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Transition State Theory in Driven Systems

Methods

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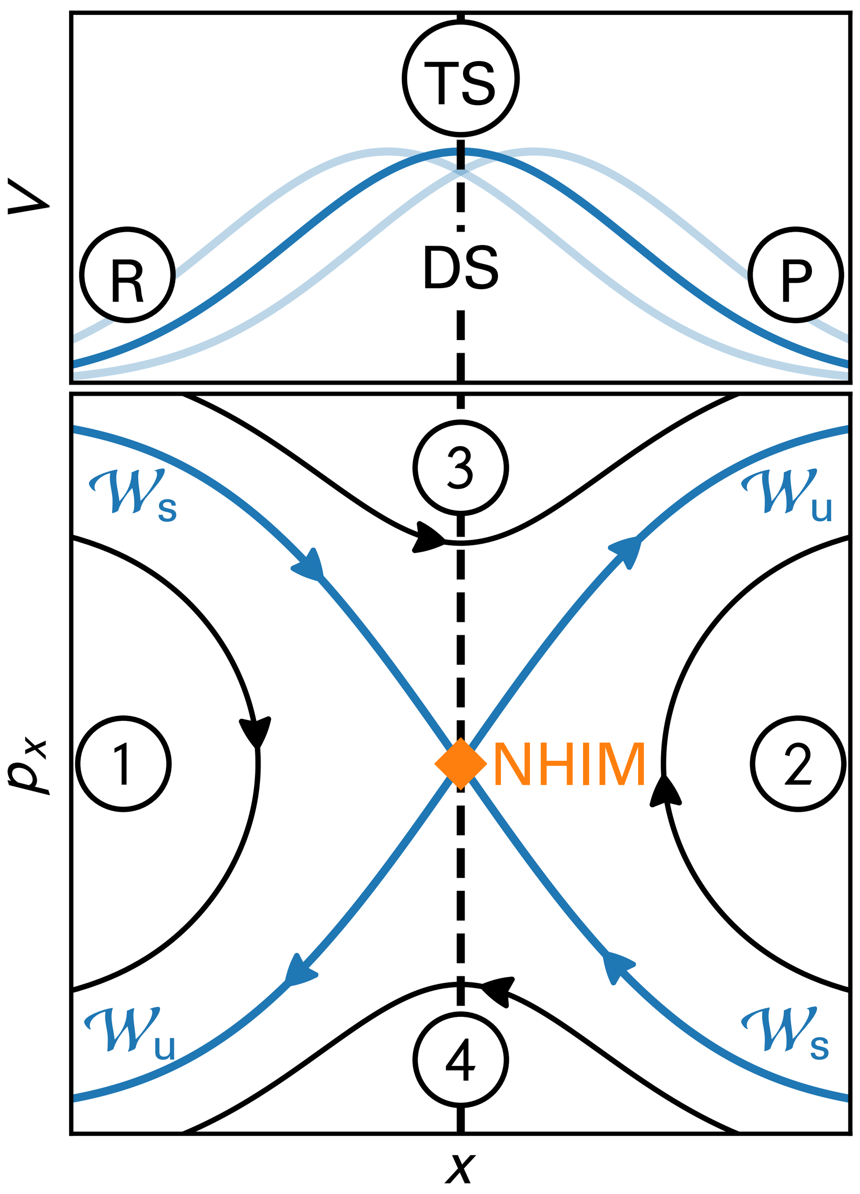
Abstract: Decay rates can be used to quantify the stability of systems. We present methods for calculating such rates in the framework of transition state theory.

Transition State Theory (TST)



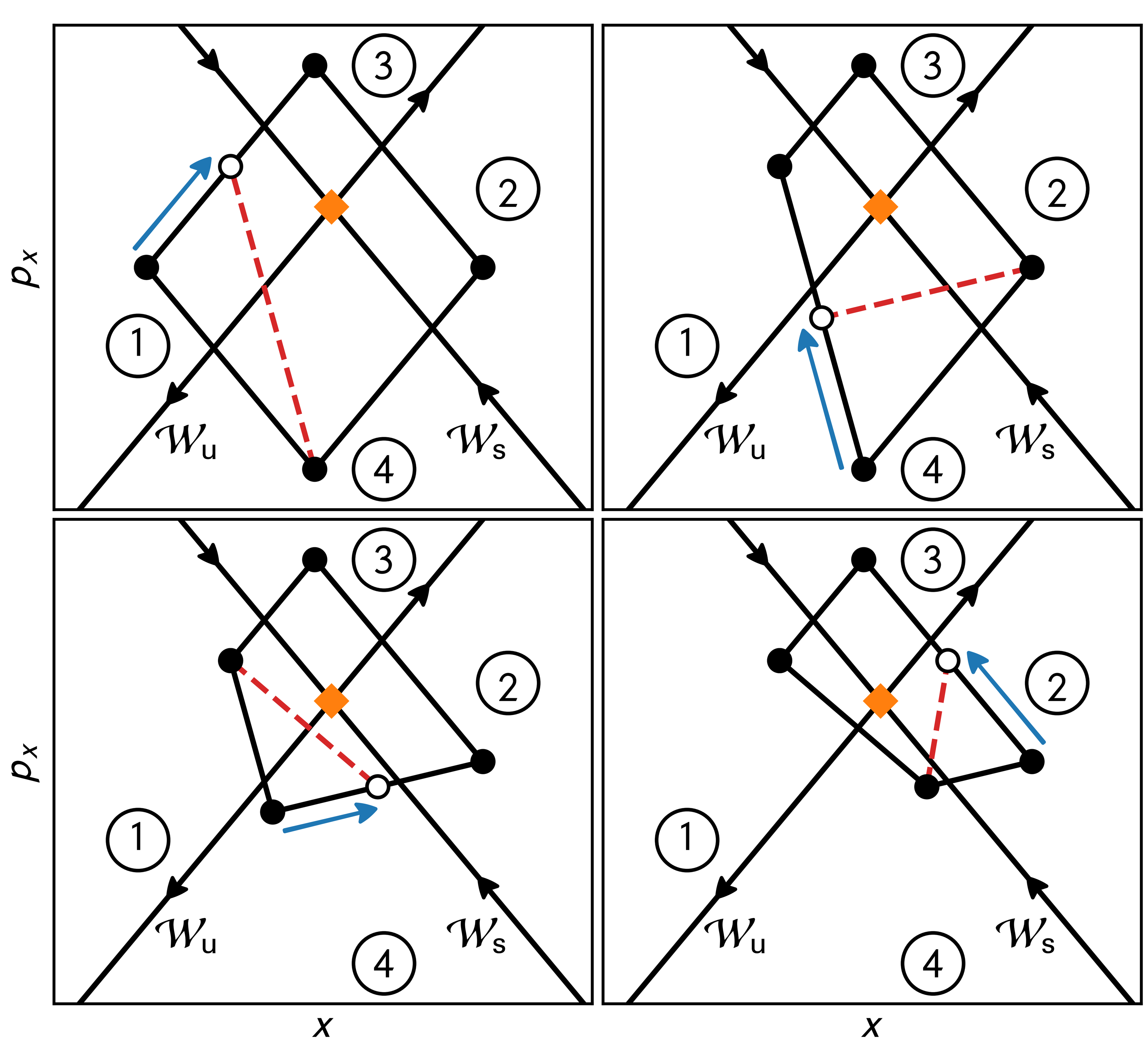
Basic concepts:

- effective particle on a PES with rank-1 saddle
- dividing surface (DS) separates reactants (R) and products (P)
- transition state (TS)
- stable and unstable manifolds ($\mathcal{W}_s$, $\mathcal{W}_u$)
- normally hyperbolic invariant manifold (NHIM)
- four reactive and nonreactive regions

An external driving makes the construction of the DS nontrivial, even in simple cases with one degree of freedom. The NHIM can act as an anchor for a recrossing-free DS.

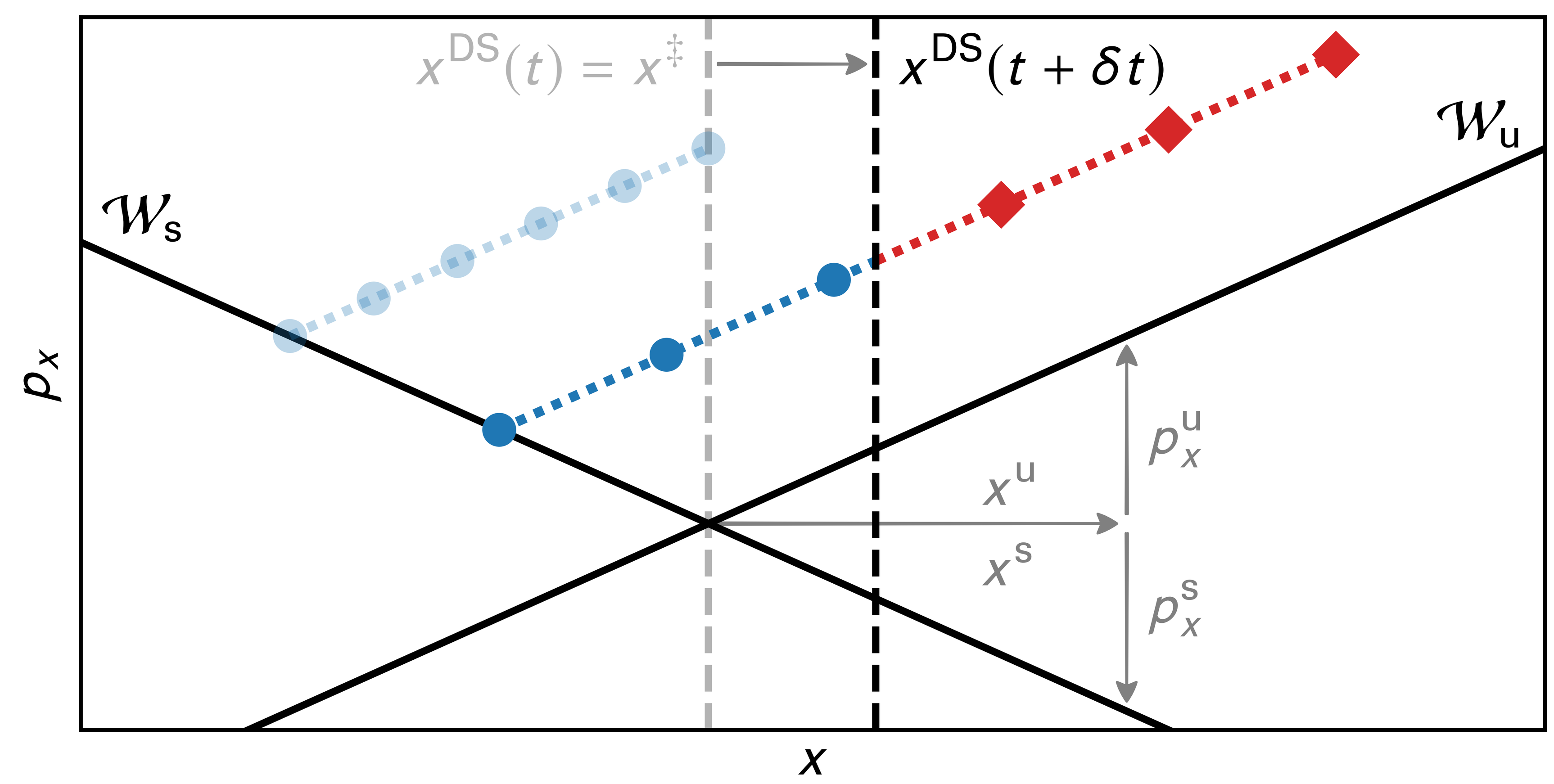
M. Feldmaier, P. Schraft, R. Bardakcioglu, J. Reiff, et al., J. Phys. Chem. B **123**, 2070–2086 (2019)

Binary Contraction Method (BCM)



R. Bardakcioglu, A. Junginger, M. Feldmaier, J. Main, and R. Hernandez, Phys. Rev. E **98**, 032204 (2018)

Local Manifold Analysis (LMA)



Flux-over-population rate:

$$k(t) = -\frac{\dot N(t)}{N(t)} = -\lim_{\delta t\to 0} \frac{N(t+\delta t)-N(t)}{N(t)\,\delta t}$$

Linearized dynamics via Jacobian:

$$\dot{\boldsymbol\gamma}(t) = \boldsymbol J\left(t;\boldsymbol\gamma^\ddagger\right)\boldsymbol\gamma(t)$$

After propagating from t to $t+\delta t$:

$$\frac{N(t+\delta t)}{N(t)} = \frac{x^s(t+\delta t)}{x^s(t)}\,\frac{x^u(t)}{x^u(t+\delta t)} = \frac{x^s(t+\delta t)}{x^u(t+\delta t)}$$

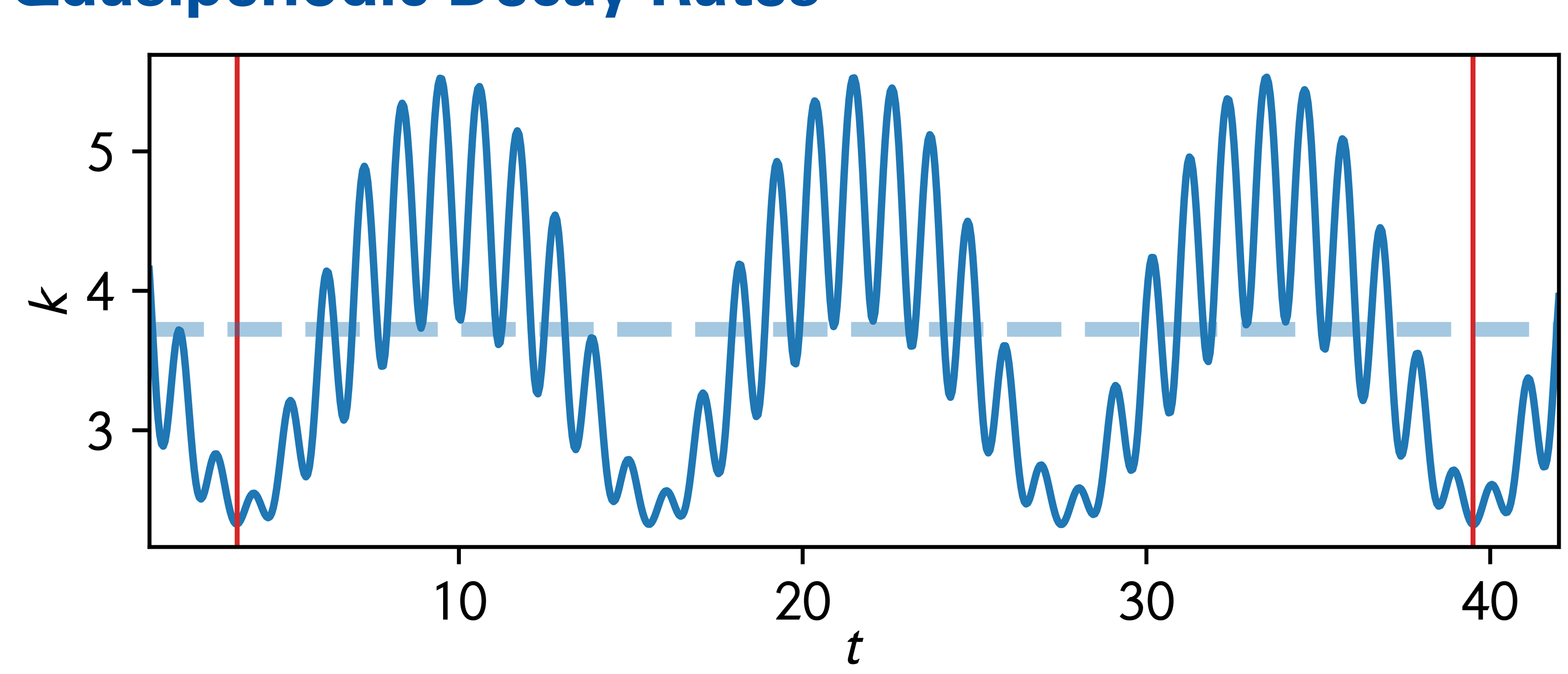
Result (including DS correction):

$$k\left(t;\boldsymbol\gamma^\ddagger\right) = J_{x,p_x}(t)\,\frac{p_x^u(t)-p_x^s(t)}{x^u(t)} - \frac{x^{DS}(t+\delta t)}{x^u(t)\,\delta t}$$

This decay rate describes the stability of trajectories on the NHIM. Instantaneous and average results agree with those obtained via ensemble propagation and Floquet analysis.

J. Reiff, J. Zatsch, J. Main, and R. Hernandez, Commun. Nonlinear Sci. Numer. Simul. **104**, 106053 (2022)

Quasiperiodic Decay Rates



Many orbits on the NHIM (and their rates) are quasiperiodic. Appropriate intervals can still yield accurate averages.

M. Feldmaier, R. Bardakcioglu, J. Reiff, J. Main, and R. Hernandez, J. Chem. Phys. **151**, 244108 (2019)

Founded by the DFG, the NSF, and the EU's Horizon 2020 Program (TraX).