TSTC Dynamics Lectures
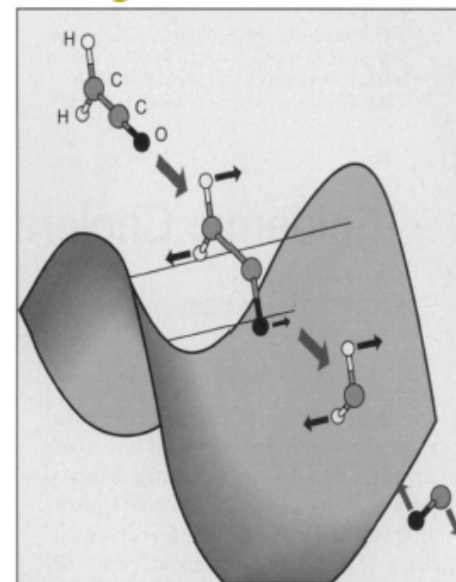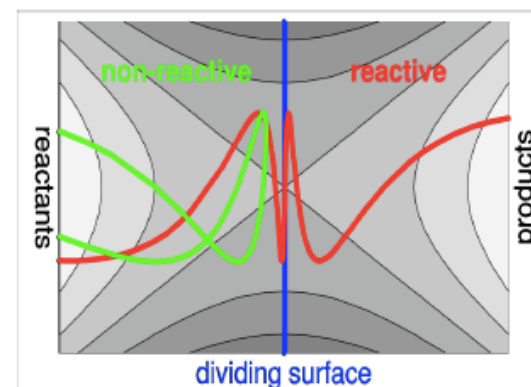## Transition State Theory
July 14-20

Ned Sibert
University of Wisconsin
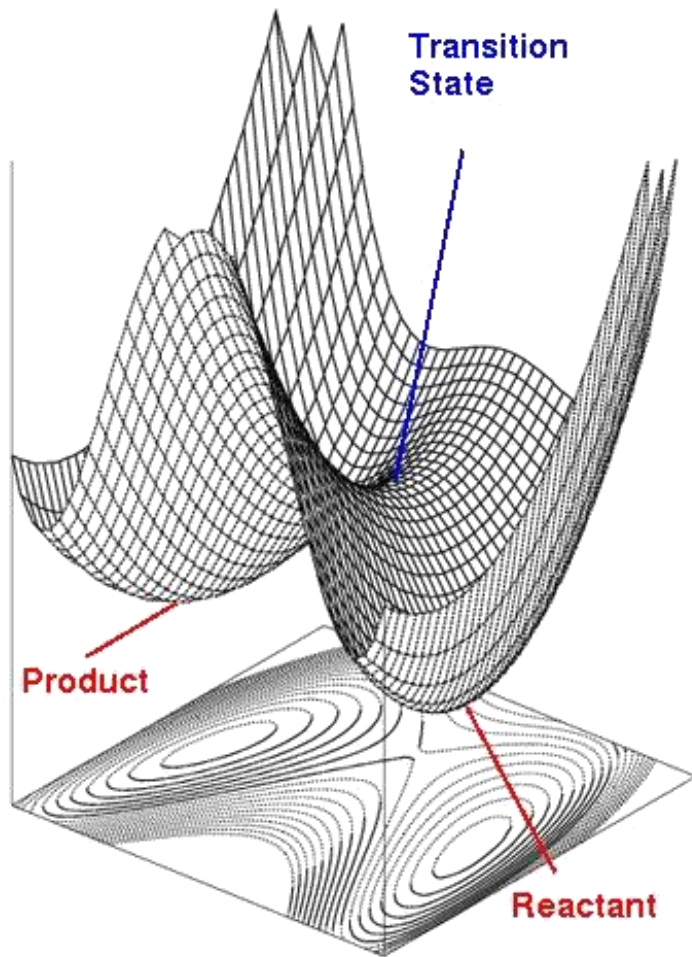
Transition State Theory

- **Objective:**
  - Calculate reaction rates
  - Obtain insight on reaction mechanism

- **Eyring, Wigner, Others..**
  - Existence of Born-Oppenheimer $V(x)$
  - Classical nuclear motions
  - No dynamical recrossings of TST

- **Keck,Marcus,Miller,Truhlar, Others...**
  - Extend to phase space
  - Variational Transition State Theory
  - Formal reaction rate formulas

- **Pechukas, Pollak...**
  - PODS—2-Dimensional non-recrossing DS

- **Full-Dimensional Non-Recrossing Surfaces**
  - Miller, Hernandez developed good action-angle variables at the TS using CVPT/Lie PT to construct semiclassical rates
  - Jaffé, Uzer, Wiggins, Berry, Others... extended to NHIM's, etc

(Marcus: Science **256** (1992) 1523)

non-reactive   reactive

reactants   products

dividing surface

TSTC
Telluride School on Theoretical Chemistry

Transition State Theory and Beyond

$$k(T) = \frac{kT}{h} \frac{Q^{\ddagger}(T)}{Q_r(T)}$$

Transition State Theory:
A Dynamical Perspective

Transition state theory is the theory for the interpretation of chemical reaction rates.

See *Current Status of Transition-State Theory*, J. Phys. Chem. **87** 2664 (1983). for an excellent review.

In a series of papers Miller [Acc. Chem. Res. 1993, 26, 174] made deep connections between TST and dynamics, building on earlier work of Pechukas and others. He also make connections with quantum mechanical scattering theory.

A Simple 1D Model for Transition State (Pechukas)
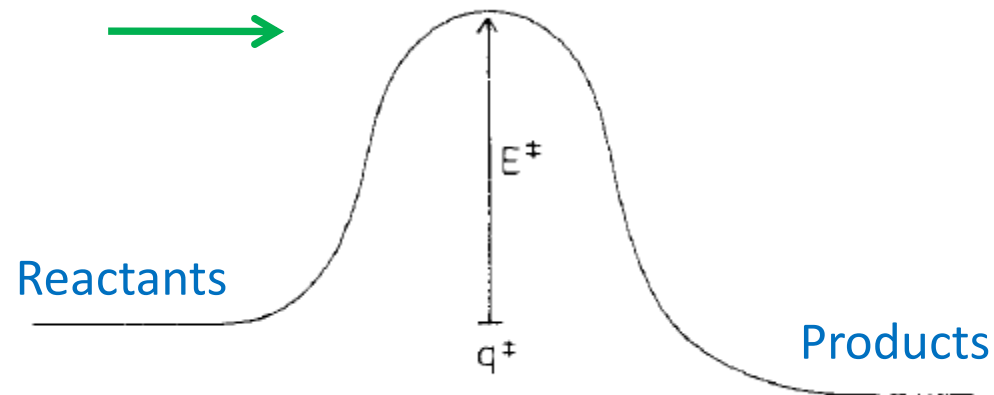
The rate constant for the above 1D model is

$$k = \int_{(2mE^\ddagger)^{1/2}}^{\infty} dp\, \frac{p}{m}\rho(p), \tag{1}$$

where $\rho(p)$ is the probability that a reactant molecule has momentum between p and $p + dp$.

If we assume that

$$\rho(p) = \exp(-p^2/2mkT)/(2\pi mkT)^{1/2} \tag{2}$$

then we can evaluate the integral to obtain

$$k = \frac{kT}{h}\frac{\exp(-E^\ddagger/mkT)}{(2\pi mkT)^{1/2}/h} \tag{3}$$

$$k = (2\pi mkT)^{-1/2} \int_{(2mE^{\ddagger})^{1/2}}^{\infty} dp \, \frac{p}{m} \exp(-p^2/2mkT),$$

We can make the whole calculation look slightly less juvenile by introducing an obscure notation and obtain

$$k = (2\pi mkT)^{-1/2} \int dp \, \frac{p}{m} \chi_r(p, q) \exp[-H(p, q)/kT],$$

where $\chi_r(p, q)$, the characteristic function = 1 for a reactive trajectory and 0 for a nonreactive trajectory. The quantity $\chi_r(p, q) \exp[-H(p, q)/kT]$ is a phase space density. Its flux through any dividing surface is constant.

The equilibrium rate constant is proportional to the classical flux of this density through the surface in phase space defined by the equation $q = constant$.

As technical aside, one sees the below expression written with and without the 'r' subscript on χ.

$$k = (2\pi mkT)^{-1/2} \int dp \, \frac{p}{m} \chi r(p,q) \exp[-H(p,q)/kT],$$

$\chi_r(p,q)=1$ for a reactive trajectory, otherwise $\chi_r(p,q)=0$.
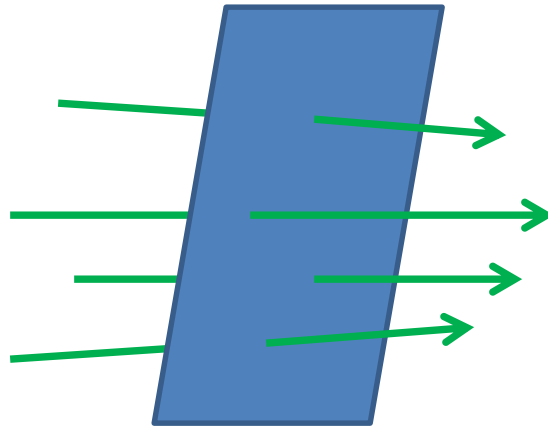$\chi(p,q) = \chi_r(p,q)+\chi_{nr}(p,q)$.

Transition state theory replaces $\chi_r(p,q^+)$ with $\chi_+(p,q^+)$ where

$$\chi_+(p,q) = 1 \quad if \quad p > 0$$
$$= 0 \; otherwise$$

Higher Dimensions

1 dimensional → F - dimensional

$$\frac{p}{m} = \frac{dq}{dt} \longrightarrow \frac{d}{dt} h\big[s(\mathbf{q})\big] = F(\mathbf{q}, \mathbf{p})$$

flux

- S(q=0) defines a F-1 dimensional hypersurface.
- h is the heaviside function.

The Flux - $F(\mathbf{p}, \mathbf{q})$

The flux is defined wrt a dividing surface $s(\mathbf{q}) = 0$.

$$F(\mathbf{q}, \mathbf{p}) = \frac{d}{dt} h[s(\mathbf{q})] = \delta[s(\mathbf{q})] v_s(\mathbf{p}, \mathbf{q}) \qquad (3)$$

where $v_s(\mathbf{p}, \mathbf{q}) \equiv ds(\mathbf{q})/dt$ is velocity along reaction coordinate.

$$\frac{ds}{dt} = \sum_{i=1}^{F} \frac{\partial s}{\partial q_i} \dot{q}_i = \sum_{i=1}^{F} \frac{\partial s}{\partial q_i} \frac{p_i}{m}$$

The Characteristic Function - $\chi(\mathbf{p}, \mathbf{q})$

$\chi(\mathbf{p}, \mathbf{q}) = 1$ if the trajectory, determined by initial conditions at time t=0, goes from reactant in the infinite past to products in the infinite future. Otherwise $\chi(\mathbf{p}, \mathbf{q}) = 0$.
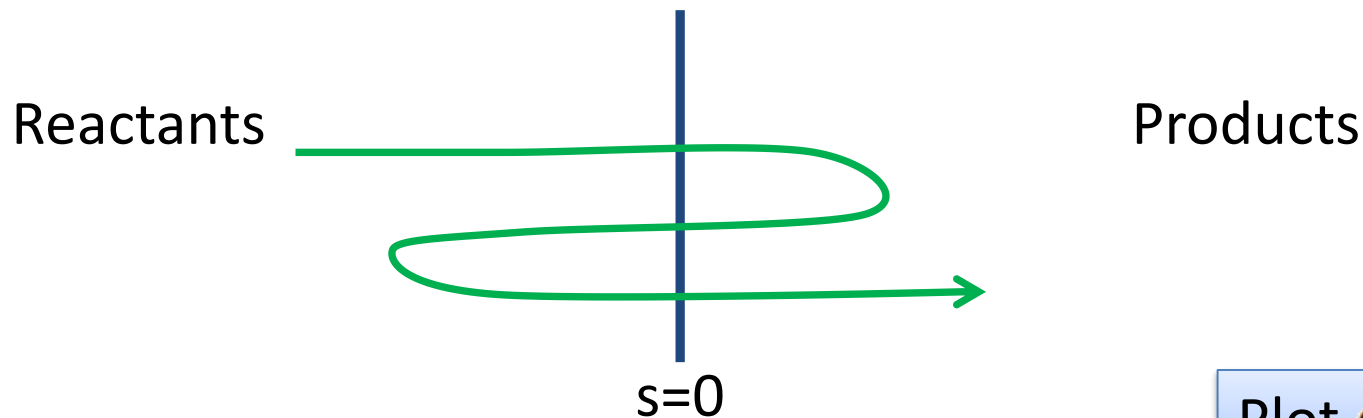
$$\chi(\mathbf{p}, \mathbf{q}) = \lim_{t \to \infty} h[s(\mathbf{q})]$$

Classical Equilibrium Rate Result

$$Q_r(T)k(T) = [h]^{-F} \int d\mathbf{p} \int d\mathbf{q} \ e^{-H(\mathbf{p},\mathbf{q})/k_B T} F(\mathbf{p},\mathbf{q})\chi(\mathbf{p},\mathbf{q}).$$

$$Q_r(T)k(T) = \lim_{t\to\infty} [h]^{-F} \int d\mathbf{p} \int d\mathbf{q} \ e^{-H(\mathbf{p},\mathbf{q})/k_B T} \delta[s(\mathbf{q})]v_s(\mathbf{p},\mathbf{q})h[s(\mathbf{q}(t))].$$

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

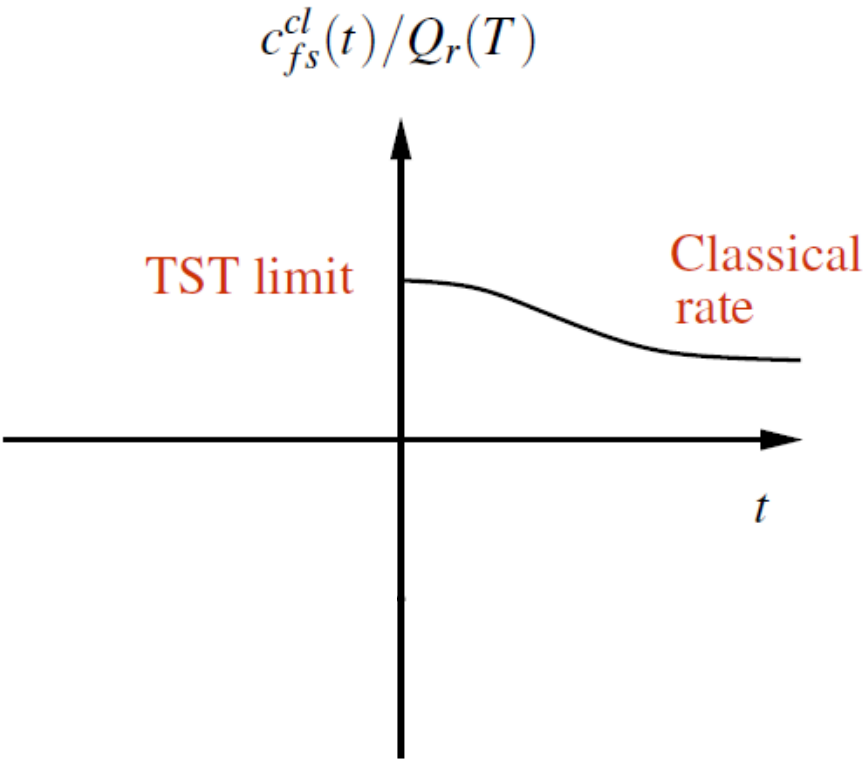Reactants   Products

s=0

Plot $c_{fs}^{cl}(t)$ for t>0.

$$Q_r(T)k(T) = [h]^{-F} \int d\mathbf{p} \int d\mathbf{q} \ e^{-H(\mathbf{p},\mathbf{q})/k_BT} F(\mathbf{p},\mathbf{q})\chi(\mathbf{p},\mathbf{q}).$$

$$Q_r(T)k(T) = \lim_{t\to\infty} [h]^{-F} \int d\mathbf{p} \int d\mathbf{q} \ e^{-H(\mathbf{p},\mathbf{q})/k_BT} \delta[s(\mathbf{q})]v_s(\mathbf{p},\mathbf{q})h[s(\mathbf{q}(t))].$$

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

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

TST limit

Classical rate

t

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

Transition State Theory

The dynamical TST approximation is

$$\chi_{\mathsf{TST}}(\mathbf{p}, \mathbf{q}) = \lim_{t \to 0^+} h[s(\mathbf{q})] = h(v_s),$$

where h is the Heaviside fn.

One also assumes an initial equilibrium distribution of reactants and no products.

In a tour de force of mathematical dexterity, Miller reduced the thermal rate constant to

$$k(T) = \frac{kT}{h} \frac{Q^{\ddagger}(T)}{Q_r(T)} \tag{4}$$

where $Q^{\ddagger}$ is the partition function on the dividing surface,

$$Q^{\ddagger}(T) = (2\pi\hbar)^{-(F-1)} \int d\mathbf{p}' \int d\mathbf{q}' \; e^{-H_{F-1}(\mathbf{p}', \mathbf{q}')/k_B T}. \tag{5}$$

Kramers theory

H.A. Kramers (1894-1952)

In Kramers theory (1940) the assumption of equilibrium in the reactant well is maintained, and attention is focussed on the barrier region. Using a model for Brownian motion over the barrier, where the reacting particle experiences friction due to the surrounding solvent molecules, Kramers was able to derive an expression for the rate constant:

$$k^{\mathsf{K}} = \frac{m\omega_b}{\zeta} k^{\mathsf{TST}}$$

where ω_b is the barrier frequency, m the mass of the reactive particle, and ζ the friction constant it experiences in its motion. This result only holds in the limit of very high friction.

Reaction coordinate
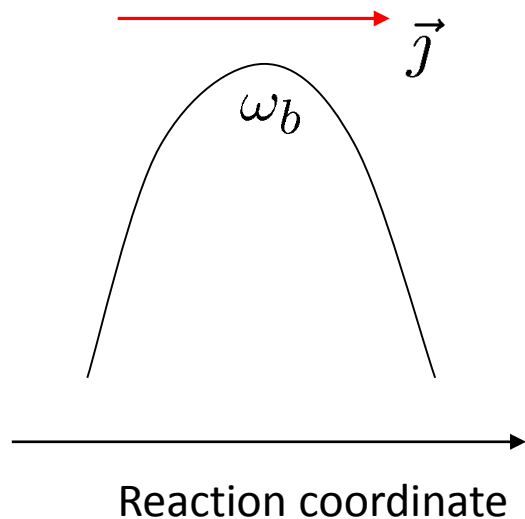
The Kramers rate is *always* lower than the rate calculated with TST. The reason is that now it is not sufficient for the particle to reach the top of the barrier, it has to have sufficient velocity to go over it, or it will be sent back to the reactant well.

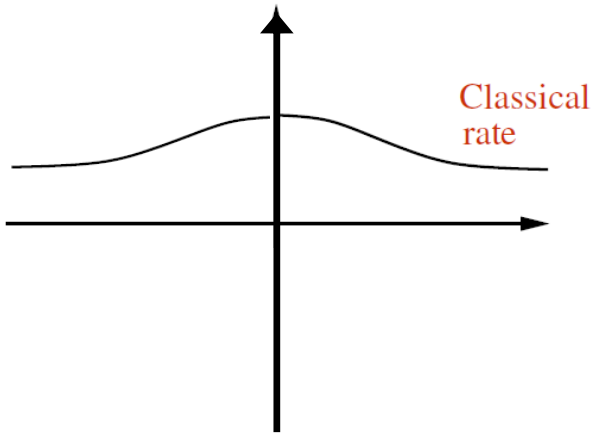Slide from Gert van der Zwan

Kramer's Turnover

The turnover, from an energy-diffusion limited regime, where rates increase with friction, to a spacial-diffusion one, in which rates do the opposite, was predicted by Kramers in his 1940.
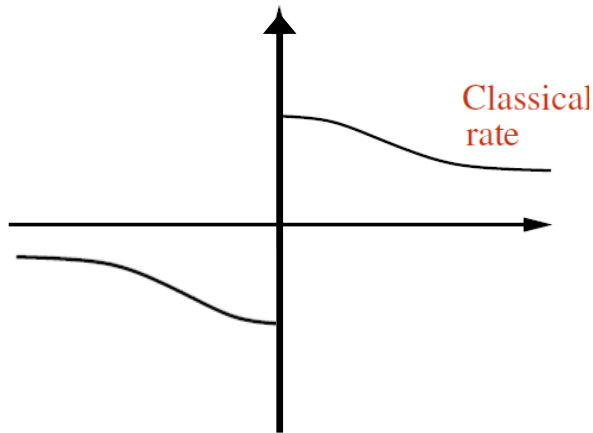
Think - Pair - Share

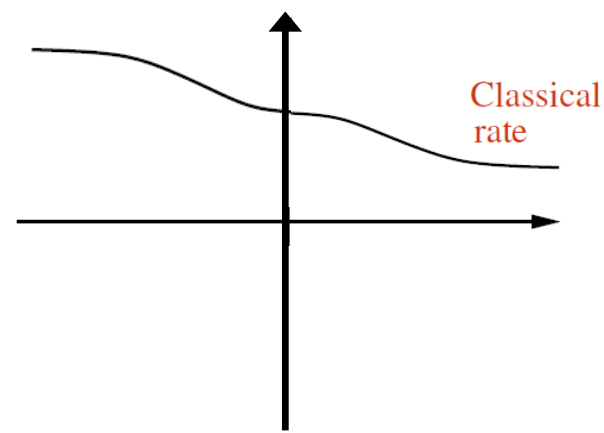What does $c_{fs}^{cl}(t)/Q_r(T)$ look like for negative time?

A)   B)   C)

$$Q_r(T)k(T) = \lim_{t\to\infty} [h]^{-F} \int d\mathbf{p} \int d\mathbf{q} \, e^{-H(\mathbf{p},\mathbf{q})/k_BT} \delta[s(\mathbf{q})] v_s(\mathbf{p},\mathbf{q}) h[s(\mathbf{q}(t))].$$

Microcanical Rate Constants

The thermal rate constant can be expressed in terms of the cumulative reactive probability $N(E)$ as

$$k(T) = [2\pi\hbar Q_r(T)]^{-1} \int_0^\infty dE \ e^{-E/k_B T} N(E), \qquad (1)$$

where

$$N(E) = (2\pi\hbar)^{-(F-1)} \int d\mathbf{p} \int d\mathbf{q} \ \delta[E - H(\mathbf{p}, \mathbf{q})] F(\mathbf{p}, \mathbf{q}) \chi(\mathbf{p}, \mathbf{q}). \quad (2)$$

Statistical Factor

Dynamical Factor

It can and will be shown that

$$N(E) = (2\pi\hbar)^{-(F-1)} \int d\mathbf{p}' \int d\mathbf{q}' \ h[E - H_{F-1}]$$

Classical to Quantum

Classical to Quantum Result

$$k(T) = [2\pi\hbar Q_r(T)]^{-1} \int_0^\infty dE \; e^{-E/k_B T} N(E),$$

$$N(E) = (2\pi\hbar)^{-(F-1)} \int d\mathbf{p}' \int d\mathbf{q}' \; h[E - H_{F-1}]$$

Assume F DOF is separable. The $F - 1$ DOF correspond to bound states with energies E_n and we replace $N(E)$ with

$$N(E) = \sum_{n'} P_{tun}(E - E_{n'})$$

to give

$$k(T) = [2\pi\hbar Q_r(T)]^{-1} \sum_{n'} \int_0^\infty dE \; e^{-E/k_B T} P_{tun}(E - E_{n'})$$

Classical to Quantum Result

$$k(T) = [2\pi\hbar Q_r(T)]^{-1} \sum_{n'} \int_0^\infty dE \; e^{-E/k_B T} P_{tun}(E - E_{n'})$$

Letting $E_F = E - E_{n'}$ one obtains

$$
\begin{aligned}
k(T) &= [2\pi\hbar Q_r(T)]^{-1} \left[\sum_{n'} e^{-E_n/k_B T} \right] \int_0^\infty dE_F e^{-E_F/k_B T} P_{tun}(E_F) \\
&= [2\pi\hbar Q_r(T)]^{-1} \left[Q^\ddagger(T) \right] \int_0^\infty dE_F e^{-E_F/k_B T} P_{tun}(E_F) \\
&= \frac{k_B T}{h} \frac{Q^\ddagger(T)}{Q_r(T)} (k_B T)^{-1} \int_0^\infty dE_F \; e^{-E_F/k_B T} P_{tun}(E_F) \\
&\equiv \kappa(T) \frac{k_B T}{h} \frac{Q^\ddagger(T)}{Q_r(T)}.
\end{aligned}
$$

We have derived the TST tunneling correction $\kappa(T)$.

Quantum Transition State Theory

If reaction coordinate is separable from the remaining DOF, then one can:

♠ quantize the $F - 1$ bound dof to obtain ϵ_n.

♠ calculate $N(E) = \sum_n P_{tun}(E - \epsilon_n)$

♠ $k(T) = \kappa(T)\dfrac{kT}{h}\dfrac{Q^{\ddagger}(T)}{Q_r(T)}$ where

$$\kappa(T) = (k_B T)^{-1}\int_0^\infty dE_F e^{-E_F/k_B T} P_{\text{tun}}(E_F)$$

♠ You need info on potential in the region of transition state.

A new tunneling path for reactions such as
H+H₂→H₂+H[a)] R. A. Marcus and Michael E. Coltrin
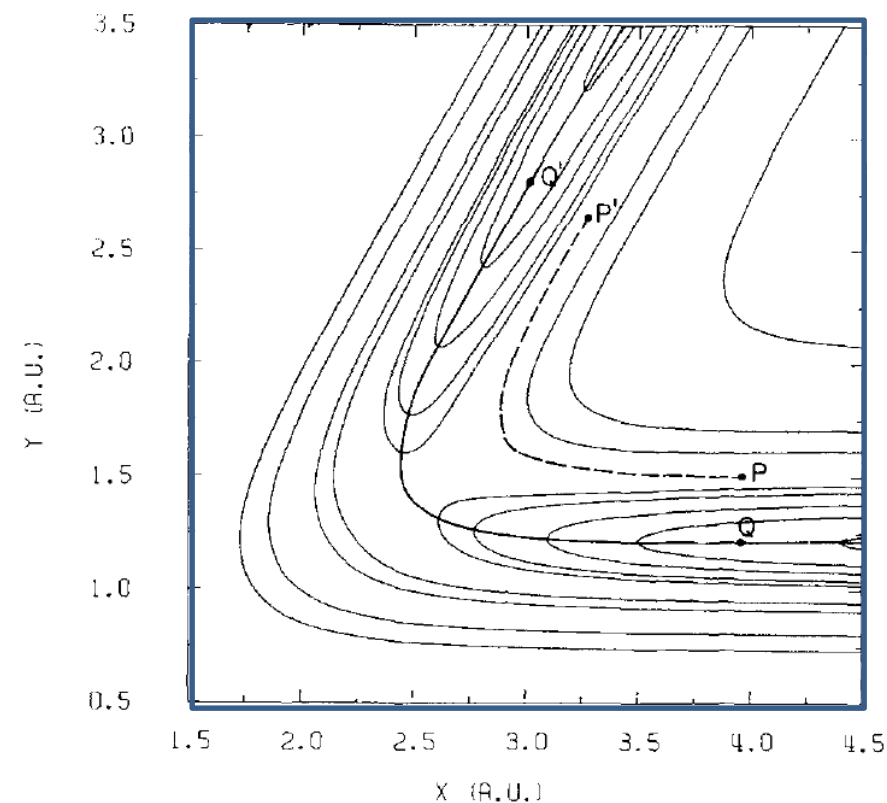
FIG. 1. Plot of potential energy contours for the H + H₂ → H₂ + H reaction using the Porter–Karplus surface. Solid line is line of steepest ascent (reaction path). Dotted line is the t-curve (limit of vibrational amplitudes in the given vibrational state, here the zero-point state). The points P and P' denote the initial and final tunneling points on the t-curve for a particular total energy. The corresponding tunneling points if tunneling occurred along the reaction path are Q and Q'.

256 Citations

Reaction probability vs intial translational energy
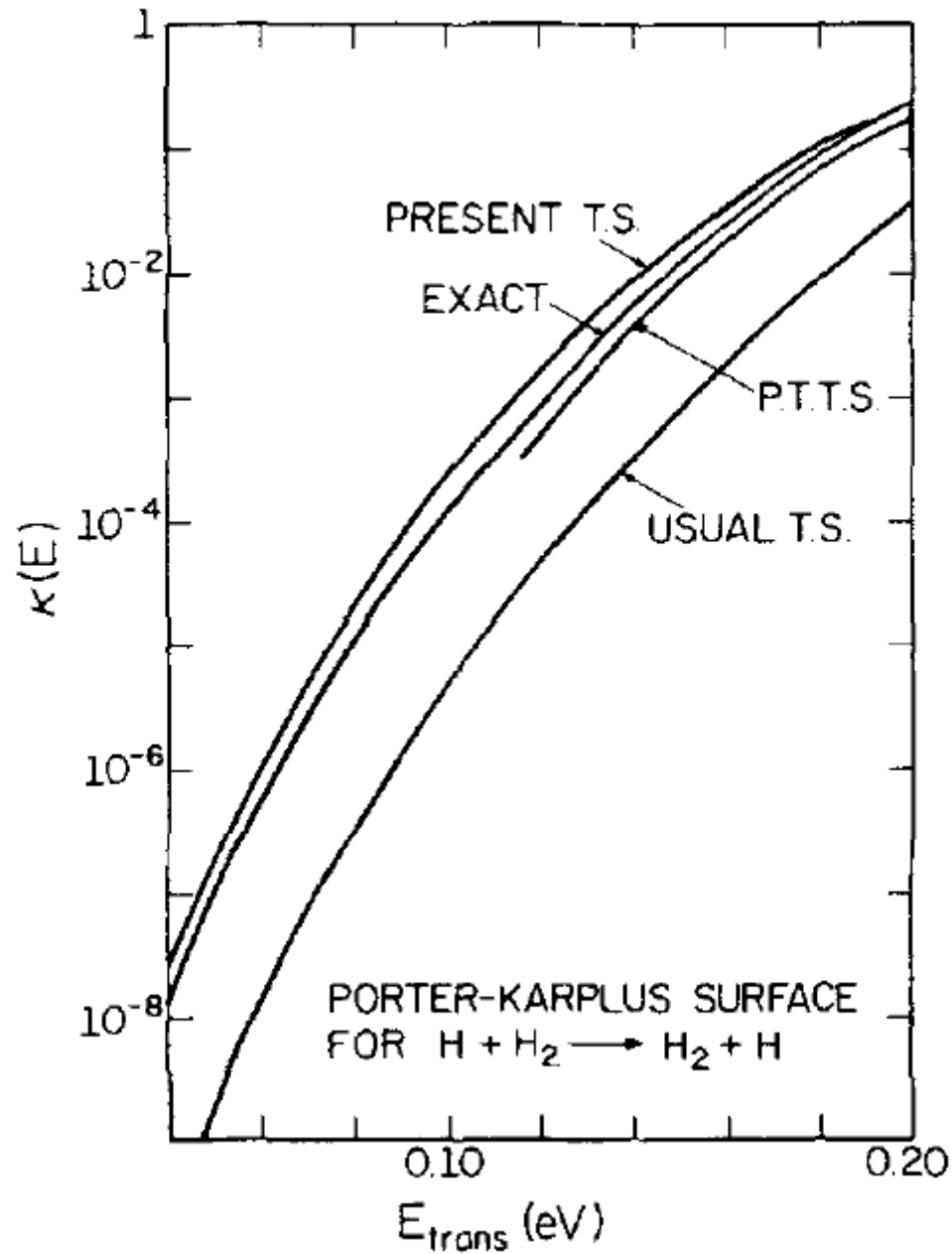
High-level direct-dynamics variational transition state theory calculations including multidimensional tunneling of the thermal rate constants, branching ratios, and kinetic isotope effects of the hydrogen abstraction reactions from methanol by atomic hydrogen

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[2]*Department of Chemistry and Supercomputing Institute, University of Minnesota, 207 Pleasant Street S. E., Minneapolis, Minnesota 55455-0431, USA*

We report a detailed theoretical study of the hydrogen abstraction reaction from methanol by atomic hydrogen. The study includes the analysis of thermal rate constants, branching ratios, and kinetic isotope effects. Specifically, we have performed high-level computations at the MC3BB level together with direct dynamics calculations by canonical variational transition state theory (CVT) with the microcanonically optimized multidimensional tunneling (μOMT) transmission coefficient (CVT/μOMT) to study both the $CH_3OH + H \rightarrow CH_2OH + H_2$ (R1) reaction and the $CH_3OH + H \rightarrow CH_3O + H_2$ (R2) reaction.

Sophisticated Comparison of Quantum and Classical Rate Theories

To obtain a quantum TST like expression we replace classical with quantum expressions

$$\heartsuit \quad (2\pi\hbar)^{-F} \int d\mathbf{p} \int \mathbf{q}[\cdots] \to tr[\cdots]$$

$$\heartsuit \quad F(\mathbf{p}, \mathbf{q}) = \frac{d}{dt} h[f(\mathbf{q})] \to \hat{F} = \frac{i}{\hbar}[\hat{H}, h(f(\mathbf{q}))]$$

$$\heartsuit \quad \chi(\mathbf{p}, \mathbf{q}) = \lim_{t \to \infty} h[f(\mathbf{q}(t))] = \int_0^\infty dt \, \frac{d}{dt} h[f(\mathbf{q})] = \int_0^\infty dt \, F(t)$$

Classical

$$N(E) = (2\pi\hbar)^{-(F-1)} \int d\mathbf{p} \int d\mathbf{q} \, \delta[E - H(\mathbf{p}, \mathbf{q})] F(\mathbf{p}, \mathbf{q}) \chi(\mathbf{p}, \mathbf{q})$$

Quantum

$$N(E) = (2\pi\hbar)^{-1} \int_0^\infty dt \, tr[\delta(E - H)] \, \hat{F}\hat{F}(t)$$

Quantum Expression Simplified

$$N(E) = (2\pi\hbar) \int_0^\infty dt \; tr[\delta(E - H) \; \hat{F}\hat{F}(t)]$$

where we will insert

$$\hat{F}(t) = e^{i\hat{H}t/\hbar}\hat{F}e^{-i\hat{H}t/\hbar}$$

Real part of integral is even.

to obtain

$$N(E) = (\pi\hbar) \int_{-\infty}^\infty dt \; tr[\delta(E - H) \; \hat{F}e^{i(\hat{H}-E)t/\hbar}\hat{F}].$$

Quantum Expression Simplified

$$N(E) = (2\pi\hbar) \int_0^\infty dt \; tr[\delta(E - H) \; \hat{F}\hat{F}(t)]$$

where we will insert

$$\hat{F}(t) = e^{i\hat{H}t/\hbar}\hat{F}^{-i\hat{H}t/\hbar}$$

δ function allows us to replace H with E.

to obtain

$$N(E) = (\pi\hbar) \int_{-\infty}^\infty dt \; tr[\delta(E - H) \; \hat{F}e^{i(\hat{H}-E)t/\hbar}\hat{F}].$$

Classical

$$N(E) = (2\pi\hbar)^{-(F-1)} \int d\mathbf{p} \int d\mathbf{q} \; \delta[E - H(\mathbf{p}, \mathbf{q})] F(\mathbf{p}, \mathbf{q}) \chi(\mathbf{p}, \mathbf{q}). \quad (2)$$

Statistical Factor

Dynamical Factor

Quantum

$$N(E) = 2(\pi\hbar)^2 \; tr[\delta(E - H) \; \hat{F}\delta(E - H)\hat{F}].$$

Where is the dynamical factor?

"In quantum mechanics, dynamics and statistics are inseparably intertwined; e.g., a wavefunction describes the *dynamical motion* of the particles and also their *statistics*."

TOPICAL REVIEW

Accurate calculations of reaction rates: predictive theory based on a rigorous quantum transition state concept

Uwe Manthe*

$$N(E) = \mathrm{Tr}[\hat{P}(E)] \qquad \hat{P}(E) = 4\hat{e}_r^{1/2}\hat{G}(E)^\dagger\hat{e}_p\hat{G}(E)\hat{e}_r^{1/2} \qquad N(E) = \sum_k p_k(E),$$

Beyond Transition State Theory

Full-dimensional time-dependent treatment for diatom–diatom reactions: The H_2+OH reaction

Dong H. Zhang[a] and John Z. H. Zhang
Department of Chemistry, New York University, New York, New York 10003

Quantum dynamics study of $H+NH_3 \rightarrow H_2+NH_2$ reaction

Xu Qiang Zhang, Qian Cui, and John Z. H. Zhang[a]
Department of Chemistry, New York University, New York, New York 10003

Ke Li Han
State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, The Chinese Academy of Science, Dalian 116023, China
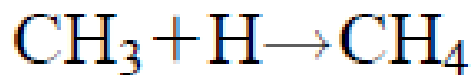
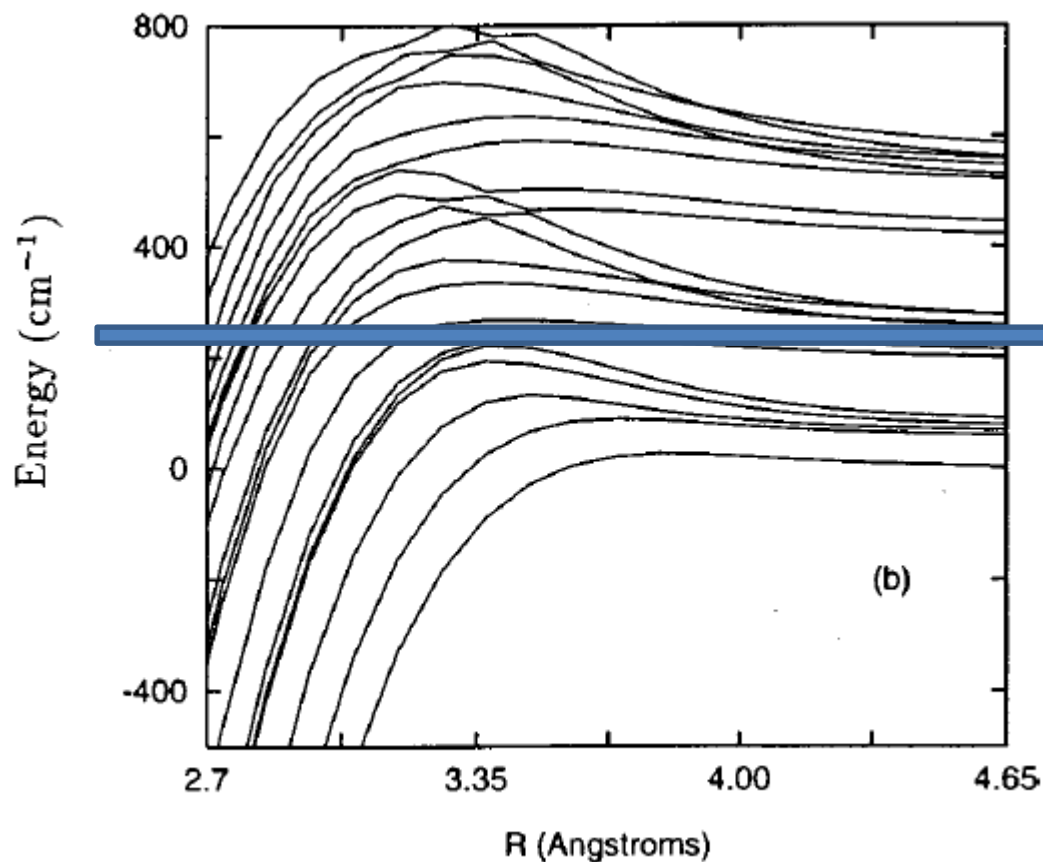## The effect of nonadiabatic coupling on the calculation of $N(E,J)$ for the methane association reaction

Kristy L. Mardis and Edwin L. Sibert III[a]
Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin, Madison, Madison, Wisconsin 53706

$$CH_3 + H \rightarrow CH_4$$

Plot of transitional modes as a function of R.

(b)

Energy (cm^{-1}) vs R (Angstroms)

SACM
and
Variational RRKM

$$k(E,J) = \frac{N(E,J)}{h\rho^R(E,J)} .$$

The microcanonical rate constant

$$k(E,J) = \frac{N(E,J)}{h\rho^R(E,J)}.$$

can be written in terms of the cummulative reaction probability.

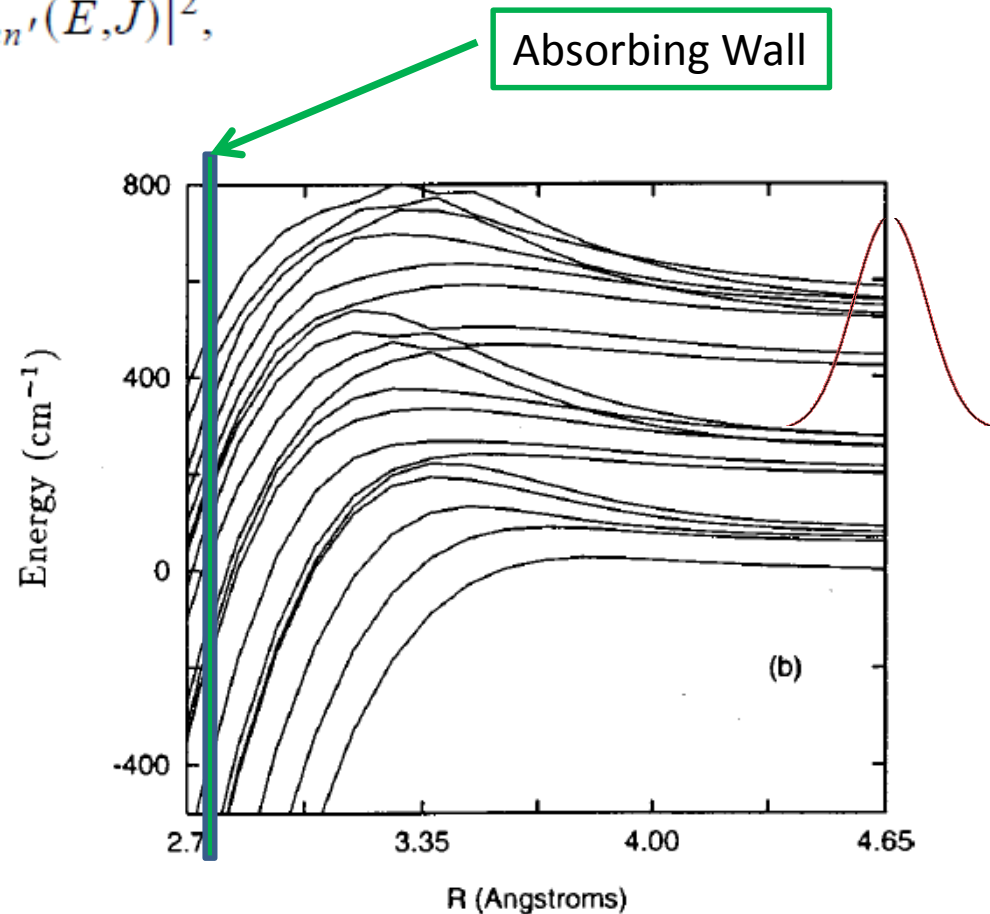$$N(E,J) = \sum_n \sum_{n'} P_{nn'}(E,J) = \sum_n \sum_{n'} |S_{nn'}(E,J)|^2,$$

$$\hat{F} = \tfrac{1}{2}[\,\delta(R-R_0)\hat{v}_R + \hat{v}_R\delta(R-R_0)\,].$$

$$\hat{F} = \sum_{n'} |n'\rangle\hat{F}\langle n'|.$$

$$P_n(E,J) = \sum_{n'} \langle\Psi^+_{nE}|n'\rangle\hat{F}\langle n'|\Psi^+_{nE}\rangle.$$

$$P^R_{nn'}(E,J) = \langle\Psi^+_{nE}|n'\rangle\hat{F}\langle n'|\Psi^+_{nE}\rangle.$$

$$\Psi^+_{nE} = \frac{1}{a_n(E)}\int_{-\infty}^{\infty} dt\, e^{(iEt/\hbar)t}\psi_n(t).$$

Absorbing Wall

(b)

Comparison of SACM, SACM with tunneling, and exact QM

(a)