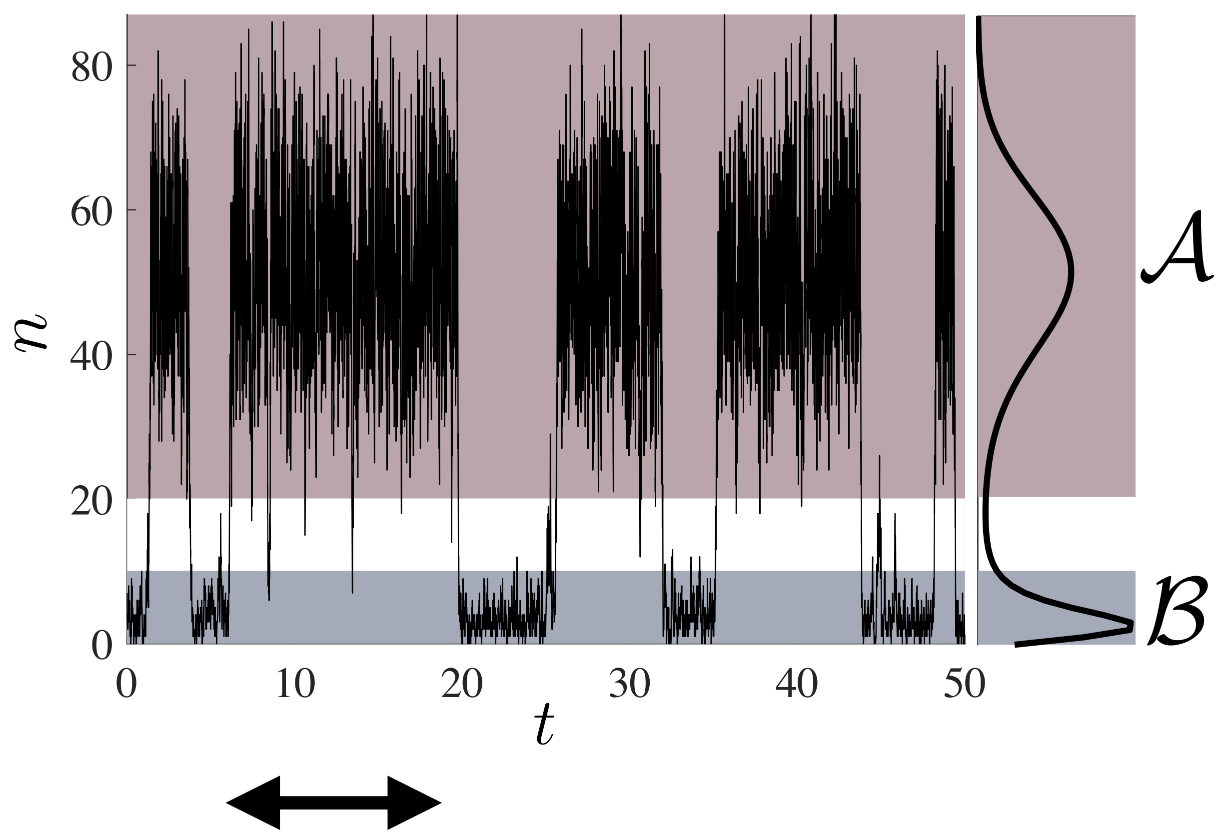
$$|p(t)\rangle = e^{\mathbb{W}t} |p(0)\rangle$$

Matrix exponentiation naturally averages over all possible trajectories

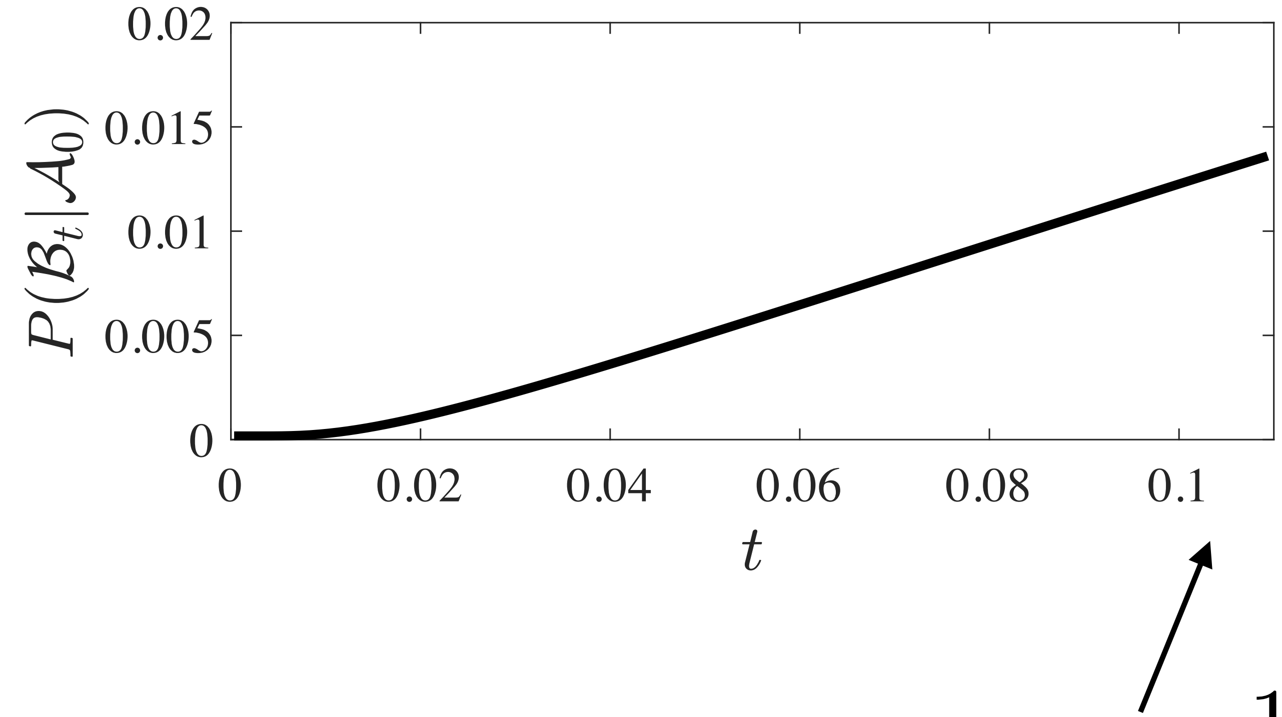
$$|p_{\mathrm{ss}}\rangle = \lim_{t \to \infty} e^{\mathbb{W}t} |p(0)\rangle$$

The maximal eigenvector gives the steady state *distribution*

Rate calculations from propagators

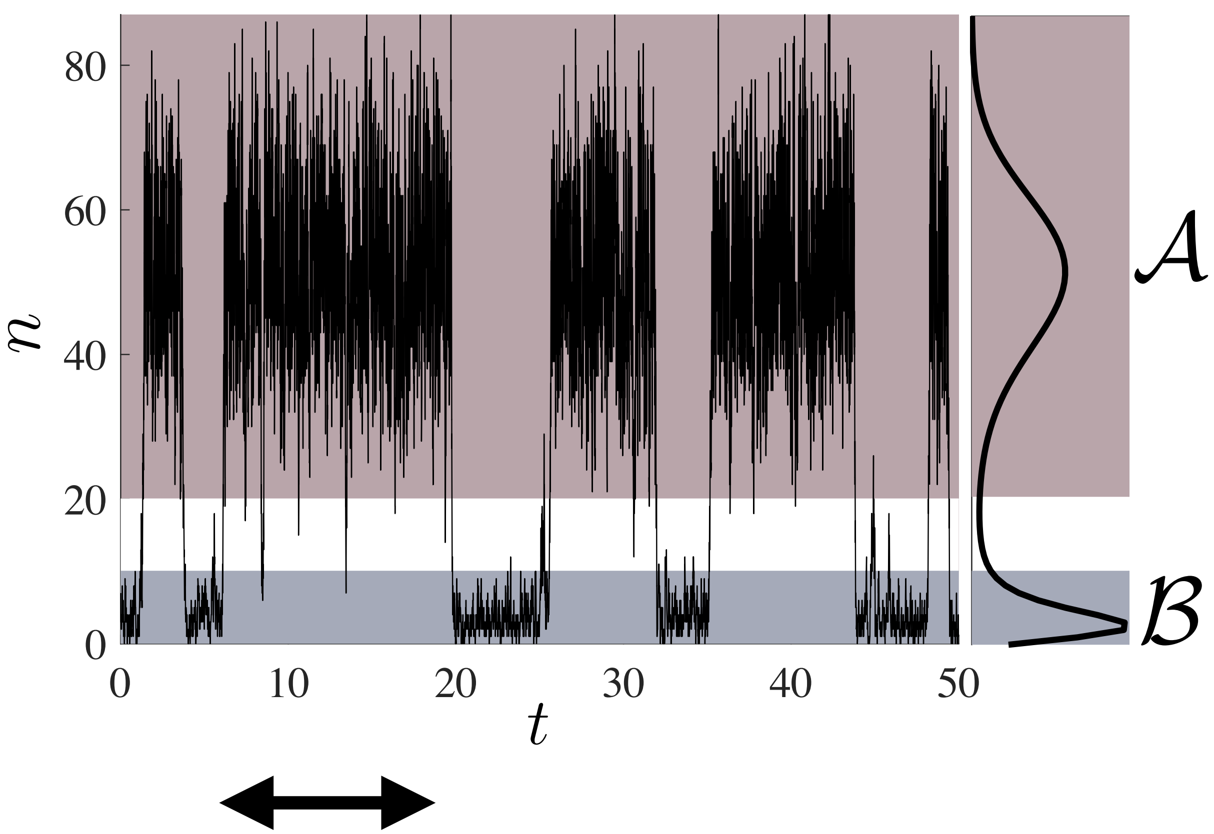


$$\approx \frac{1}{k}$$

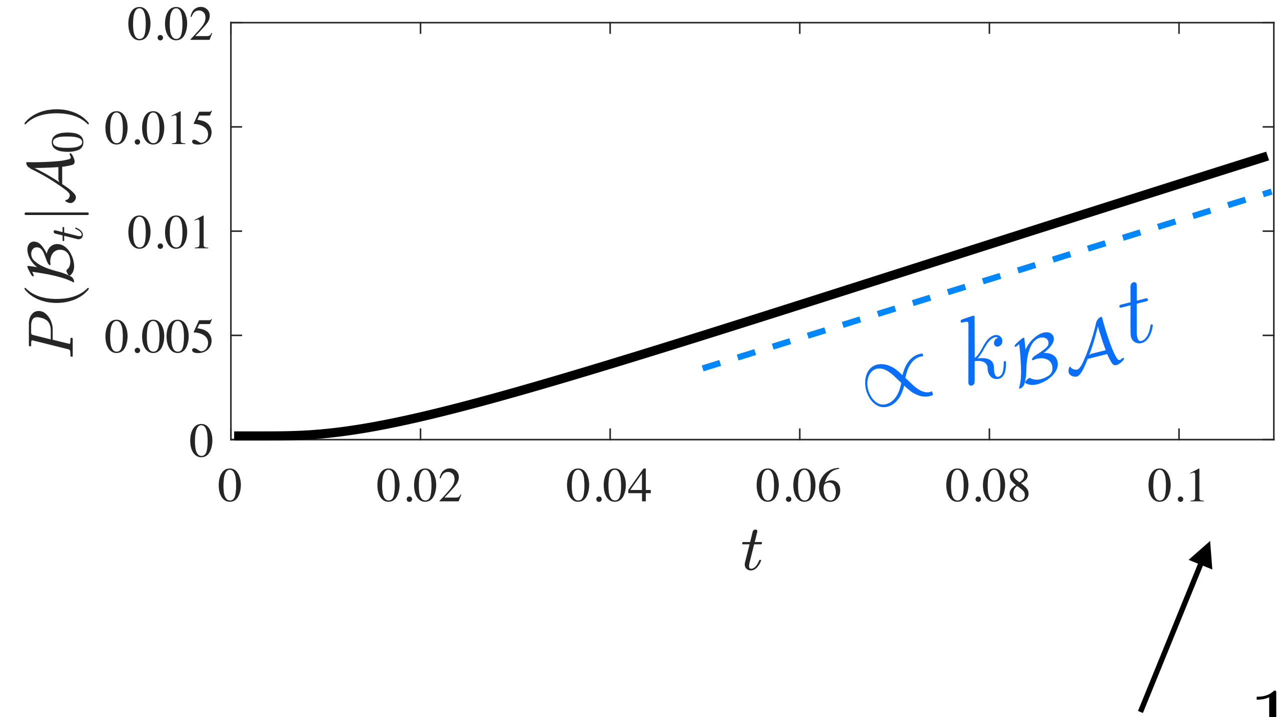


$$t << \frac{1}{k}$$

Rate calculations from propagators



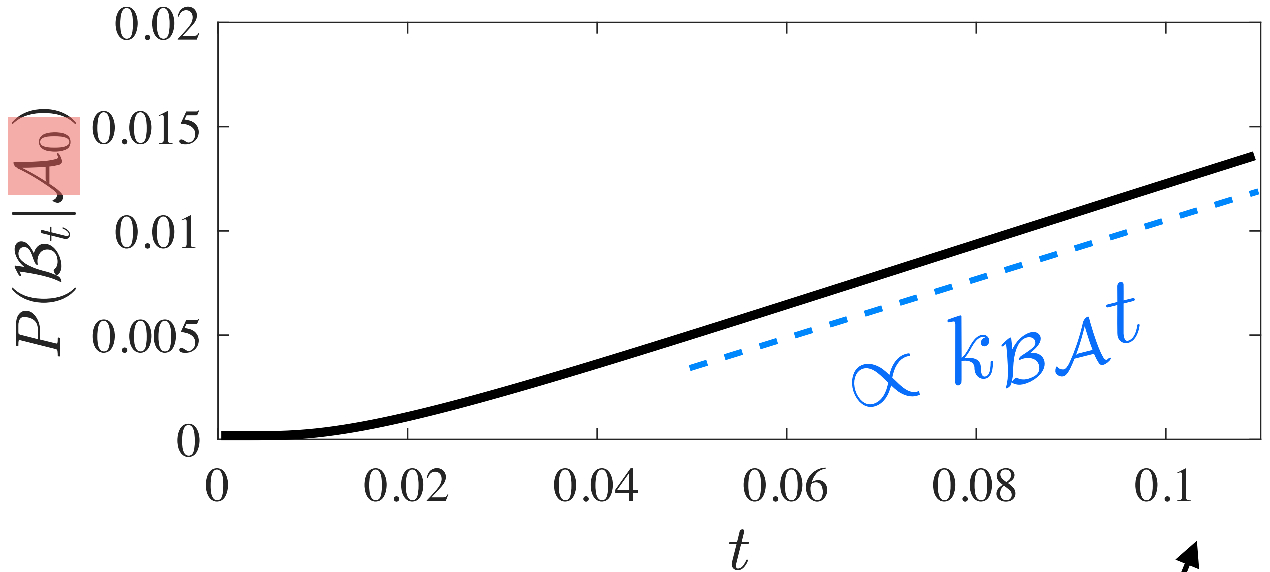
$\approx \frac{1}{k}$



$t << \frac{1}{k}$

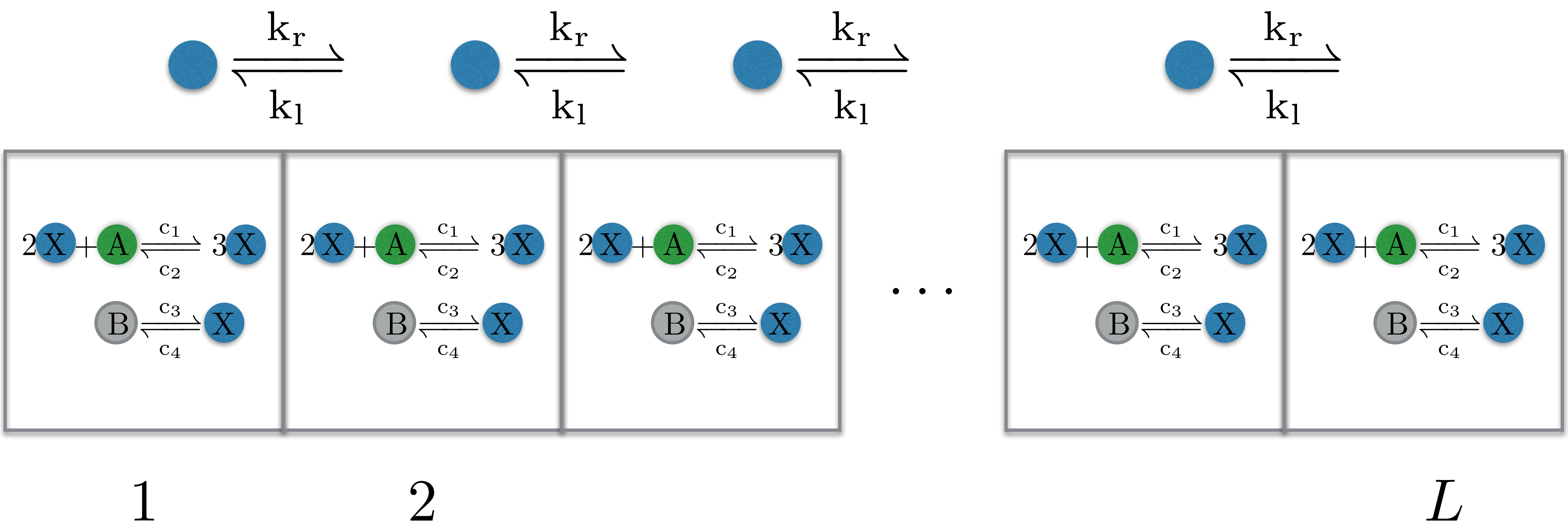
Rate calculations from propagators

$$\frac{\langle \mathbf{1} | \hat{\mathcal{P}}_{\mathcal{B}} e^{\mathbb{W}t} \hat{\mathcal{P}}_{\mathcal{A}} | p_{\text{ss}} \rangle}{\langle \mathbf{1} | \hat{\mathcal{P}}_{\mathcal{A}} | p_{\text{ss}} \rangle}$$

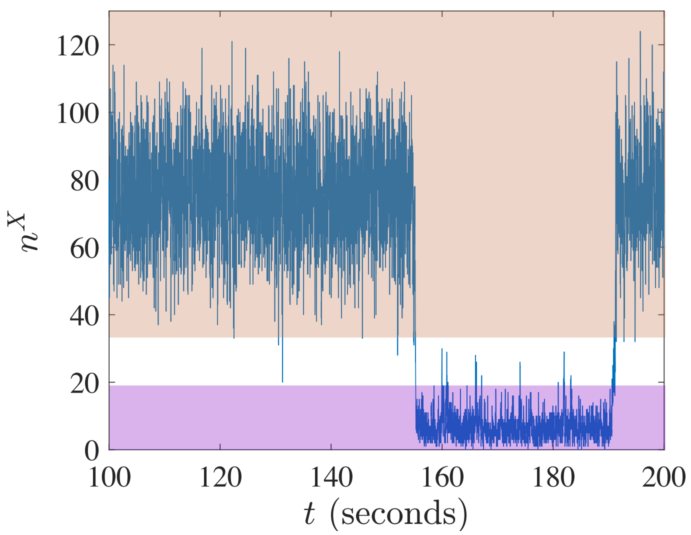


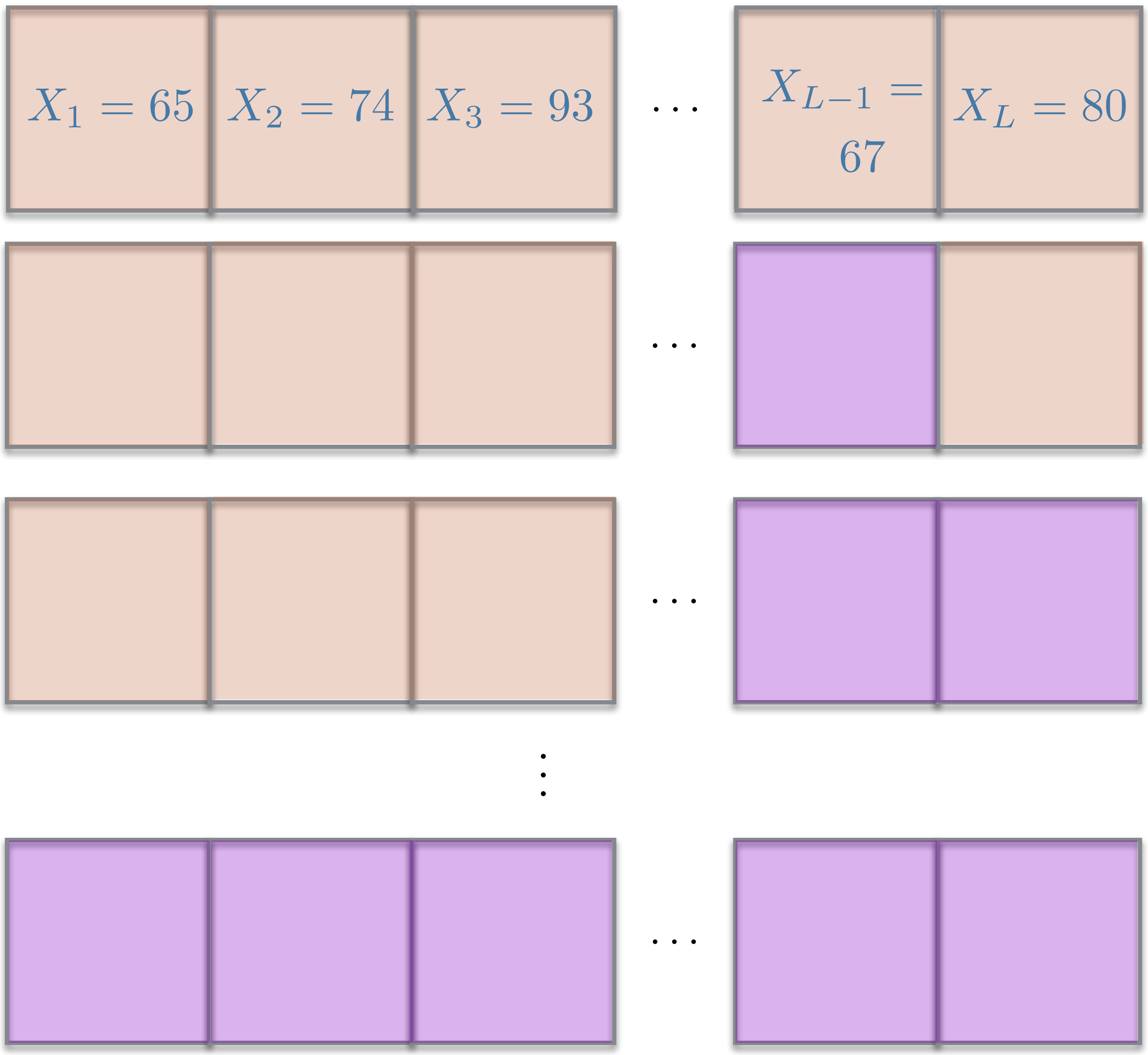
$$t << \frac{1}{k}$$

Reaction Diffusion

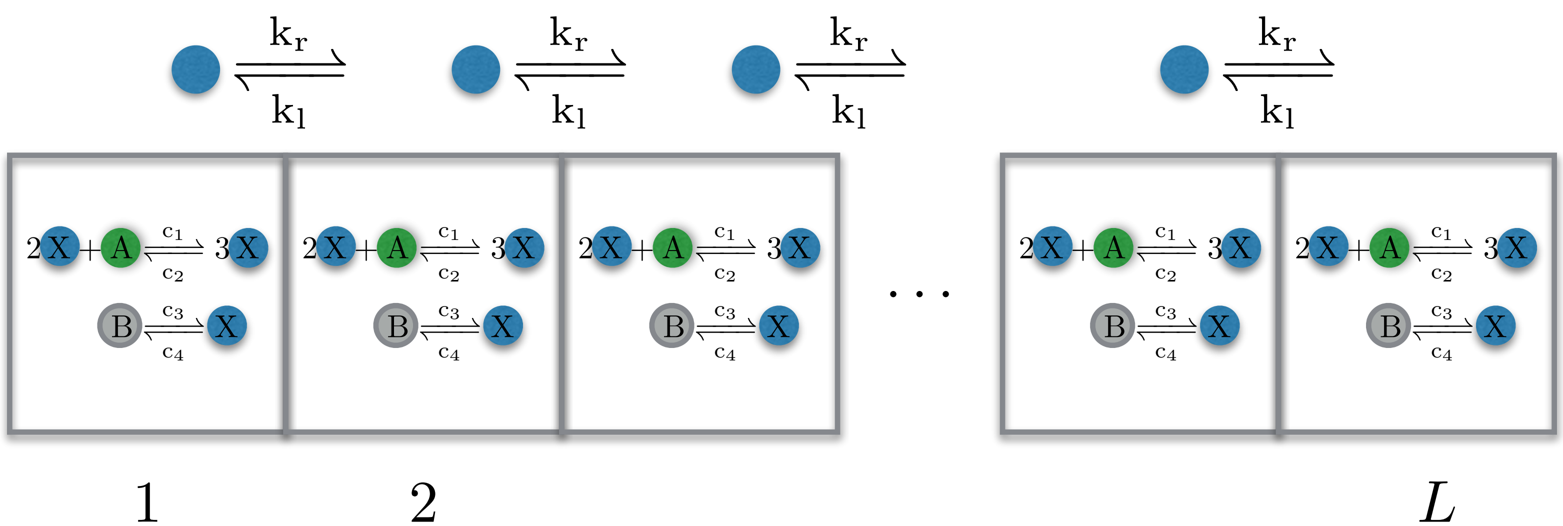


Collective hops from high-X to low-X states...





Two different issues...



Gillespie realizations

Time between events shrinks as system size grows

Evolution of distribution

Many-body problem

$$|p\rangle = \begin{pmatrix} p_{X=0} \\ p_{X=1} \\ p_{X=2} \\ p_{X=3} \\ \vdots \end{pmatrix} \qquad \mathbb{W}_B = \begin{pmatrix} -n_B c_3 & c_4 & 0 & 0 & \cdots \\ n_B c_3 & -n_B c_3 - c_4 & 2c_4 & 0 & \\ 0 & n_B c_3 & -n_B c_3 - 2c_4 & 3c_4 & \\ 0 & 0 & n_B c_3 & -n_B c_3 - 3c_4 & \\ & \vdots & & & \ddots \end{pmatrix}$$

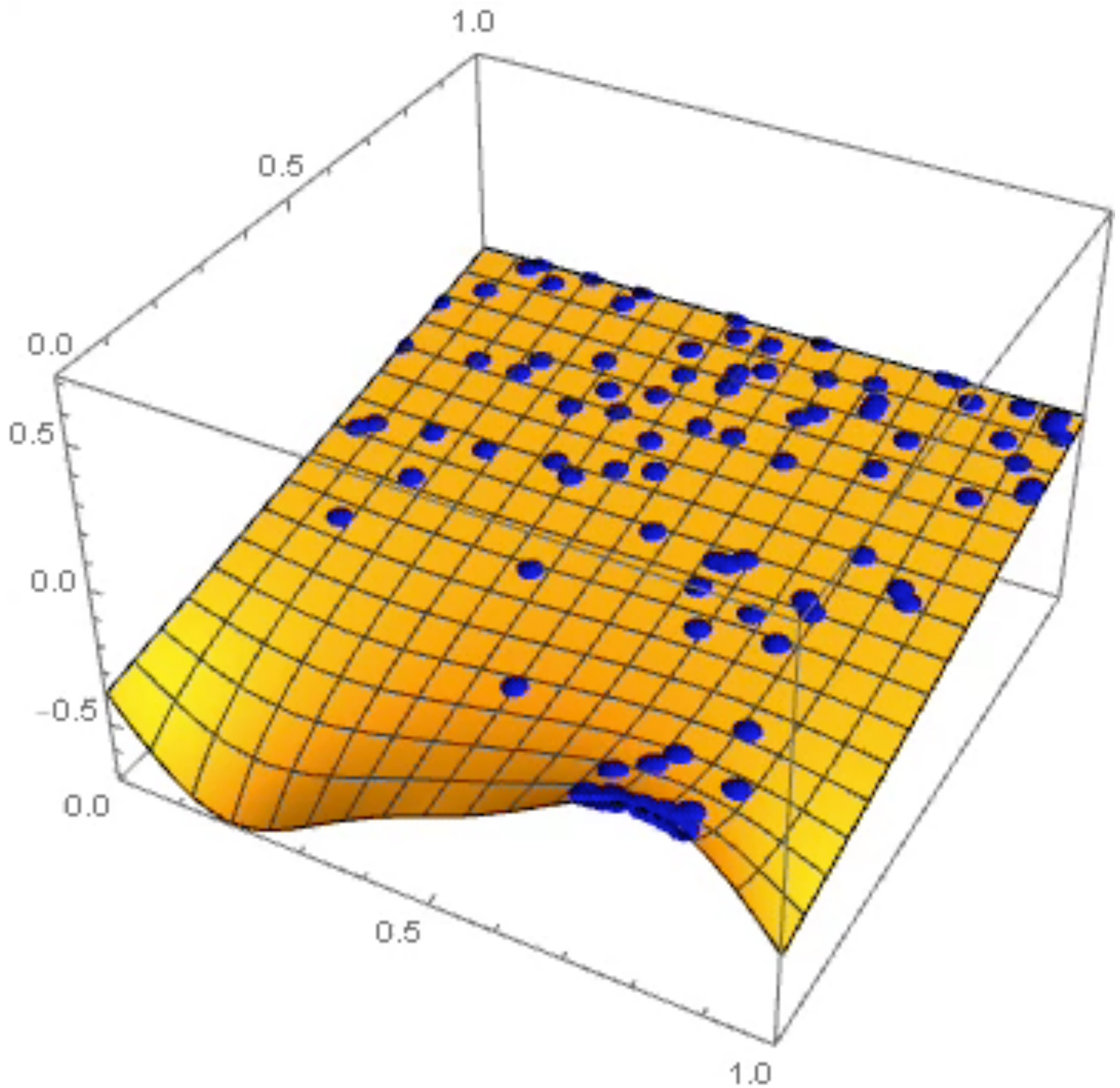
Act II:
Tensor Networks

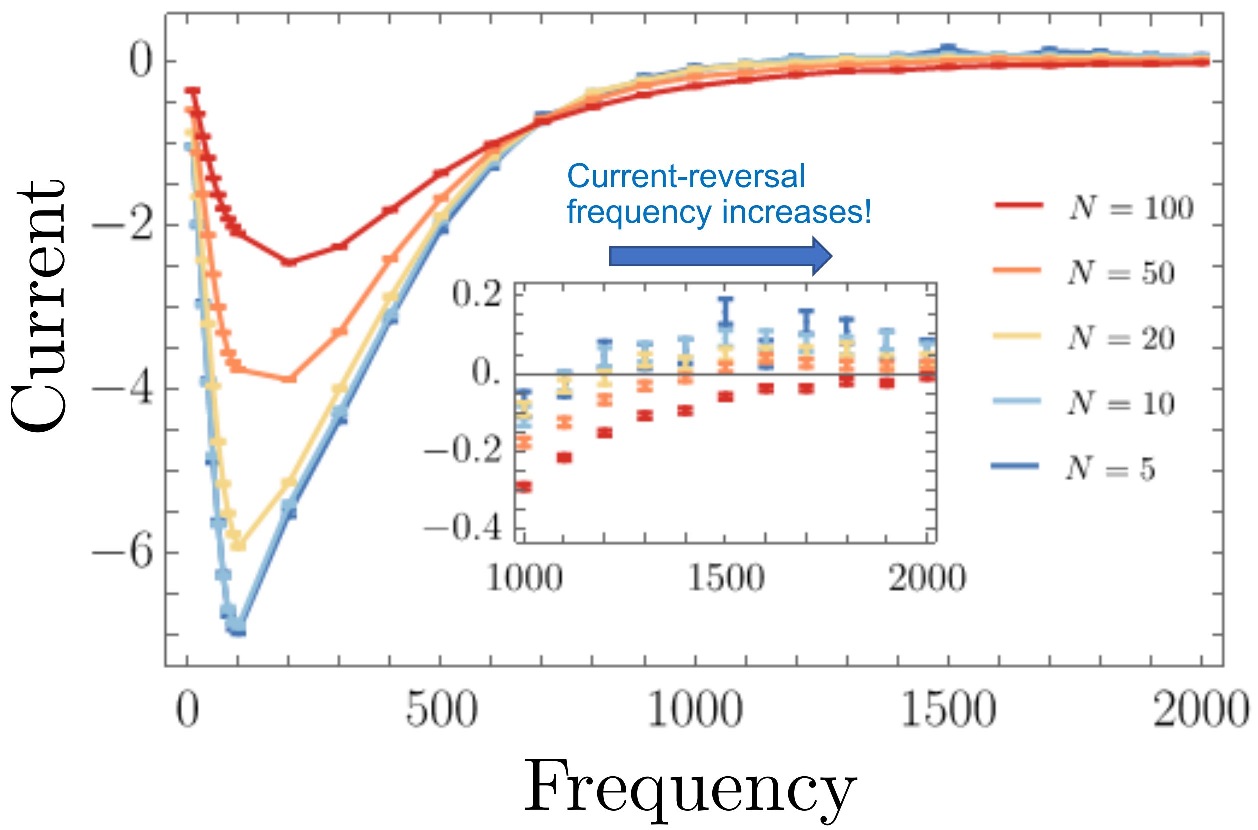
Nils Strand
Graduate Student

Hadrien Vroylandt
Currently at Sorbonne Université

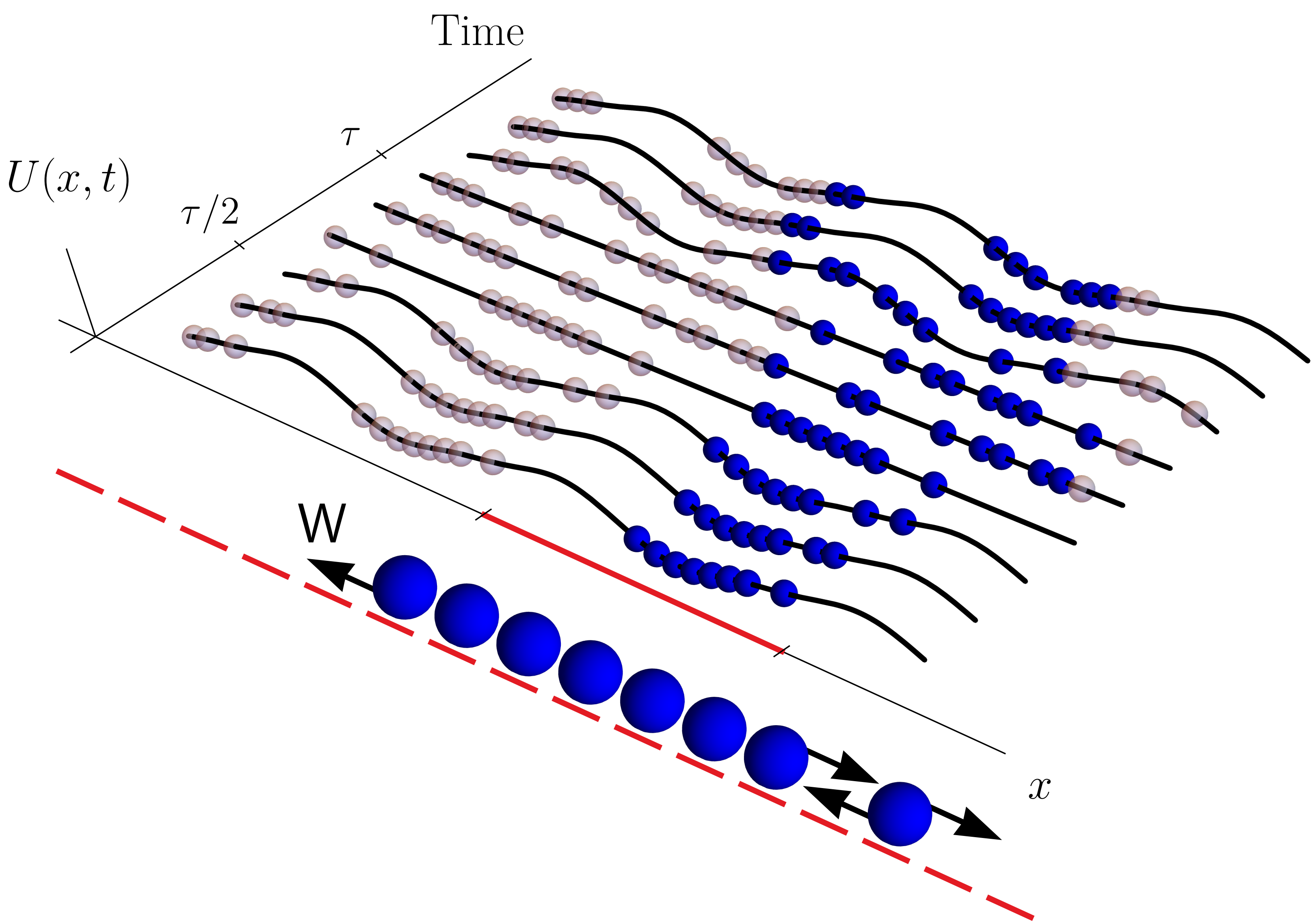
N.E. Strand, H. Vroylandt, and T.R. Gingrich, *JCP*, 156, 221103, 2022.
N.E. Strand, H. Vroylandt, and T.R. Gingrich, *JCP*, 157, 054109, 2022.

Ratchets and Current Reversals





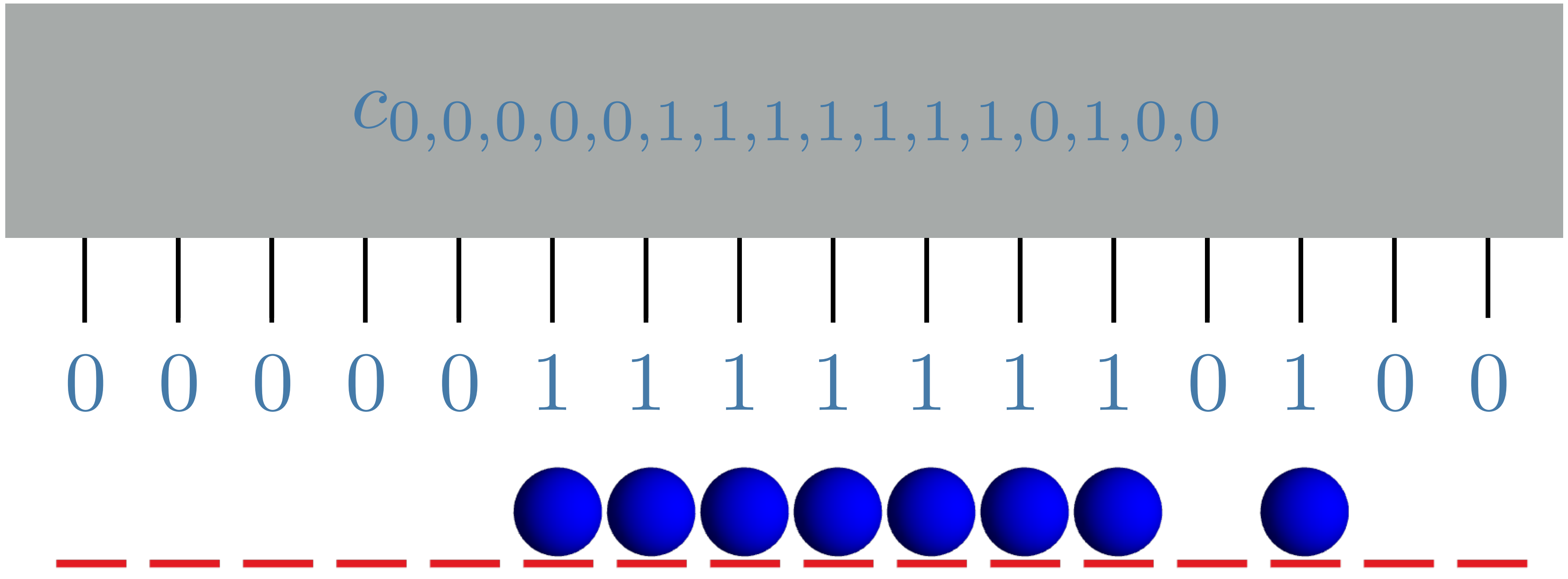
What would it take to evolve a 1d flashing ratchet in distribution?



$$|p\rangle = \sum_{X_1,X_2,\ldots,X_L} c_{X_1,X_2,\ldots,X_L} \, |X_1, X_2, \ldots, X_L\rangle$$

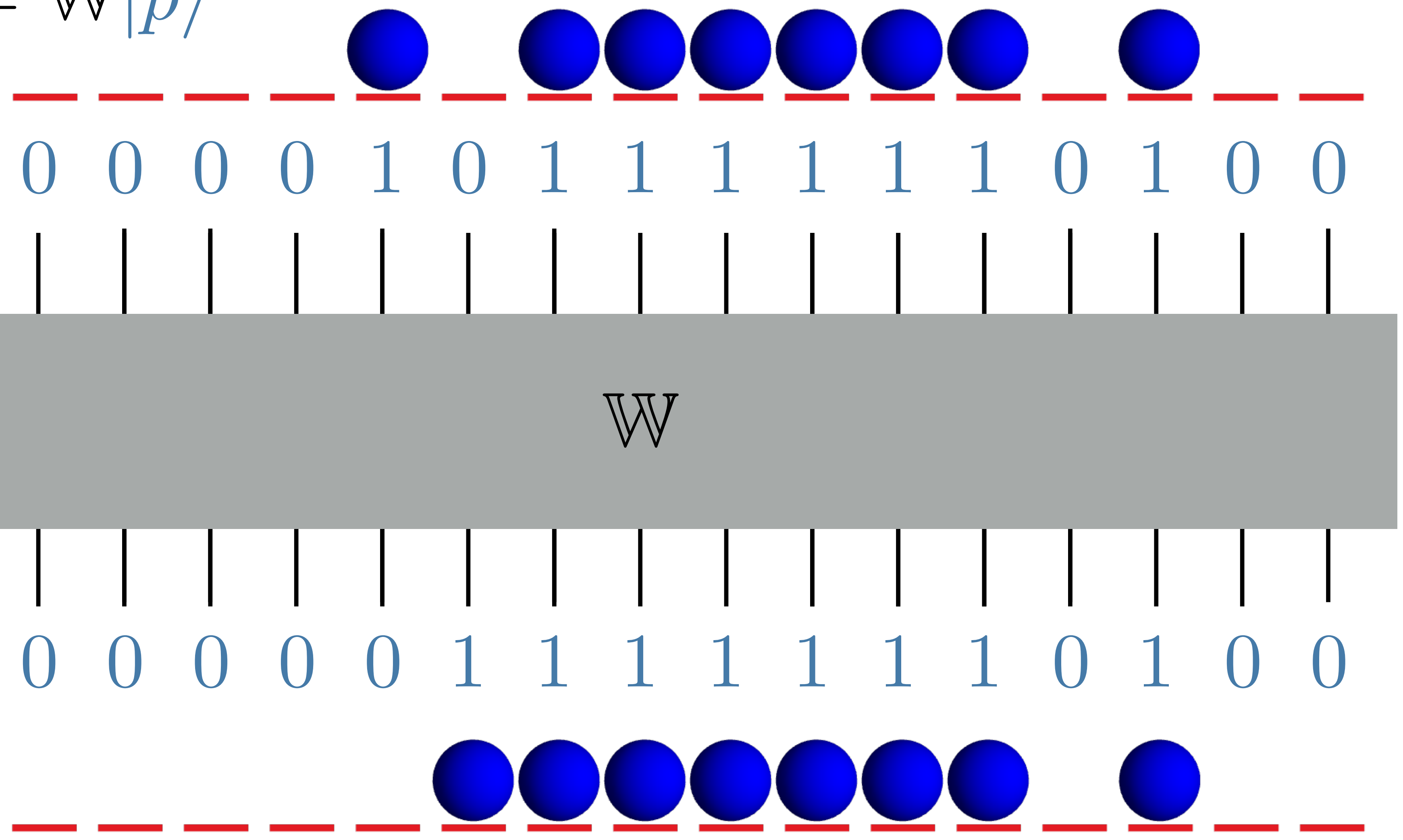
The distribution over microstates is encoded in a rank L tensor

$$|p\rangle = \sum_{X_1, X_2, \ldots, X_L} c_{X_1, X_2, \ldots, X_L} \, |X_1, X_2, \ldots, X_L\rangle$$



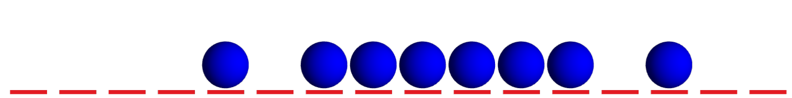
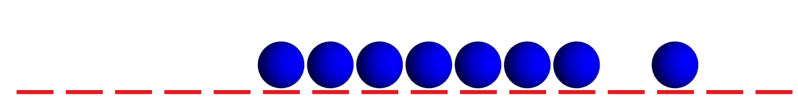
The rate matrix for transitions between microstates is a rank 2L tensor

$$\frac{\partial\,|p\rangle}{\partial t} = \mathbb{W}|p\rangle$$



A second-quantized representation

$$\mathbb{W} = \sum_{i=1}^{L} \left[r_{i\to i+1}(a_i a_{i+1}^\dagger - n_i v_{i+1}) + r_{i+1\to i}(a_i^\dagger a_{i+1} - v_i n_{i+1}) \right]$$

$\langle$  $|\mathbb{W}|$  $\rangle = r_{6\to 5}$

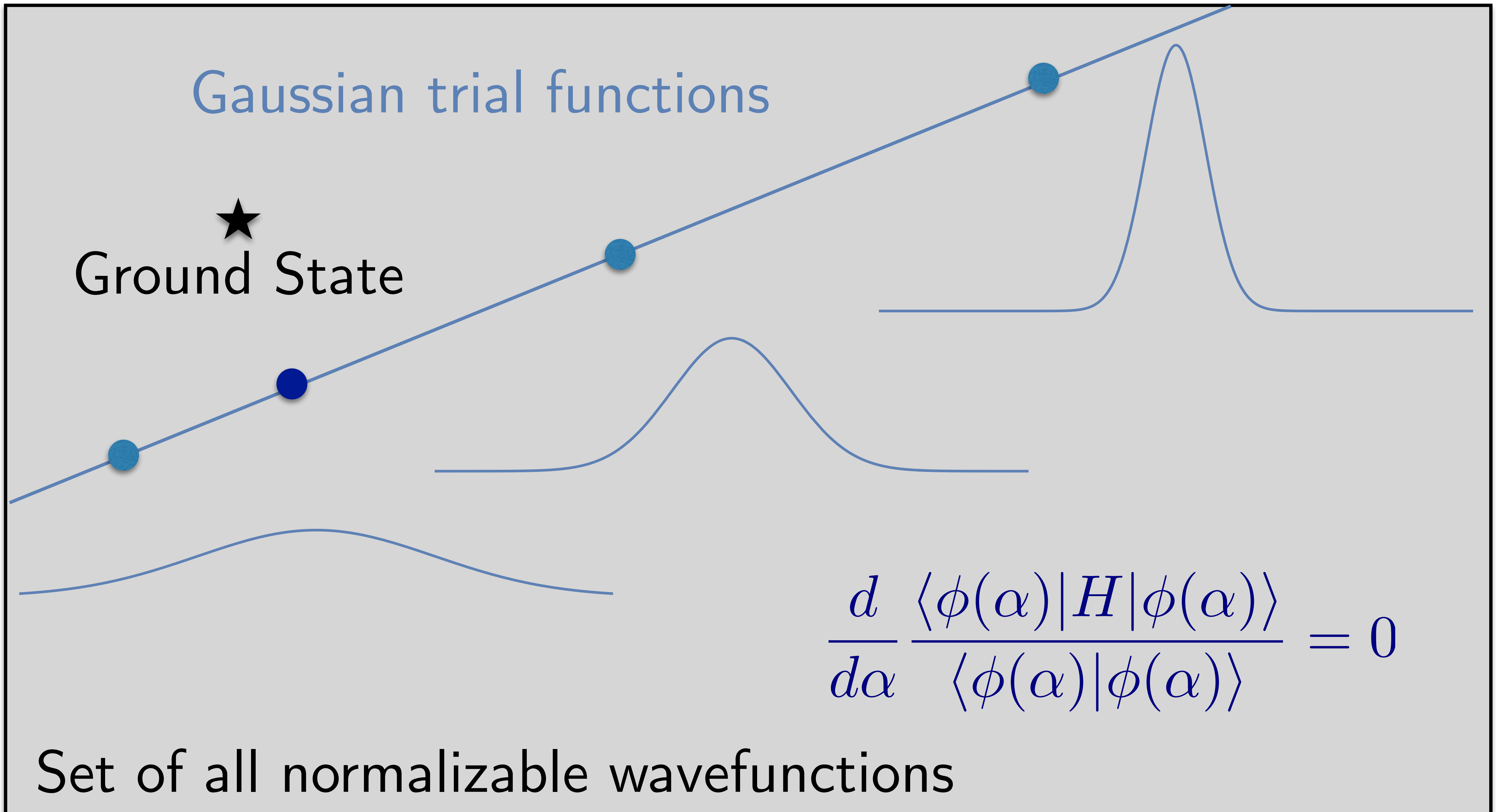
This Doi-Peliti form can't save me from the fact that there are too many microstates to enumerate their probabilities:

$$|p\rangle = \sum_{X_1, X_2, \ldots, X_L} c_{X_1, X_2, \ldots, X_L} |X_1, X_2, \ldots, X_L\rangle$$

We need a variational principle a la quantum mechanics.

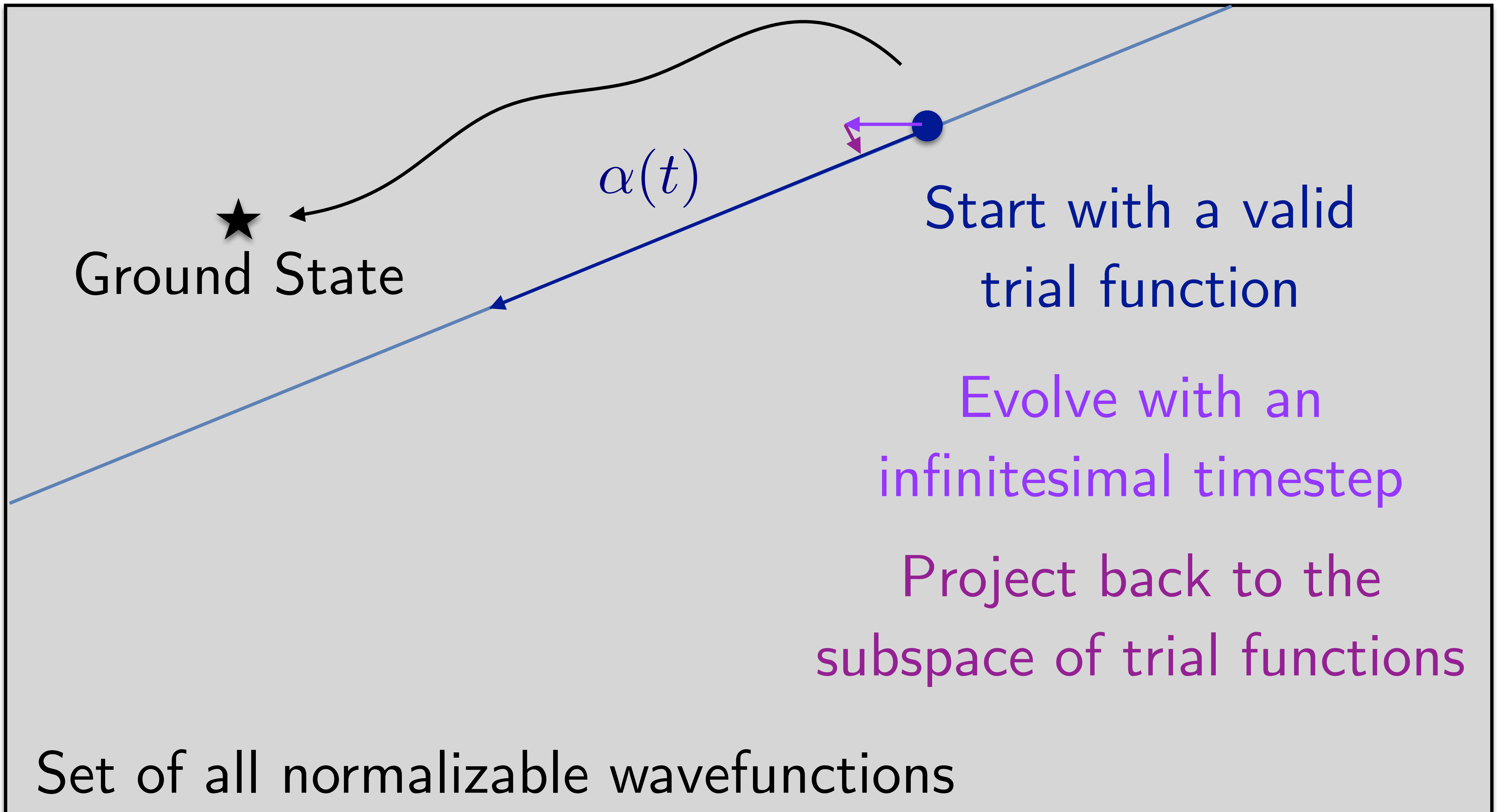
[Doi 1976, Peliti 1985]

A variational principle

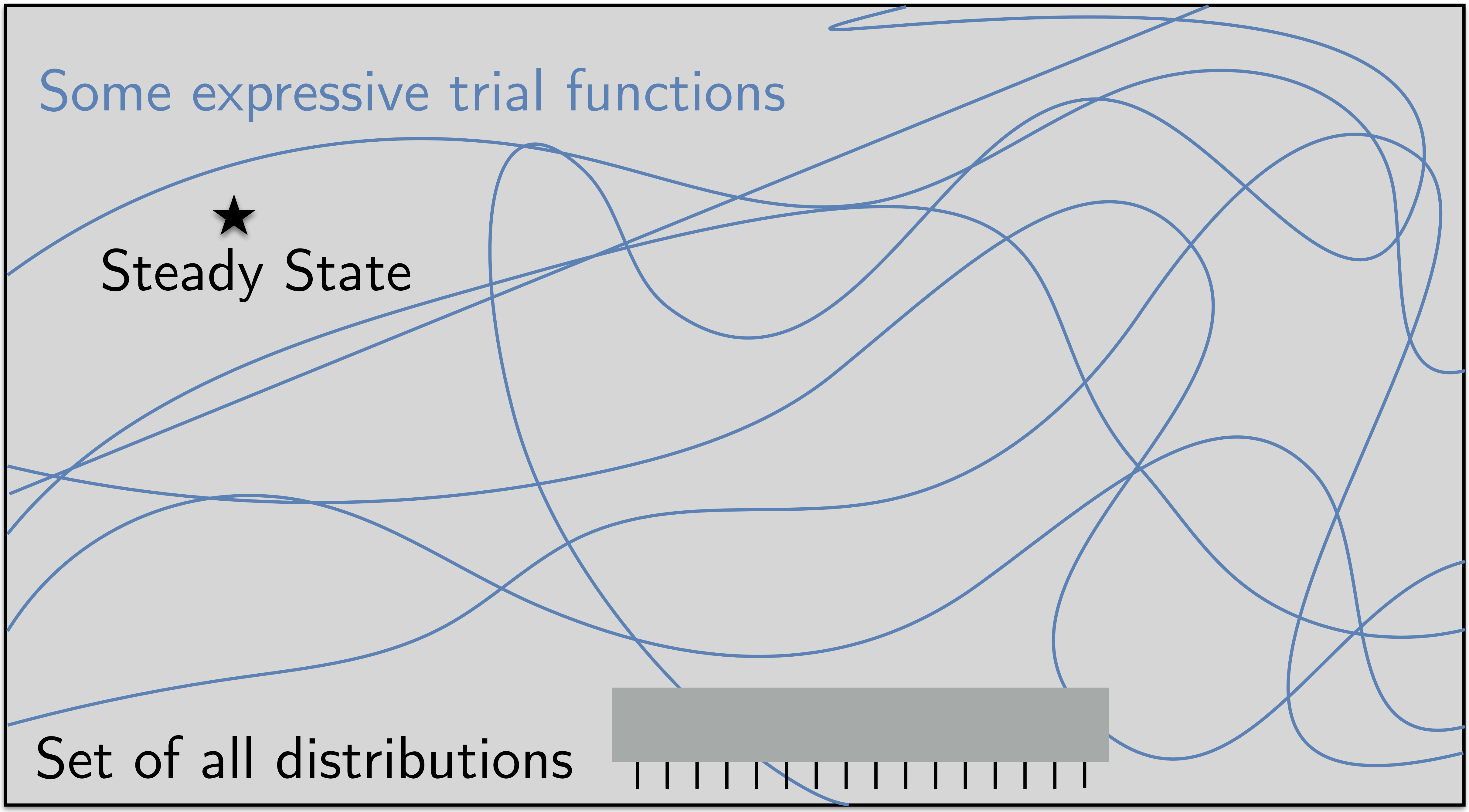


$$\frac{d}{d\alpha}\frac{\langle\phi(\alpha)|H|\phi(\alpha)\rangle}{\langle\phi(\alpha)|\phi(\alpha)\rangle} = 0$$

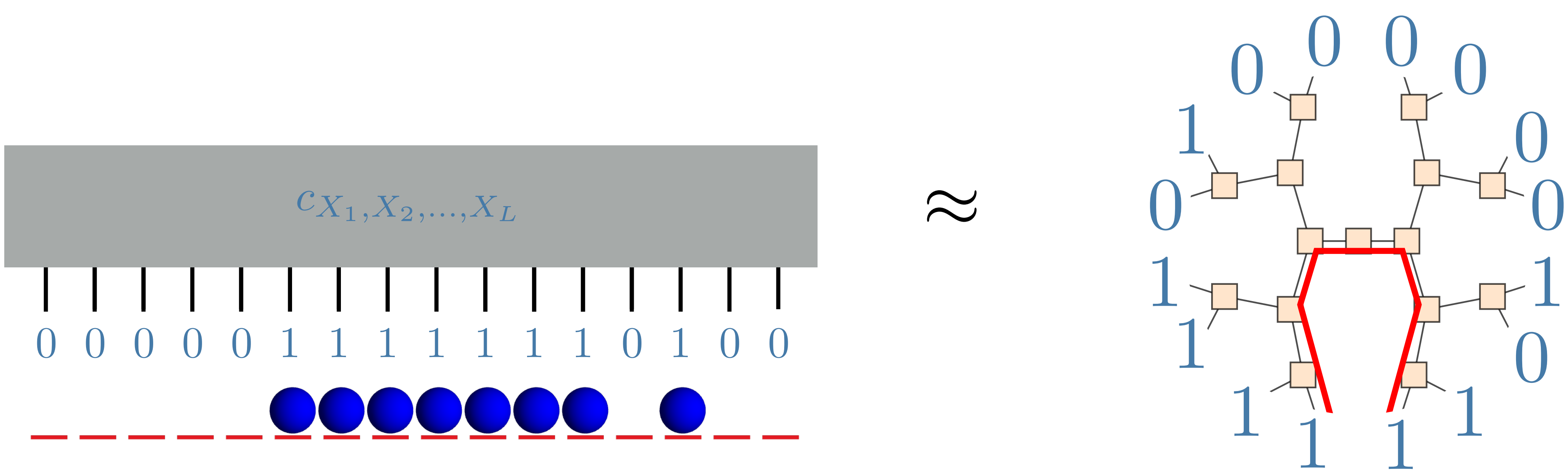
A time-dependent variational principle (TDVP)

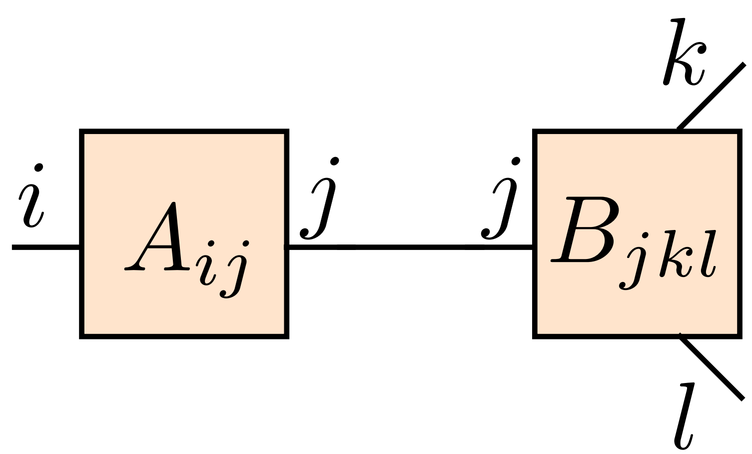


A variational principle



Tensor networks as variational trial functions

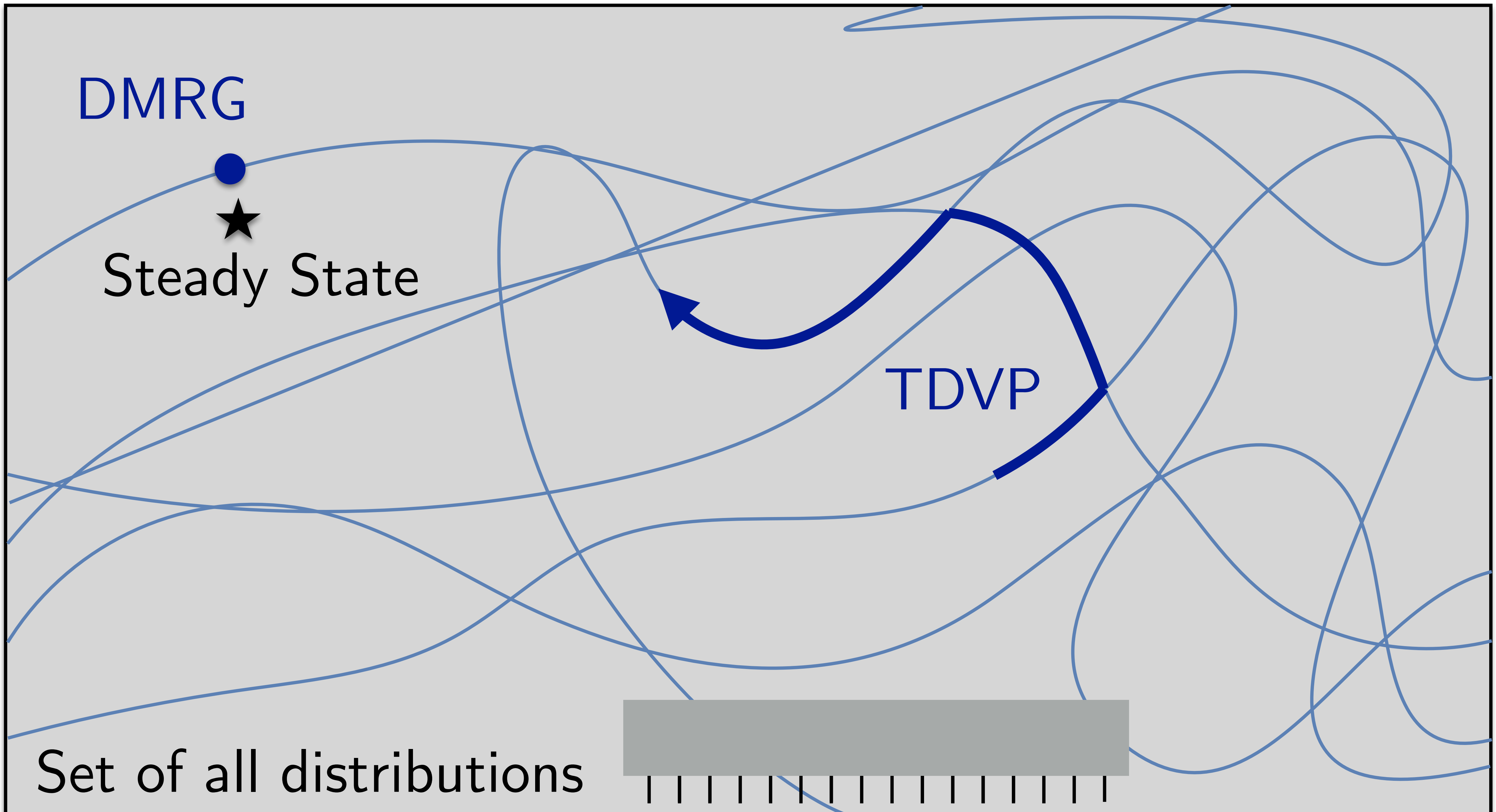




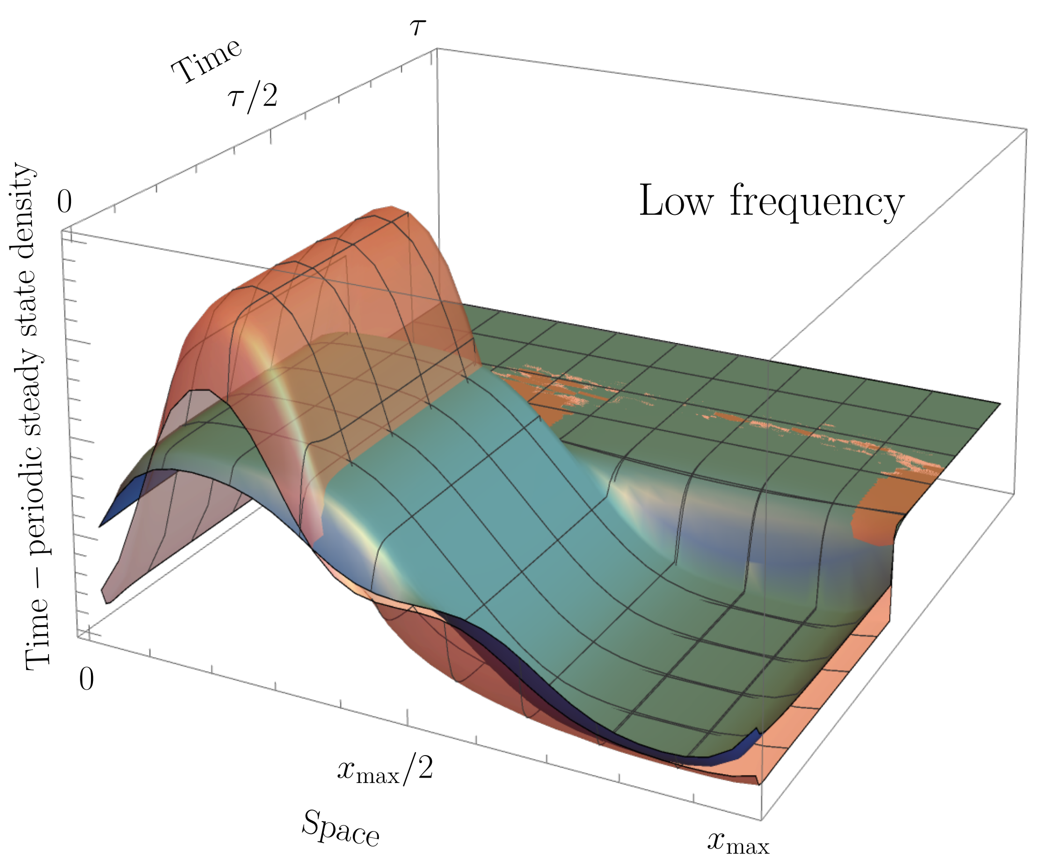
$$= \sum_{j=1}^{???} A_{ij} B_{jkl}$$

D. Bauernfeind and M. Aichhorn, SciPost Phys. (2020).

A TN variational principle



TDVP can extract time-periodic steady states

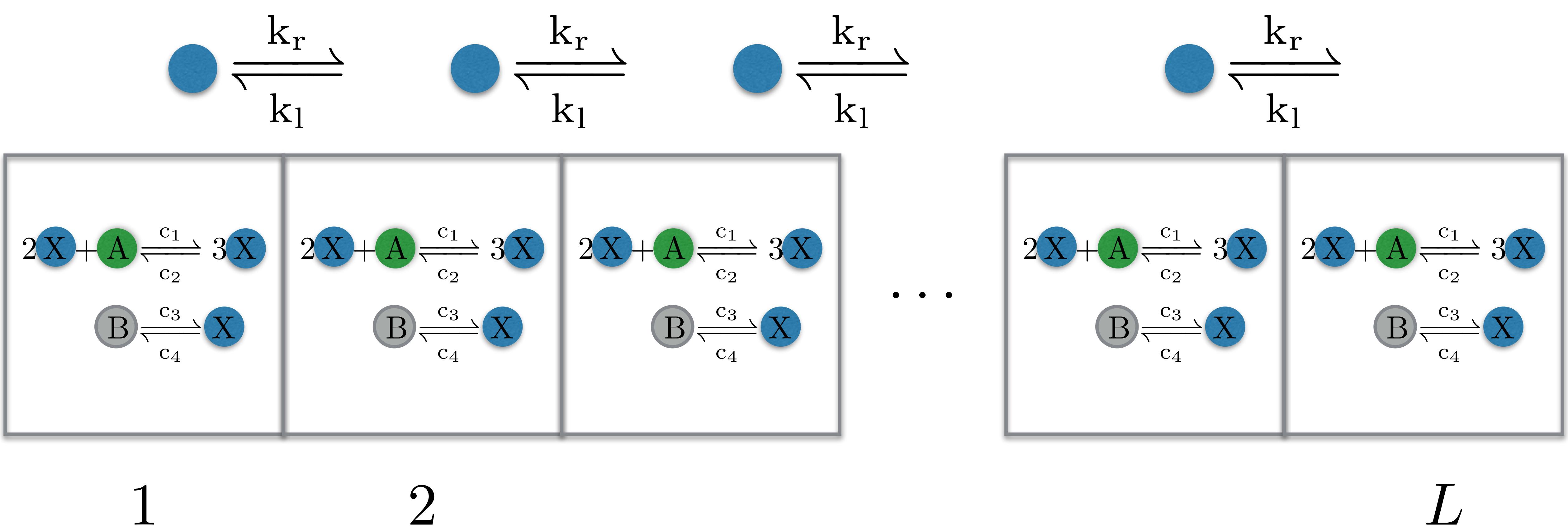


N.E. Strand, H. Vroylandt, and T.R. Gingrich, *JCP*, 156, 221103, 2022.

Act III: Putting It Together

S.B. Nicholson and T.R. Gingrich, arXiv:2301.03717, 2023.

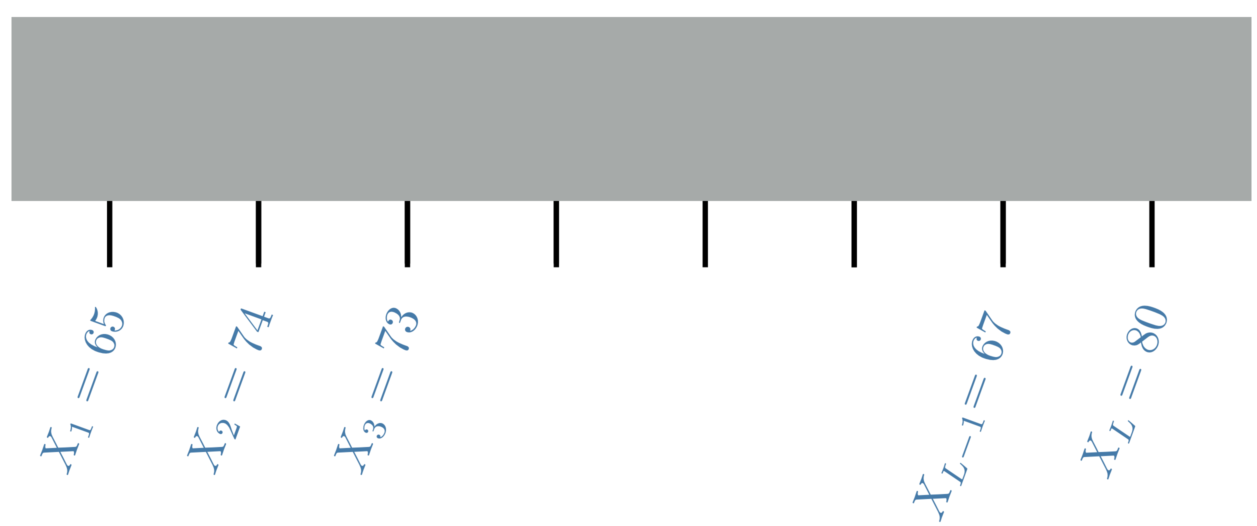
Reaction Diffusion



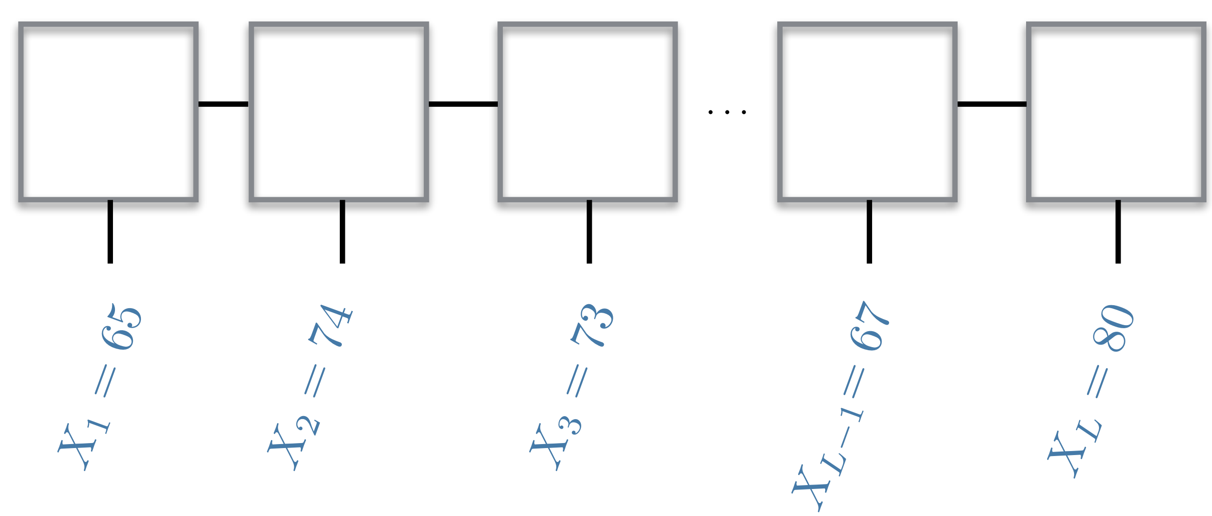
Matrix Product State (MPS) Ansatz

$$|p\rangle = \sum_{X_1, X_2, \ldots, X_L} c_{X_1, X_2, \ldots, X_L} |X_1, X_2, \ldots, X_L\rangle$$

$c_{65,74,\ldots,80} =$



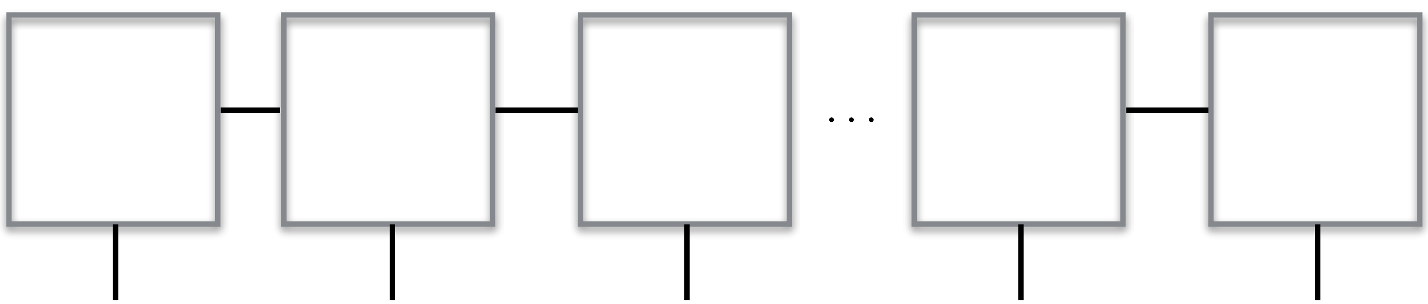
$\approx$



The spirit of the procedure...

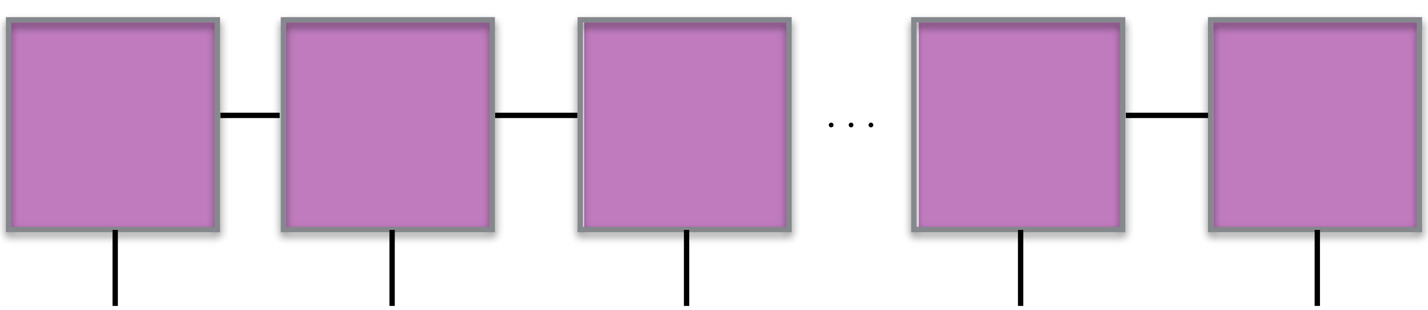
$$|p(t)\rangle = e^{\mathbb{W}t}|p(0)\rangle$$

$c_{X_1,X_2,\ldots,X_L} \approx$



Time t

$\approx$



Time $t + \Delta t$

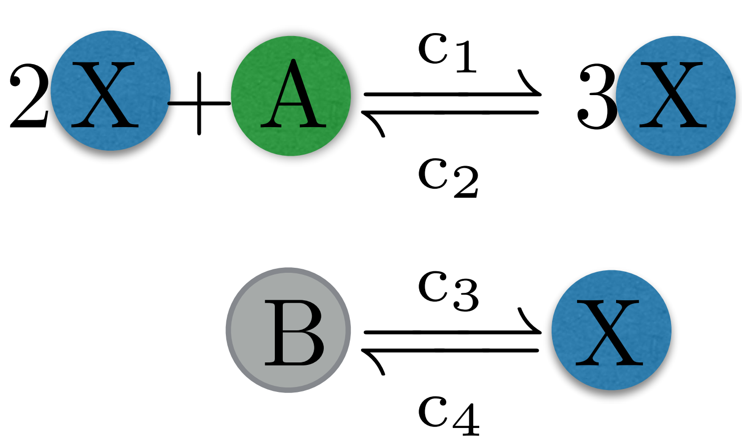
But how...?

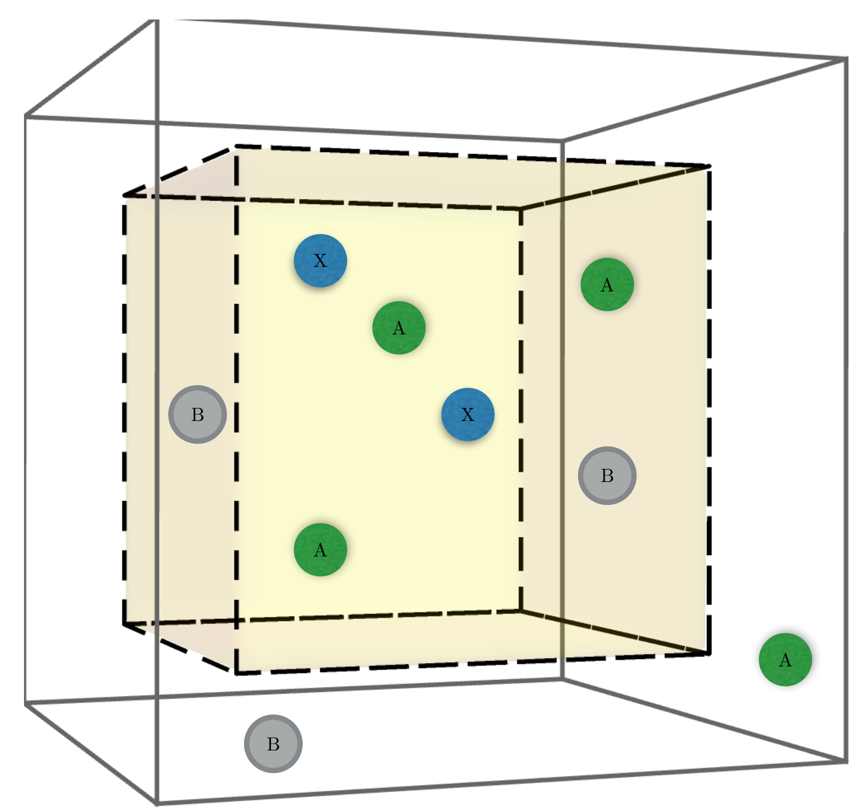
Doi-Peliti

$$\mathbb{W} = \mathbb{W}_{\mathrm{A}} + \mathbb{W}_{\mathrm{B}}$$

$$x^{\dagger 2}\left[\left(c_1 x^\dagger + c_2\left(\mathbb{I} - x^\dagger\right)x\right)x^2\right] \qquad x^\dagger(c_3 - c_4)x + c_4$$

Schlögl



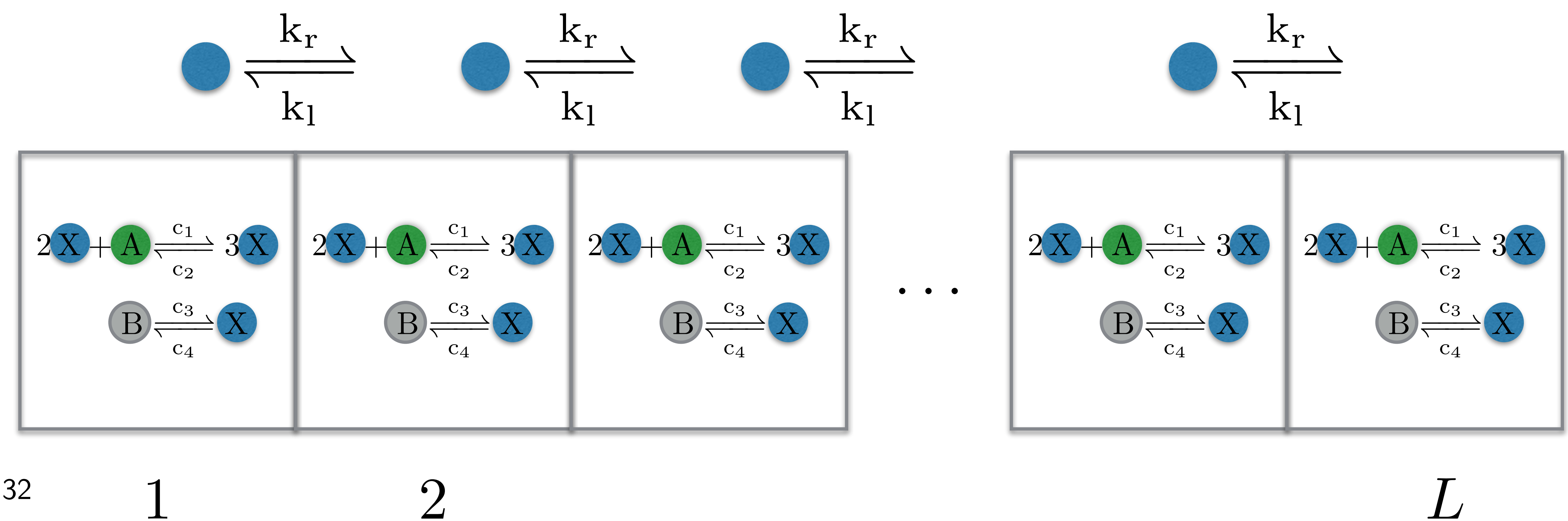


Doi-Peliti

$$\mathbb{W} = \mathbb{W}_{\mathrm{A}} + \mathbb{W}_{\mathrm{B}} + \mathbb{W}_{\mathrm{diff}}$$

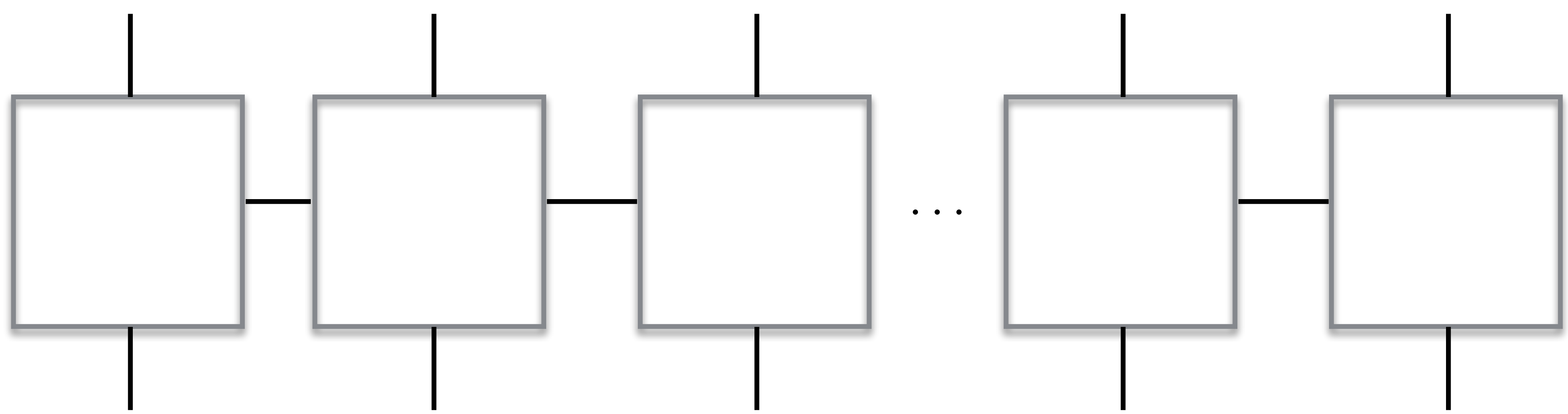
$$\sum_l {x_l^\dagger}^2 \left[\left(c_1 x_l^\dagger + c_2 \left(\mathbb{I} - x_l^\dagger \right) x_l \right) x_l^2 \right] + x_l^\dagger (c_3 - c_4) x_l + c_4$$

$$+ \sum_l k \left[\left(x_{l+1}^\dagger - x_l^\dagger \right) \left(x_l - x_{l+1} \right) \right]$$



Locality of interactions...

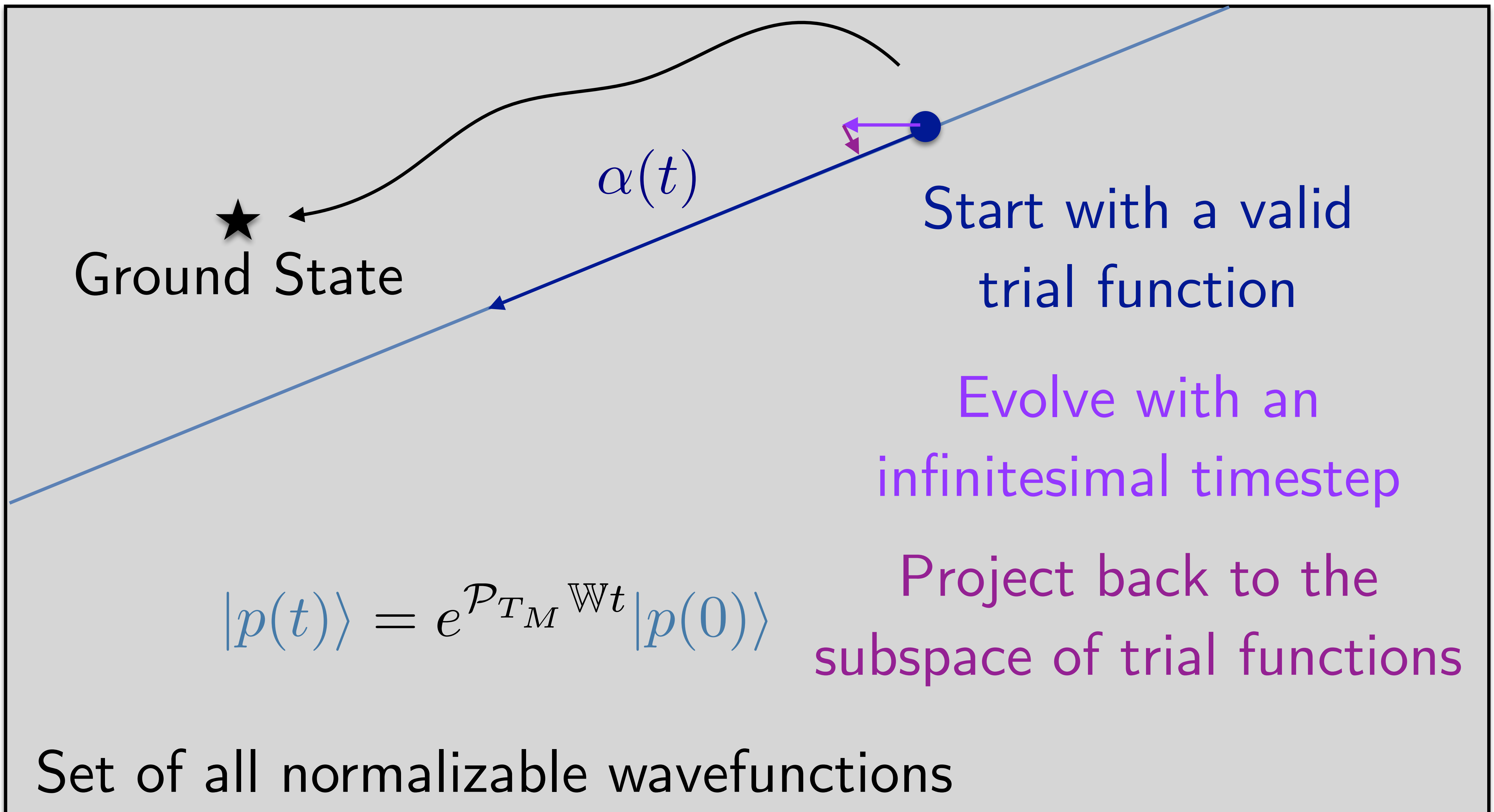
$$\mathbb{W} = \mathbb{W}_{\mathrm{A}} + \mathbb{W}_{\mathrm{B}} + \mathbb{W}_{\mathrm{diff}}$$

$=$ 

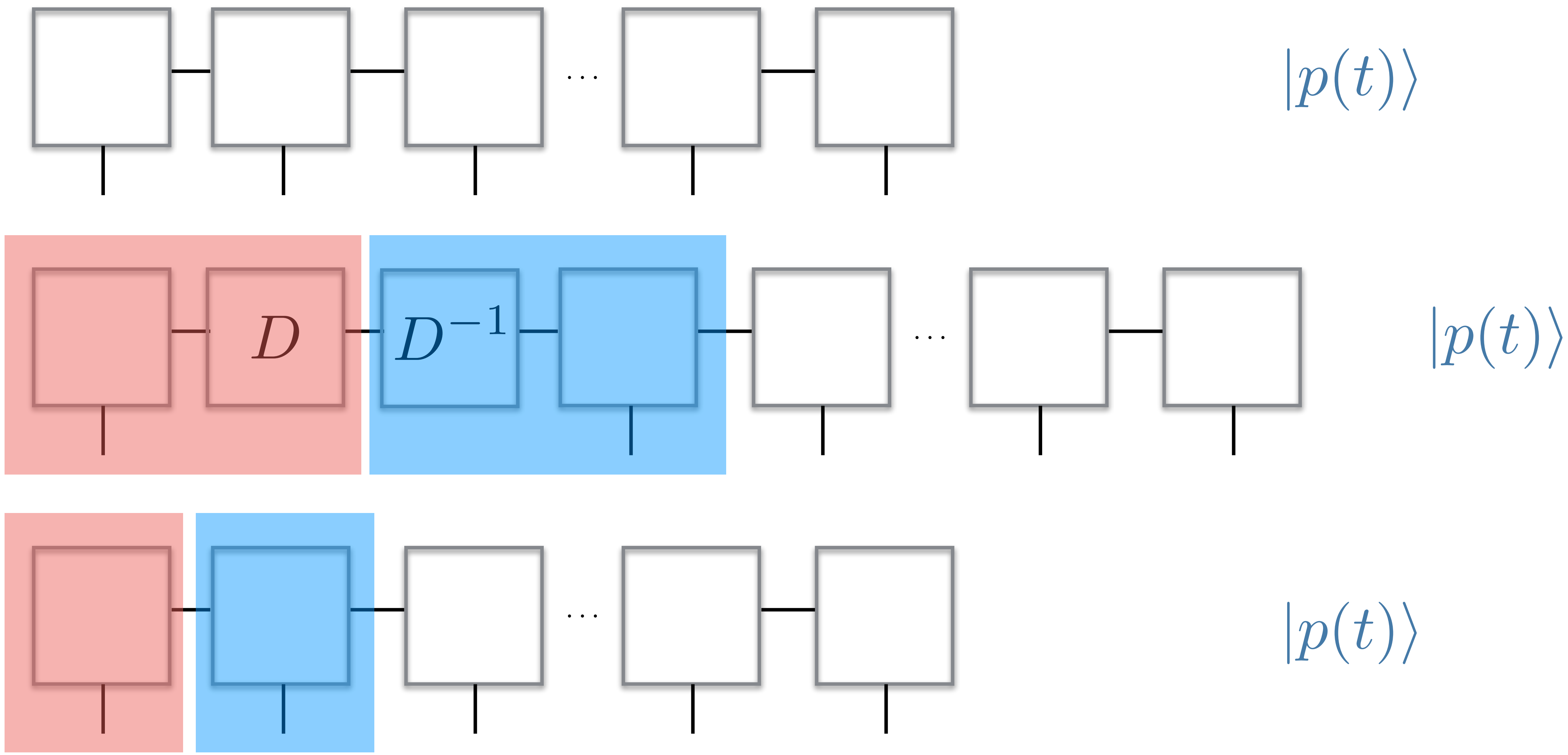
Matrix Product Operator (MPO)

$|p(t)\rangle = e^{\mathbb{W}t}|p(0)\rangle$ would leave the MPS manifold.

A time-dependent variational principle (TDVP)

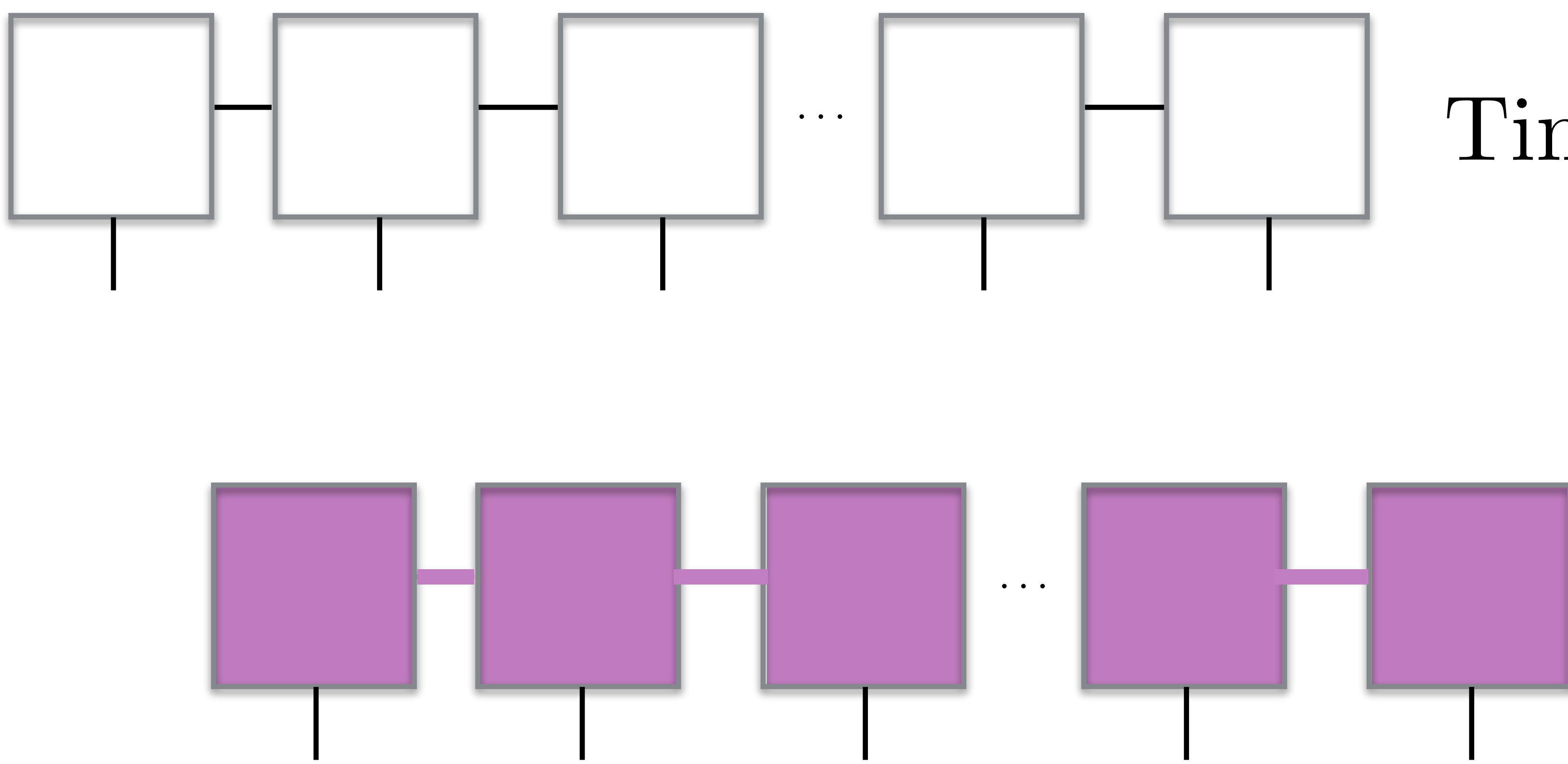


The algorithm furthermore leverages gauge freedoms in very clever ways



Single-site MPS TDVP

$$|p(t)\rangle = e^{\mathcal{P}_{T_M}\mathbb{W}t}|p(0)\rangle$$



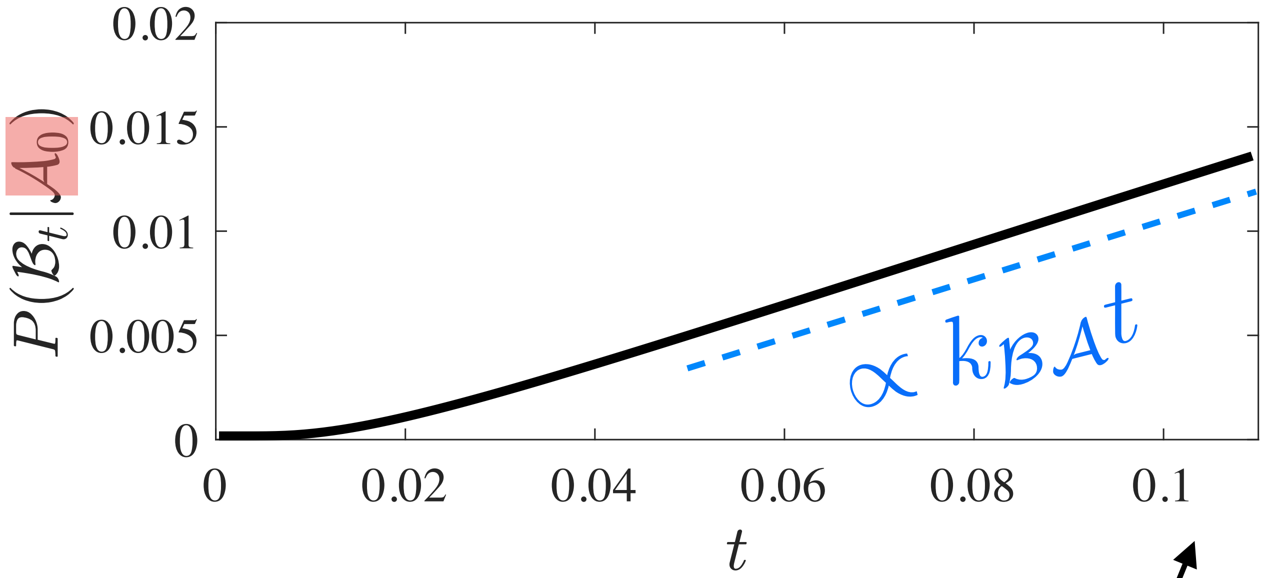
Time t

Time $t + \Delta t$

Haegeman et al. PRL (2011); Paeckel et al. Annals of Physics (2019); Haegeman et al. PRB (2016); Lubich et al. SIAM Numerical Analysis (2015)

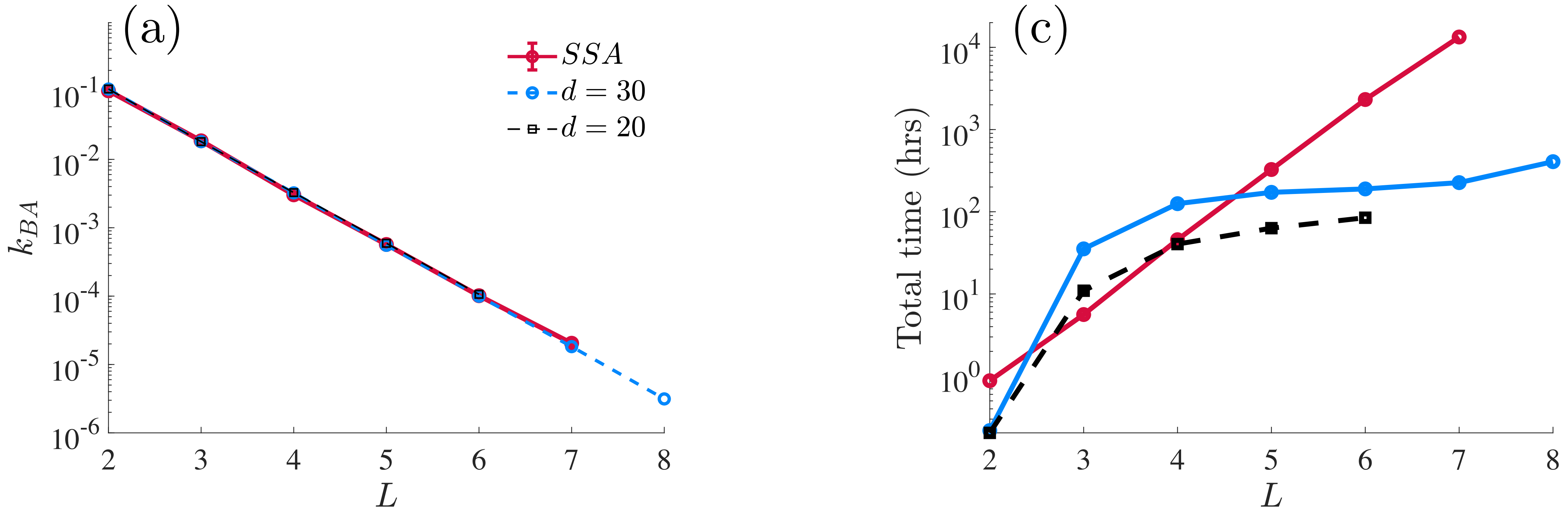
Rate calculations from propagators

$$\frac{\langle \mathbf{1}| \hat{\mathcal{P}}_{\mathcal{B}} e^{\mathbb{W}t} \hat{\mathcal{P}}_{\mathcal{A}} |p_{\text{ss}}\rangle}{\langle \mathbf{1}| \hat{\mathcal{P}}_{\mathcal{A}} |p_{\text{ss}}\rangle}$$



$$t << \frac{1}{k}$$

Can it work? Can it be useful?



S.B. Nicholson and T.R. Gingrich, arXiv:2301.03717, 2023.

Schuyler Nicholson
Postdoctoral Scholar

Emanuele Penocchio
Postdoctoral Scholar

Kathleen Krist
Postdoctoral Scholar

Nils Strand
Graduate Student

Rueih-Sheng (Ray) Fu
Graduate Student

Geyao Gu
Graduate Student

Jonah Greenberg
Graduate Student

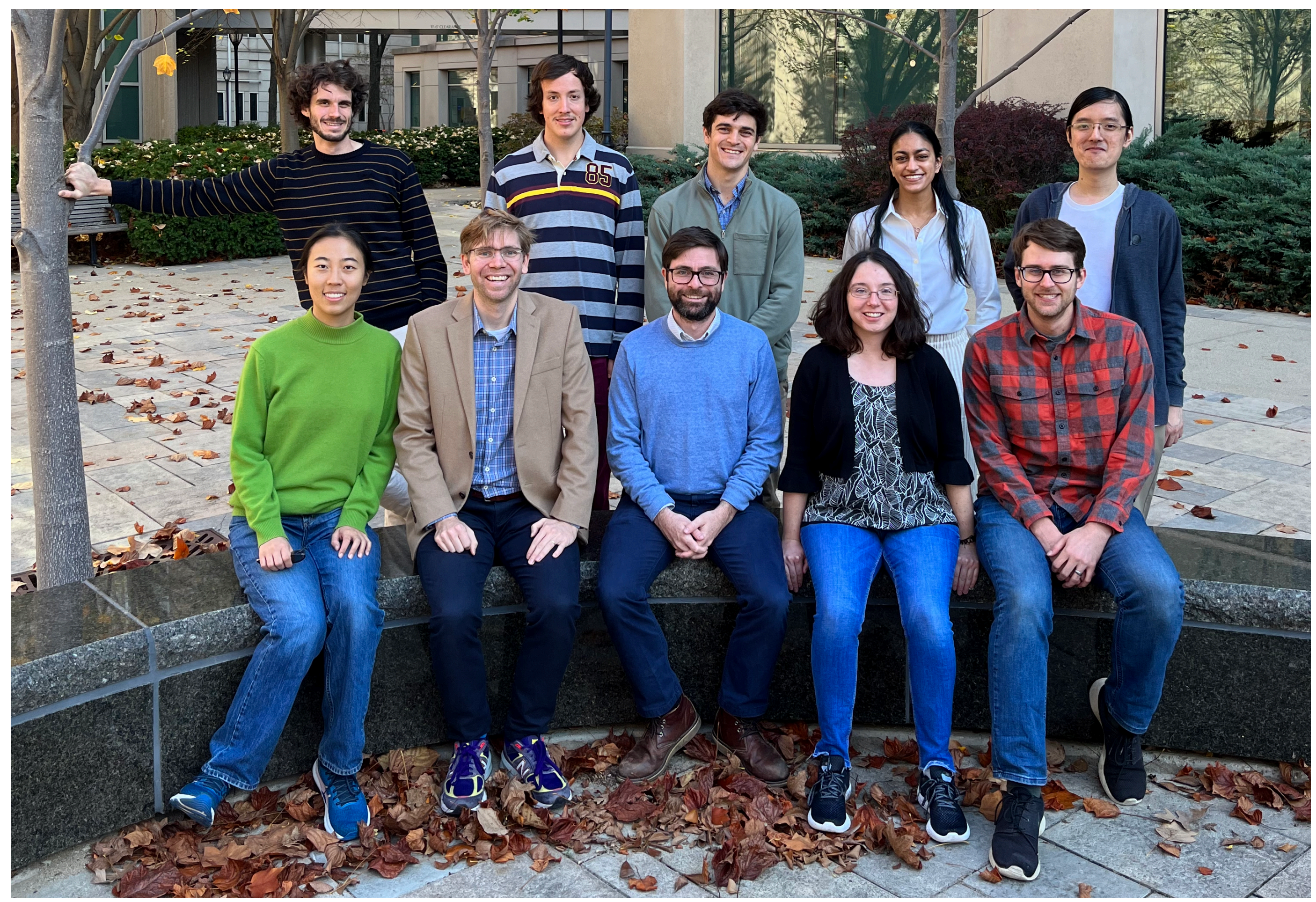
Kate Murphy
Graduate Student

Ashini Shah
Undergraduate Student

Alex Albaugh
Currently an Assistant Professor at Wayne State University

Niles Babin
Currently an Undergraduate at Harvey Mudd College

Hadrien Vroylandt
Currently at Sorbonne Université



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GORDON AND BETTY MOORE FOUNDATION

N.E. Strand, H. Vroylandt, and T.R. Gingrich, *JCP*, 156, 221103, 2022.
N.E. Strand, H. Vroylandt, and T.R. Gingrich, *JCP*, 157, 054109, 2022.
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