Transition state theory for solvated reactions beyond recrossing-free dividing surfaces

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Transition state theory for solvated reactions beyond recrossing-free dividing surfaces

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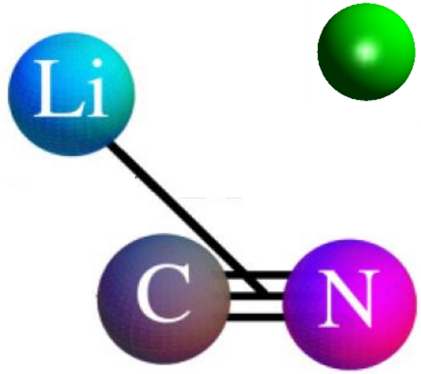
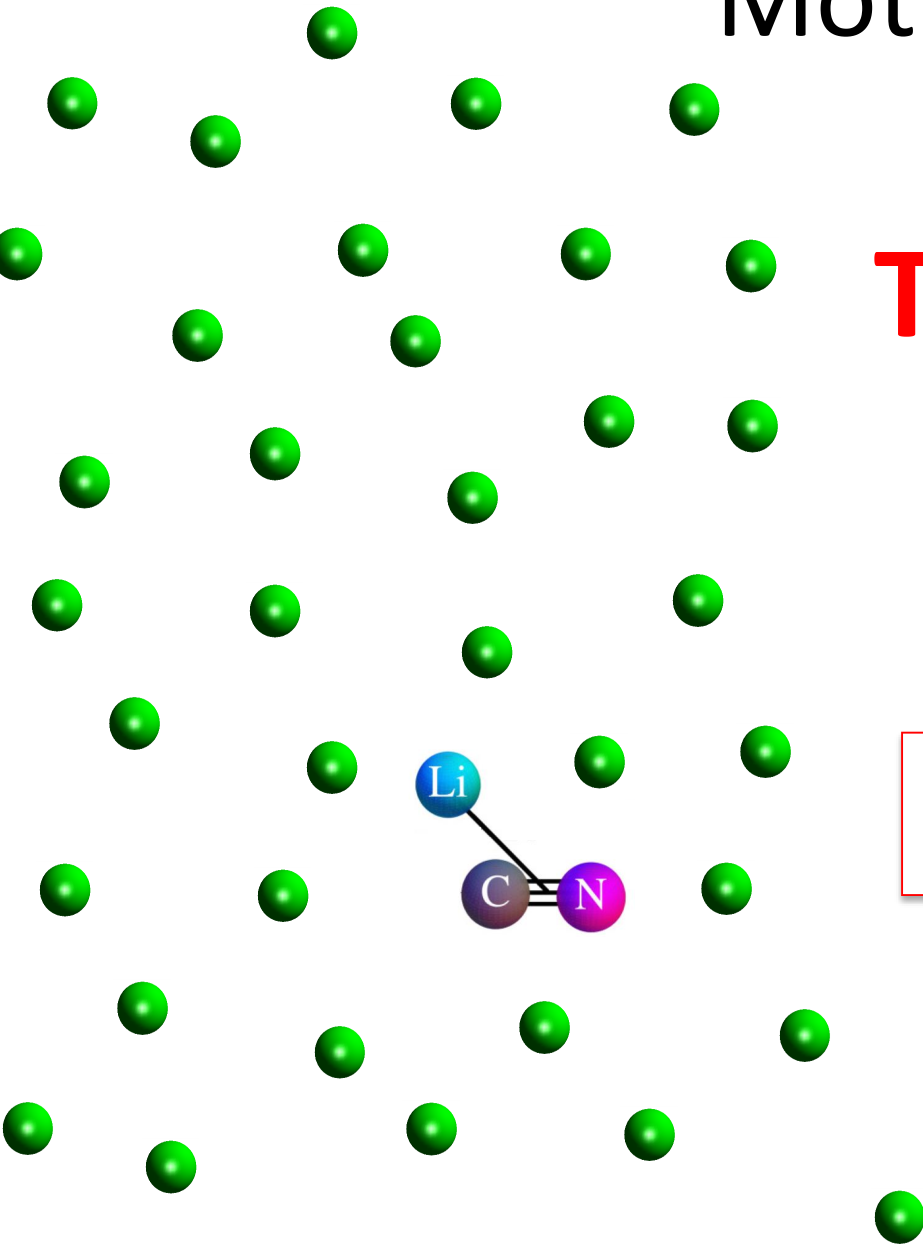
Motivation

Rate calculations are computationally very **demanding**

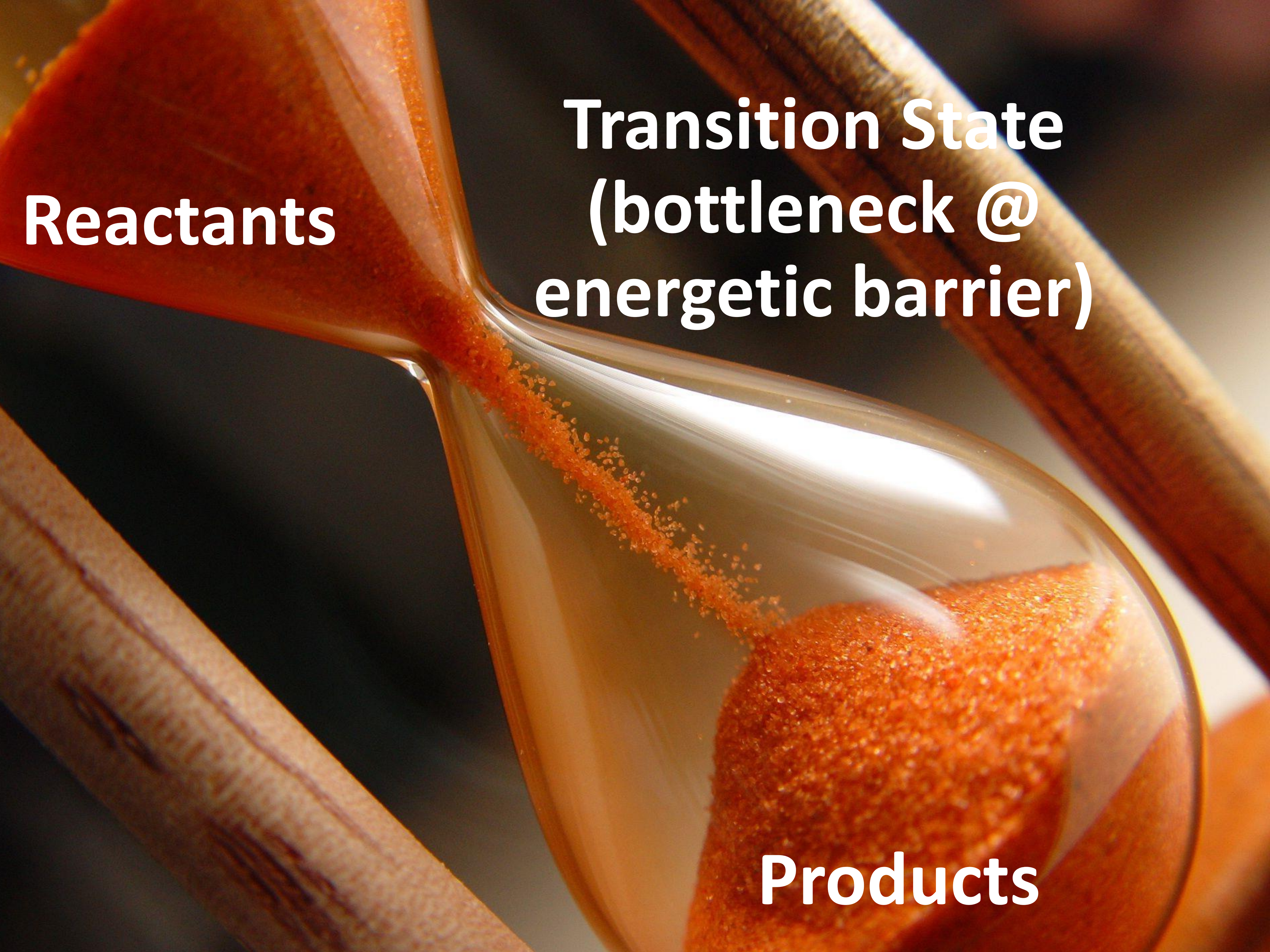


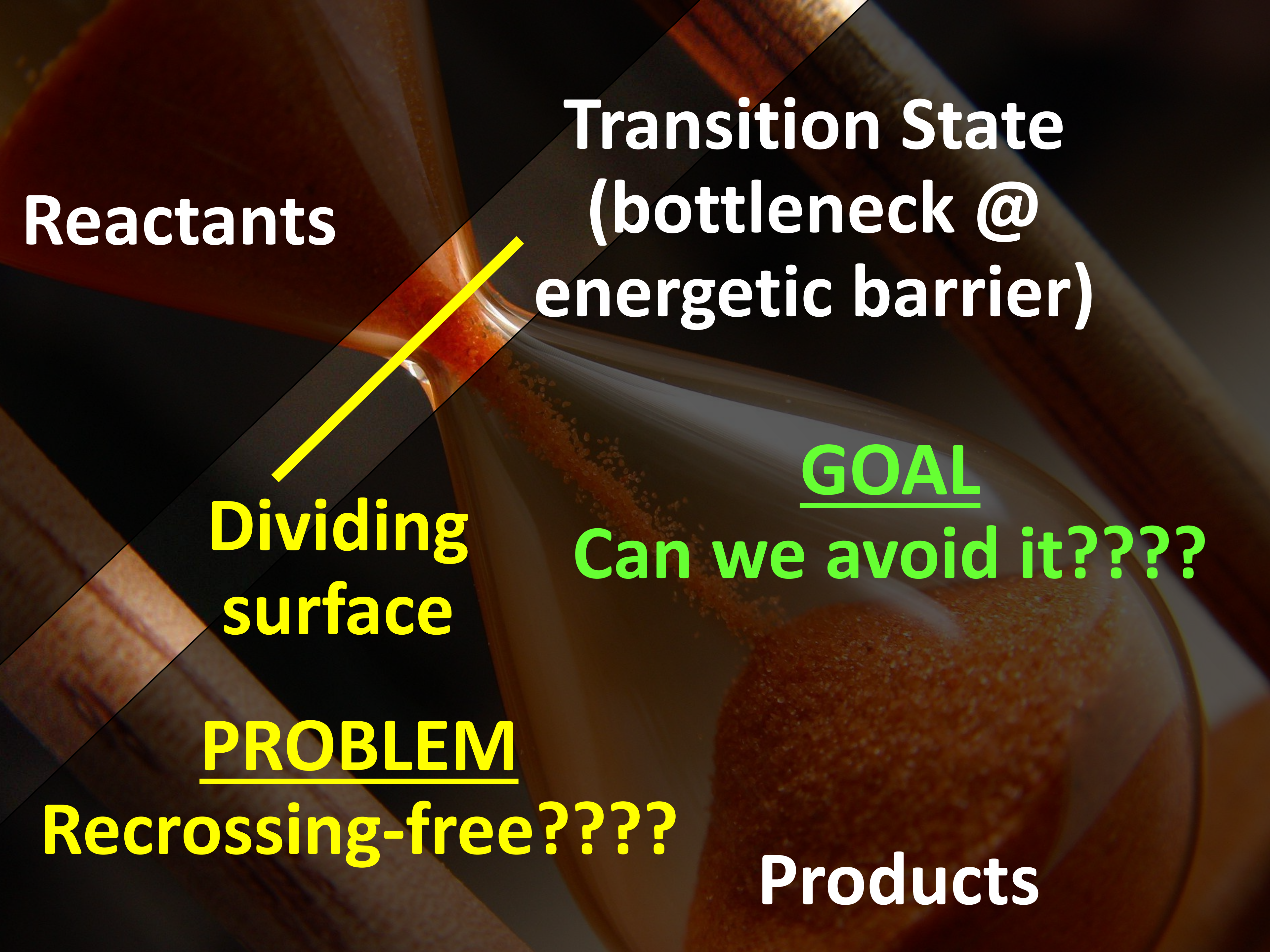
Motivation



Transition State Theory

?


Reactants
Transition State
(bottleneck @
energetic barrier)
Products


Transition State
(bottleneck @
energetic barrier)
Reactants
Dividing
surface
GOAL
Can we avoid it????
PROBLEM
Recrossing-free????
Products

Outline

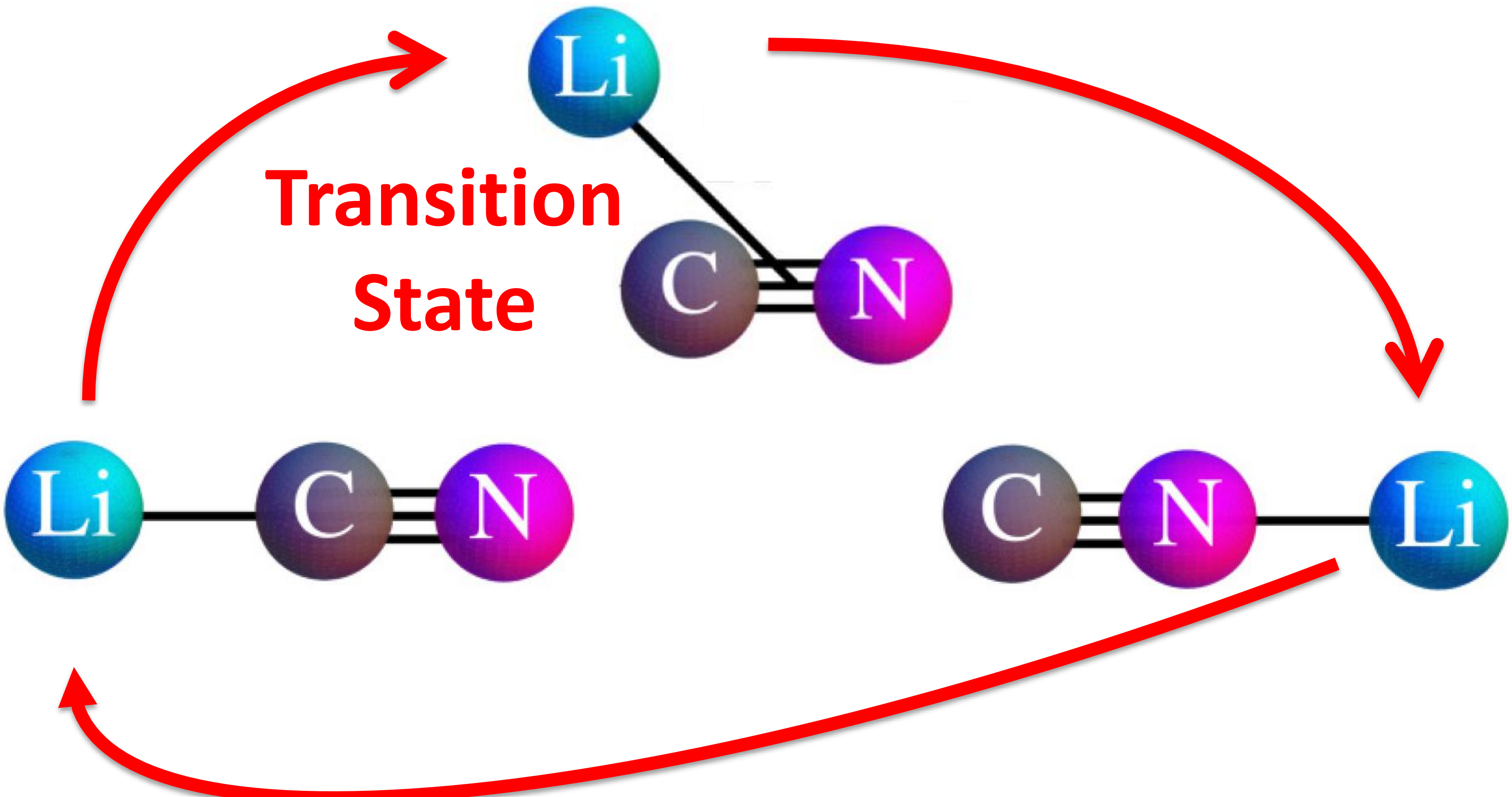
1. **System and model under study**

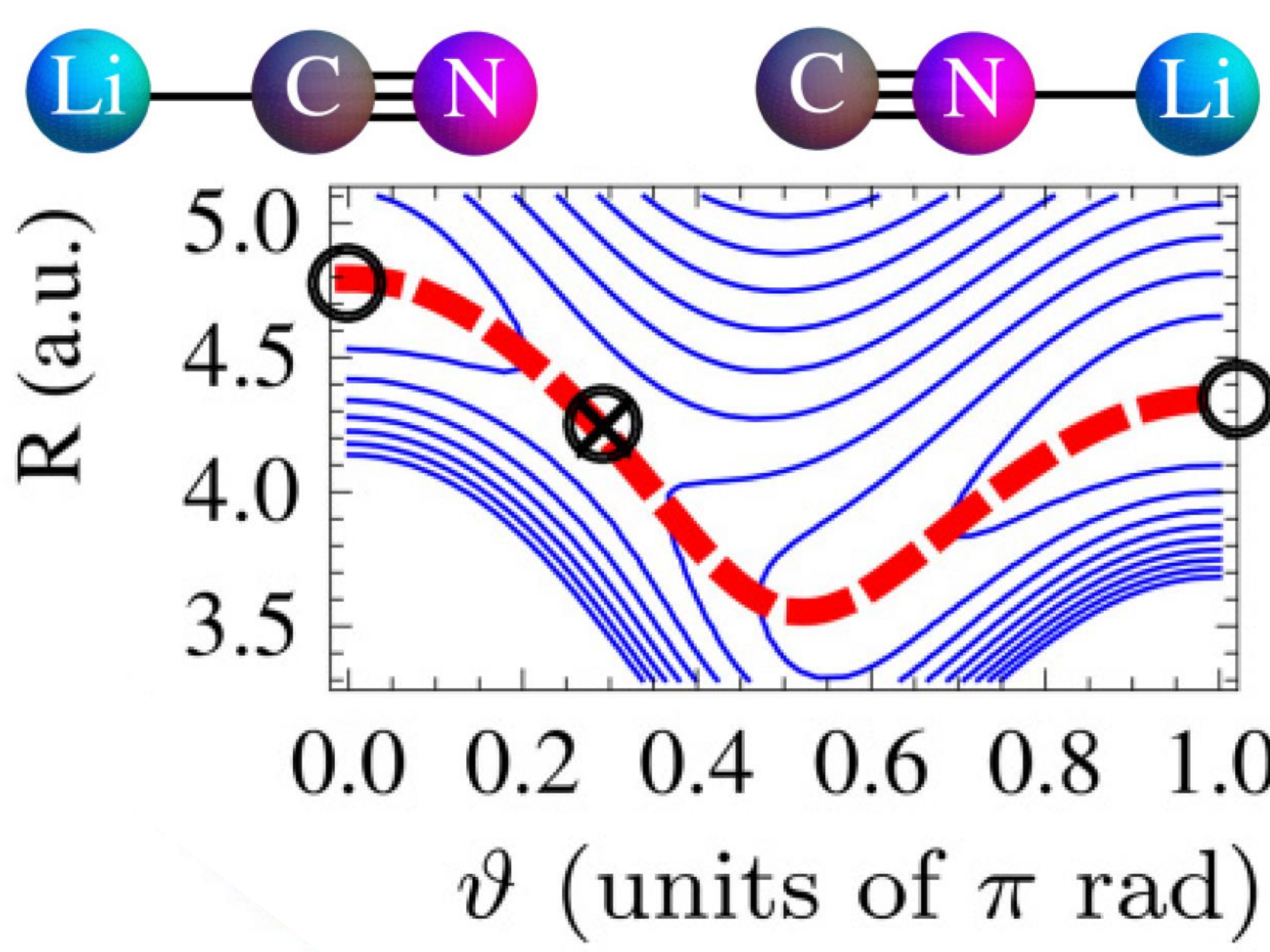
2. A recrossing-free dividing surface?

3. Results

4. Conclusions

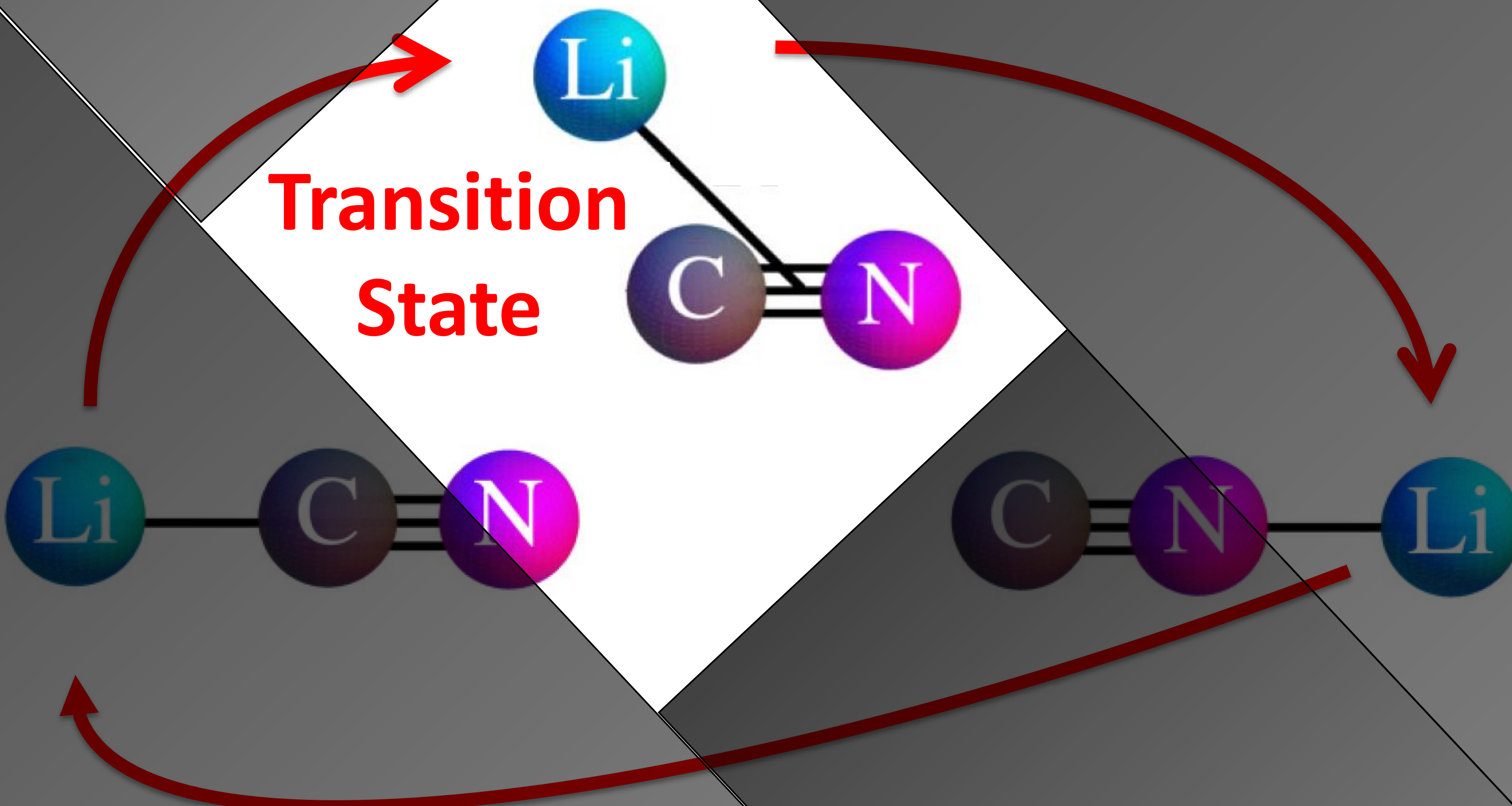
System
LiCN/LiCN isomerizing reaction





Li
C
N
C
N
Li
R (a.u.)
5.0
4.5
4.0
3.5
0.0
0.2
0.4
0.6
0.8
1.0
ϑ (units of π rad)

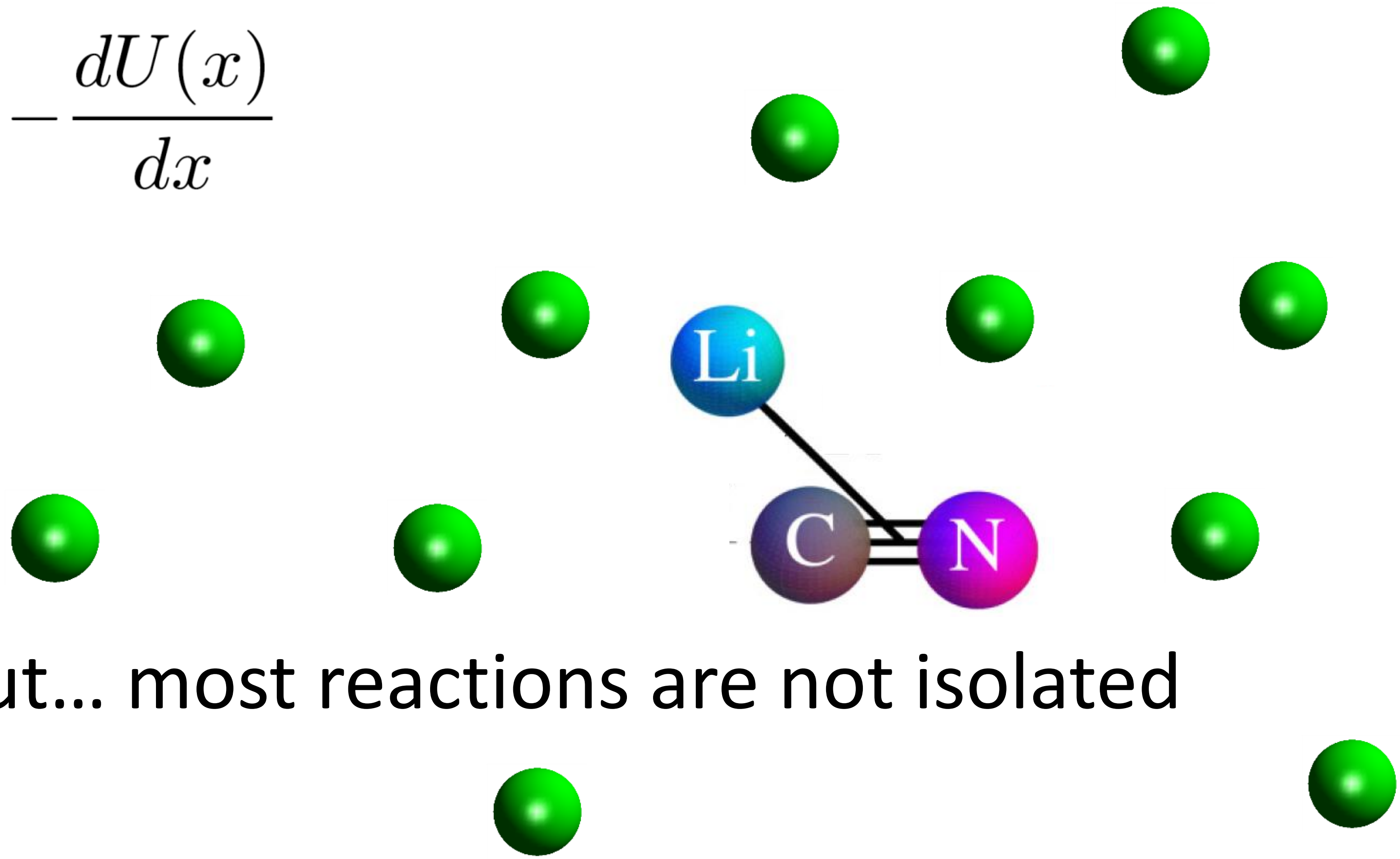
System
LiCN/LiCN isomerizing reaction



Model

$$m\ddot{x} = -\frac{dU(x)}{dx}$$

Argon bath



But… most reactions are not isolated

Model: Generalized Langevin Equation

$$m\ddot{x} = -\frac{dU(x)}{dx} - m\int_{-\infty}^{t} \gamma(t-s)\,\dot{x}(s)\,ds + mR_\alpha(t)$$

Potencial force

Friction (memory)

Environment force

$$\langle R_\alpha(t) R_\alpha(0)\rangle = \frac{k_\mathrm{B}T}{m}\gamma(t) = \frac{k_\mathrm{B}T}{m}\frac{\gamma_0}{\tau}e^{-t/\tau}$$

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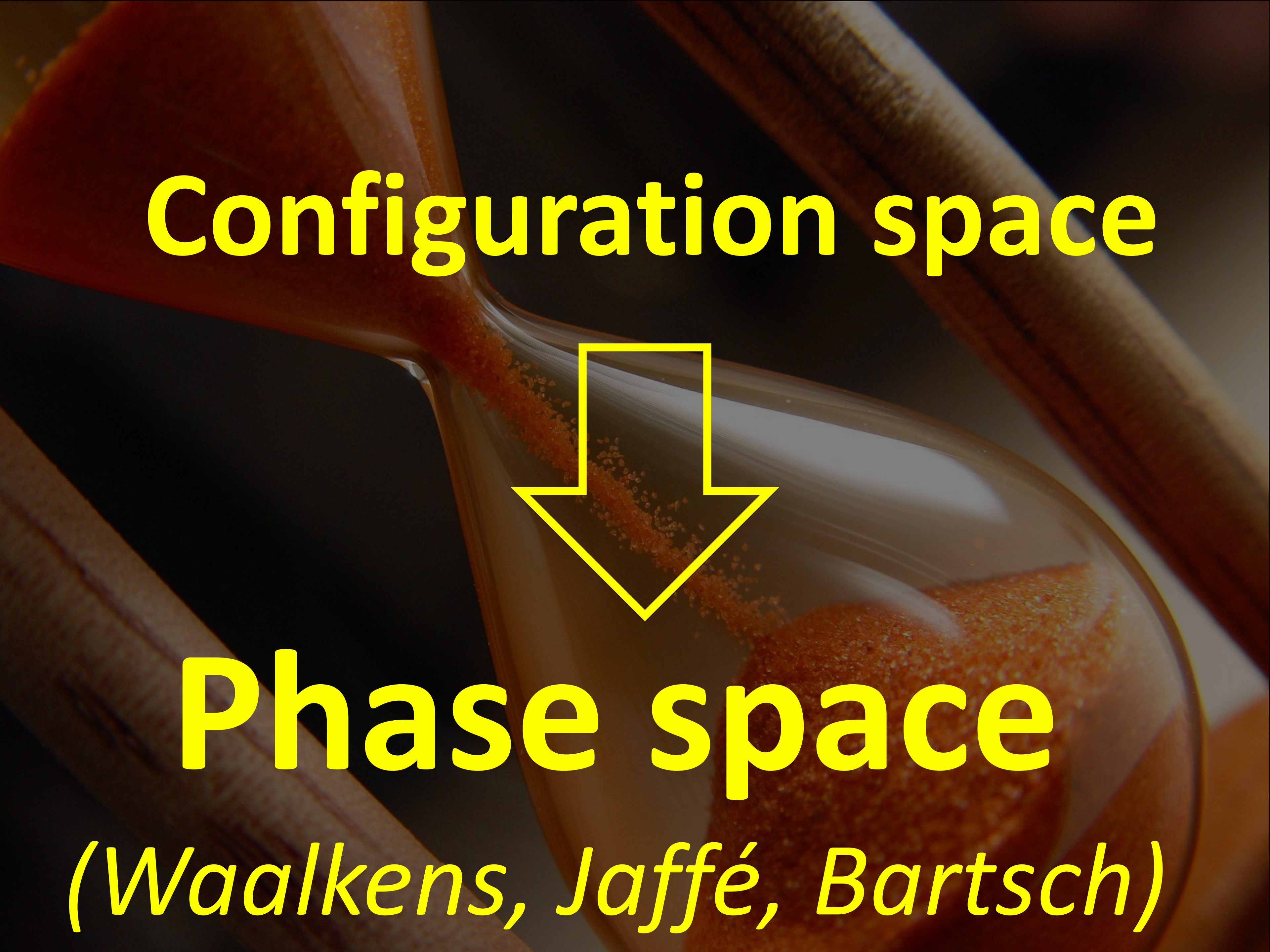
A recrossing-free dividing surface?

TS trajectory
(T. Bartsh)

Separatrices

(invariant manifolds)


Configuration space
Phase space
(Waalkens, Jaffé, Bartsch)

Method

1. Make a **Taylor expansion** of the potential around the saddle point @ energetic barrier (transition state)
2. Add a new **variable** to account for the memory effects in the bath
3. Compute the **TS trajectory**
4. Identifify the **structures** that **separate** reactive from nonreactive trajectories.

Method (solution of GLE)

$$m\ddot{x} = -\frac{dU(x)}{dx} - m\int_{-\infty}^{t} \gamma(t-s)\,\dot{x}(s)\,ds + mR_{\alpha}(t)$$

1. Substitute the effect of the **memory** with a **new variable** *(Martens, Ferrari…)*

$$\zeta = -\int_{-\infty}^{t} \gamma(t-s)\,\dot{x}(s)\,ds$$

Method

Then, the equations of motion read…

$$\dot{x} = v$$

$$\dot{v} = -\frac{1}{m}\frac{dU(x)}{dx} + \zeta$$

$$\dot{\zeta} = -\frac{\gamma_0}{\tau}v - \frac{1}{\tau}\zeta + \xi_\alpha(t)$$

White noise!

$$\langle \xi_\alpha(t)\xi_\alpha(s)\rangle_\alpha = \frac{2k_{\mathrm{B}}T\,\gamma_0}{m\tau^2}\,\delta(t-s)$$

Method

2. Change to **diagonal coordinates**

$$(\lambda_i - \lambda_j)(\lambda_i - \lambda_k)\, z_i = (\lambda_j \lambda_k + \omega_{\mathrm{b}}^2) x - (\lambda_j + \lambda_k) v + \zeta$$

where the equations of motion read...

$$\dot{z}_i = \lambda_i z_i + K_i\, f(x) + \frac{1}{F_i}\, \xi_\alpha(t)$$

Method

3. Change to **diagonal coordinates**

$$\Delta z_i(t) = z_i(t) - z_i^{\ddagger}(t)$$

$$z_i^{\ddagger}(t) = \frac{1}{F_i} S[\lambda_i, \xi_\alpha; t]$$

TS trajectory

$$S_{t'}[\mu, g; t] = \begin{cases} -\int_t^{\infty} g(t') \, \exp(\mu(t-t'))\, dt' & : \ \mathrm{Re}\,\mu > 0, \\ +\int_{-\infty}^{t} g(t') \, \exp(\mu(t-t'))\, dt' & : \ \mathrm{Re}\,\mu < 0. \end{cases}$$

Method

The equations of motion in diagonal coordinates

$$\Delta \dot{z}_i = \lambda_i \Delta z_i + K_i f(x)$$

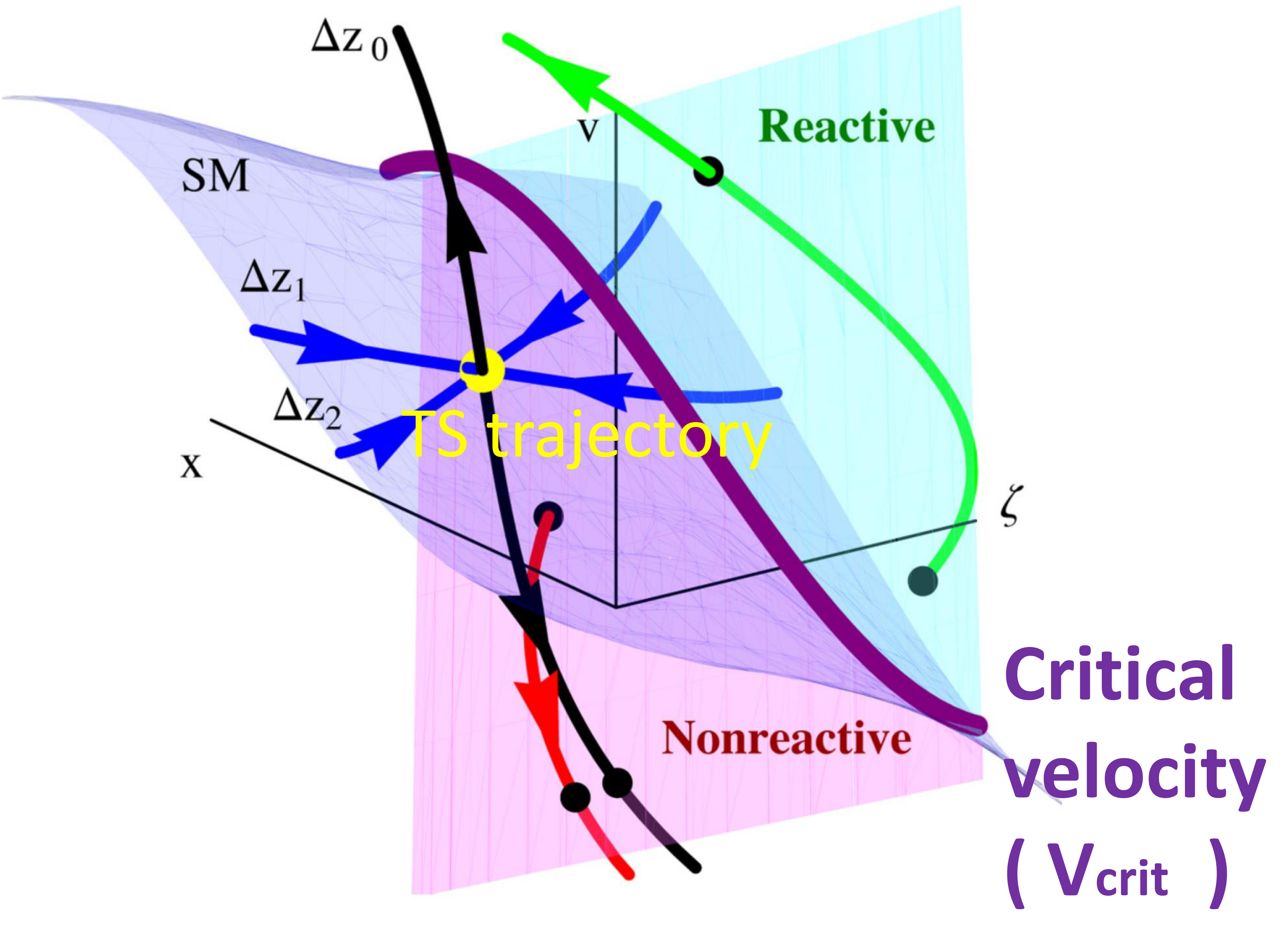
$$\Delta z_j(t) = \Delta z_j(0) e^{\lambda_j t}$$

Method

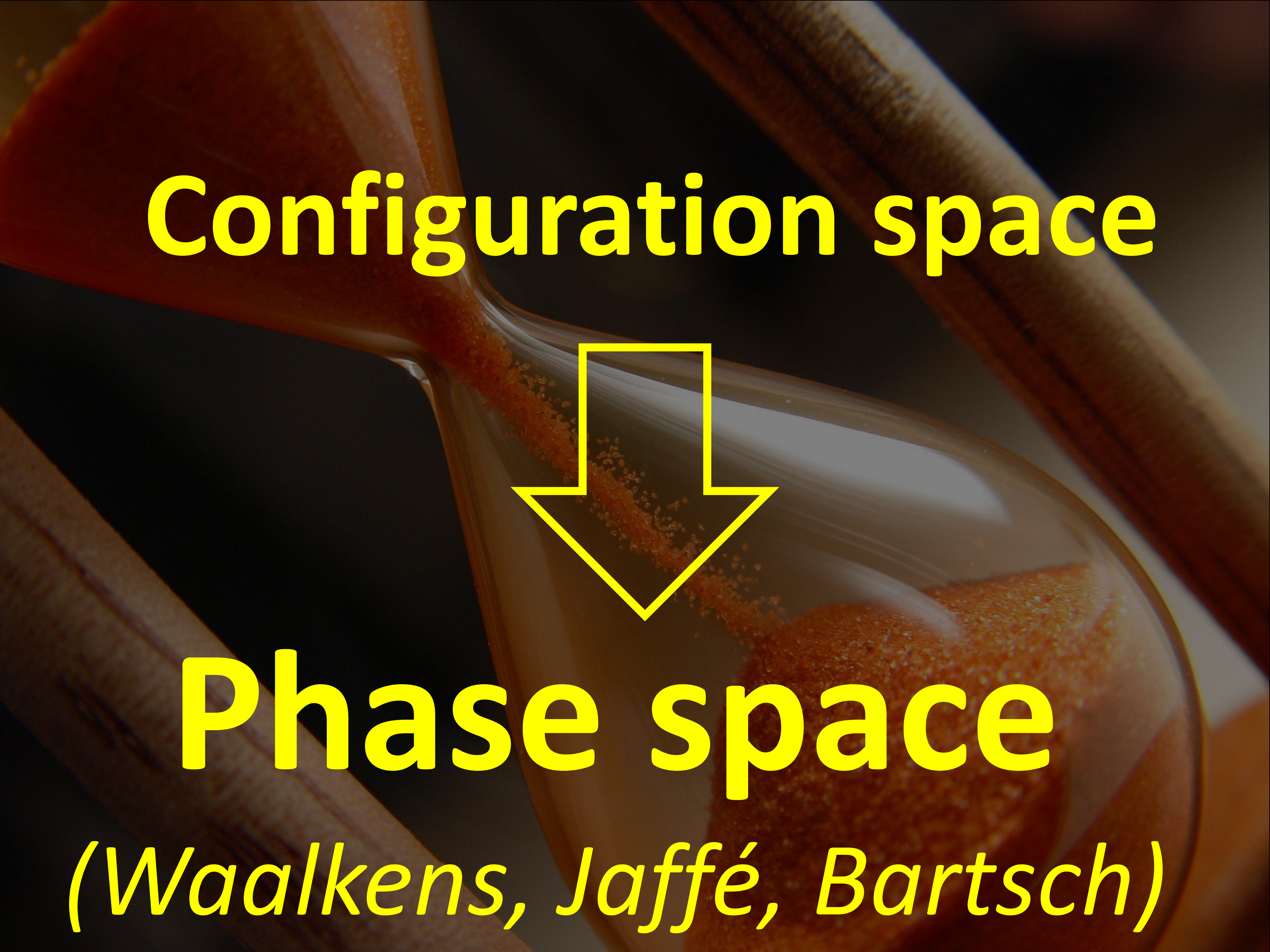
The equations of motion in diagonal coordinates

$$\Delta \dot{z}_i = \lambda_i \Delta z_i + K_i f(x)$$

$$\Delta z_j(t) = \Delta z_j(0) e^{\lambda_j t}$$ + h.c.t.



Δz 0
SM
v
Reactive
Δz1
Δz2
x
TS trajectory
ζ
Nonreactive
Critical
velocity
(Vcrit)


Configuration space
Phase space
(Waalkens, Jaffé, Bartsch)

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Results

- Using **invariant manifolds**, we can identify **reactive trajectories** uniquely.
- We have obtained **explicit anharmonic corrections** to **Grote-Hynes** expression (also in potentials with several dof!).

Transmission factor

$$\kappa = \frac{k_{\text{exact}}}{k_{\text{TST}}} = \left\langle e^{-mV^{\ddagger\,2}/2k_{\text{B}}T} \right\rangle_{\alpha,\zeta}$$

$$\kappa = \kappa^{(0)} + \varepsilon\kappa^{(1)} + \varepsilon^2\kappa^{(2)} + \ldots$$

Transmission factor

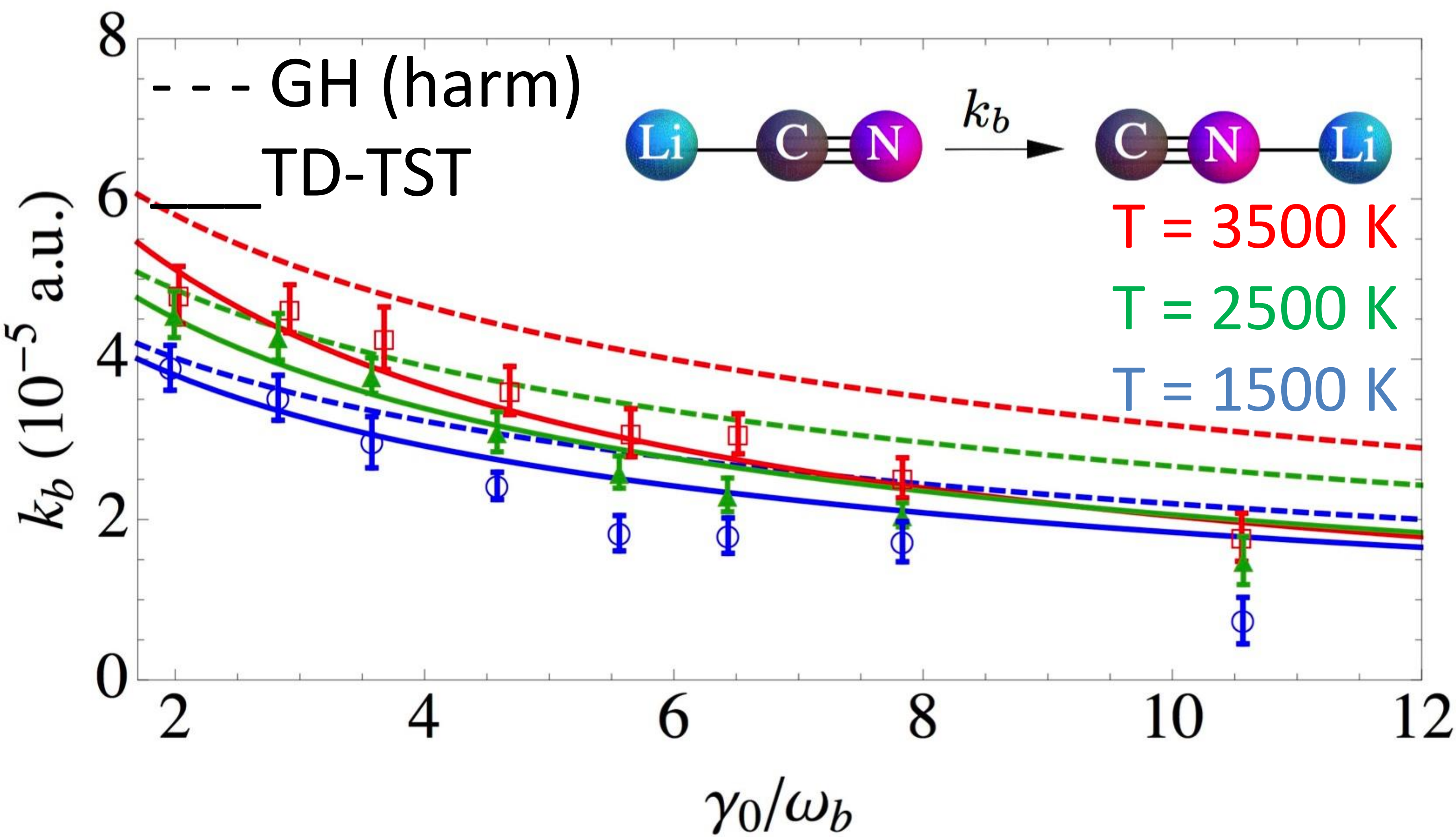
$$\kappa = \kappa^{(0)} + \varepsilon\kappa^{(1)} + \varepsilon^2\kappa^{(2)} + \ldots$$

$$\kappa^{(0)} = \frac{\lambda_0}{\omega_\mathrm{b}}$$

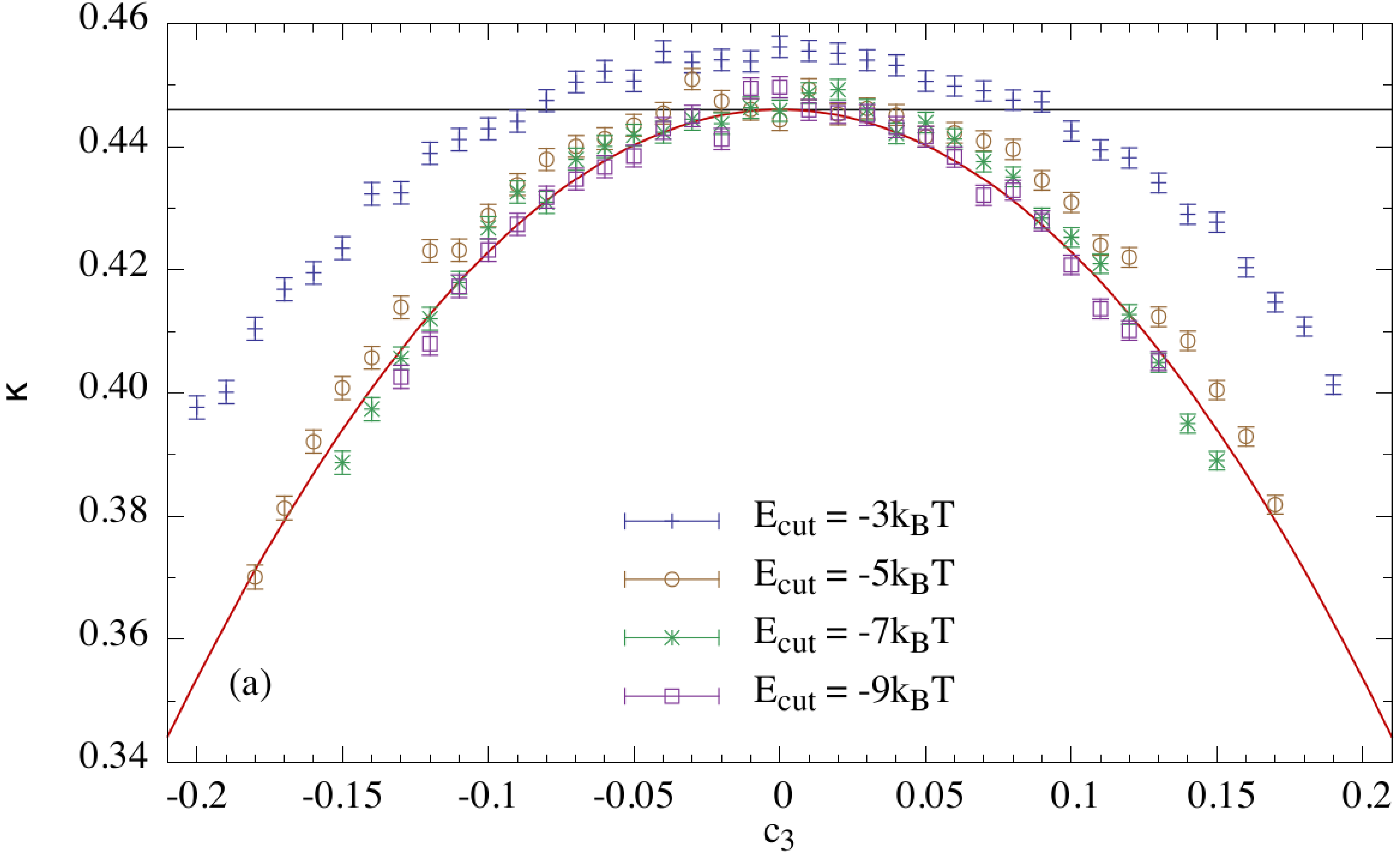
Grote-Hynes expression (harmonic limit)

$$\kappa^{(2)} = -\frac{c_3^2\, k_\mathrm{B} T}{6m\omega_\mathrm{b}^6} \frac{\mu\left(\mu^2-1\right)^2}{\left(\mu^2+\nu^2\right)\left[\mu^4+2\mu^2\left(\nu^2-2\right)+4\nu^2\right]\left[\mu^4+\mu^2\left(\nu^2-1\right)+\nu^2\right]^2\left[4\mu^4+\mu^2\left(2\nu^2-1\right)+\nu^2\right]} \times$$
$$\Big[2\left(10\mu^4+41\mu^2+10\right)\nu^{10}+\left(110\mu^4+329\mu^2-12\right)\mu^2\nu^8+2\left(115\mu^4+197\mu^2-28\right)\mu^4\nu^6+$$
$$2\left(115\mu^4+22\mu^2+8\right)\mu^6\nu^4+2\left(55\mu^4-94\mu^2+6\right)\mu^8\nu^2+5\left(4\mu^4-17\mu^2+4\right)\mu^{10}\Big]$$
$$-\frac{3\,c_4\, k_\mathrm{B} T}{4m\,\omega_\mathrm{b}^4} \frac{\mu\left(\mu^2-1\right)^2\left(\mu^2+\nu^2\right)^2}{\left[\mu^4+\mu^2\left(\nu^2-1\right)+\nu^2\right]^2}$$

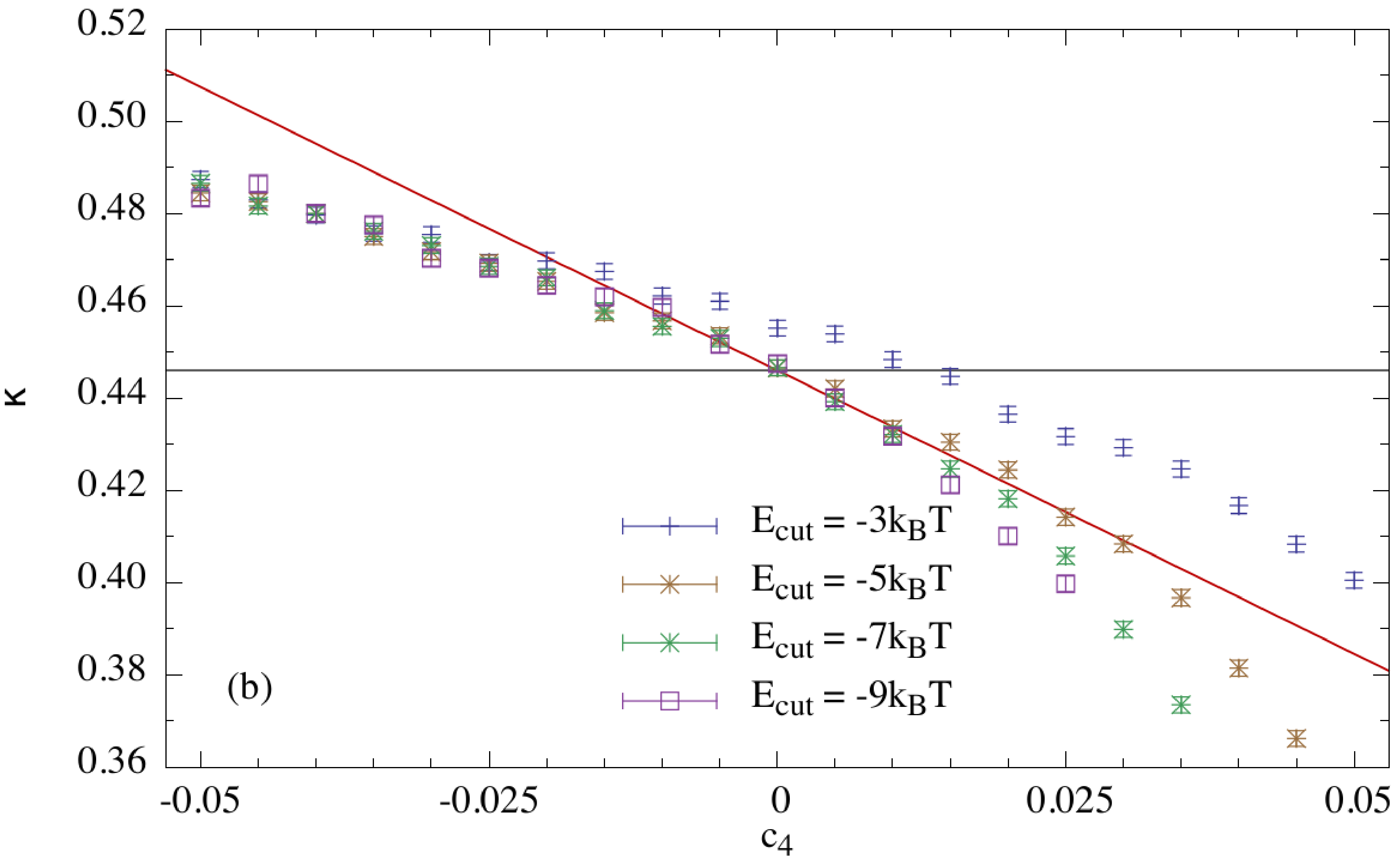
LiCN -> LiCN reaction rates



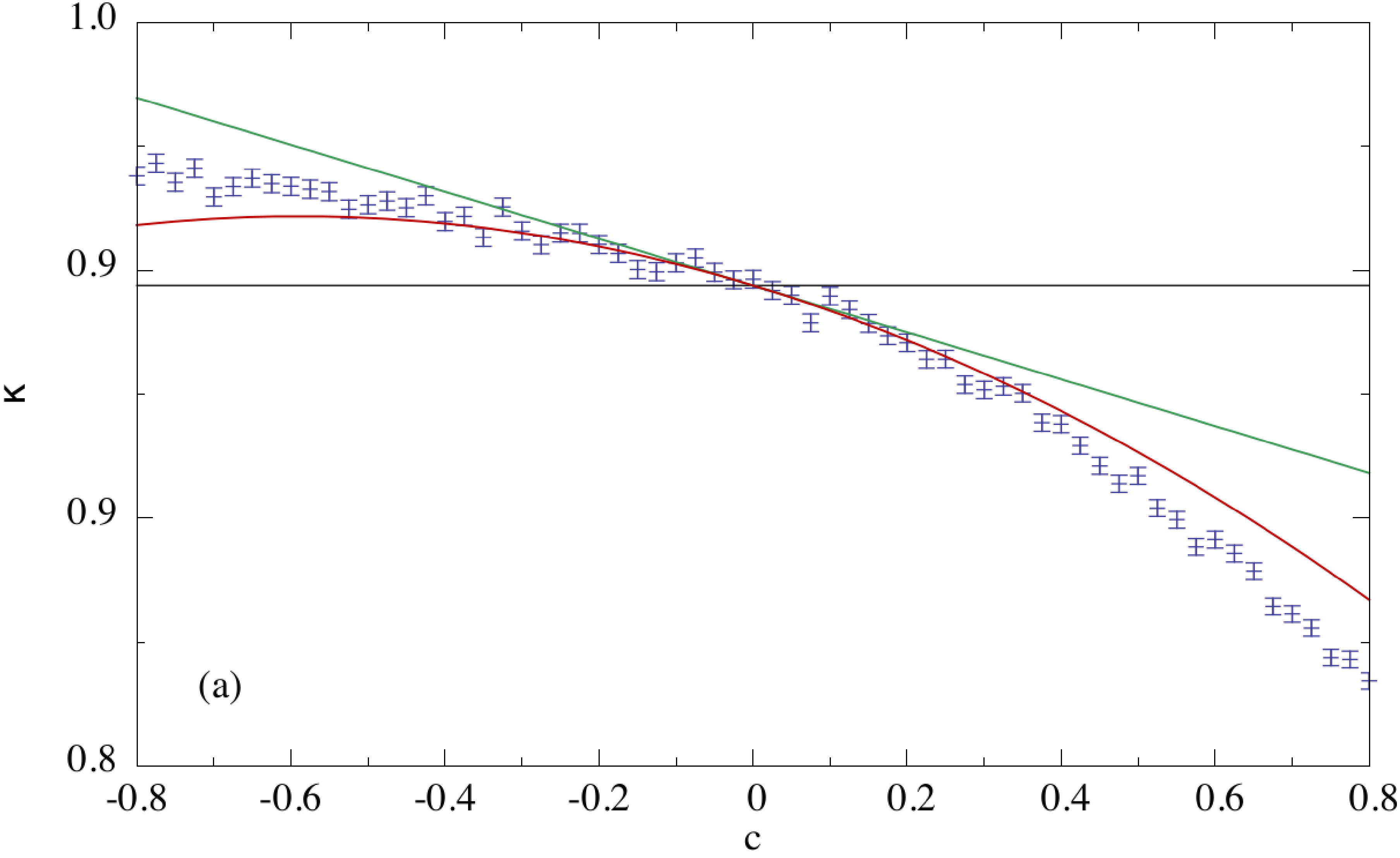
Cubic potential



Quartic potential



Potential with 2 dof



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Conclusions

Conclusion

The **geometry** of the **phase space** provides valuable information of **reactivity** (with a laser, white noise, colored noise…)