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Ring-polymer instanton theory

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Recap of first lecture

- Steepest-descent approximation to path integral gives

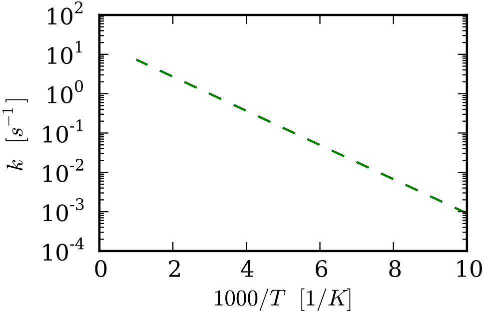
$$K(x', x'', \tau) = \Lambda^N \int \mathrm{e}^{-S(\mathbf{x})/\hbar}\, \mathrm{d}\mathbf{x} \sim \sum_{\text{cl. traj}} \sqrt{\frac{C}{2\pi\hbar}}\, \mathrm{e}^{-S(\tilde{\mathbf{x}})/\hbar}$$

  where C depends on the product of eigenvalues of the polymer Hessian.
- A minimum-action path is equivalent to a classical trajectory in imaginary time (or on the upside-down surface).
- Minimum-action paths can be located using standard optimization algorithms.

Classical Rate theory

Arrhenius law

$$k = A\mathrm{e}^{-\beta E_\mathrm{a}}$$



- Arrhenius. "Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren." *Z. Phys. Chem.* **4**, 226 (1889).

Eyring TST

$$k = A\mathrm{e}^{-\beta E_\mathrm{a}}$$

where prefactor is ratio of partition functions

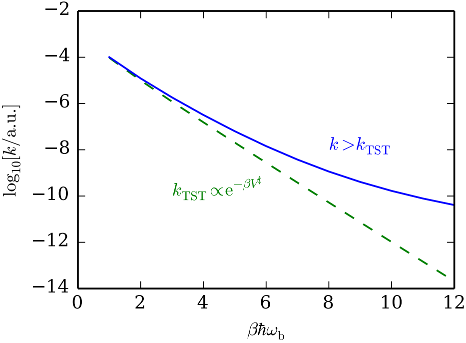
$$A = \frac{1}{2\pi\beta\hbar}\frac{Z^\ddagger}{Z_\mathrm{r}}$$

and activation energy is barrier height

$$E_\mathrm{a} = V^\ddagger$$

- Eyring. “The theory of absolute reaction rates.” *Trans. Faraday Soc.* **34**, 41 (1938).

Tunnelling

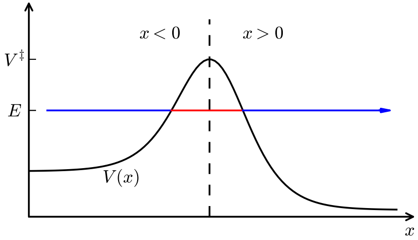


- high temperature
- thermal activation

- low temperature
- tunnelling

Classical description of tunnelling

$$E = \frac{p^2}{2m} + V(x)$$
$$p = \sqrt{2m[E - V(x)]}$$



- therefore p is imaginary if $E < V(x)$
- tunnelling can be described by classical trajectories in imaginary time

Reaction rate

Exact definition

$$kZ_{\mathrm{r}} = \int_0^\infty \mathrm{Tr}\left[\mathrm{e}^{-\beta\hat{H}}\hat{F}\hat{F}(t)\right]\mathrm{d}t$$
$$= \frac{1}{2}\int_{-\infty}^{\infty} \mathrm{Tr}\left[\hat{F}\mathrm{e}^{-\hat{H}(\tau_0-\mathrm{i}t)/\hbar}\hat{F}\mathrm{e}^{-\hat{H}(\tau_1+\mathrm{i}t)/\hbar}\right]\mathrm{d}t,$$

where

$$\hat{F} = \frac{1}{2m}\left[\hat{p}\,\delta(\hat{x}) + \delta(\hat{x})\,\hat{p}\right]$$
$$\beta\hbar = \tau_0 + \tau_1$$

- Miller, Schwartz & Tromp. "Quantum mechanical rate constants for bimolecular reactions." *J. Chem. Phys.* **79**, 4889 (1983).

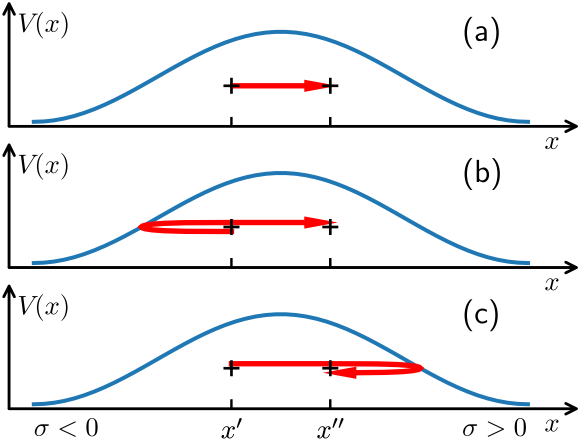
Instanton rate theory

$$kZ_\mathrm{r} = \frac{1}{8m^2}\int_{-\infty}^{\infty} \mathrm{Tr}\left[A(x',x'',t)\delta(x')\delta(x'')\right] \mathrm{d}x'\mathrm{d}x''$$

where

$$\begin{aligned} A(x',x'',t) = {} & \langle x'|\hat{p}\,\mathrm{e}^{-\hat{H}(\tau_0-\mathrm{i}t)/\hbar}|x''\rangle\langle x''|\hat{p}\,\mathrm{e}^{-\hat{H}(\tau_1+\mathrm{i}t)/\hbar}|x'\rangle \\ & + \langle x'|\hat{p}\,\mathrm{e}^{-\hat{H}(\tau_0-\mathrm{i}t)/\hbar}\,\hat{p}|x''\rangle\langle x''|\mathrm{e}^{-\hat{H}(\tau_1+\mathrm{i}t)/\hbar}|x'\rangle \\ & + \langle x'|\mathrm{e}^{-\hat{H}(\tau_0-\mathrm{i}t)/\hbar}|x''\rangle\langle x''|\hat{p}\,\mathrm{e}^{-\hat{H}(\tau_1+\mathrm{i}t)/\hbar}\,\hat{p}|x'\rangle \\ & + \langle x'|\mathrm{e}^{-\hat{H}(\tau_0-\mathrm{i}t)/\hbar}\,\hat{p}|x''\rangle\langle x''|\mathrm{e}^{-\hat{H}(\tau_1+\mathrm{i}t)/\hbar}\,\hat{p}|x'\rangle \end{aligned}$$

Instanton rate theory



3 classical trajectories: $\mu \in \{0, -, +\}$

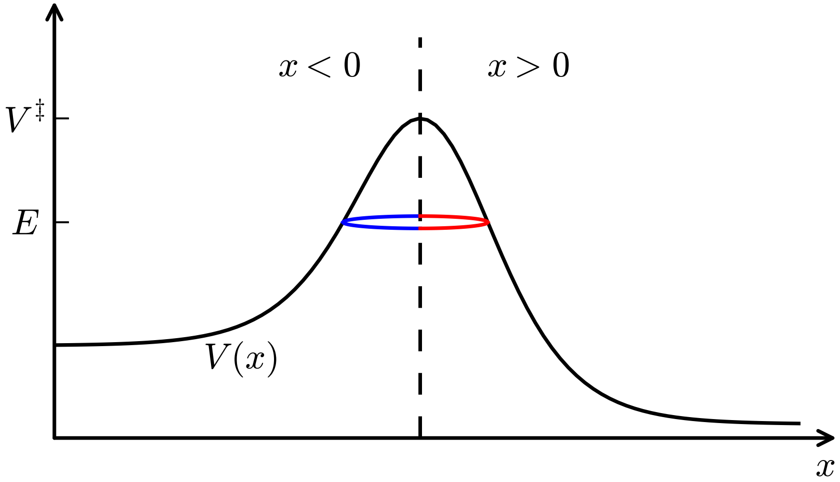
Instanton rate theory

$$A(x', x'', t) \sim \sum_{\mu\nu} A_{\mu\nu}(x', x'', t)$$

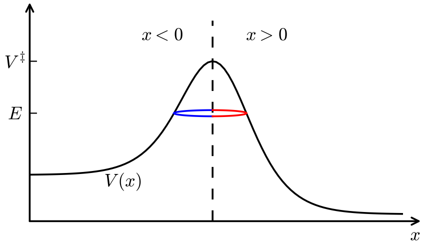
$$A_{\pm\mp}(x', x'', t) = 4|p'||p''| K_{\pm}(x', x'', \tau_0 - \mathrm{i}t) K_{\mp}(x'', x', \tau_1 + \mathrm{i}t)$$

$$\begin{aligned} kZ_{\mathrm{r}} &\sim \frac{1}{8m^2} \iiint_{-\infty}^{\infty} 2A_{+-}(x', x'', t)\, \delta(x')\delta(x'')\, \mathrm{d}x'\mathrm{d}x''\mathrm{d}t \\ &= \iiint_{-\infty}^{\infty} \frac{|p'||p''|}{m^2} \sqrt{\frac{C_+}{2\pi\hbar}} \sqrt{\frac{C_-}{2\pi\hbar}}\, \mathrm{e}^{-S/\hbar}\, \delta(x')\delta(x'')\, \mathrm{d}x'\mathrm{d}x''\mathrm{d}t, \\ &= \frac{|p'||p''|}{m^2} \sqrt{\frac{C_+}{2\pi\hbar}} \sqrt{\frac{C_-}{2\pi\hbar}} \sqrt{\frac{2\pi\hbar}{-\mathrm{d}^2S/\mathrm{d}\tau^2}}\, \mathrm{e}^{-S/\hbar} \end{aligned}$$

Instanton rate theory

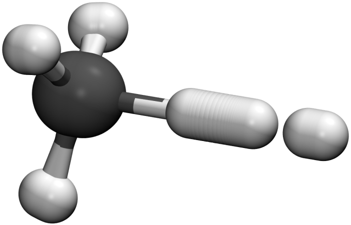


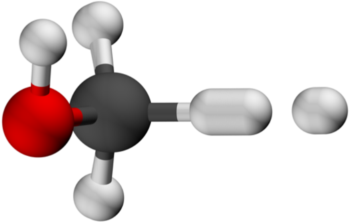
Periodic orbit



- τ_0 and τ_1 chosen such that $\frac{\partial S}{\partial \tau} = 0$
- N.B. $\frac{\partial S_0}{\partial \tau_0} = E_0$ and $\frac{\partial S_1}{\partial \tau_1} = E_1$
- so instanton obeys $E_0 = E_1$, i.e. both trajectories have the same energy
- they also match their momenta such that it is a periodic orbit

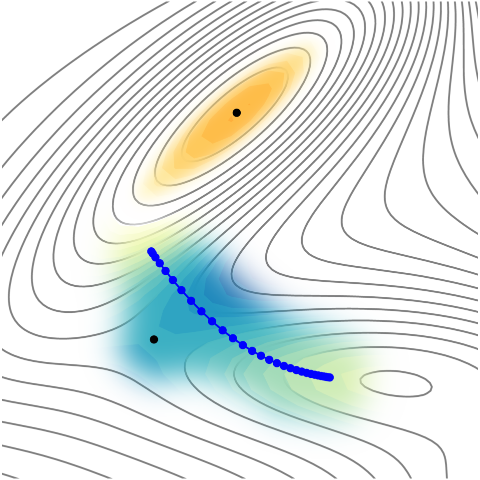
Ab initio quantum rate theory

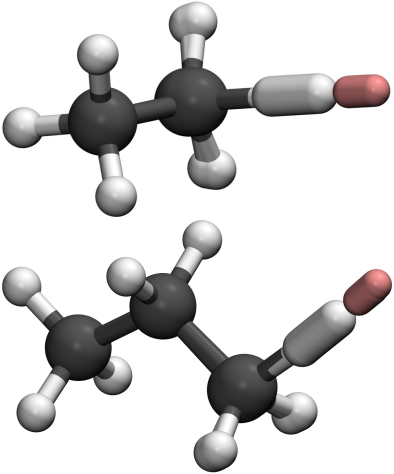




- ring-polymer instanton located numerically
- on the fly: RCCSD(T)-F12/VTZ
- implemented in MOLPRO and i-PI
- easy to combine with machine-learning PES
- Much larger systems: see Yair Litman's talk

Gaussian process regression

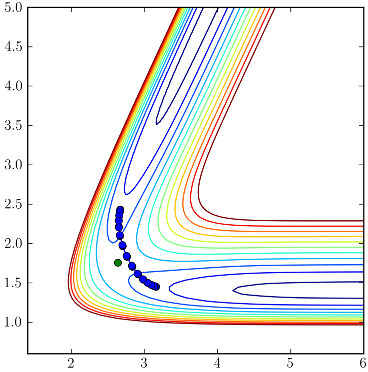




- Laude, Calderini, Tew & J.O.R. “Ab initio instanton rate theory made efficient using Gaussian process regression.” *Faraday Discuss.* **212**, 237 (2018); arXiv:1805.02589 [physics.chem-ph].

Relationship to ring polymers

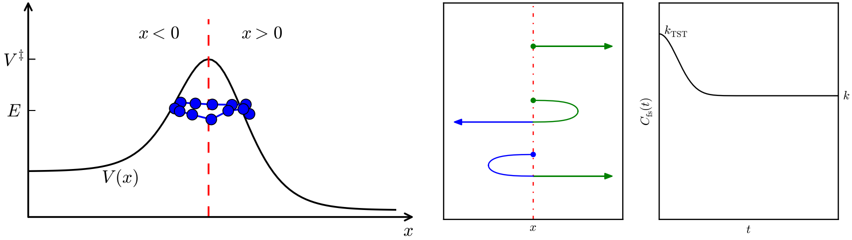
- Tunnelling favours thin (mass-weighted) barriers
- Optimal pathway does not follow minimum energy path through transition state
- Instanton can be found as a 1st-order saddle point on ring-polymer surface
- Eigenvalues of ring-polymer hessian: 1 negative (downhill), 1 zero (for permutation), maybe 5 or 6 zeros for translations & rotations, the rest are positive.



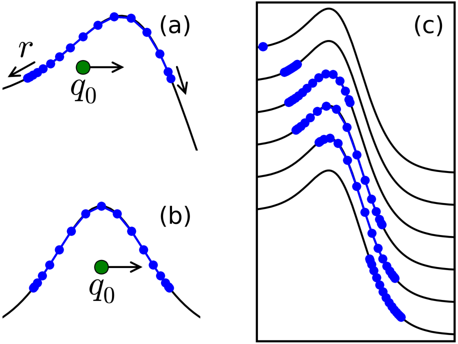
Ring-polymer transition-state theory

Short-time limit of RPMD rate theory:

$$k_{\mathrm{RPTST}} Z_{\mathrm{r}} = \iint \mathrm{e}^{-\beta_N H_N(\mathbf{p},\mathbf{x})} \delta\left[\sigma(\mathbf{x})\right] \dot{\sigma}(\mathbf{x},\mathbf{p}) h\left[\dot{\sigma}(\mathbf{x},\mathbf{p})\right] \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{p}$$
$$= A \int \mathrm{e}^{-S_\circ(\mathbf{x})/\hbar} \delta\left[\sigma(\mathbf{x})\right] \mathrm{d}\mathbf{x}$$
$$\sim B \mathrm{e}^{-S_\circ(\tilde{\mathbf{x}})/\hbar}$$



Ring-polymer instanton



- J.O.R. & Althorpe. "Ring-polymer molecular dynamics rate-theory in the deep-tunneling regime: Connection with semiclassical instanton theory." *J. Chem. Phys.* **131**, 214106 (2009).

Crossover temperature

Put all beads at classical transition-state with imaginary frequency, $\bar{\omega}_\mathrm{b}$.

$$\eta_k^2 = \frac{4}{\beta_N^2 \hbar^2} \sin^2 k\pi/N - \bar{\omega}_\mathrm{b}^2$$

For the lowest modes where $k \ll N$, this is given approximately by

$$\eta_k^2 \approx \frac{4k^2\pi^2}{\beta^2\hbar^2} - \bar{\omega}_\mathrm{b}^2$$

Crossover temperature is defined as

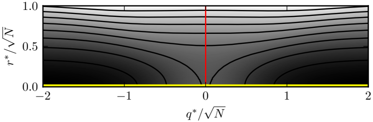
$$\beta_\mathrm{c} = 2\pi/\hbar\bar{\omega}_\mathrm{b}$$

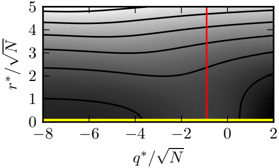
Free-energy plots (in ring-polymer normal-mode space)

Asymmetric barrier

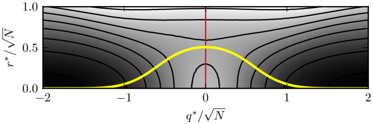
Symmetric barrier

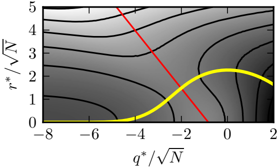
high temp



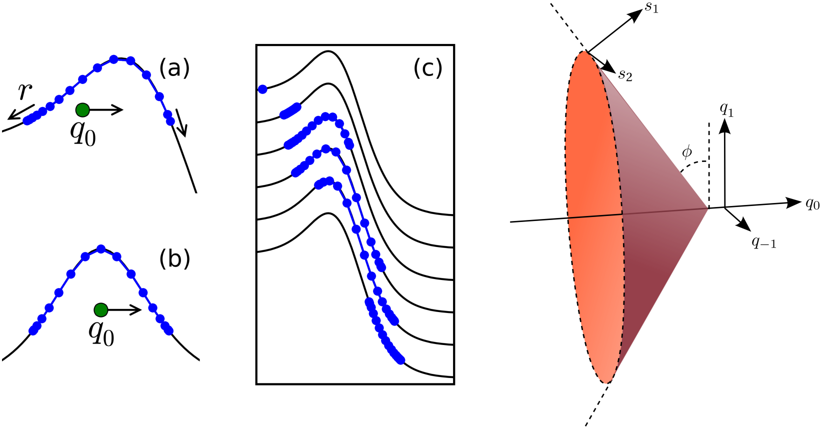


low temp





Optimal ring-polymer dividing surface



- J.O.R. & Althorpe. "Ring-polymer molecular dynamics rate-theory in the deep-tunneling regime: Connection with semiclassical instanton theory." *J. Chem. Phys.* **131**, 214106 (2009).

Results

Asymmetric Eckart barrier

$\beta\hbar\omega_b$	RPMD	Centroid	RPTST	σ-inst	QM	Inst.	h-RPTST
2	1.18	1.18	1.18	...	1.20	...	1.19
4	1.96	1.98	1.98	...	2.01	...	2.20
6	5.28	5.61	5.61	...	5.32	...	21.3
8	28	36	30	28	26.1	28.1	33.1
10	320	540	330	260	251	232	321
12	5900	16000	6300	4200	4060	3690	5910

- J.O.R. & Althorpe. “Ring-polymer molecular dynamics rate-theory in the deep-tunneling regime: Connection with semiclassical instanton theory.” *J. Chem. Phys.* **131**, 214106 (2009).

Rate theories

Method	Recrossing	Anharmonic	ZPE	Tunnelling
classical	✓	✓	✗	✗
cl TST	✗	✓	✗	✗
Eyring TST	✗	✗	✓	✗
instanton	✗	✗	✓	✓
RP-TST	✗	✓	✓	✓
RPMD	✓	✓	✓	✓

Summary of most important concepts

- Instanton rate is derived from first principles from exact rate theory using only an asymptotic approximation in $\hbar$
- Instanton pathway gives uniquely defined optimal tunnelling pathway
- Instanton rate strongly related to RPTST and hence to RPMD rate theory
- Centroid free-energy barrier alone may not give correct information on rate
- RPTST optimal dividing surface is a cone shape in normal-mode space
- RPMD recrossing corrects for suboptimal dividing surface

Reading List

- J.O.R. "Perspective: Ring-polymer instanton theory." *J. Chem. Phys.* **148**, 200901 (2018).
- J.O.R. "Ring-polymer instanton theory." *Int. Rev. Phys. Chem.* **37**, 171 (2018).
- J.O.R. & Althorpe. "Ring-polymer molecular dynamics rate-theory in the deep-tunneling regime: Connection with semiclassical instanton theory." *J. Chem. Phys.* **131**, 214106 (2009).
- Hele & Althorpe. "Derivation of a true ($t \to 0_+$) quantum transition-state theory. I. Uniqueness and equivalence to ring-polymer molecular dynamics transition-state-theory." *J. Chem. Phys.* **138**, 084108 (2013).