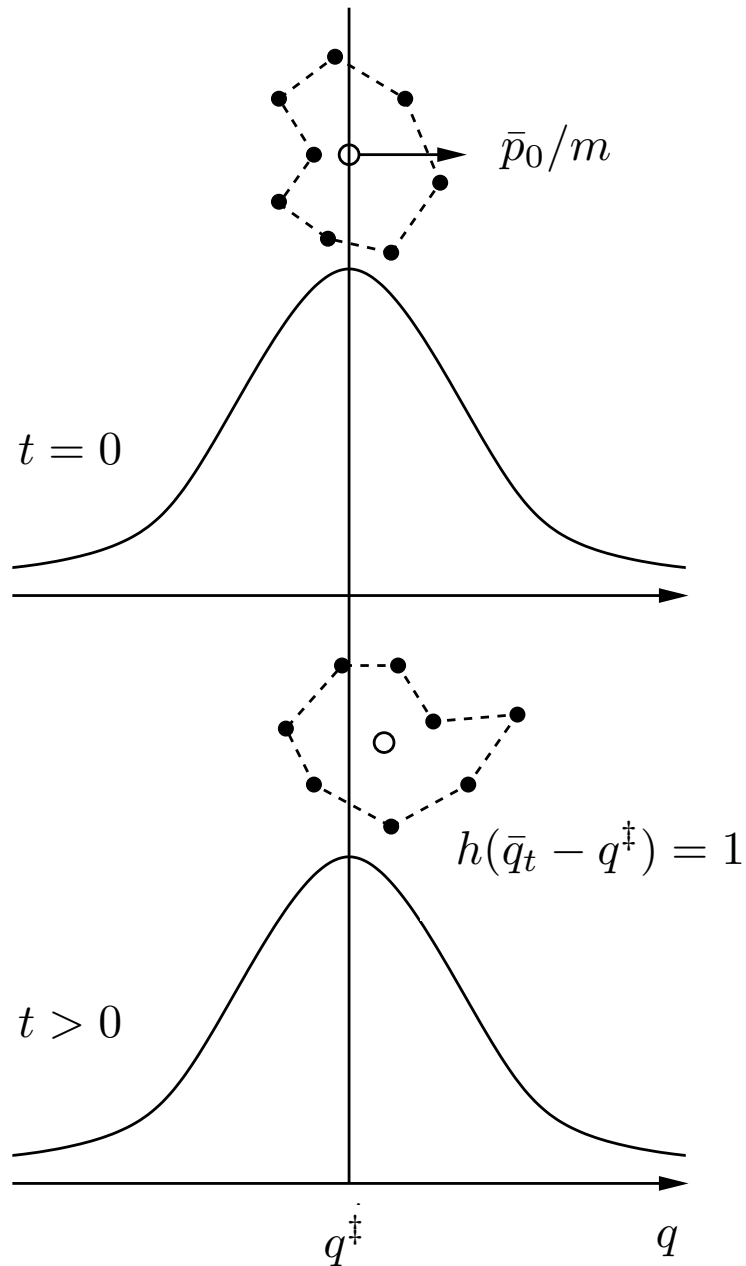


Ring polymer rate theory



David Manolopoulos
Department of Chemistry
University of Oxford

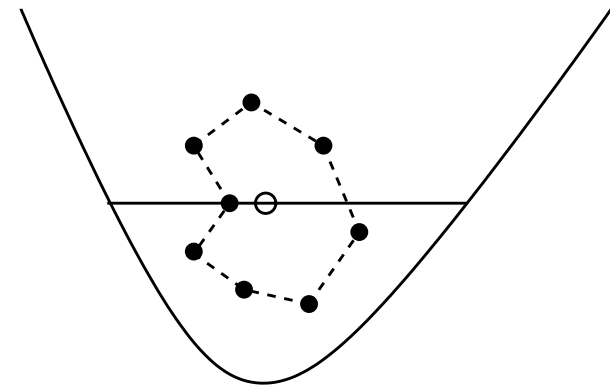
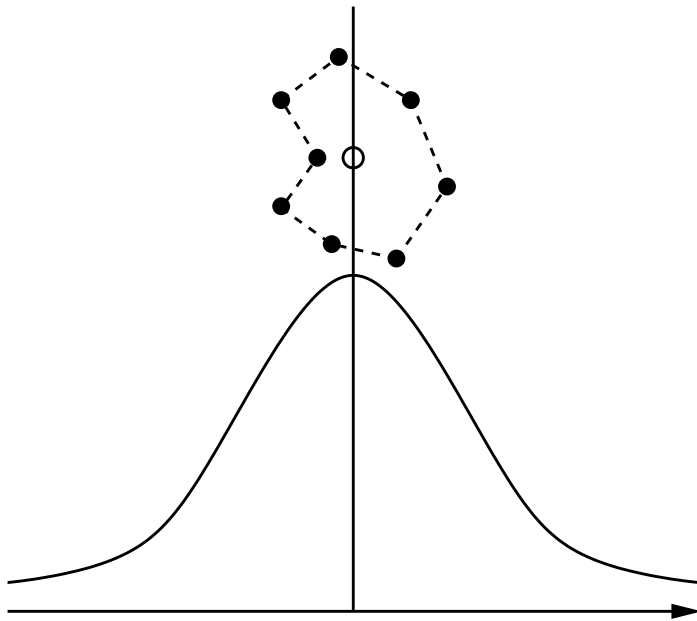
Mariapfarr Workshop 2019
Lecture III

I. A killer application

Recall that RPMD includes both

tunneling and

zero point energy



which are *the* dominant quantum mechanical effects in chemical reaction rates!

2. Ring polymer rate theory

Consider a simple 1d barrier transmission problem:

The exact QM rate coefficient is^{1,2}

$$k(T) = \frac{1}{Q_r(T)} \lim_{t \rightarrow \infty} \tilde{c}_{fs}(t)$$

where

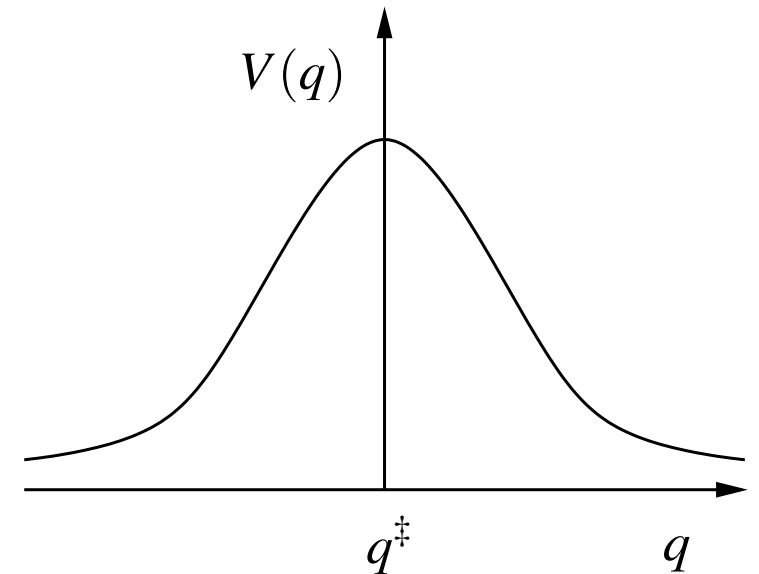
$$\tilde{c}_{fs}(t) = \frac{1}{\beta} \int_0^\beta d\lambda \operatorname{tr} \left[e^{-(\beta-\lambda)\hat{H}} \hat{F}(0) e^{-\lambda\hat{H}} \hat{h}(t) \right]$$

with

$$\hat{F} = \frac{i}{\hbar} \left[\hat{H}, \hat{h} \right] \quad \text{and} \quad \hat{h} = h(\hat{q} - q^\ddagger).$$

Flux

Side



NB:

1. $k(T)$ is independent of q^\ddagger .
2. $\tilde{c}_{fs}(t \rightarrow 0_+) \sim t^{1/2} \rightarrow 0$.

The classical limit:

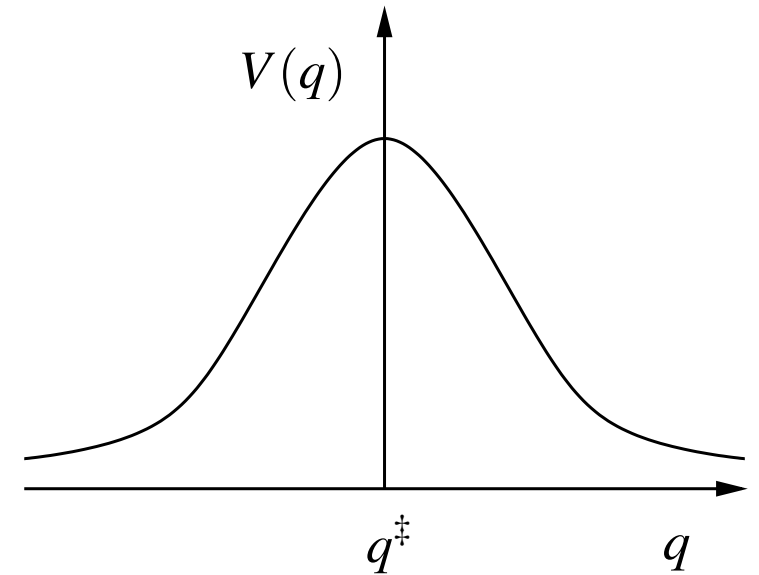
The classical limit rate coefficient is

$$k^{\text{cl}}(T) = \frac{1}{Q_r(T)} \lim_{t \rightarrow \infty} c_{fs}^{\text{cl}}(t)$$

where

$$\tilde{c}_{fs}(t) = \frac{1}{2\pi\hbar} \int dp_0 \int dq_0 e^{-\beta H(p_0, q_0)} \\ \times \underbrace{\delta(q_0 - q^\ddagger) \frac{p_0}{m}}_{\text{Flux (t = 0)}} \times \underbrace{h(q_t - q^\ddagger)}_{\text{Side (t > 0)}}$$

Flux (t = 0) **Side (t > 0)**

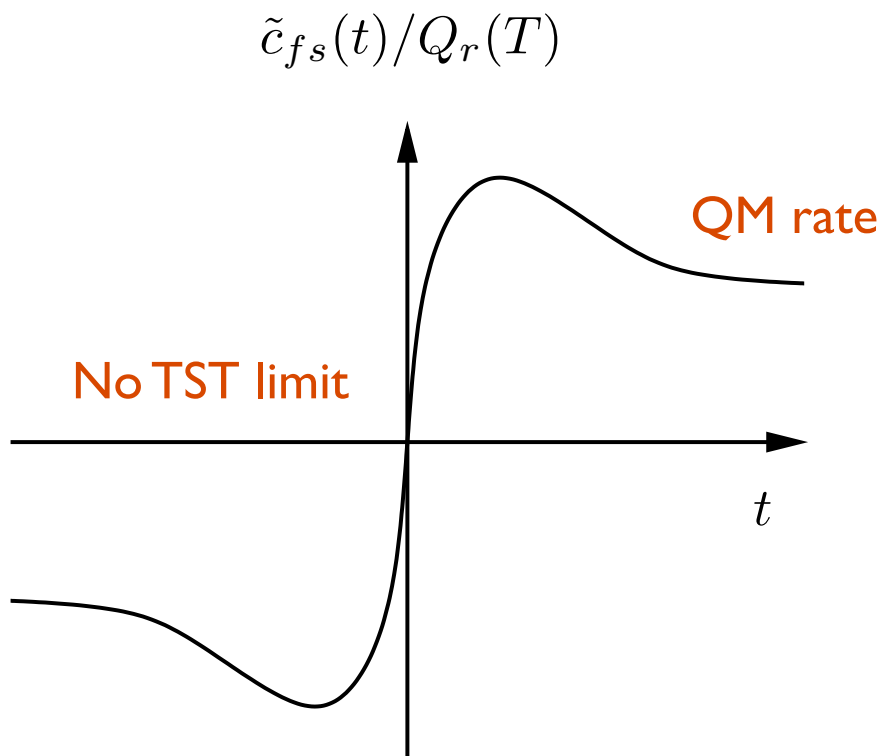


NB:

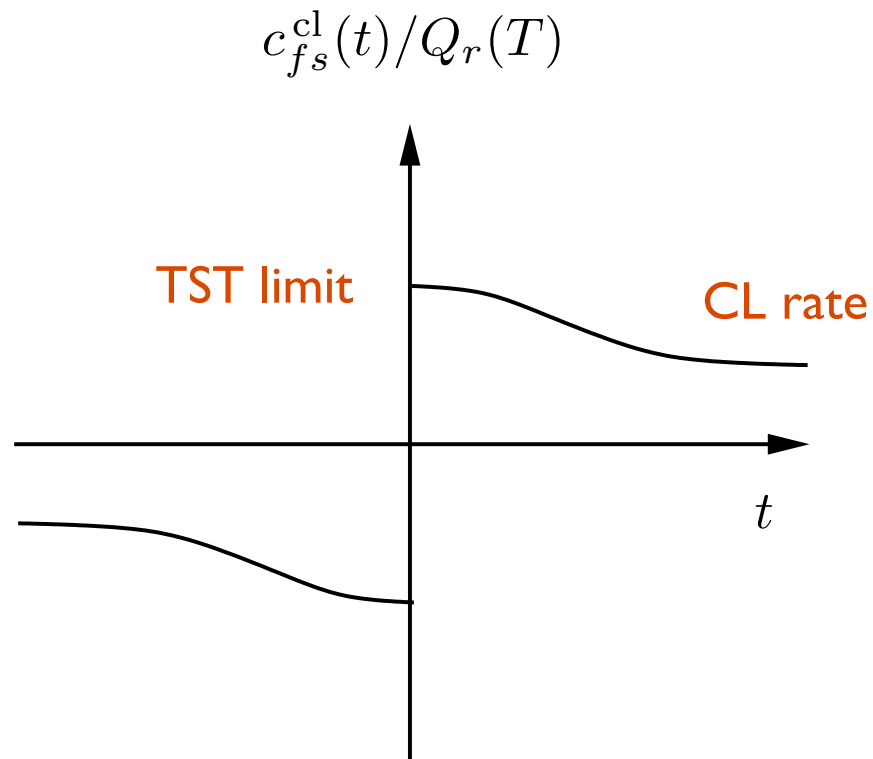
1. $k^{\text{cl}}(T)$ is independent of q^\ddagger .
2. As $t \rightarrow 0_+$, $h(q_t - q^\ddagger) \rightarrow h(p_0)$, giving

$$k^{\text{TST}}(T) = \frac{1}{Q_r(T)} c_{fs}^{\text{cl}}(t \rightarrow 0_+) = \frac{1}{2} \langle |\dot{q}| \rangle_{\text{cl}} e^{-\beta V(q^\ddagger)}.$$

Quantum



Classical



$$k^{\text{TST}}(T) = \frac{1}{Q_r(T)} c_{fs}^{cl}(t \rightarrow 0_+)$$

“Quantum transition state theory”

The centroid density QTST rate is^{3,4}

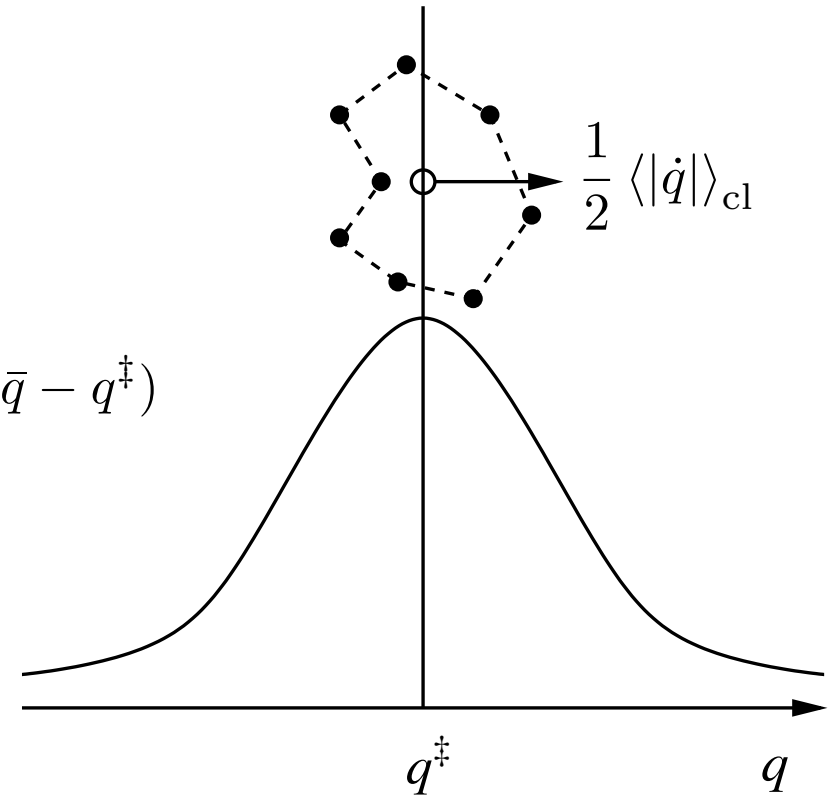
$$k^{\text{QTST}}(T) = \frac{1}{2} \langle |\dot{q}| \rangle_{\text{cl}} Q(q^\ddagger) / Q_r(T)$$

where

$$Q(q^\ddagger) = \frac{1}{(2\pi\hbar)^n} \int d\mathbf{p} \int d\mathbf{q} e^{-\beta_n H_n(\mathbf{p}, \mathbf{q})} \delta(\bar{q} - q^\ddagger)$$

with

$$\bar{q} = \frac{1}{n} \sum_{j=1}^n q_j.$$



NB:

1. $e^{-\beta V(q^\ddagger)} \rightarrow Q(q^\ddagger) / Q_r(T)$ includes (some) tunneling (good).
2. However, $k^{\text{QTST}}(T)$ is *exponentially* sensitive to q^\ddagger (bad).

Ring polymer rate theory:

The RPMD rate coefficient is^{5,6}

$$k^{\text{RPMD}}(T) = \frac{1}{Q_r(T)} \lim_{t \rightarrow \infty} \bar{c}_{fs}(t)$$

where

$$\begin{aligned} \bar{c}_{fs}(t) = & \frac{1}{(2\pi\hbar)^n} \int d\mathbf{p}_0 \int d\mathbf{q}_0 e^{-\beta_n H_n(\mathbf{p}_0, \mathbf{q}_0)} \\ & \times \delta(\bar{q}_0 - q^\ddagger) \frac{\bar{p}_0}{m} h(\bar{q}_t - q^\ddagger) \end{aligned}$$

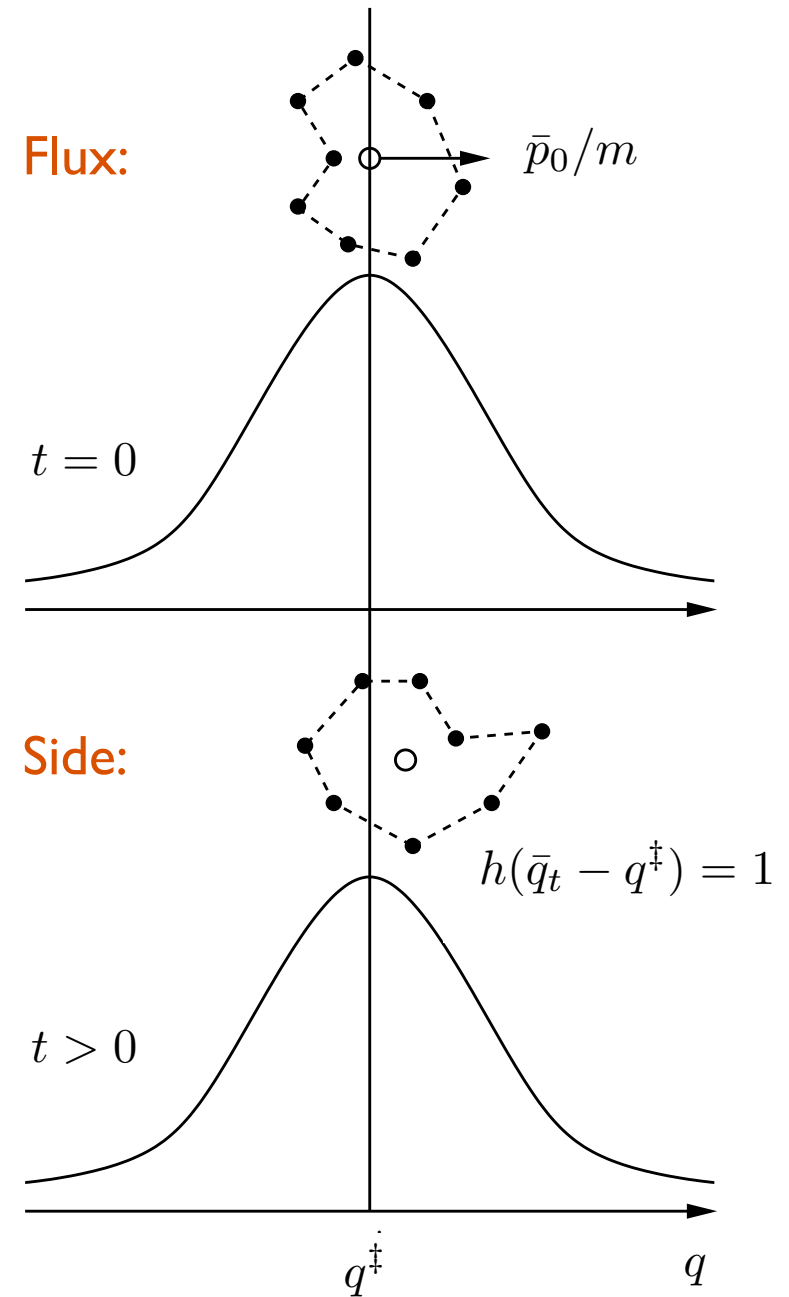
and

$$\bar{q} = \frac{1}{n} \sum_{j=1}^n q_j, \quad \bar{p} = \frac{1}{n} \sum_{j=1}^n p_j.$$

NB: With these definitions,

$$k^{\text{QTST}}(T) = \frac{1}{Q_r(T)} \bar{c}_{fs}(t \rightarrow 0_+).$$

So $k^{\text{RPMD}}(T)$ is to $k^{\text{QTST}}(T)$ what $k^{\text{cl}}(T)$ is to $k^{\text{TST}}(T)$!

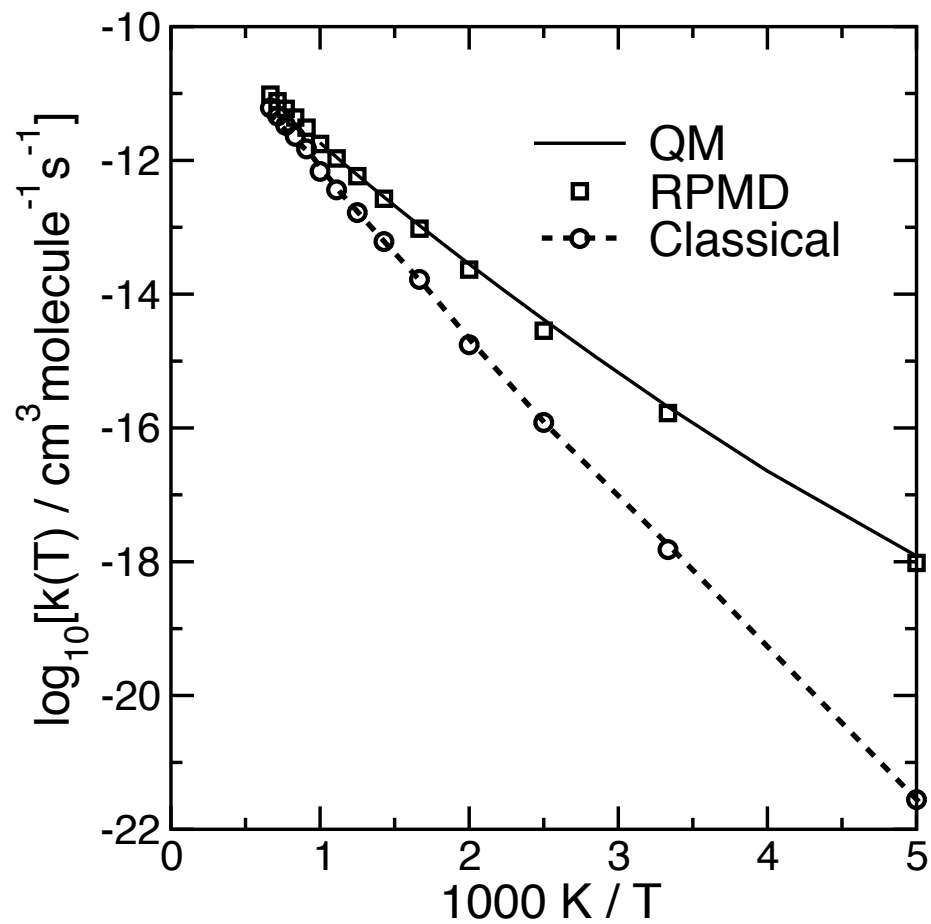
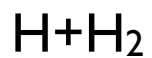


The RPMD rate is:

1. Full dimensional
2. Parameter free
3. Simple to compute
4. Exact in the high temperature limit
5. Exact for a parabolic barrier
6. Independent of the choice of dividing surface
7. Consistent with the QM equilibrium constant

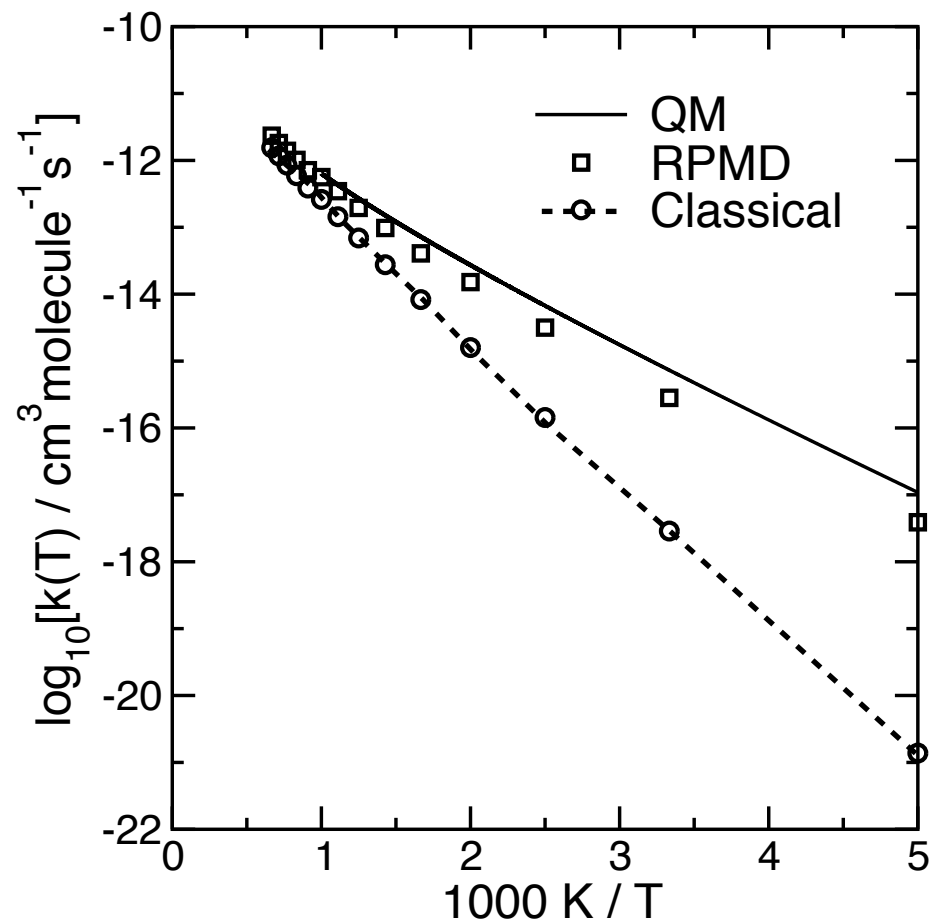
...and it has one further highly desirable feature:

3. Gas phase examples^{7,8}



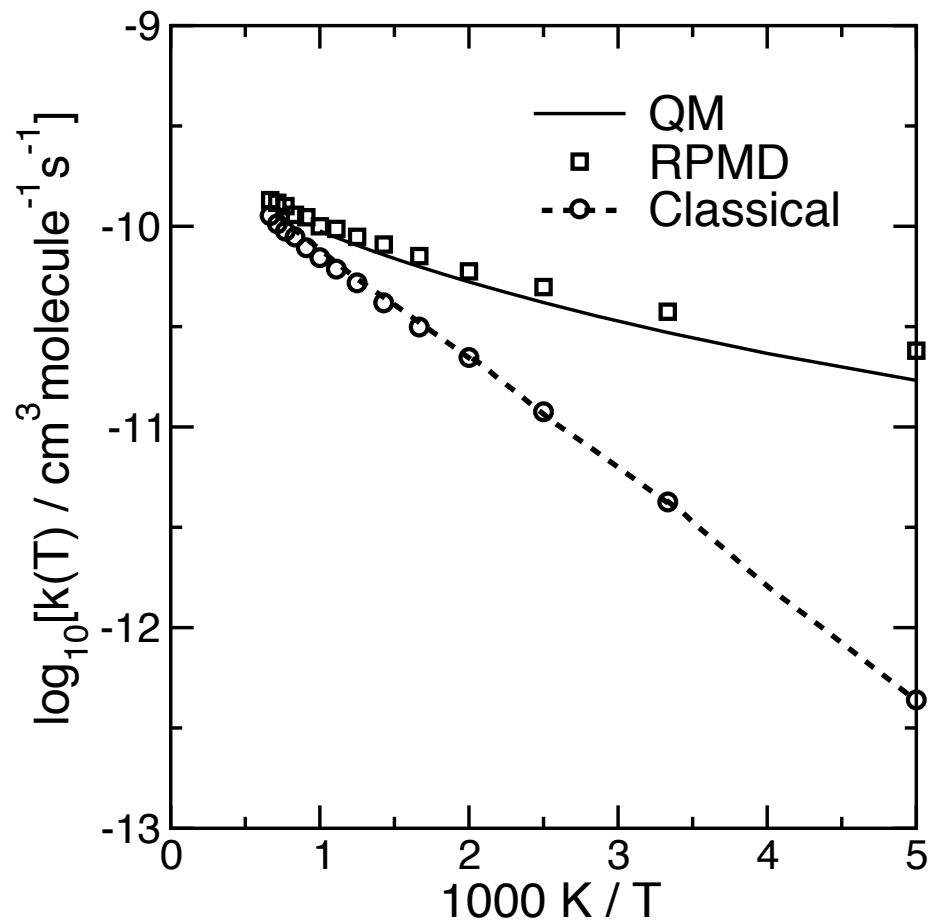
*Symmetric barrier. $T_c = 345 \text{ K}$.
RPMD is out by -21% at 200 K .*

Cl+HCl



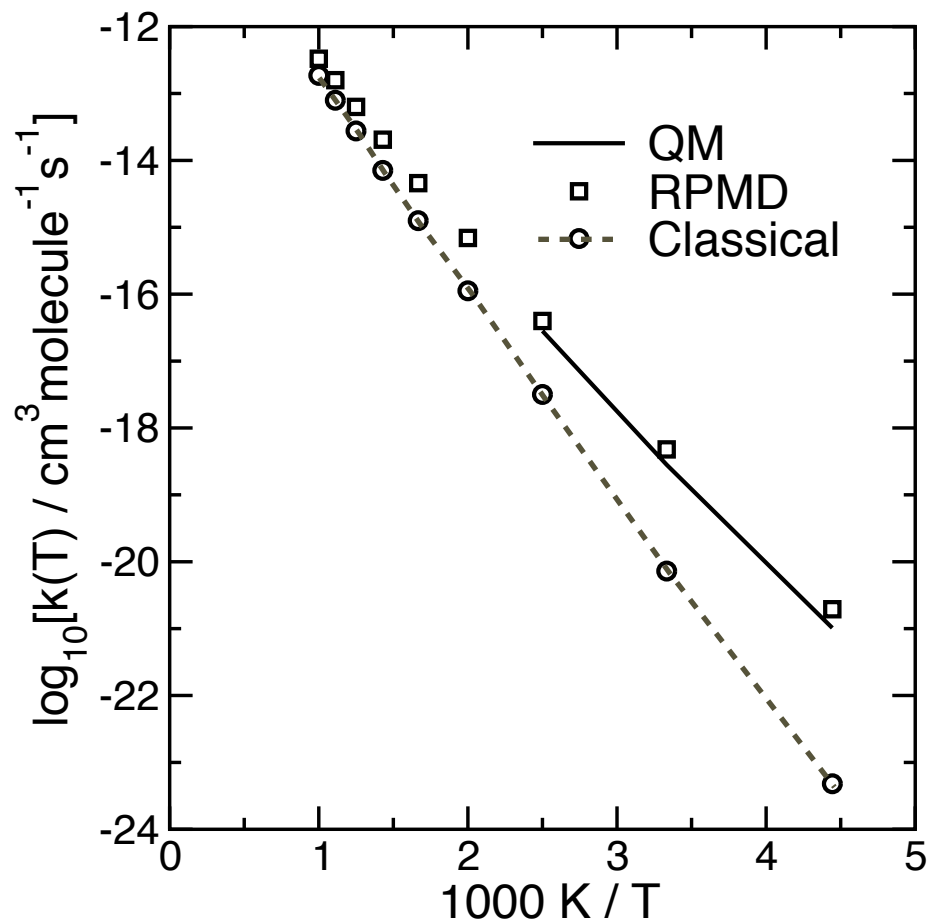
*Symmetric barrier. $T_c = 320 \text{ K}$.
RPMD is out by -64% at 200 K .*

F+H₂



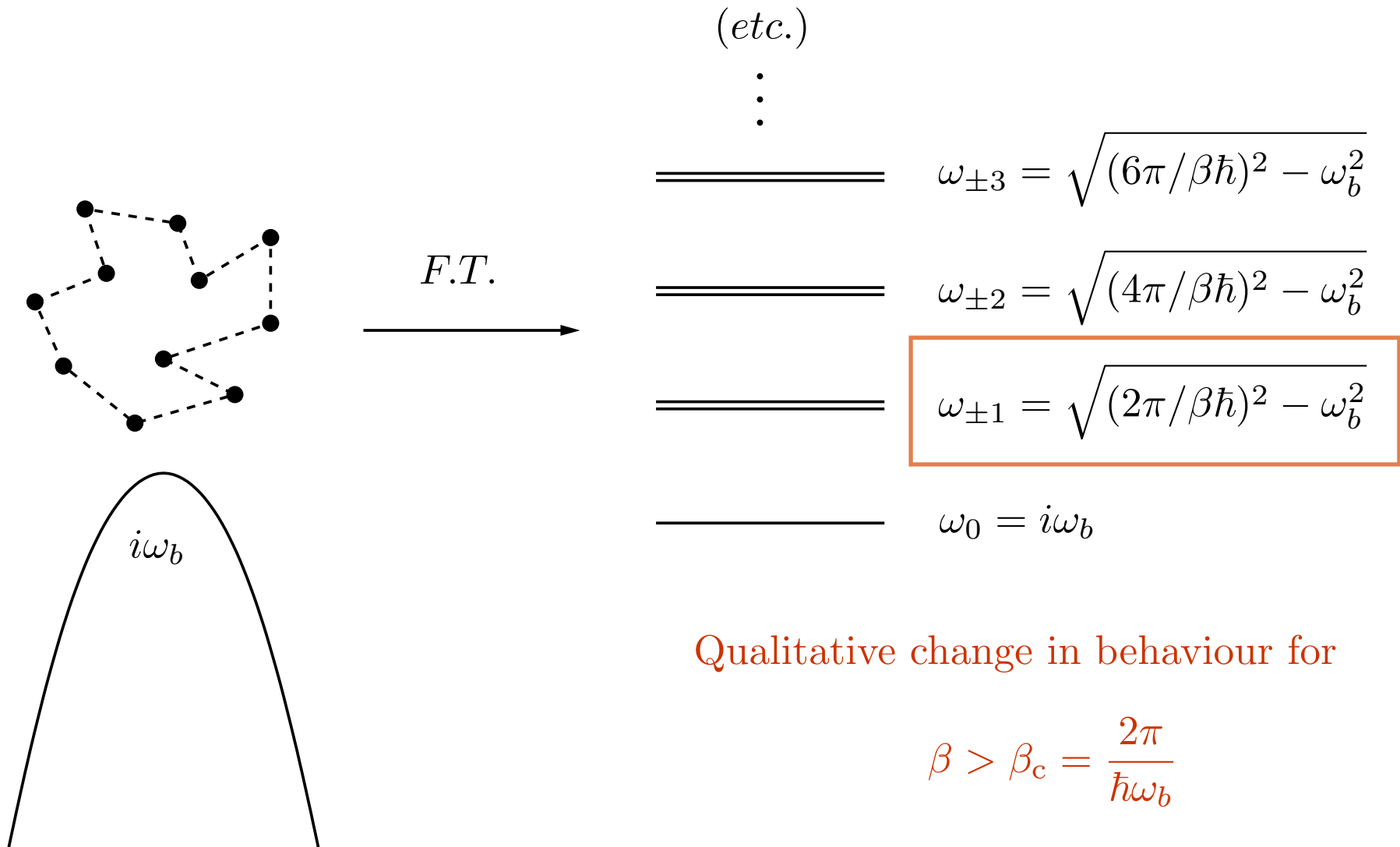
*Asymmetric barrier. $T_c = 264$ K.
RPMD is out by +46% at 200 K.*

H+CH₄



*Asymmetric barrier. $T_c = 296 \text{ K}$.
RPMD is out by +92% at 225 K.*

The deep tunneling regime⁹



Qualitative change in behaviour for

$$\beta > \beta_c = \frac{2\pi}{\hbar\omega_b}$$

$$T < T_c = \frac{\hbar\omega_b}{2\pi k_B}$$

Ring-polymer molecular dynamics rate-theory in the deep-tunneling regime: Connection with semiclassical instanton theory

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(Received 14 October 2009; accepted 4 November 2009; published online 3 December 2009)

We demonstrate that the ring-polymer molecular dynamics (RPMD) method is equivalent to an automated and approximate implementation of the “Im F” version of semiclassical instanton theory when used to calculate reaction rates in the deep-tunneling regime. This explains why the RPMD method is often reliable in this regime and also shows how it can be systematically improved. The geometry of the beads at the transition state on the ring-polymer potential surface describes a finite-difference approximation to the “instanton” trajectory (a periodic orbit in imaginary time $\beta\hbar$ on the inverted potential surface). The deep-tunneling RPMD rate is an approximation to the rate obtained by applying classical transition-state theory (TST) in ring-polymer phase-space using the optimal dividing surface; this TST rate is in turn an approximation to a free-energy version of the Im F instanton rate. The optimal dividing surface is in general a function of several modes of the ring polymer, which explains why centroid-based quantum-TSTs break down at low temperatures for asymmetric reaction barriers. Numerical tests on one-dimensional models show that the RPMD rate tends to overestimate deep-tunneling rates for asymmetric barriers and underestimate them for symmetric barriers, and we explain that this is likely to be a general trend. The ability of the RPMD method to give a dividing-surface-independent rate in the deep-tunneling regime is shown to be a consequence of setting the bead-masses equal to the physical mass. © 2009 American Institute of Physics. [doi:10.1063/1.3267318]

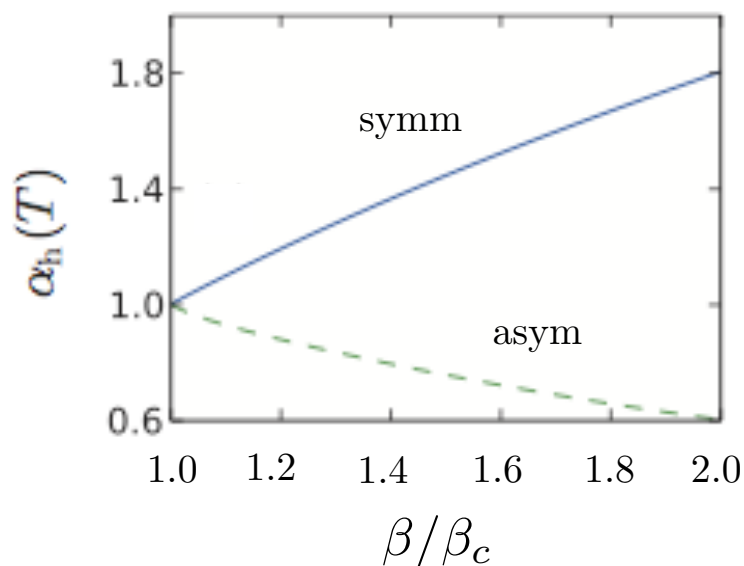
Ring-polymer molecular dynamics rate-theory in the deep-tunneling regime: Connection with semiclassical instanton theory

Jeremy O. Richardson and Stuart C. Althorpe

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

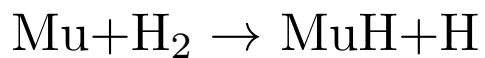
(Received 14 October 2009; accepted 4 November 2009; published online 3 December 2009)

We demonstrate that the ring-polymer automated and approximate implementation when used to calculate reaction rates in this regime a geometry of the beads at the transition finite-difference approximation to the “i on the inverted potential surface). The obtained by applying classical transition optimal dividing surface; this TST rate Im F instanton rate. The optimal dividing ring polymer, which explains why cent for asymmetric reaction barriers. Numer rate tends to overestimate deep-tunnelin symmetric barriers, and we explain that method to give a dividing-surface-indep consequence of setting the bead-masses *Physics*. [doi:10.1063/1.3267318]

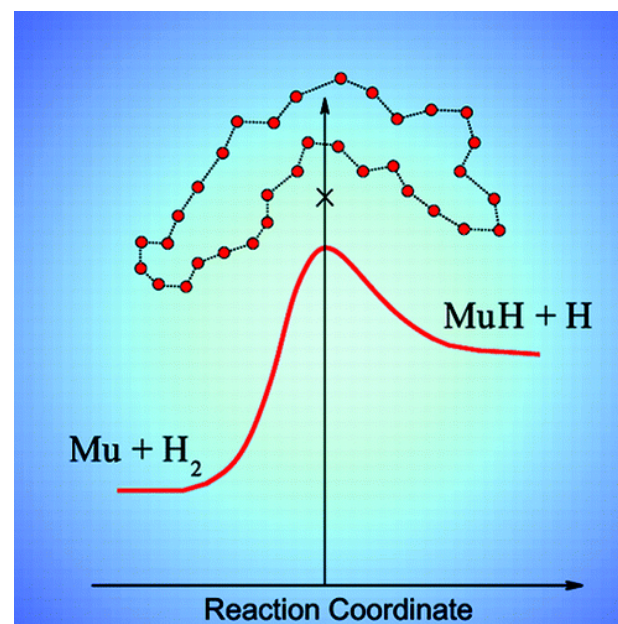
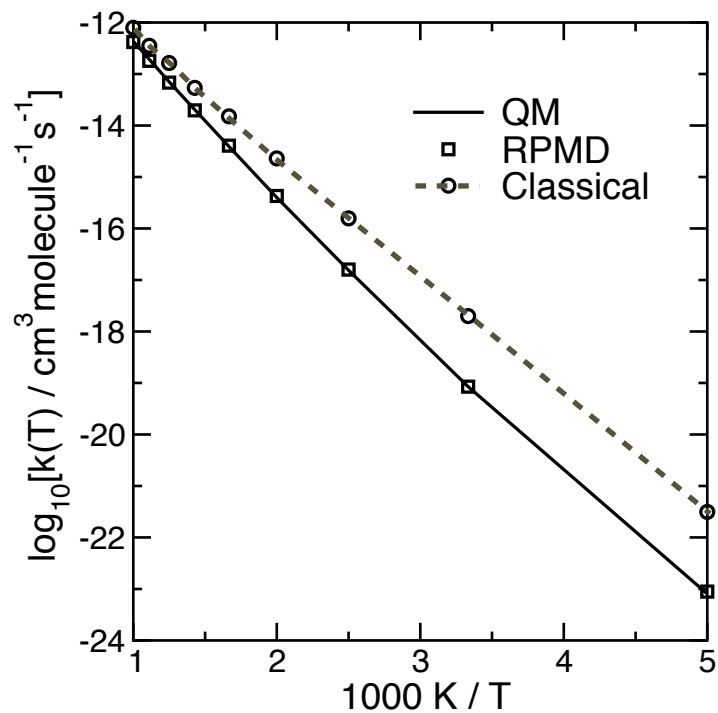


$$k_{\text{RPMD}}^{\text{oTST}}(T) = \frac{1}{\alpha(T)} k_{\text{inst}}(T)$$

So RPMD is pretty good at tunneling.
But what about zero-point energy?



Perez de Tudela *et al.* (2012)¹⁰



Asymmetric barrier. ZPE dominated.
RPMD is out by just +5% at 200 K.



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RPMDRATE: Bimolecular chemical reaction rates from ring polymer molecular dynamics[☆]

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^b Department of Mechanical and Aerospace Engineering, Combustion Energy Frontier Research Center, Princeton University, Princeton, NJ 08544, United States

The reactions studied with this software so far include:

Triatomic activated	H+H ₂ , F+H ₂ , Cl+HCl
Triatomic insertion	C(¹ D)+H ₂ , S(¹ D)+H ₂
Tetratomic	Cl+O ₃ , HCl+OH
Pentatomic	F+NH ₃
Hexatomic	H+CH ₄ , Cl+CH ₄ , O+CH ₄
Heptatomic	OH+CH ₄
Enneatomic	H+C ₂ H ₆

(etc. — this list is already out of date!)

4. Condensed phase examples

A. A system-bath model⁵

This model consists of a quartic double well coupled to a bath of harmonic oscillators:

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + V(\hat{q}_1) + \sum_{i=2}^f \left[\frac{\hat{p}_i^2}{2m} + \frac{1}{2} m \omega_i^2 \left(\hat{q}_i - \frac{c_i \hat{q}_1}{m \omega_i^2} \right)^2 \right]$$

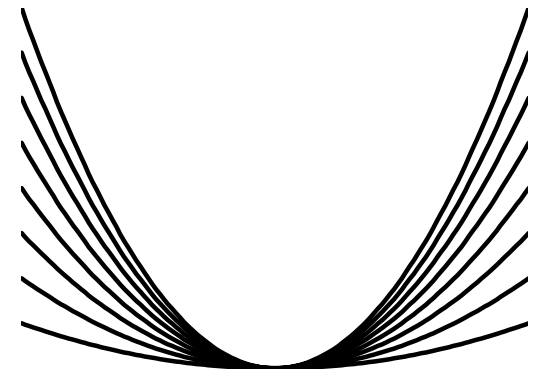
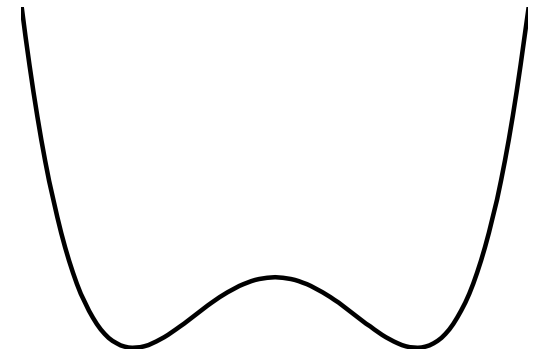
with

$$V(\hat{q}_1) = -a_2 \hat{q}_1^2 + a_4 \hat{q}_1^4$$

and

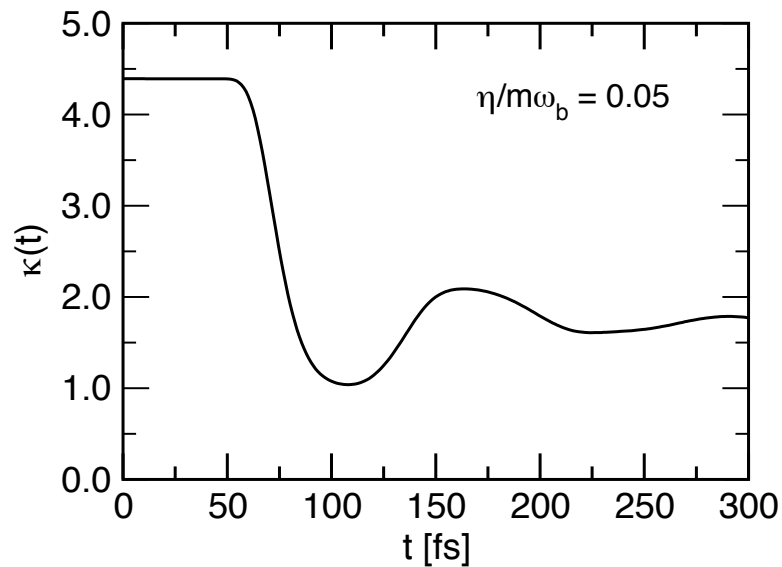
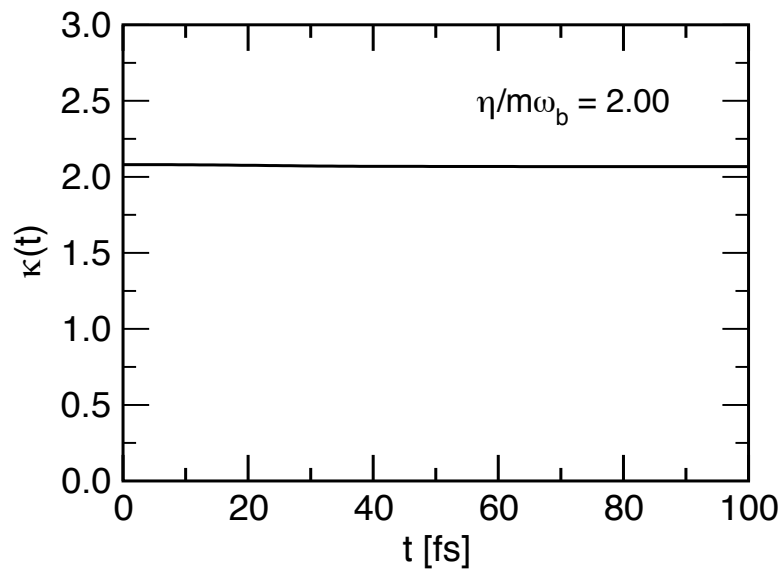
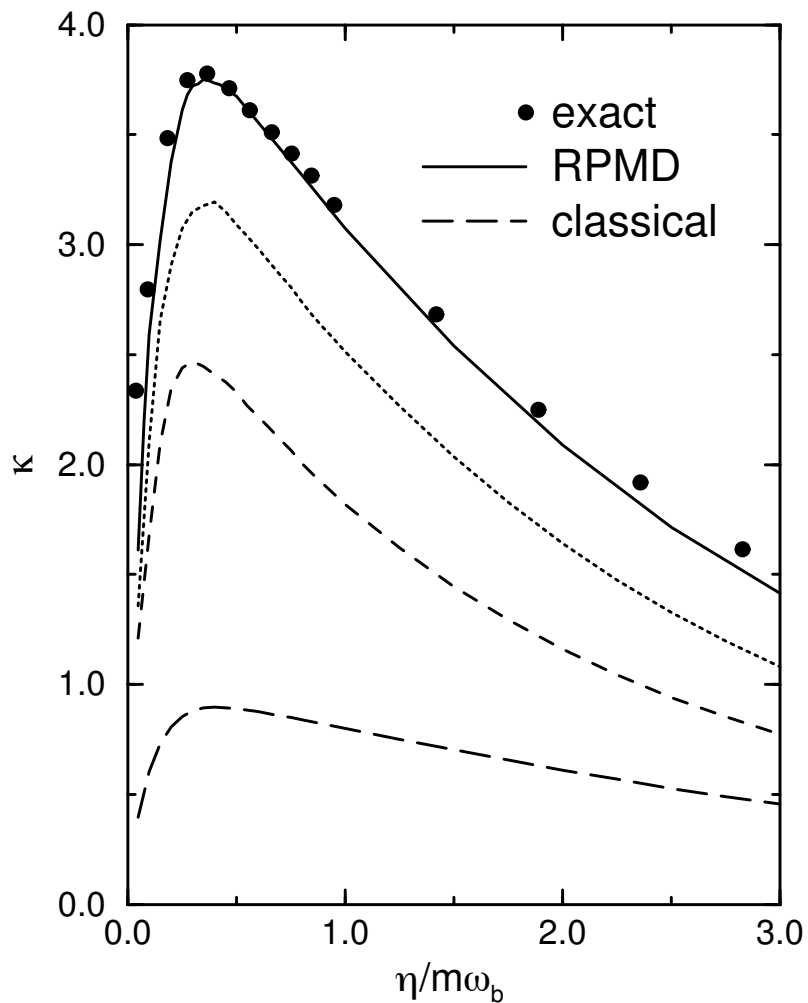
$$J(\omega) = \eta \omega e^{-\omega/\omega_c} \simeq \frac{\pi}{2} \sum_{i=2}^f \frac{c_i^2}{m \omega_i} \delta(\omega - \omega_i).$$

Parameters chosen to model a proton transfer reaction in solution.



System-bath model at 200 K

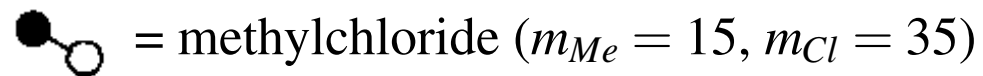
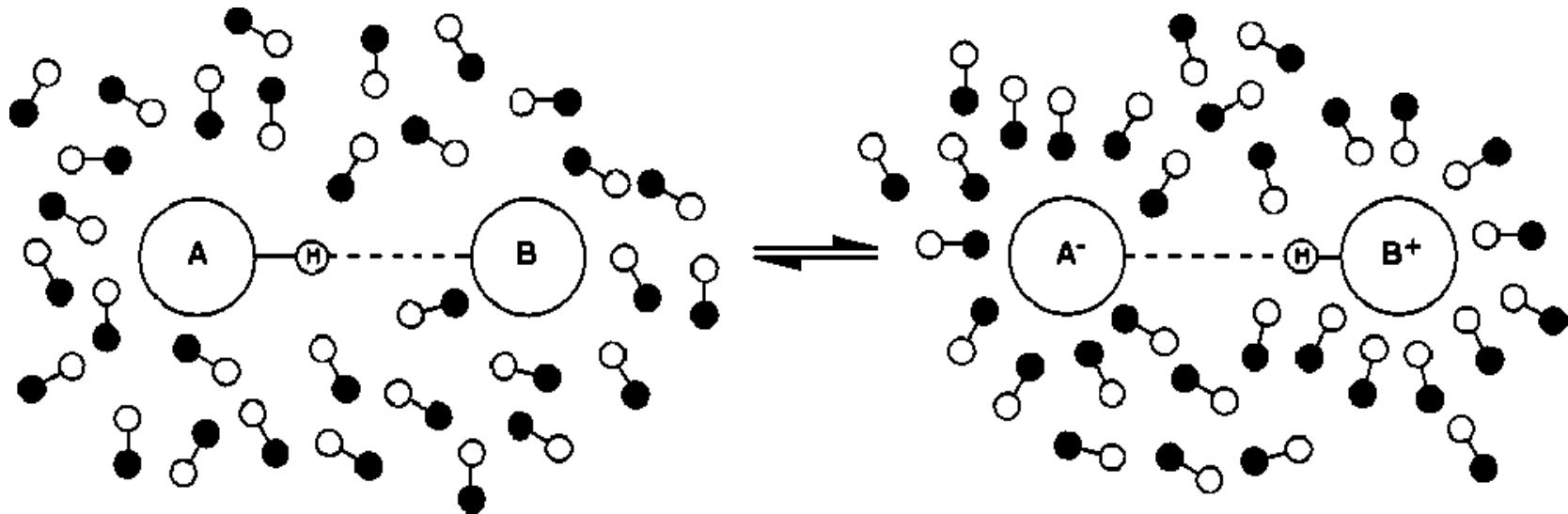
$$\kappa(t) = \frac{\bar{c}_{fs}(t)}{Q_r(T)k_{1d}^{\text{TST}}(T)}; \quad \kappa = \lim_{t \rightarrow \infty} \kappa(t)$$



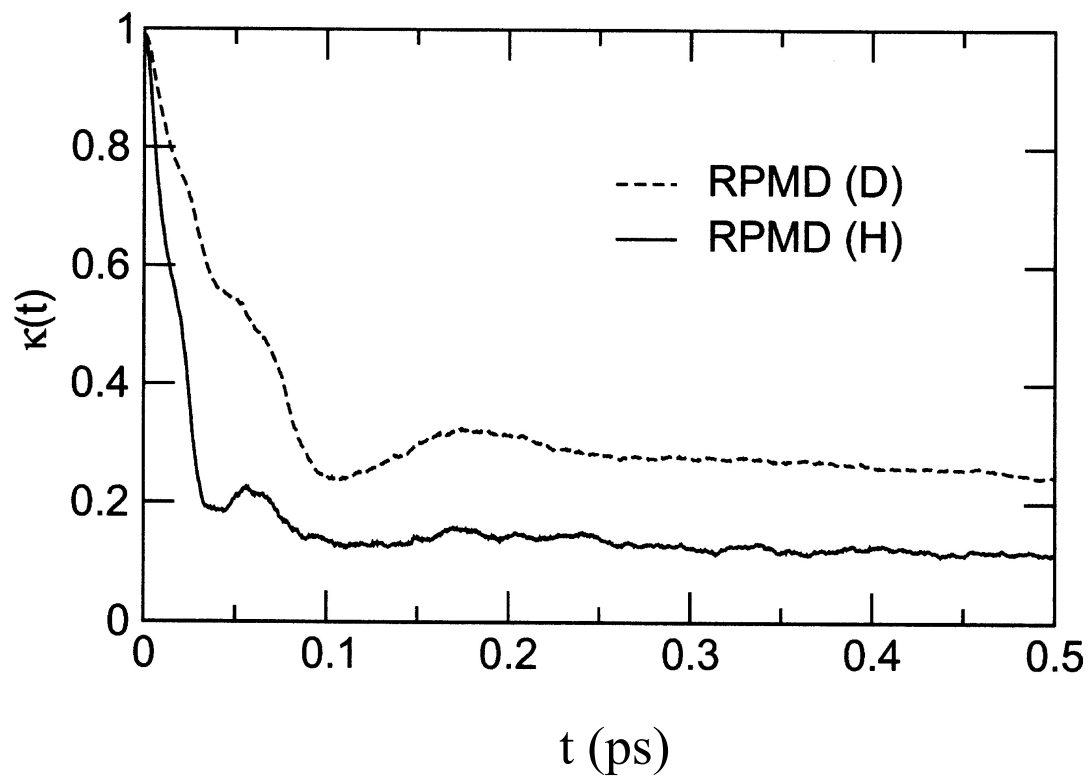
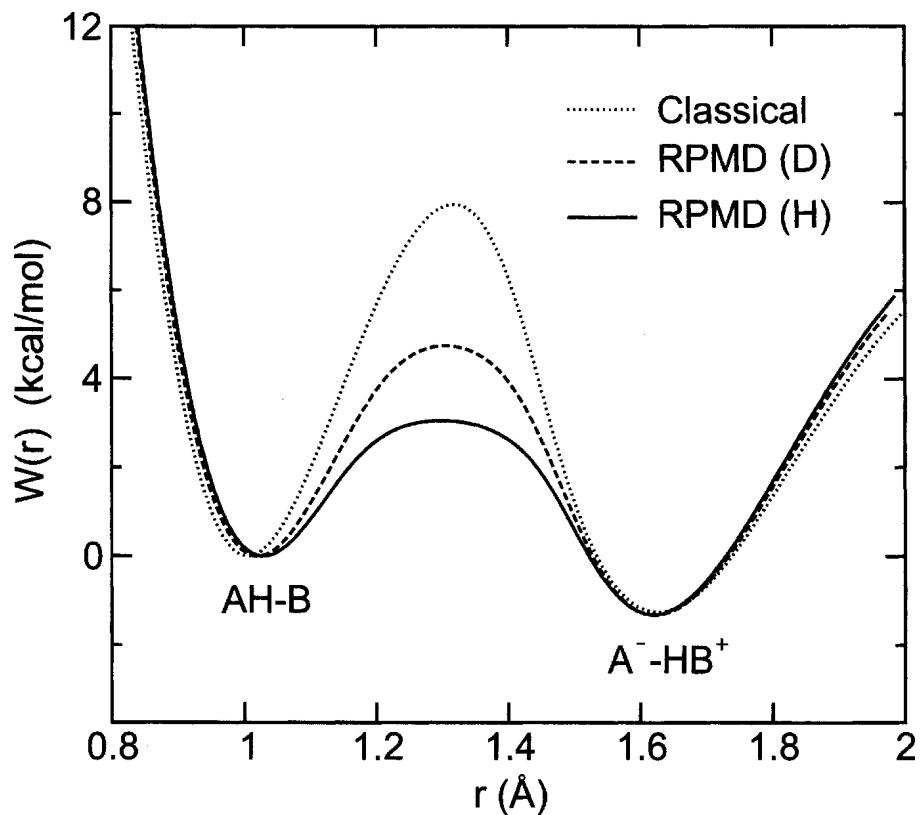
Correct quantum turnover behaviour... ...and transition state recrossing dynamics.

B. Proton transfer in a polar solvent¹¹

Illustration from S.Y.Kim and S.Hammes-Schiffer, JCP 2003:

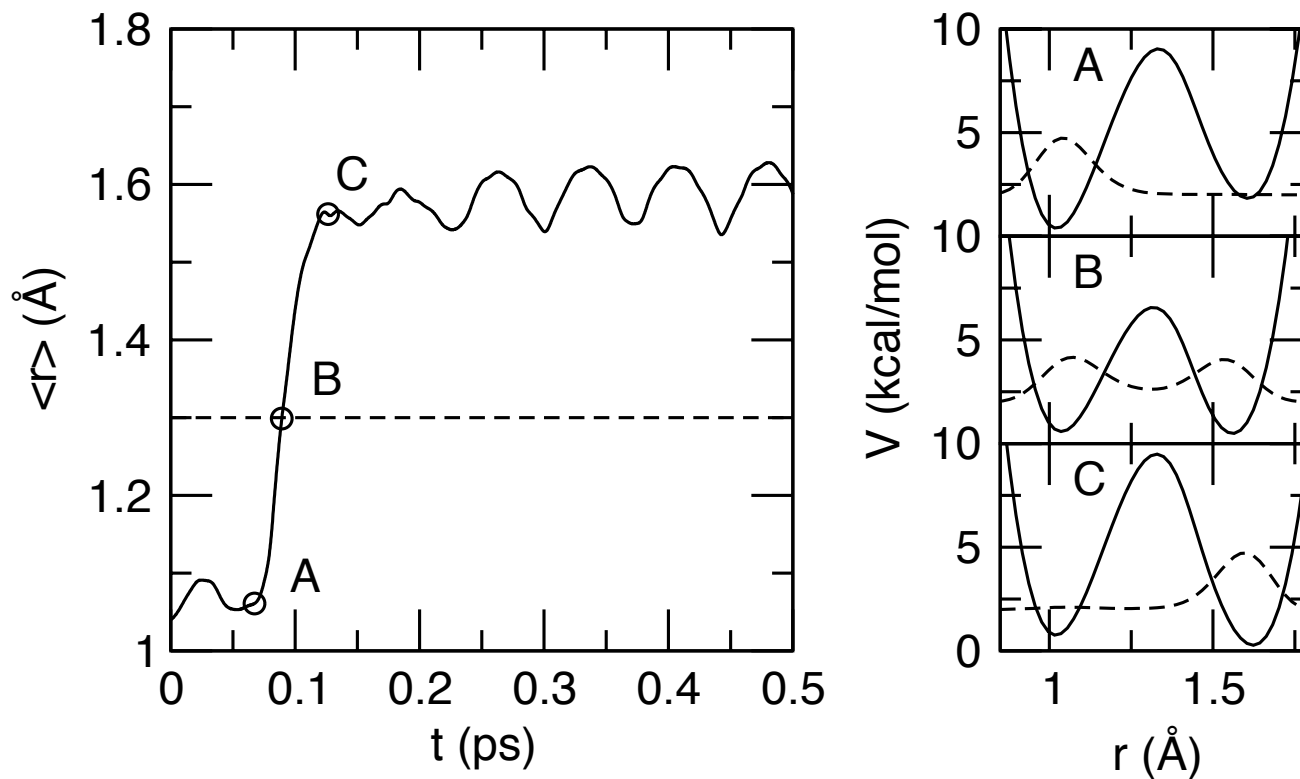


Results for H and D transfer (with $r = r_{AH} =$ proton transfer coordinate)



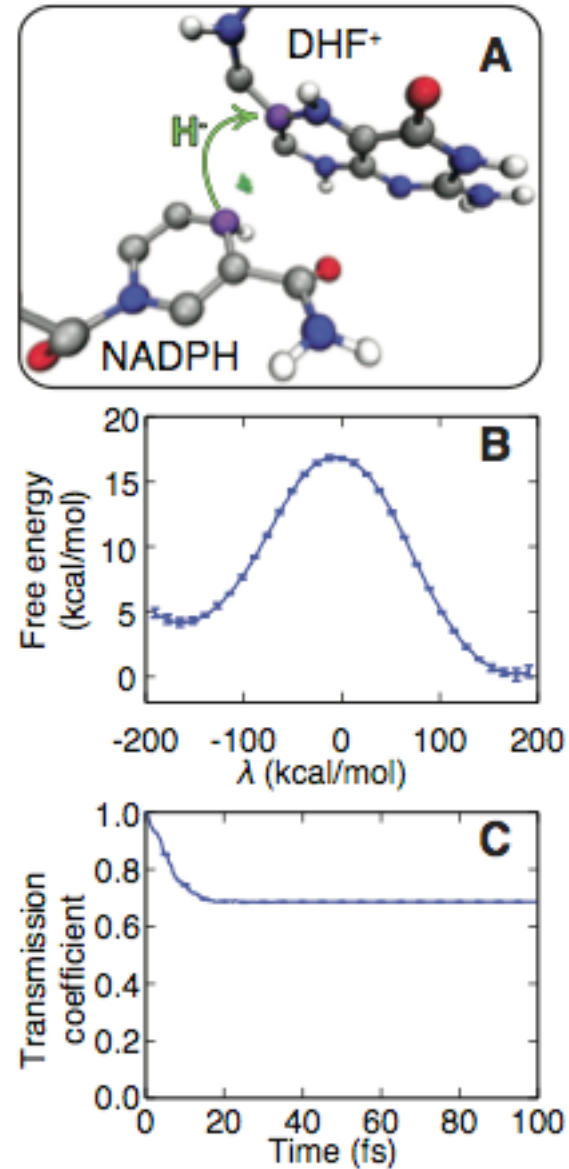
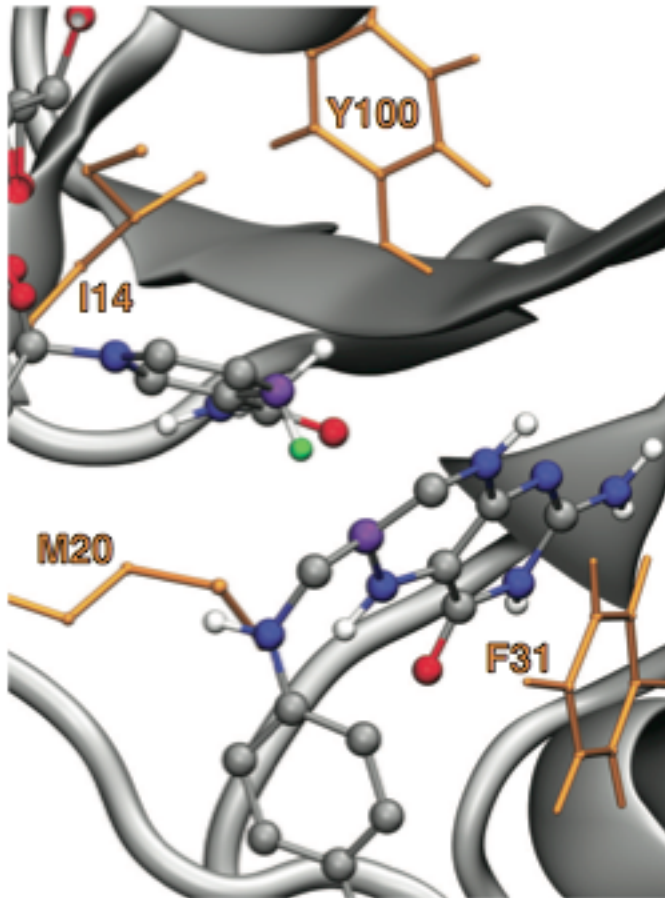
Method	$k_H / 10^{10} \text{ s}^{-1}$	$k_D / 10^{10} \text{ s}^{-1}$	k_H / k_D
QTST	13.5	0.34	40
RPMD	1.62	0.085	19

But the solvent polarisation does not...



...and this reaction coordinate gives exactly the same RPMD rate!

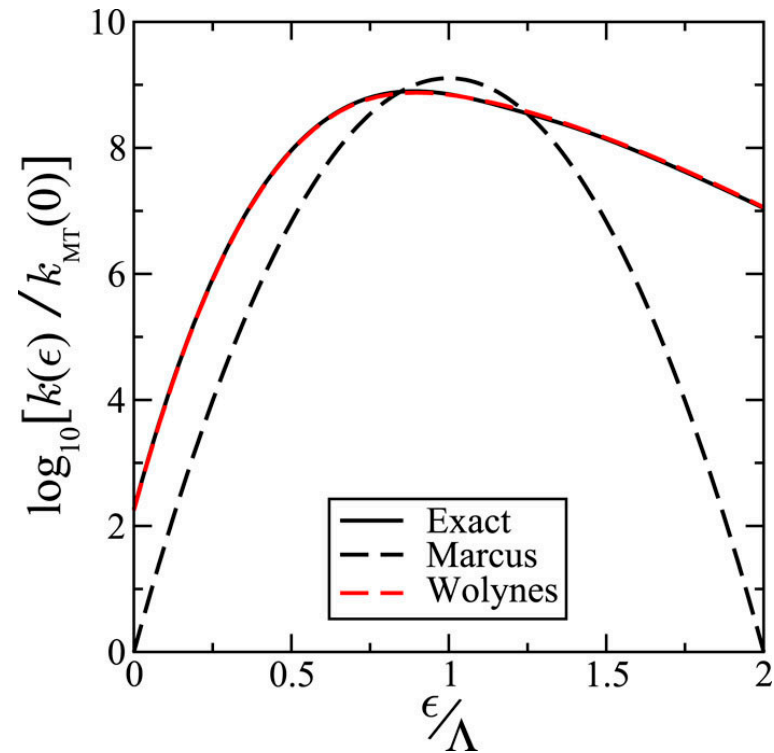
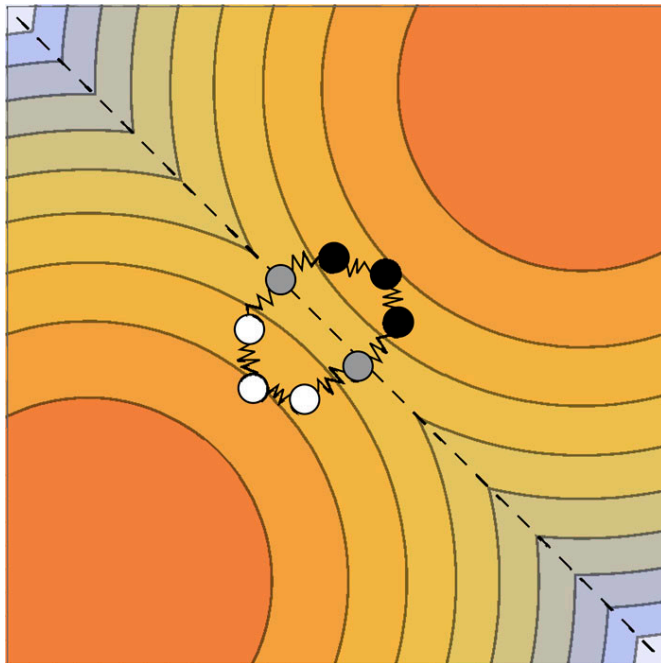
C. “Dynamics and dissipation in enzyme catalysis”¹²



N. Boekelheide *et al.*
PNAS 108, 16159 (2011)

E. And finally...

Having “solved” the adiabatic rate problem, we are now working on non-adiabatic (electron transfer) rates.^{13,14}



See Joseph Lawrence's talk on Friday for more details!

5. References

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