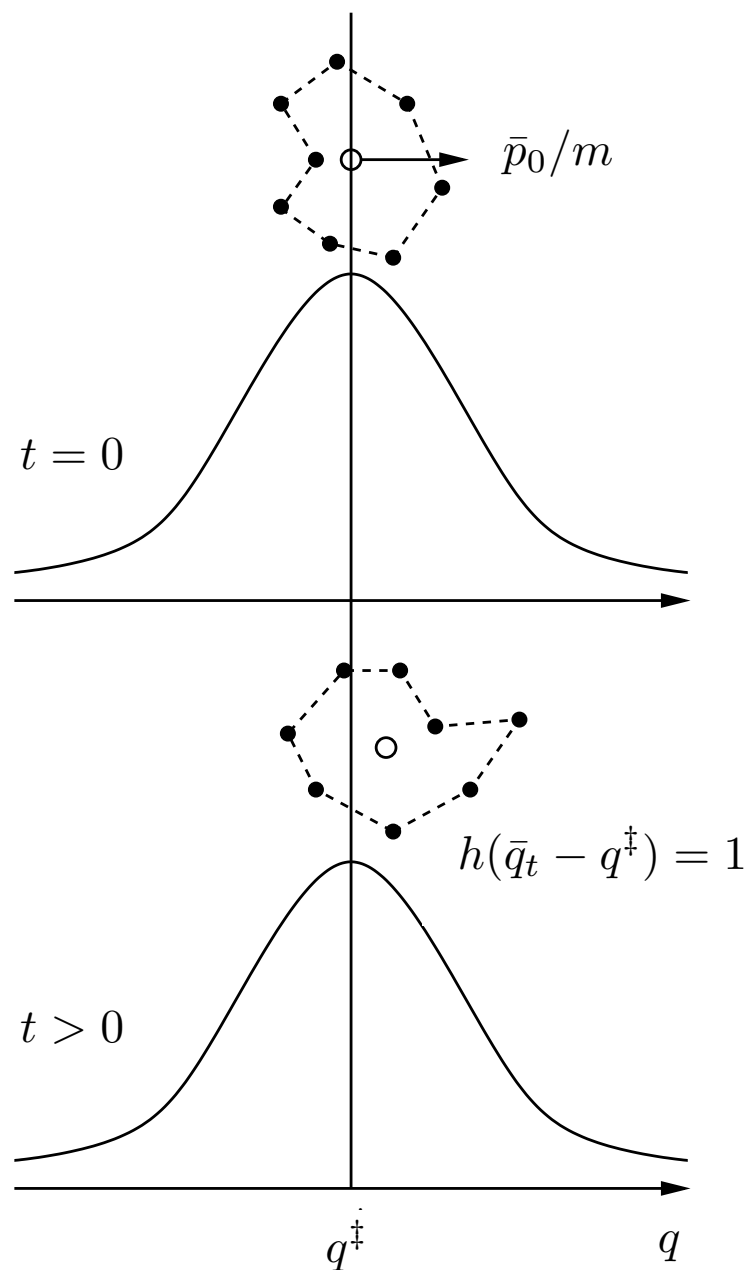# Ring polymer rate theory

David Manolopoulos
Department of Chemistry
University of Oxford
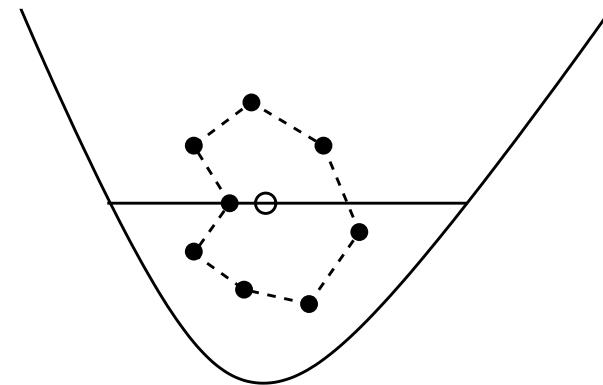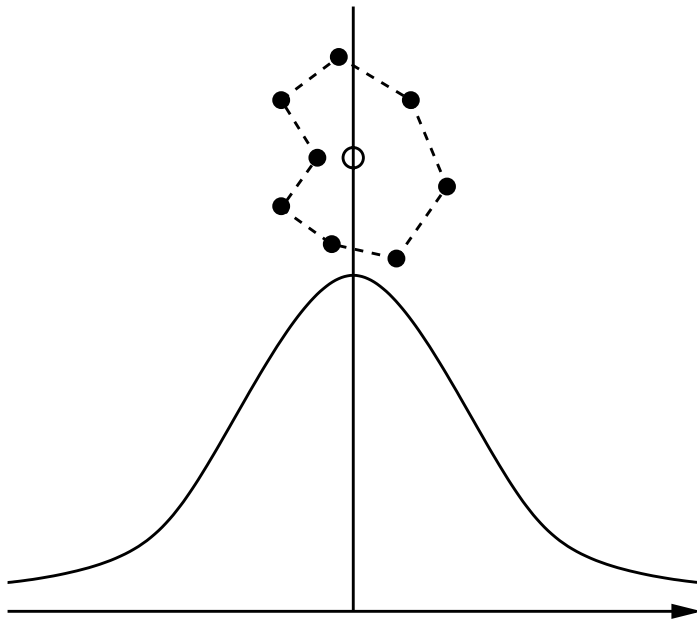
Mariapfarr Workshop 2019
Lecture III

1. 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]

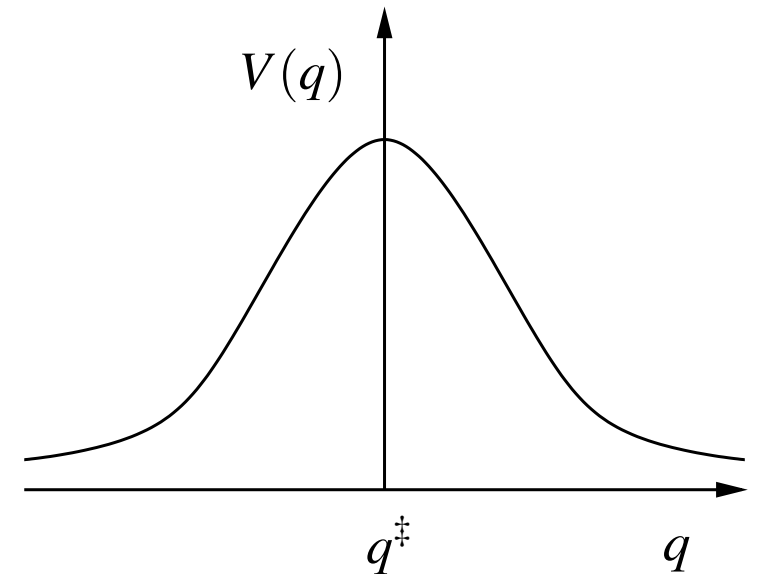$$k(T) = \frac{1}{Q_r(T)} \lim_{t \to \infty} \tilde{c}_{fs}(t)$$

where

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

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 $q^\ddagger$.
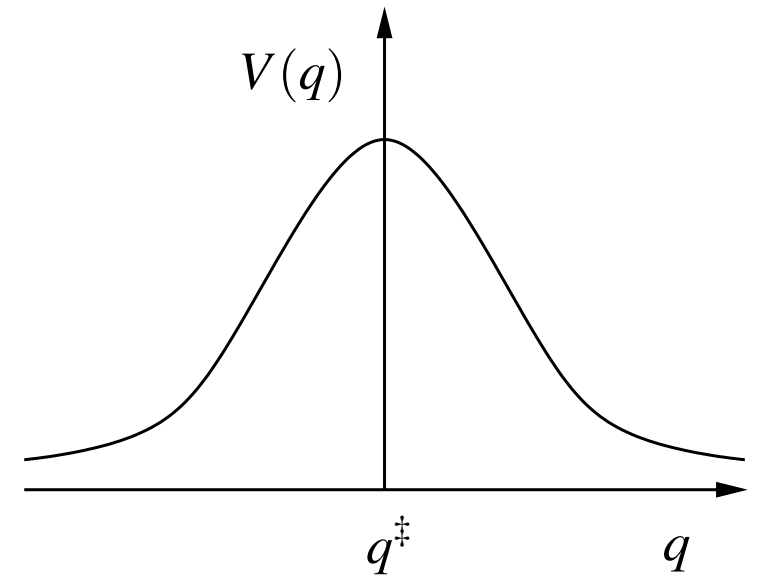
2. $\tilde{c}_{fs}(t \to 0_+) \sim t^{1/2} \to 0.$

The classical limit:

The classical limit rate coefficient is

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

where

$$\tilde{c}_{fs}(t) = \frac{1}{2\pi\hbar} \int dp_0 \int dq_0 \, e^{-\beta H(p_0, q_0)}$$

$$\times \underbrace{\delta(q_0 - q^{\ddagger})\frac{p_0}{m}}_{\text{Flux (t = 0)}} \times \underbrace{h(q_t - q^{\ddagger})}_{\text{Side (t > 0)}}.$$
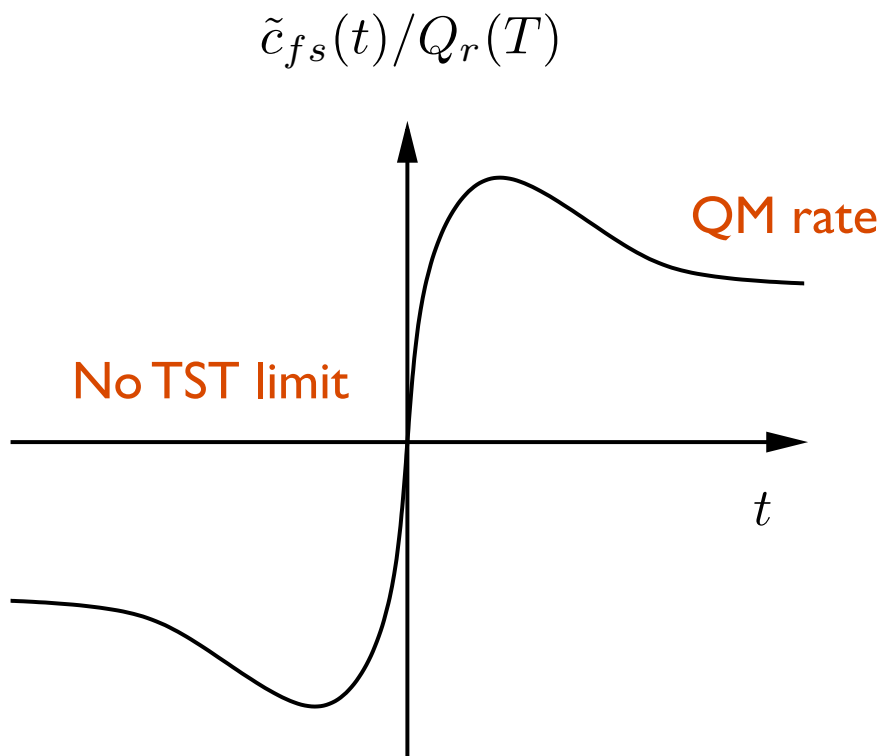
NB:
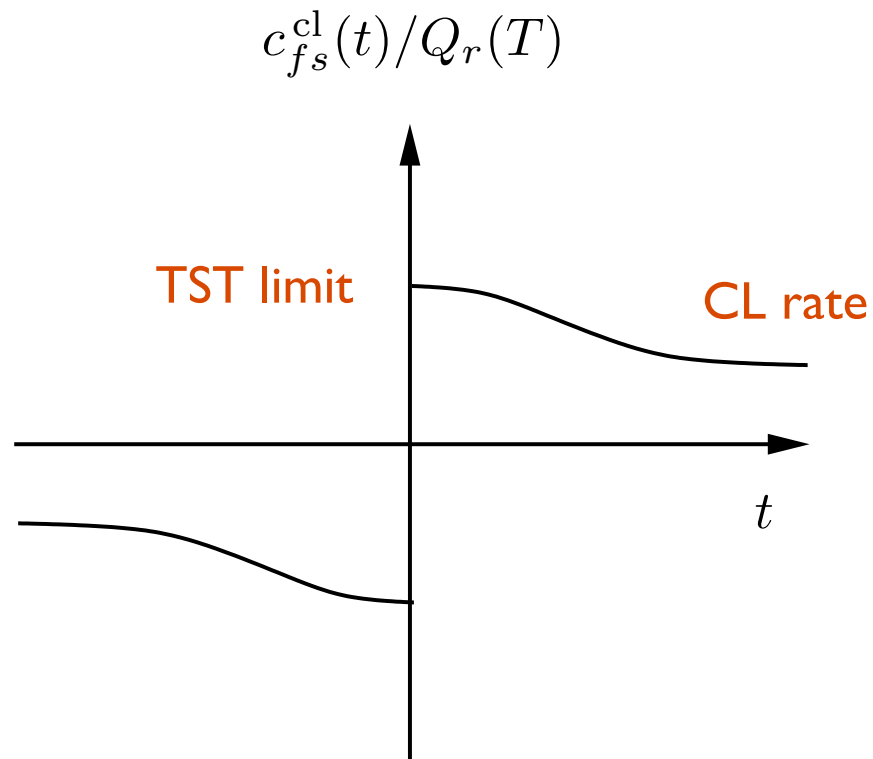
1. $k^{\mathrm{cl}}(T)$ is independent of $q^{\ddagger}$.

2. As $t \to 0_+$, $h(q_t - q^{\ddagger}) \to h(p_0)$, giving

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

Quantum

$\tilde{c}_{fs}(t)/Q_r(T)$

QM rate

No TST limit

t

Classical

$c_{fs}^{\mathrm{cl}}(t)/Q_r(T)$

TST limit

CL rate

t

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

"Quantum transition state theory"

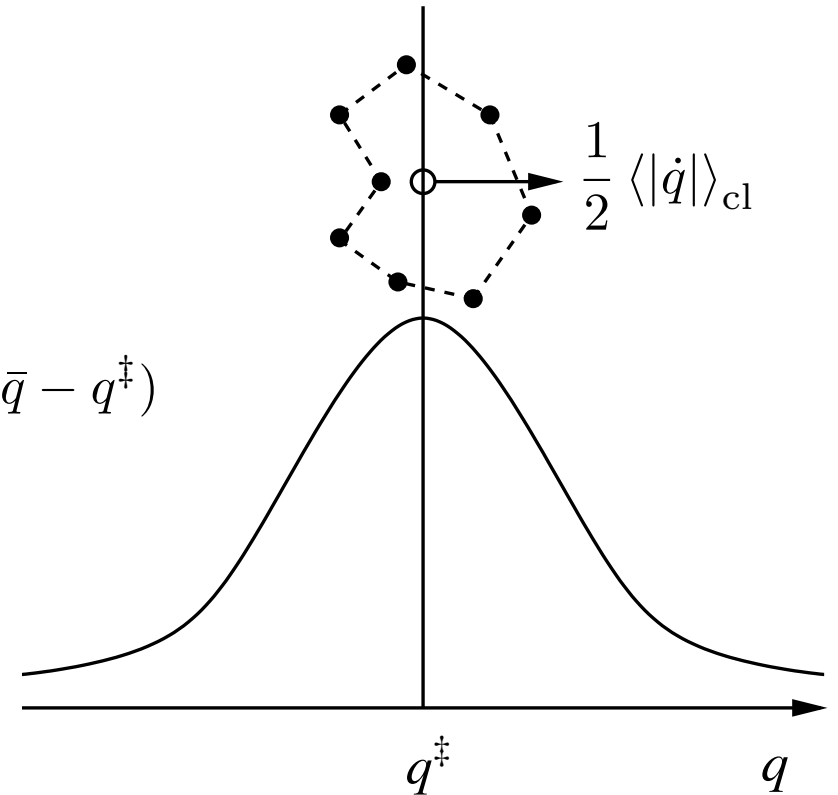The centroid density QTST rate is[3,4]

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

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

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

$$\frac{1}{2} \langle |\dot{q}| \rangle_{\text{cl}}$$

NB:

1. $e^{-\beta V(q^{\ddagger})} \to Q(q^{\ddagger})/Q_r(T)$ 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]

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

where

$$\bar{c}_{fs}(t) = \frac{1}{(2\pi\hbar)^n} \int d\mathbf{p}_0 \int d\mathbf{q}_0 \, e^{-\beta_n H_n(\mathbf{p}_0, \mathbf{q}_0)}$$

$$\times \, \delta(\bar{q}_0 - q^{\ddagger}) \frac{\bar{p}_0}{m} h(\bar{q}_t - q^{\ddagger})$$
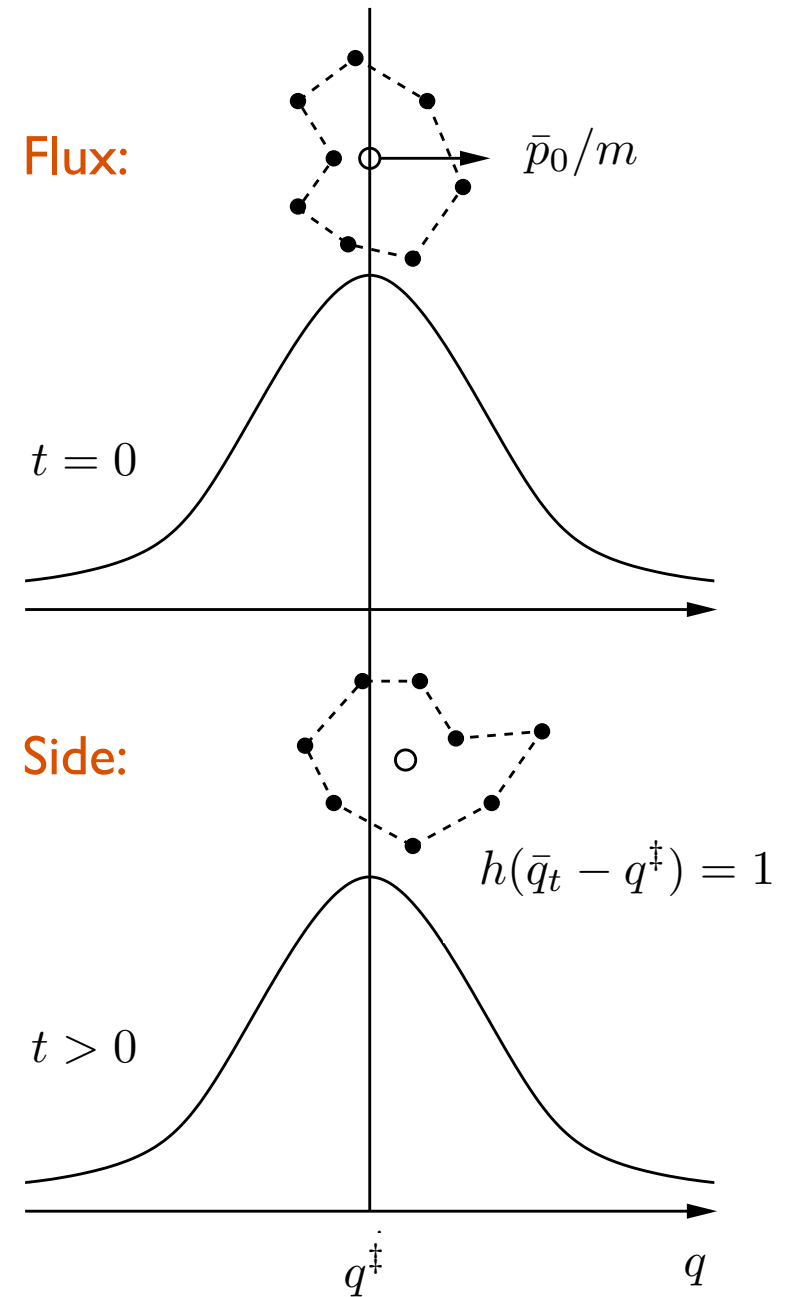
and

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

NB: With these definitions,

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

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

Flux:

$\bar{p}_0/m$

$t = 0$

Side:

$h(\bar{q}_t - q^{\ddagger}) = 1$

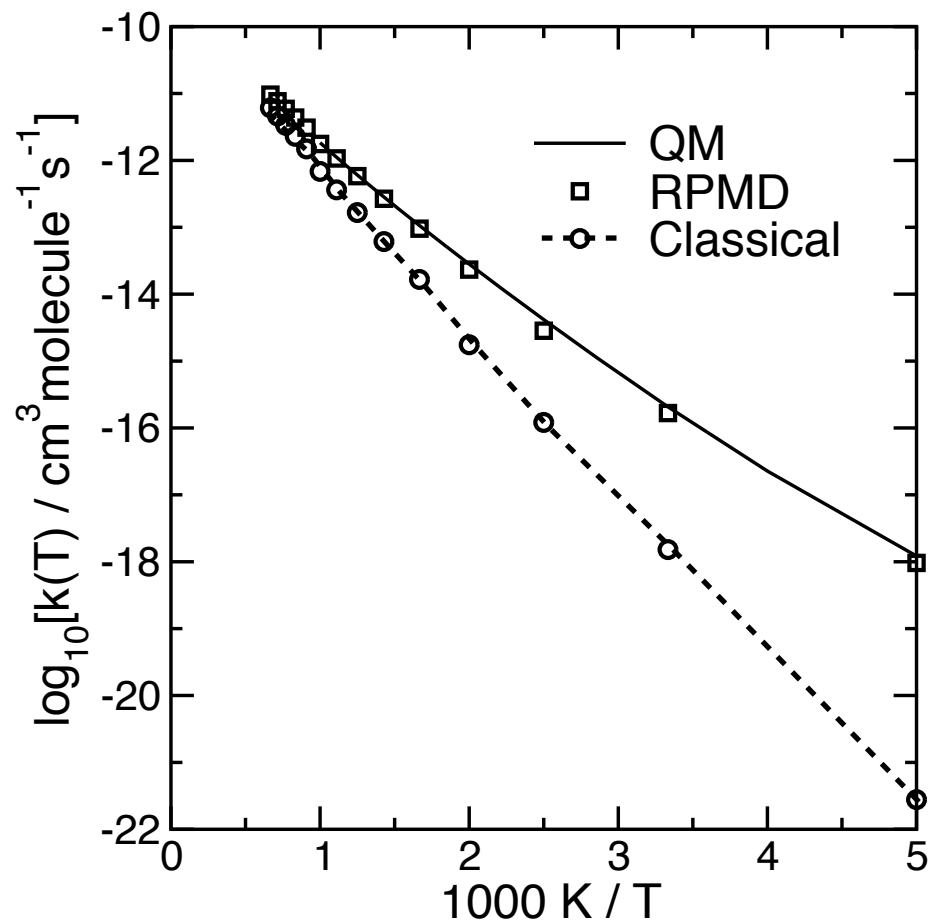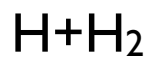$t > 0$

$q^{\ddagger}$

q

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
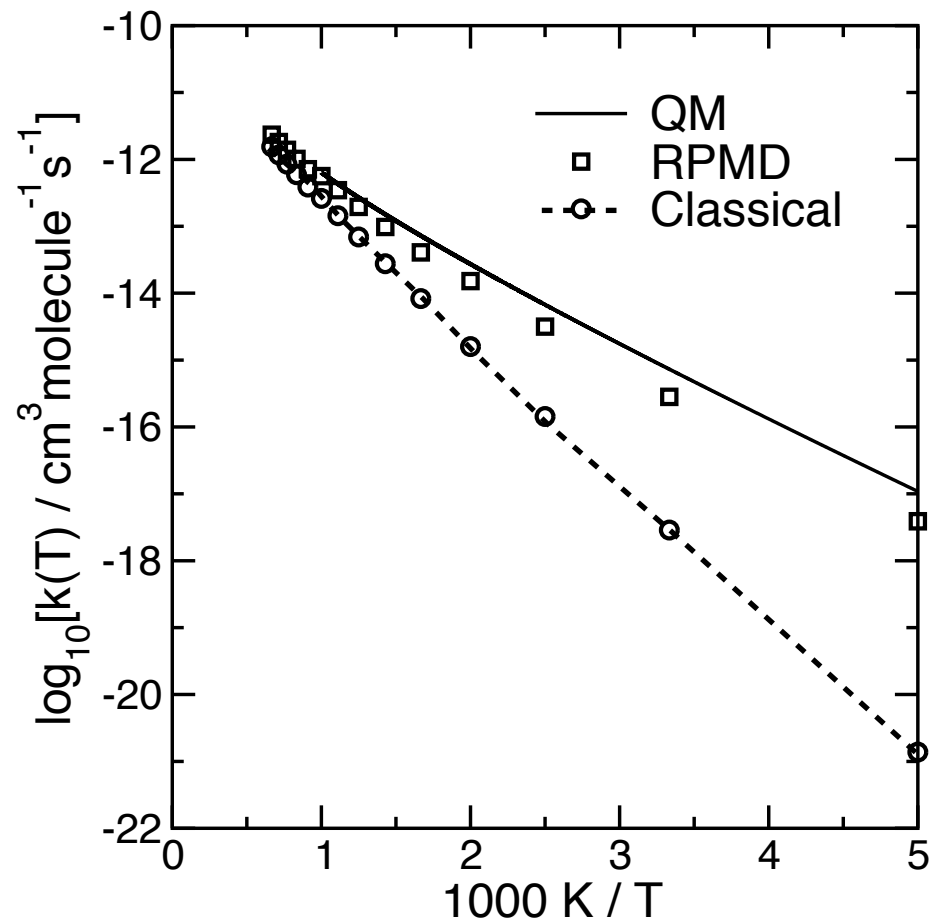
7. Consistent with the QM equilibrium constant

…and it has one further highly desirable feature:

H+H$_2$

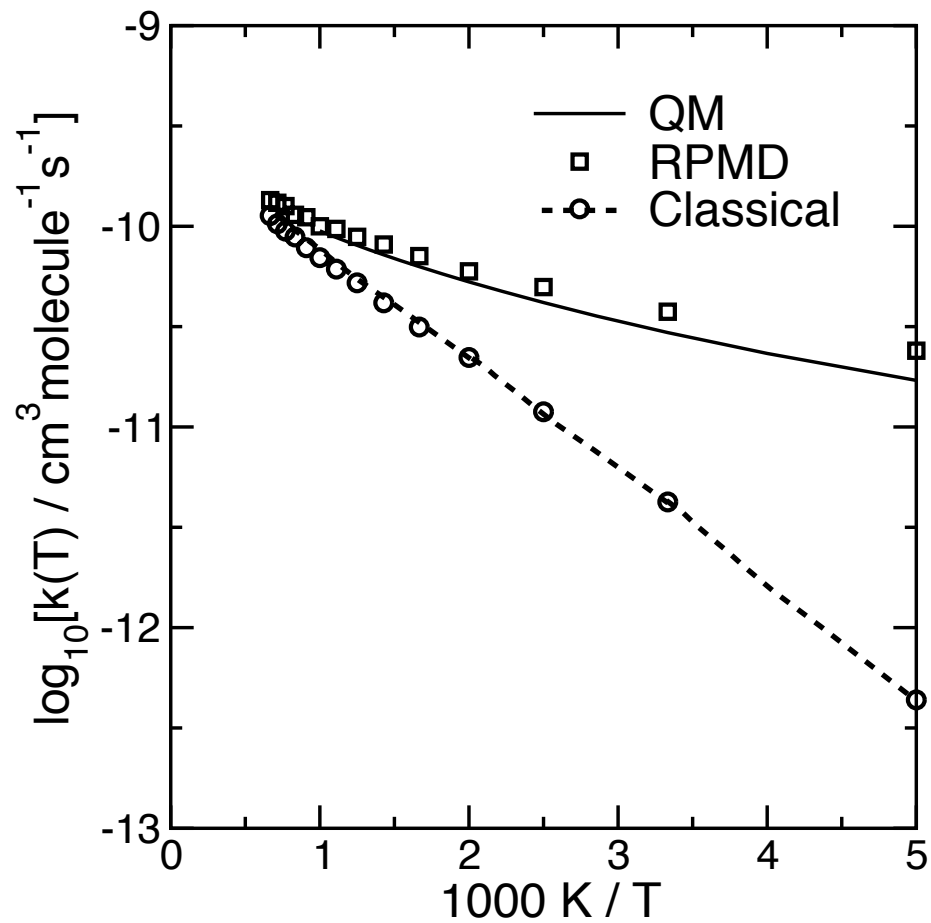Symmetric barrier. T_c = 345 K.
RPMD is out by −21% at 200 K.

Cl+HCl

QM
RPMD
Classical

Symmetric barrier. T_c = 320 K.
RPMD is out by −64% at 200 K.

F+H$_2$

$\log_{10}[k(T)$ / cm^{3}molecule^{-1}s^{-1}]

1000 K / T

QM
RPMD
Classical

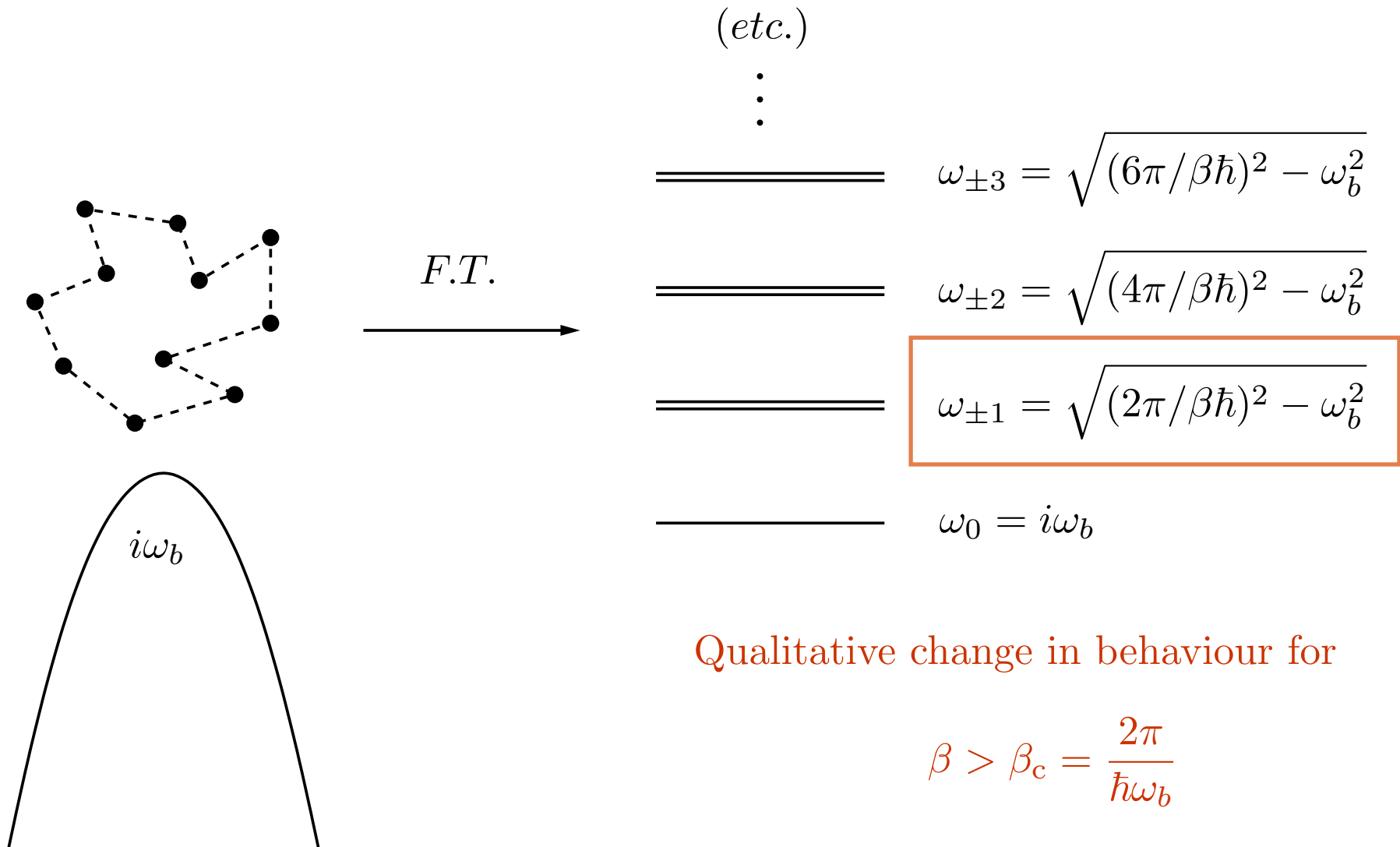*Asymmetric barrier. T_c = 264 K.*
RPMD is out by +46% at 200 K.

H+CH$_4$
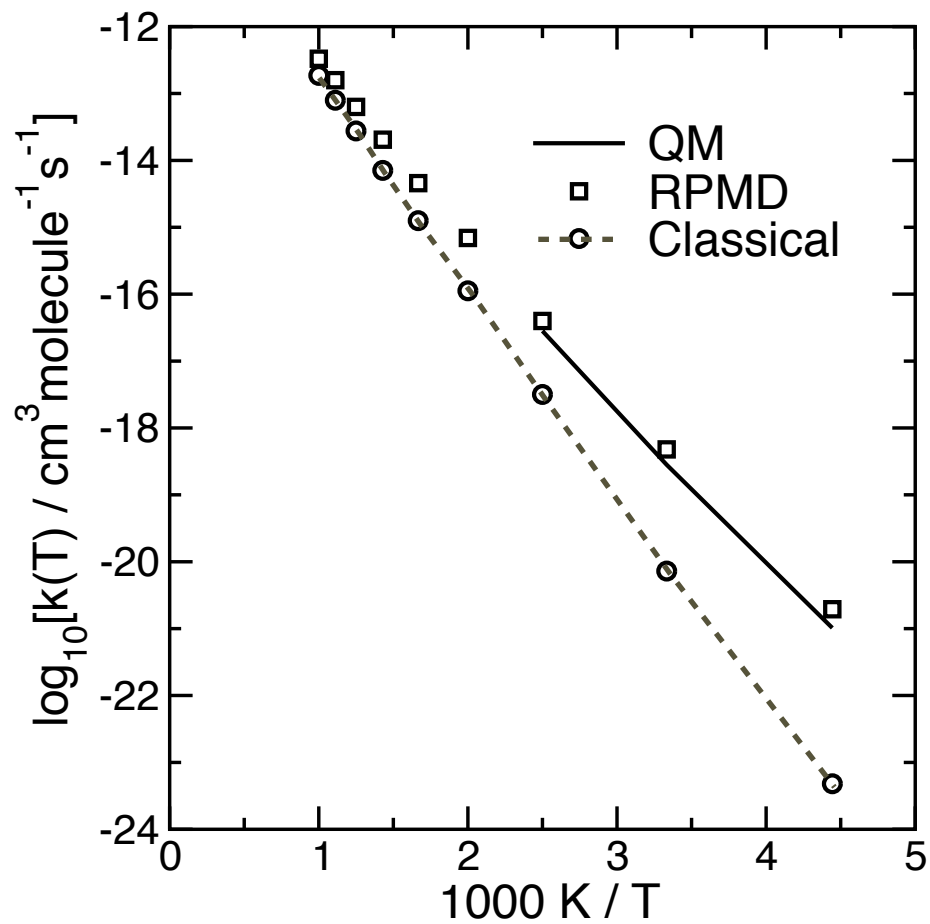
Asymmetric barrier. T_c = 296 K.
RPMD is out by +92% at 225 K.

The deep tunneling regime[9]

$(etc.)$

$\vdots$

$\omega_{\pm 3} = \sqrt{(6\pi/\beta\hbar)^2 - \omega_b^2}$

$\overset{F.T.}{\longrightarrow}$

$\omega_{\pm 2} = \sqrt{(4\pi/\beta\hbar)^2 - \omega_b^2}$

$\boxed{\omega_{\pm 1} = \sqrt{(2\pi/\beta\hbar)^2 - \omega_b^2}}$

$\omega_0 = i\omega_b$

$i\omega_b$

Qualitative change in behaviour for

$$\beta > \beta_{\mathrm{c}} = \frac{2\pi}{\hbar\omega_b}$$

$$T < T_{\mathrm{c}} = \frac{\hbar\omega_b}{2\pi k_{\mathrm{B}}}$$

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

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

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obtained by applying classical transition
optimal dividing surface; this TST rate
Im F instanton rate. The optimal dividin
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
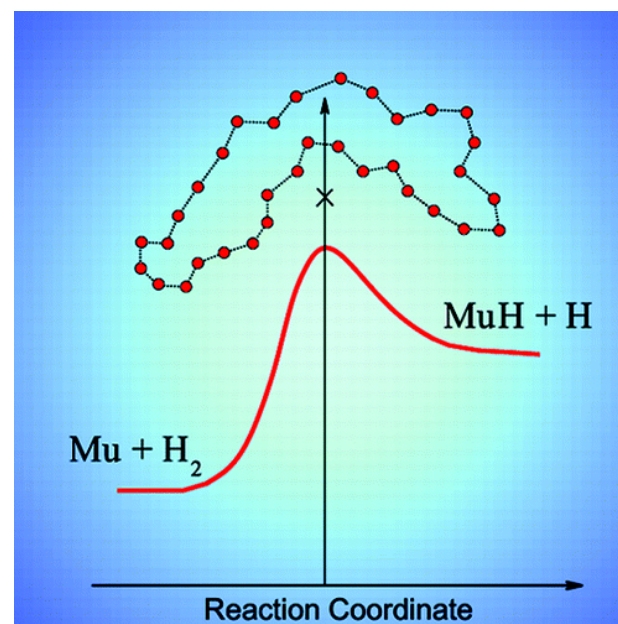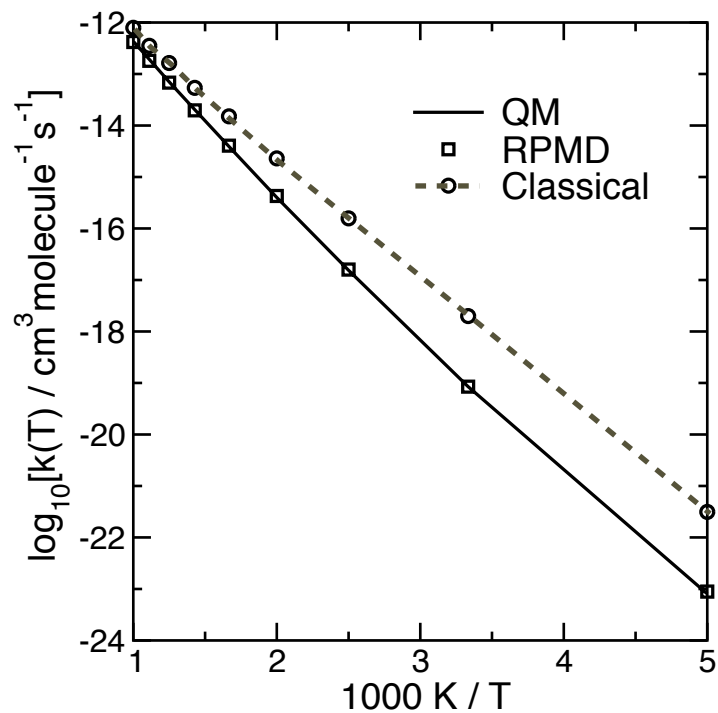consequence of setting the bead-masses
Physics. [doi:10.1063/1.3267318]
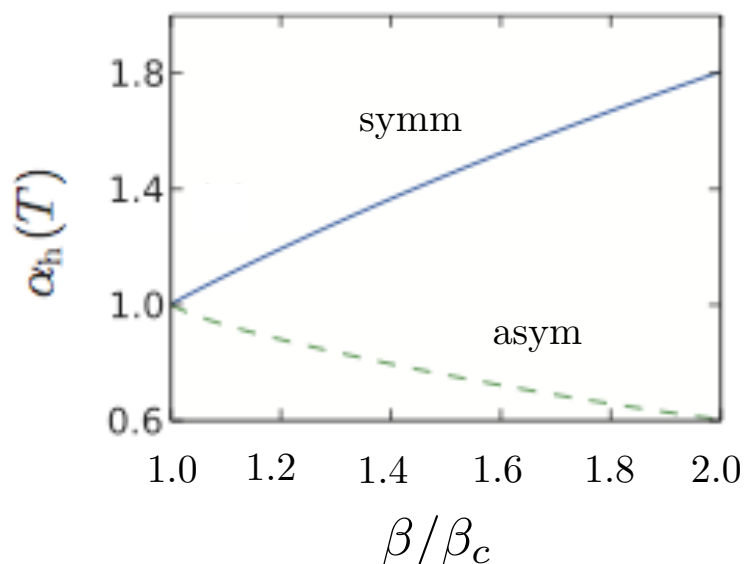
$$k_{\mathrm{RPMD}}^{\mathrm{oTST}}(T) = \frac{1}{\alpha(T)} k_{\mathrm{inst}}(T)$$

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

$$Mu + H_2 \rightarrow MuH + H$$
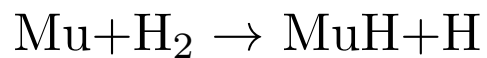
Perez de Tudela *et al.* (2012)[10]

Asymmetric barrier. ZPE dominated.

RPMD is out by just +5% at 200 K.

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

Yu.V. Suleimanov [a,b,*], J.W. Allen [a], W.H. Green [a]

[a] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States
[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	$C(^1D)+H_2$, $S(^1D)+H_2$
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	$H+C_2H_6$

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

4. Condensed phase examples

A. A system-bath model[5]

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

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + V(\hat{q}_1) + \sum_{i=2}^{f} \left[\frac{\hat{p}_i^2}{2m} + \frac{1}{2} m\omega_i^2 \left(\hat{q}_i - \frac{c_i \hat{q}_1}{m\omega_i^2} \right)^2 \right]$$
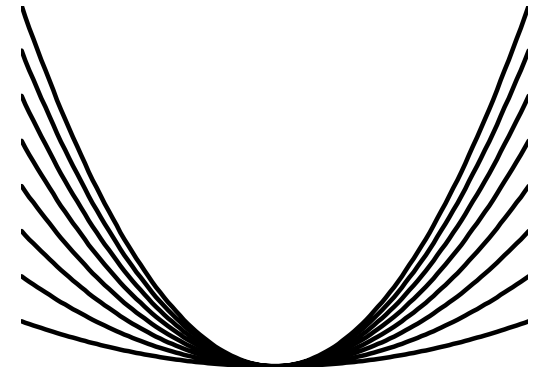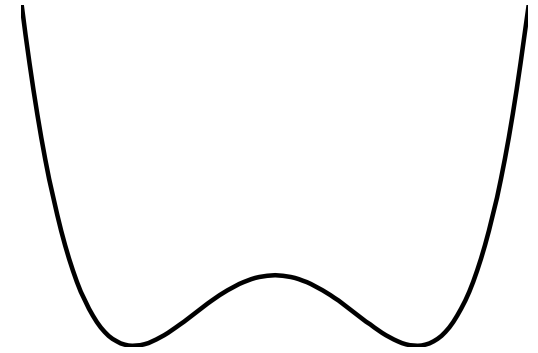
with
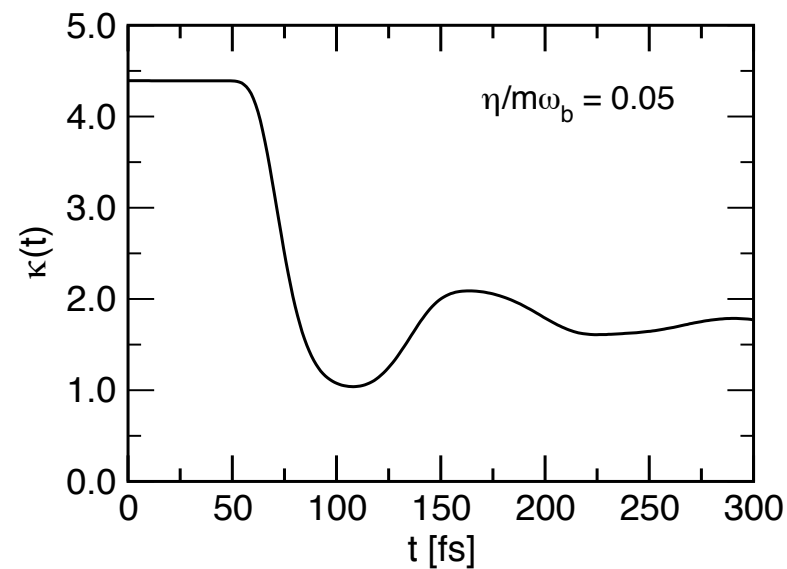
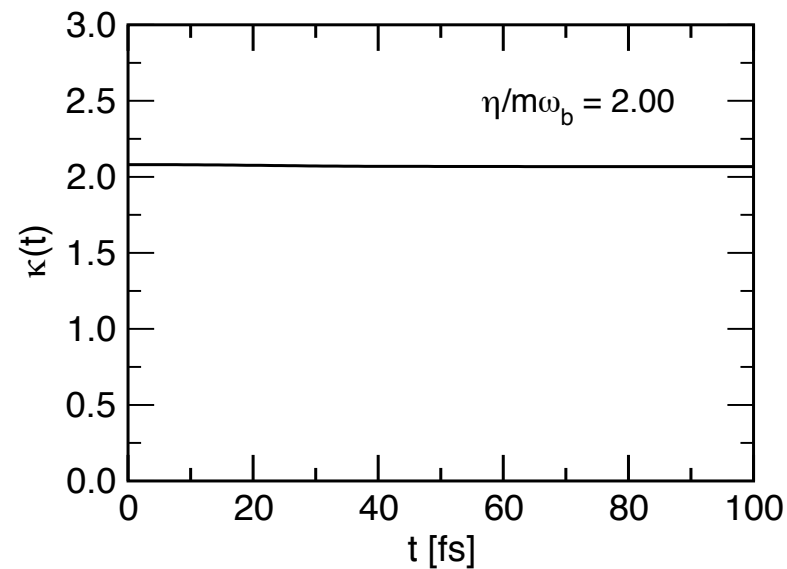$$V(\hat{q}_1) = -a_2 \hat{q}_1^2 + a_4 \hat{q}_1^4$$
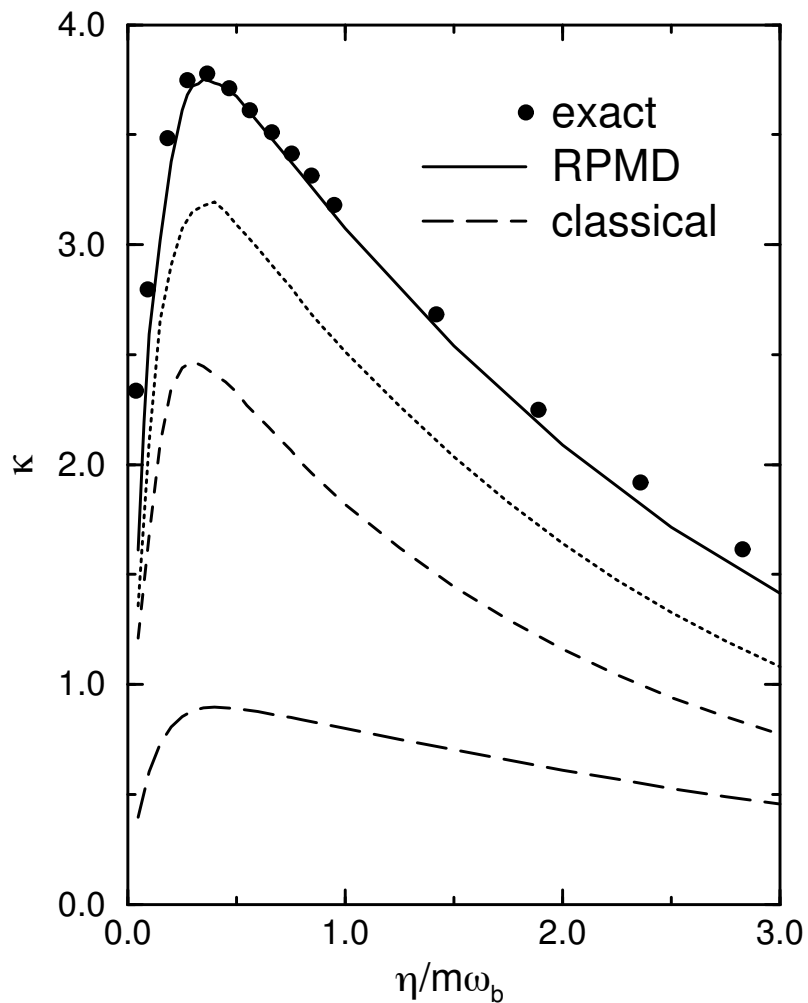
and

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

Parameters chosen to model a proton transfer reaction in solution.
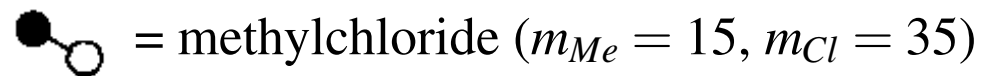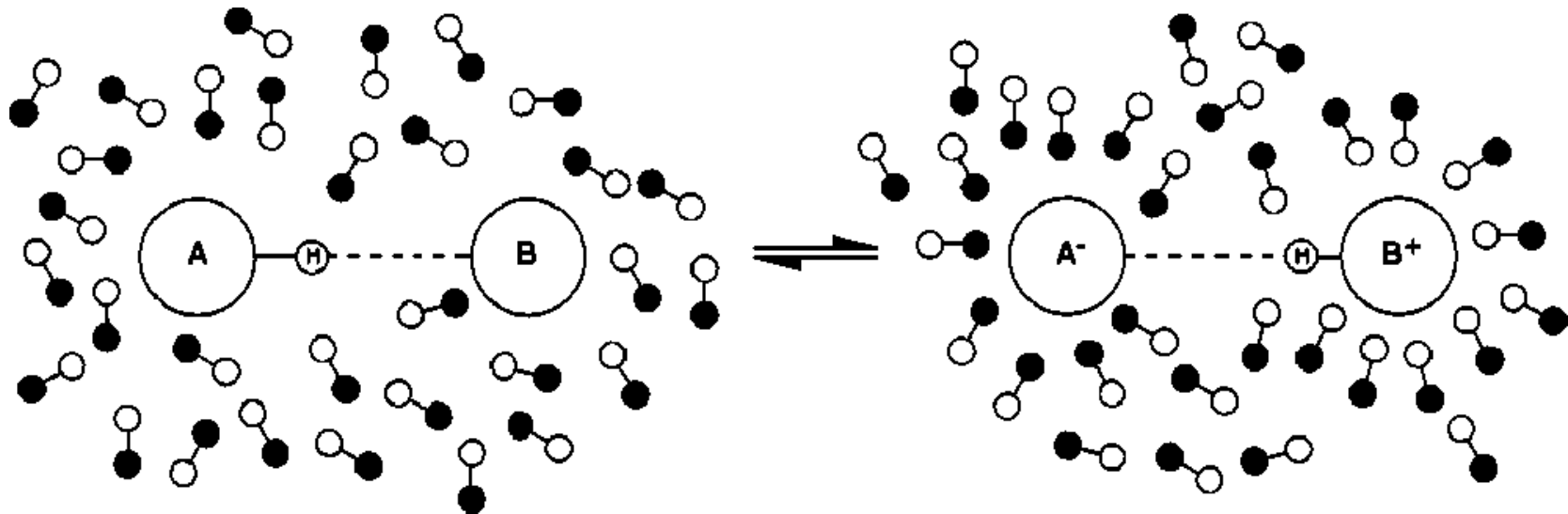
System-bath model at 200 K

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

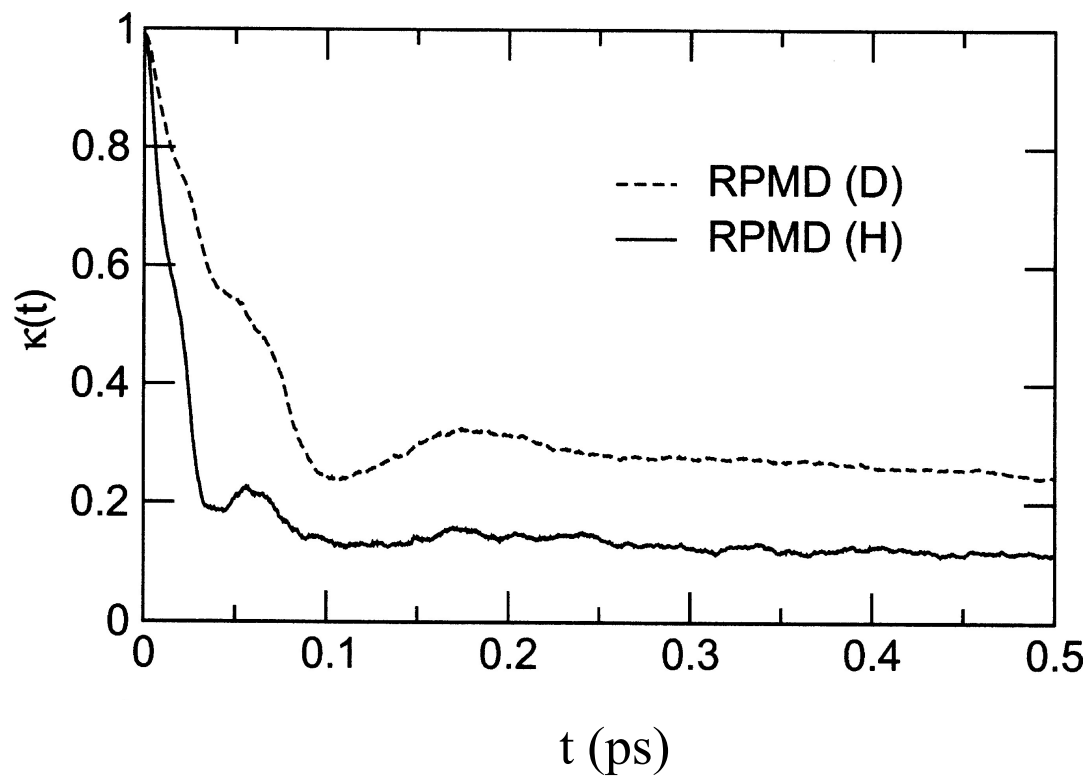Correct quantum turnover behaviour…   …and transition state recrossing dynamics.

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

A—(H) = phenol $(m_A = 93)$ B = trimethylamine $(m_B = 59)$

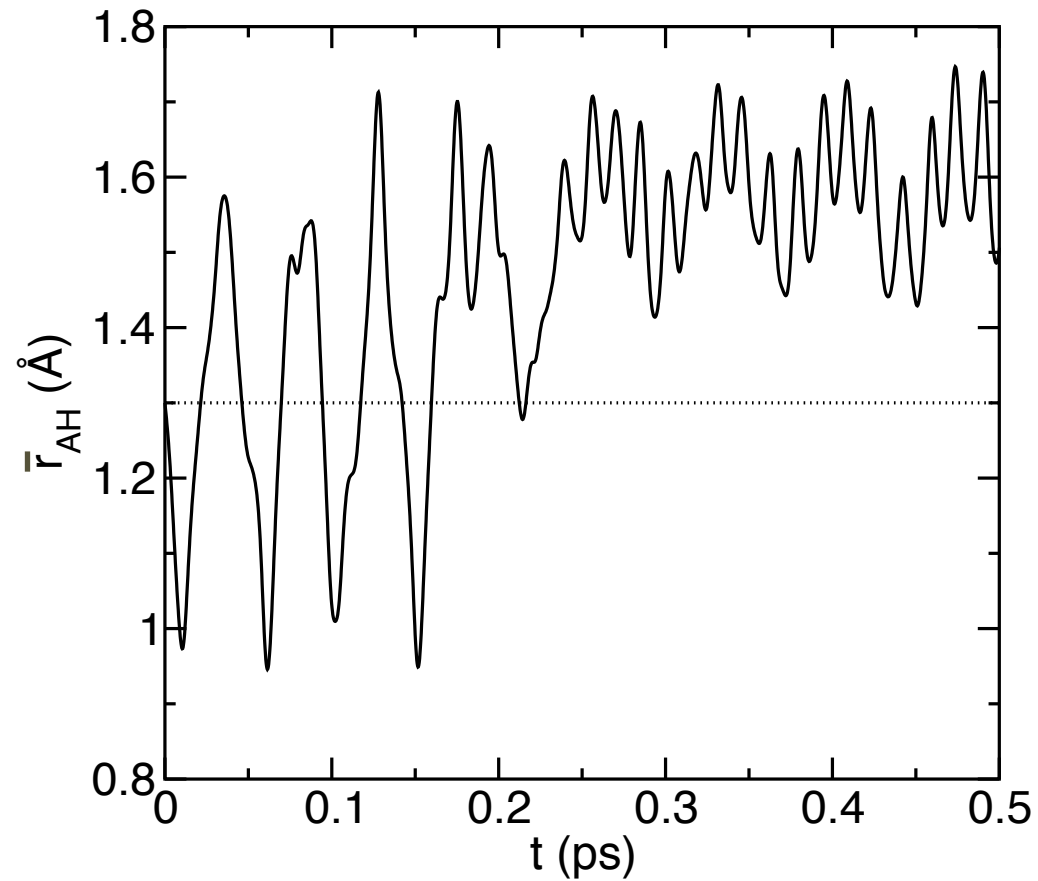●○ = methylchloride $(m_{Me} = 15, m_{Cl} = 35)$

Results for H and D transfer (with $r = r_{AH}$ = proton transfer coordinate)
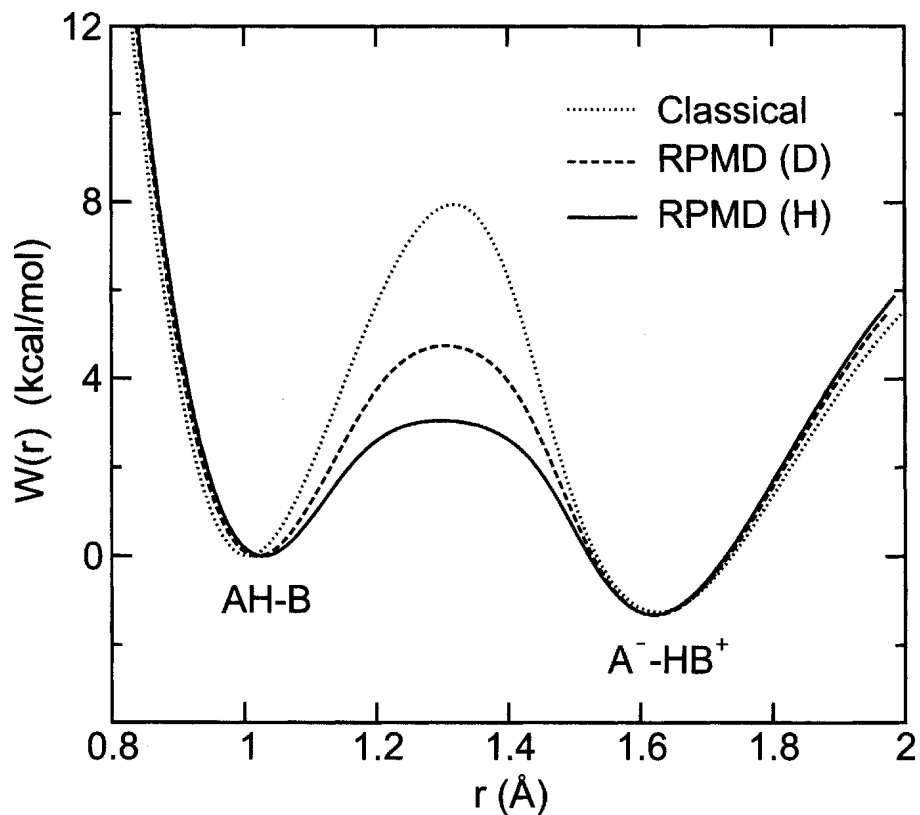
Method	k_H / 10^{10} s^{-1}	k_D / 10^{10} s^{-1}	k_H / k_D
QTST	13.5	0.34	40
RPMD	1.62	0.085	19

The proton transfer coordinate exhibits significant recrossing…
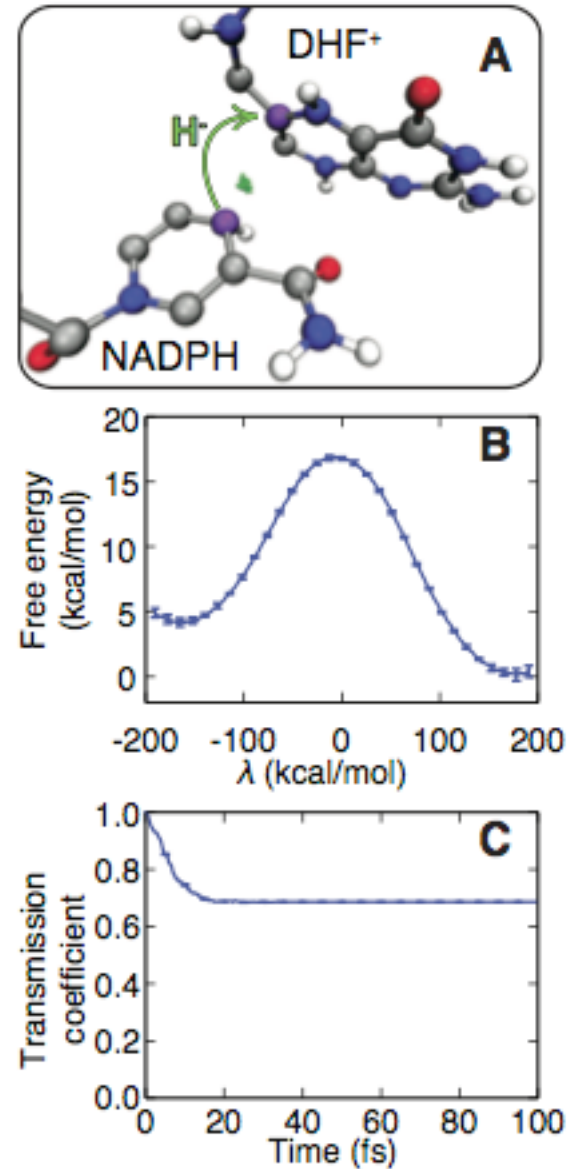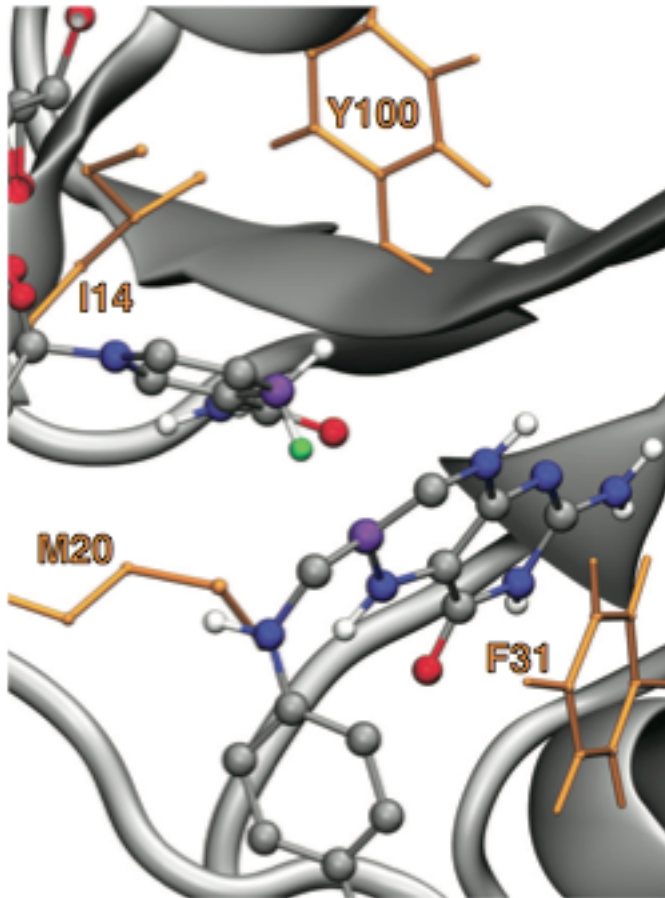(shown here for a representative trajectory)

…owing to the heavy-light-heavy mass combination.

But the solvent polarisation does not…
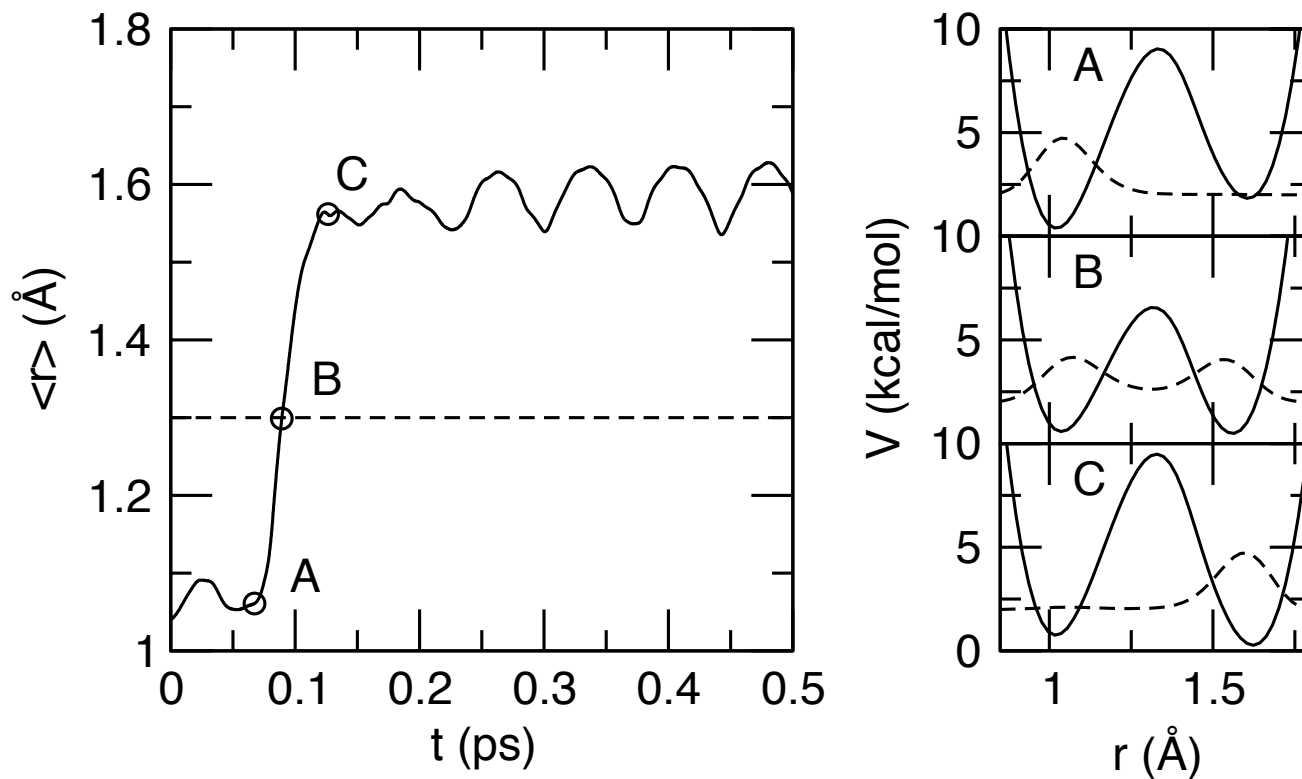
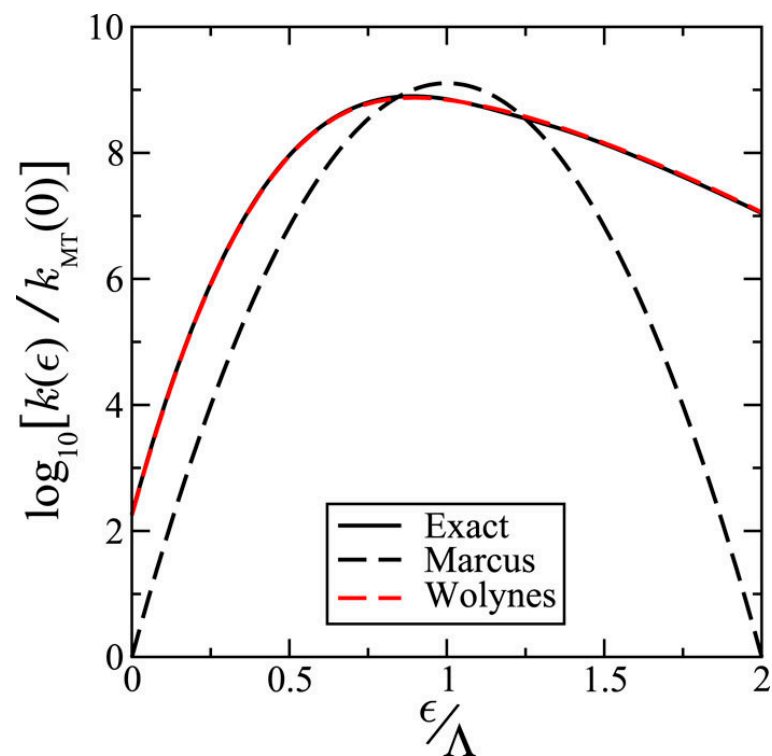…and this reaction coordinate gives exactly the same RPMD rate!
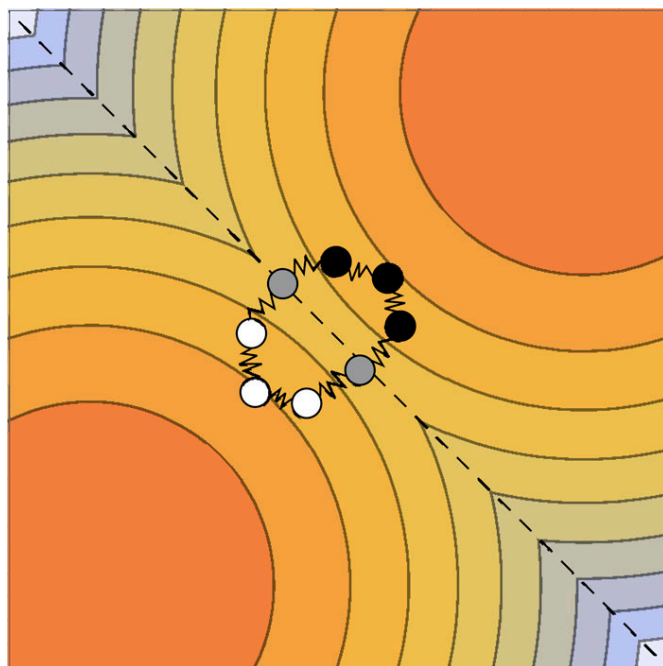
N. Boekelheide *et al.*
PNAS 108, 16159 (2011)

D. 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!

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