Calculations of tunneling in atomic and spin systems

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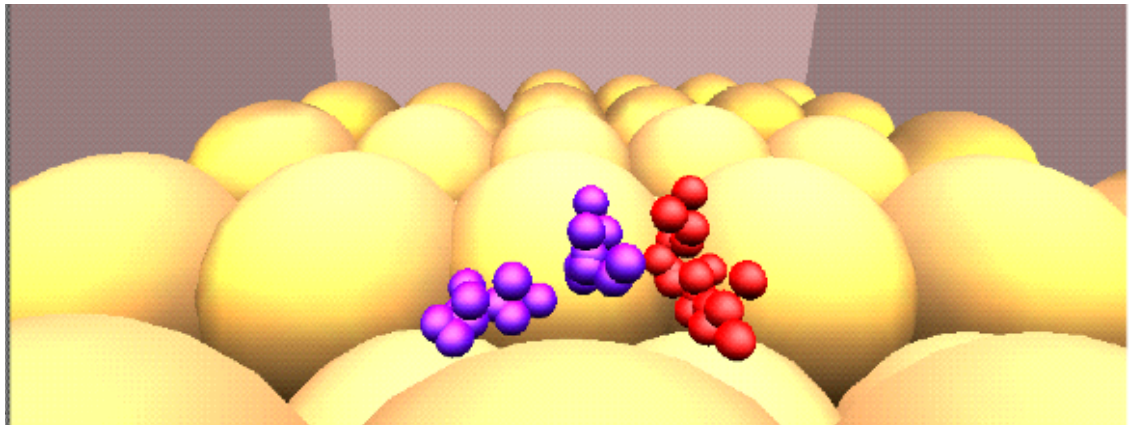
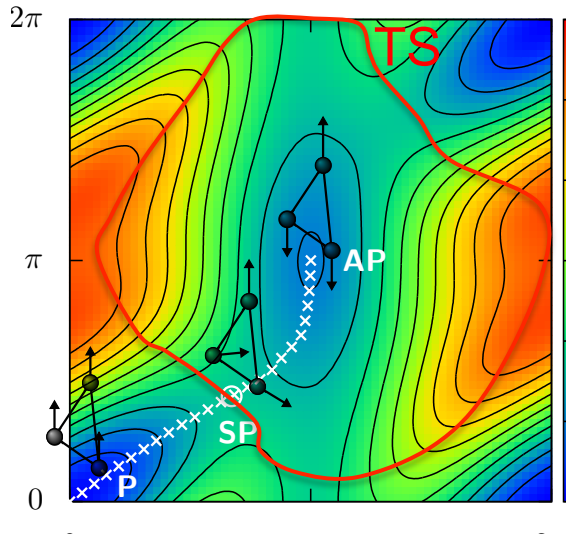
Overview:

- Statistical Feynman path integral description of the quantum stat. mech.
- Onset temperature for tunneling in atomic systems.
- Calculations of thermally assisted tunneling in atomic systems, QTST.

  Application to Eckart barrier, H_2 desorption, H-atom diffusion.
- Onset temperature for tunneling in magnetic systems.

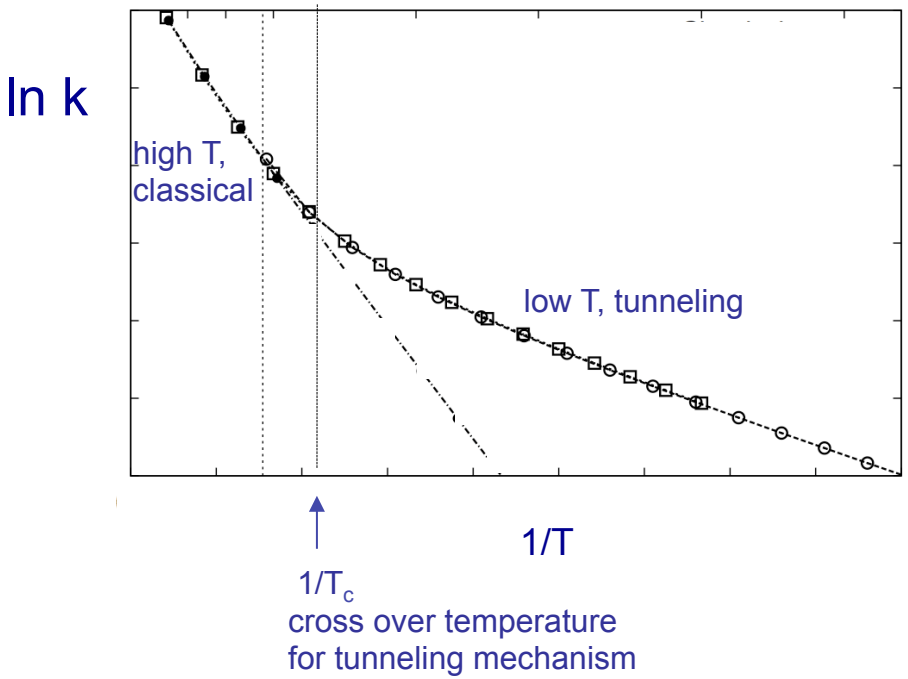
  Application to a molecular magnet containing a Mn_4 unit and a dimer of such molecules.





Extension of rate theory to quantum systems

Estimate the rate of thermal transitions including tunneling as a possible transition mechanism, extend transition state theory to include tunneling.



Tunneling becomes the dominant transition mechanism at low enough temperature.

Can be important at or near room temperature.

Examples: H_2 desorption, H-diffusion, proton reactions.

Find rate constant for a given temperature

Time dependent (wave packet) or time independent Schrödinger equation can, in principle, be used to calculate the reaction probability (transmission coefficient) as a function of energy, P(E).
A rate constant can then be found by evaluating a Boltzmann average

$$k(T) = \int_0^\infty P(E) e^{-E/k_B T} dE$$

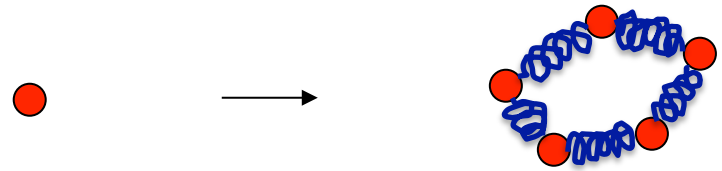
But, this is difficult to do in practice:

- Hard to solve the Shcrödinger equation for many degrees of freedom (max. around 6, typically). Need to select.
- The range in energy relevant at around room temperature is low and that makes wave packet calculations even harder and extrapolations are needed.

Instead, apply a ***statistical approach*** to find k(T) directly

Quantum statistical mechanics

Use statistical Feynman path integrals:



$$k_s = mP\left(\frac{2\pi k_B T}{h}\right)^2$$

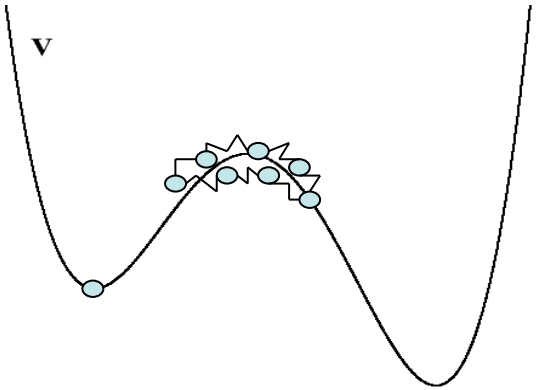
qantum stat. mech. classical stat. mech.

$$V(\vec{r}) \;\rightarrow\; V^{eff}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_P) = \sum_i^P \left(k_s(\vec{r}_i - \vec{r}_{i-1})^2 + V(\vec{r}_i)/P\right)$$

The statistical mechanical partition function of a quantum particle is mathematically the same as the partition function of a closed chain of replicas connected by temperature dependent springs.

Should take the limit as P goes to infinity, i.e. infinitely many replicas of the system.

The distribution of replicas represents quantum delocalization. They get pulled inn to a point as mass or T become large.



Derivation of FPI representation of quantum partition function

The thermally averaged expectation value for an observable is

$$\langle \hat{A} \rangle = Q^{-1} \int dx \langle x | e^{-\hat{\mathcal{H}}/k_B T} \hat{A} | x \rangle$$

Where Q is the partition function $Q = \int dx \langle x | e^{-\hat{\mathcal{H}}/k_B T} | x \rangle$

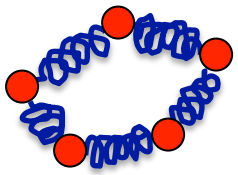
Use Trotter formula for operators $\lim_{P\to\infty} \left(e^{\hat{A}/P} e^{\hat{B}/P} \right)^P = e^{\hat{A}+\hat{B}}$

and insert the identity operator to rewrite the partition function as

$$\begin{aligned} Q &= \lim_{P\to\infty} \int dx_1 \int dx_2 \ldots \int dx_P \langle x_1 | e^{-\hat{\mathcal{H}}/k_B T P} | x_2 \rangle \\ &\quad \langle x_2 | e^{-\hat{\mathcal{H}}/k_B T P} | x_3 \rangle \ldots \langle x_{P-1} | e^{-\hat{\mathcal{H}}/k_B T P} | x_P \rangle \end{aligned}$$

Use free particle propagator from x_i to x_{i+1} at high the temperature PT

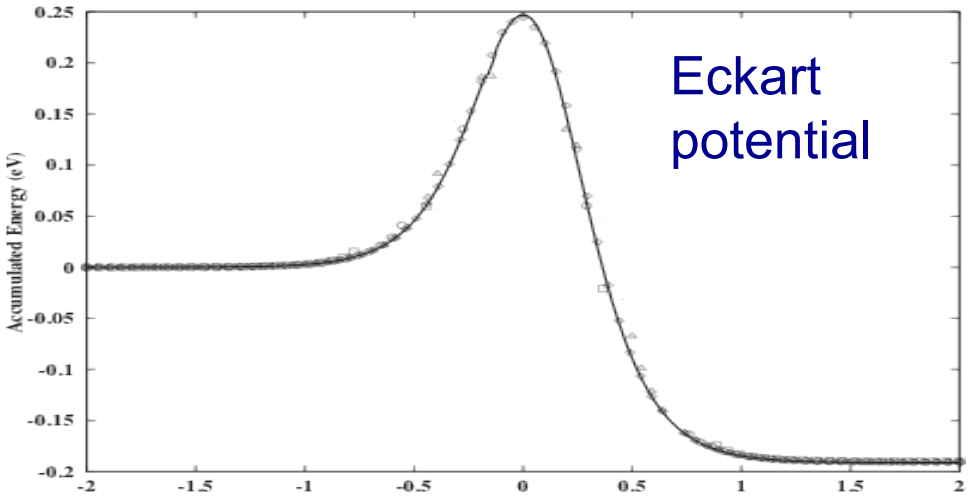
$$\begin{aligned} Q &\approx \left(\frac{m k_B T P}{2\pi\hbar^2} \right)^{P/2} \int dx_1 \ldots dx_P \\ &\quad \exp\left(\left(-\frac{1}{2} m P \left(\frac{k_B T}{\hbar} \right)^2 \sum_{i=1}^{P} (x_{i+1} - x_i)^2 + V(x_i)/P \right) / k_B T \right) \end{aligned}$$



This is equivalent to the classical partition function for a closed chain with P particles connected by springs.

One-dimensional example: Eckart barrier

V(x)



Eckart potential

Example paths along the line:

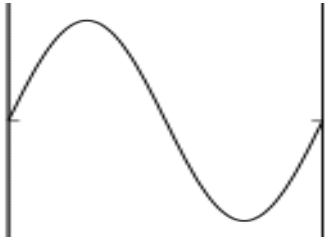
x(τ)

τ

small quantum delocalization

τ

intermediate quantum delocalization



τ

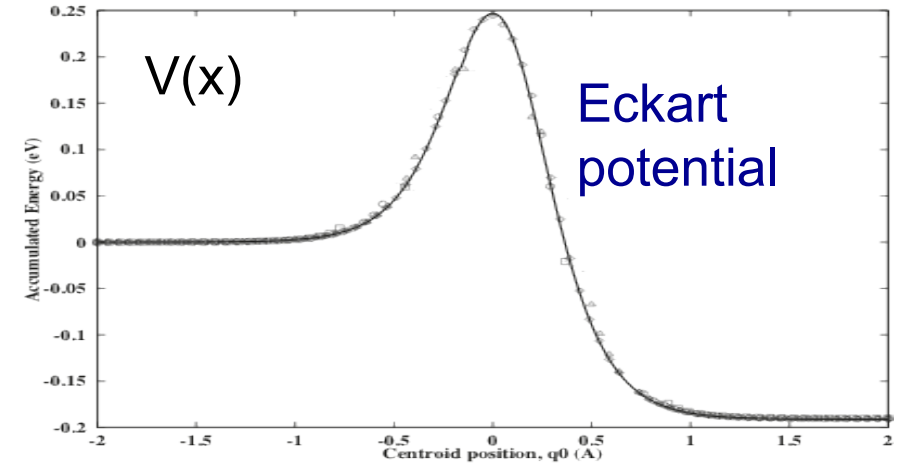
large quantum delocalization

What does the potential surface for the ring polymer, V^{eff}, look like?

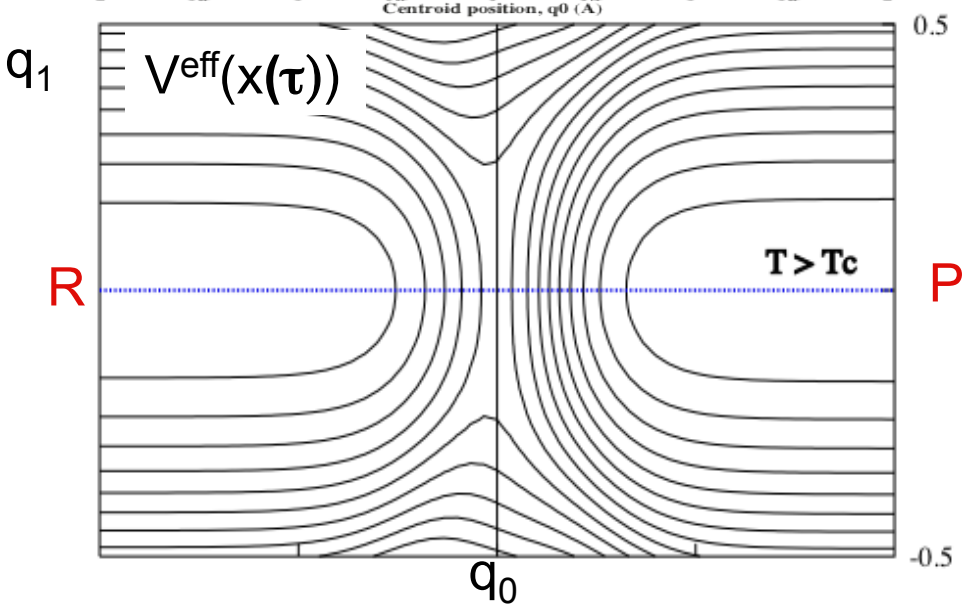
Visualize the potential surface for the ring polymer, V^{eff}

Hard to visualize the effective potential, even a 1-dimensional problem becomes high-dimensional (many variables) when FPIs are introduced.

As an example,
consider Feynman paths that can be written as $\mathbf{x(\tau)=q_0 + q_1 \sin(2\pi\,\tau/p)}$
i.e. only keep two components
in a Fourier expansion.



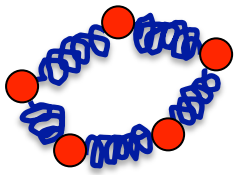
Then, construct a contour plot showing the value of the *potential energy for ring polymers* as a function of q_0 and q_1, $V^{eff}(q_0,q_1)$.



The effective potential surface, V^{eff}, is T dependent

The spring constants are temperature dependent

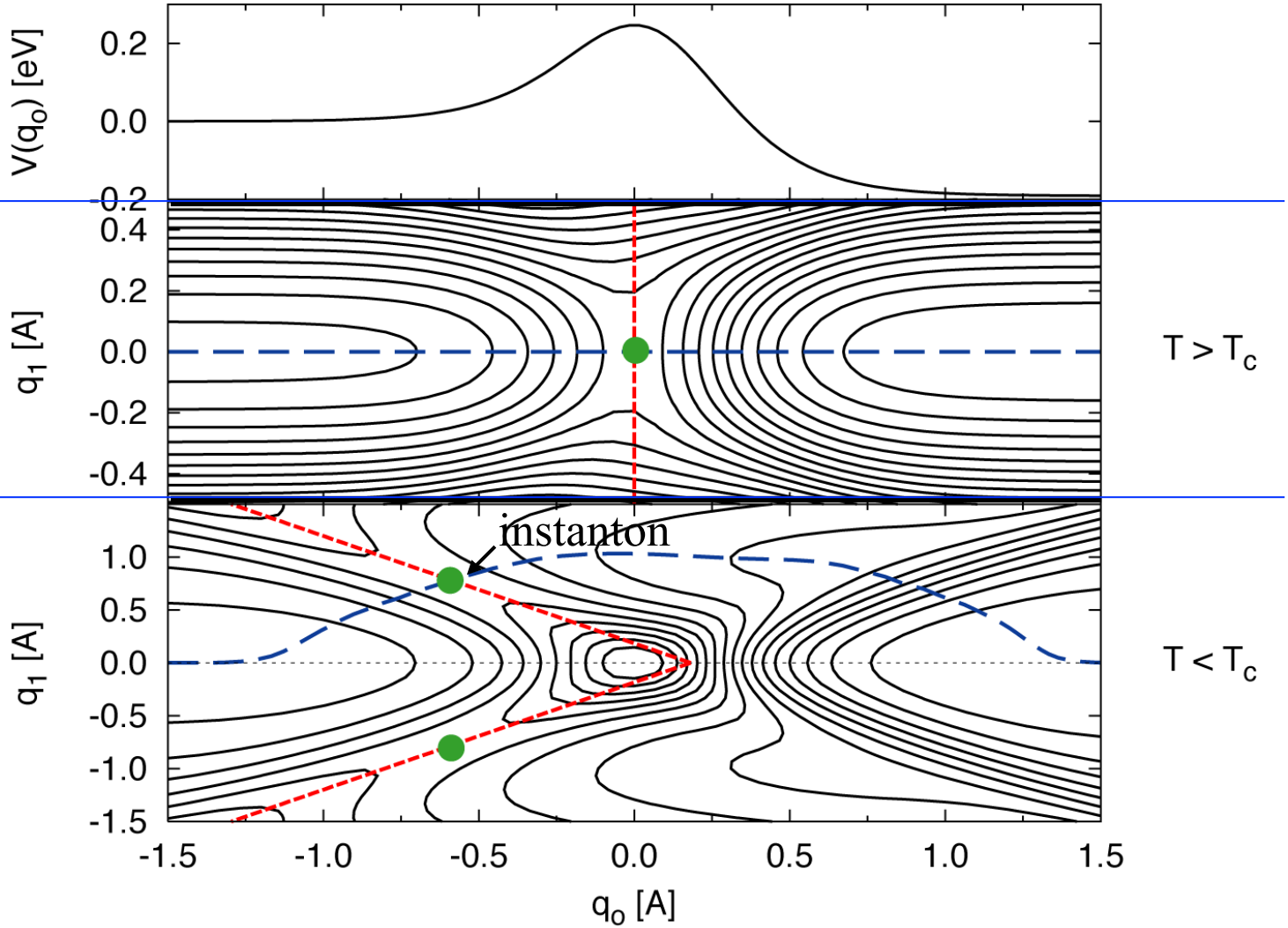
$$k_{spring} = \mu P \left(\frac{k_B T}{\hbar} \right)^2$$



Eckart potential

Above T_c classical over-the-barrier mechanism

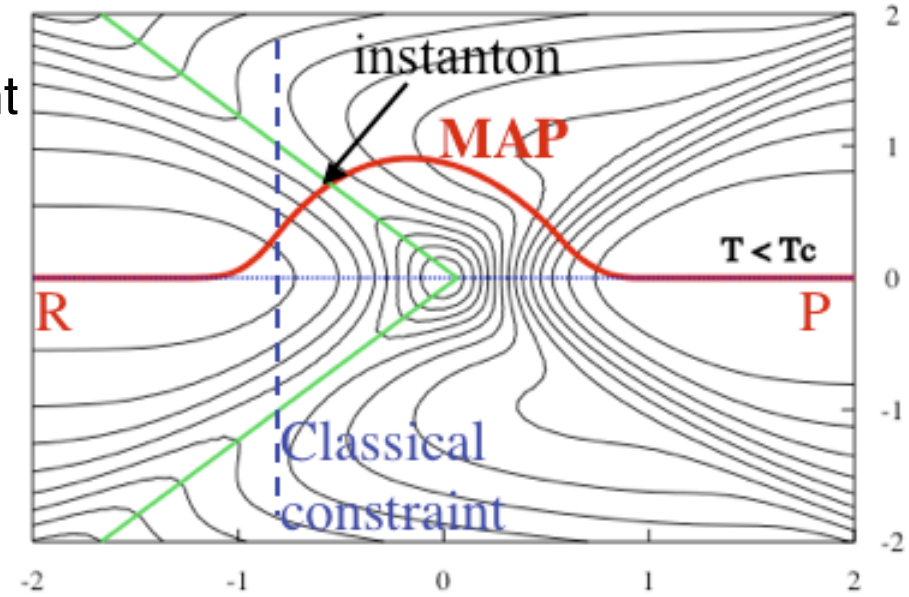
Below T_c new saddle points form (*instantons*), i.e. tunneling mechanism



Quantum transition state theory based on FPIs

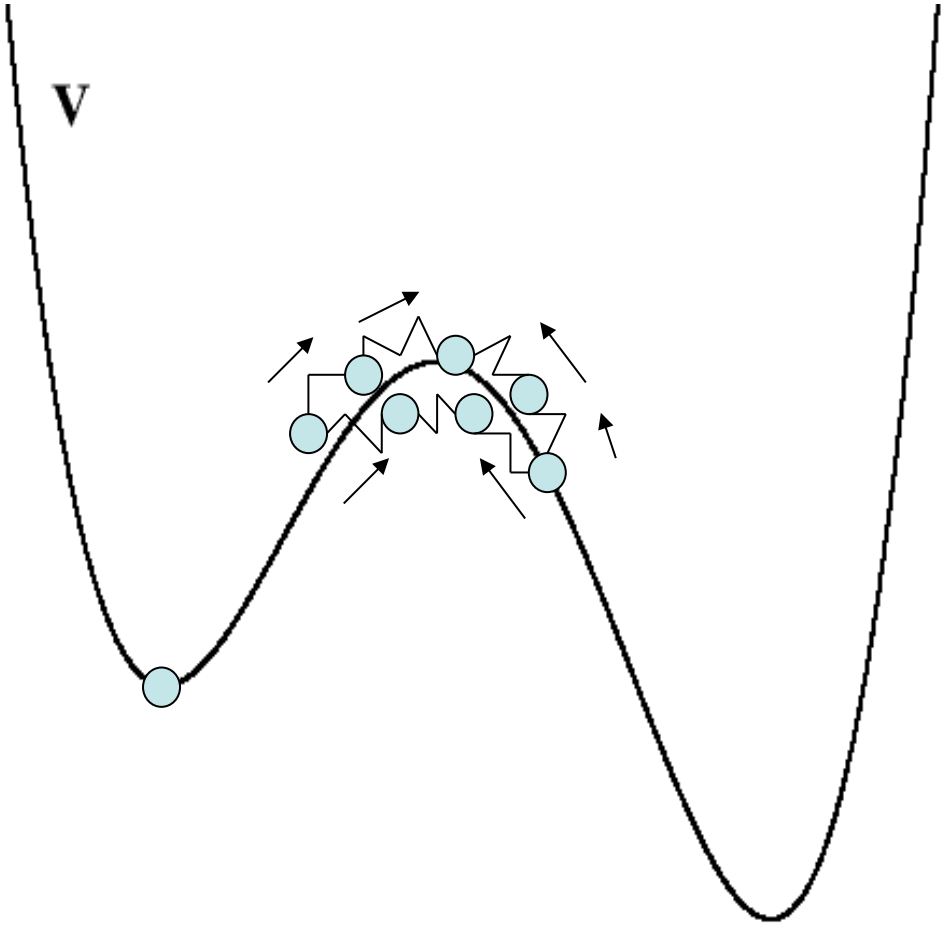
Estimate the rate at which closed Feynman paths move from the reactant region, R, to the product region, P.

The definition of the quantum transition state needs to involve both position and shape of the closed Feynman paths in order to confine the system to the bottleneck region around the instanton (not enough to specify just the location of the centroid!).



QTST: a full free energy calculation of such a transition state.
Find optimal, conical TST dividing surface for the Feyman Paths
(*Mills, Schenter, Jónsson, Chemical Phys. Lett. 1997*)

At what temperature does tunneling become important?



Ω is the magnitude of the imaginary frequency of the unstable mode at the saddle point on the classical minimum energy path

$$k_{spring} = \mu P \left(\frac{k_B T}{\hbar} \right)^2$$

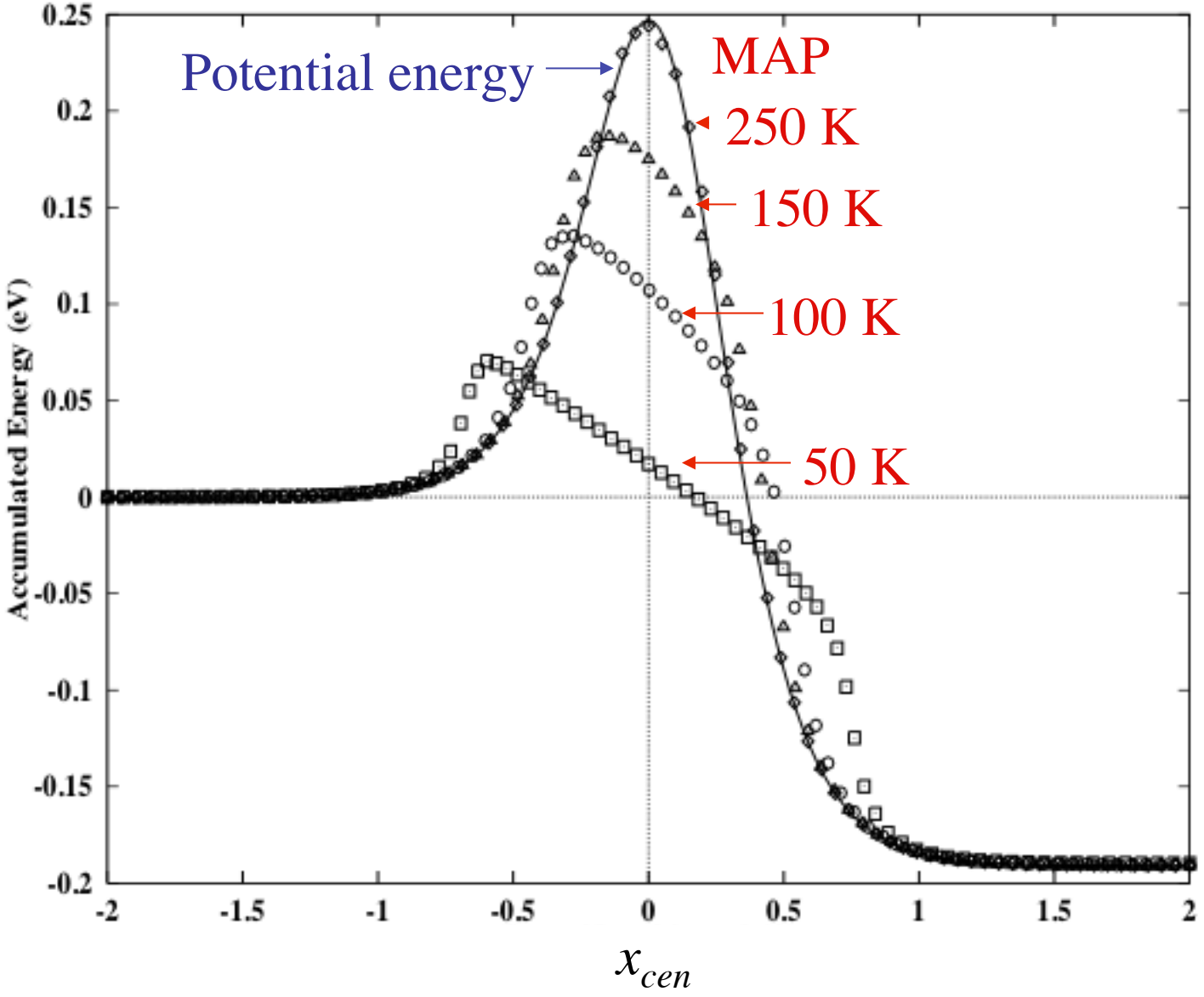
The temperature at which the spring constant matches the curvature of the barrier is

$$T_c = \frac{\hbar \Omega}{2\pi k_B}$$

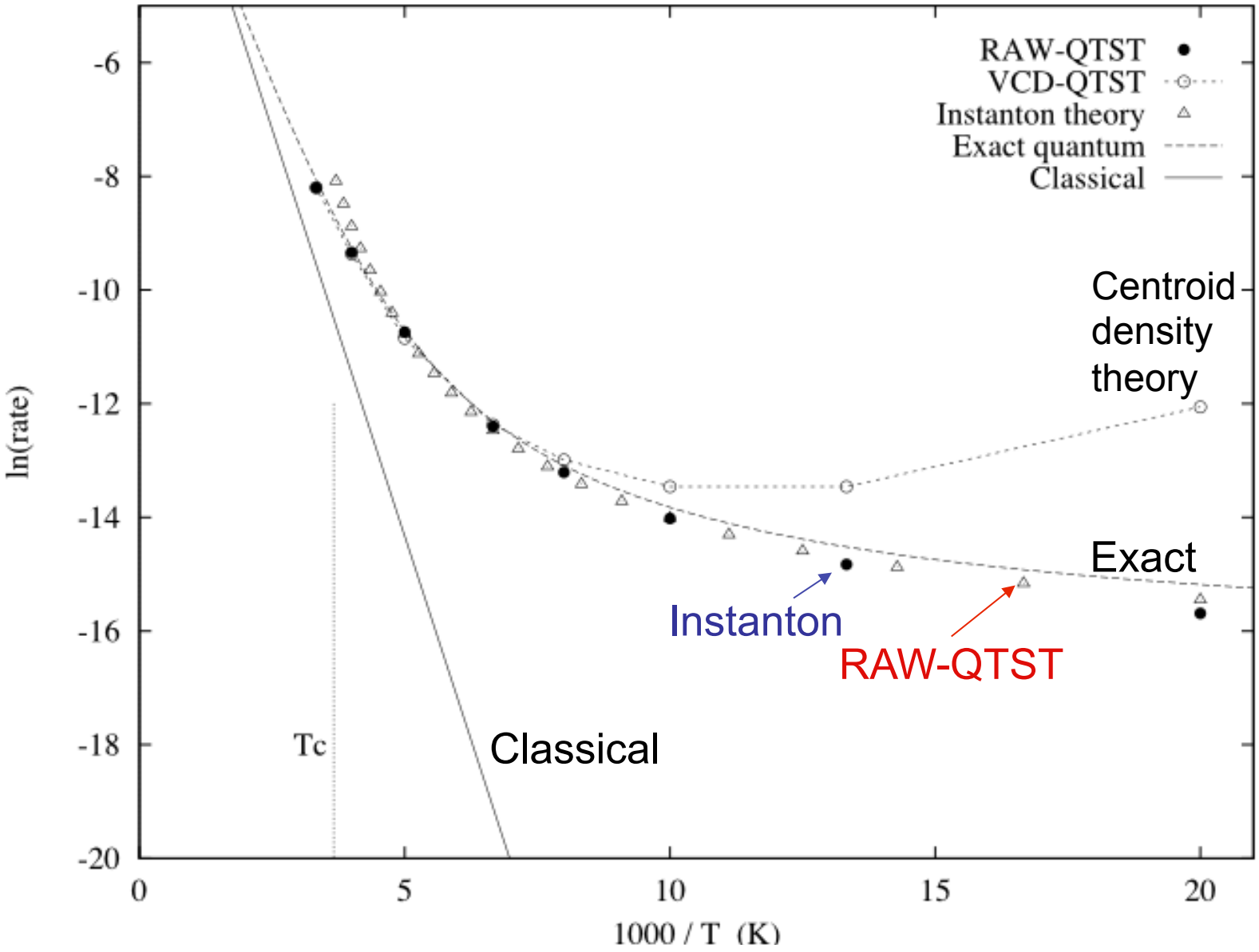
Gillan, *J. Phys. C* **20**, 3621 (1987)

Below T_c the dominant transition mechanism is tunneling.

Free energy of a quantum dividing surface for the Eckart potential representing roughly a F + H-H -> F-H + H reaction

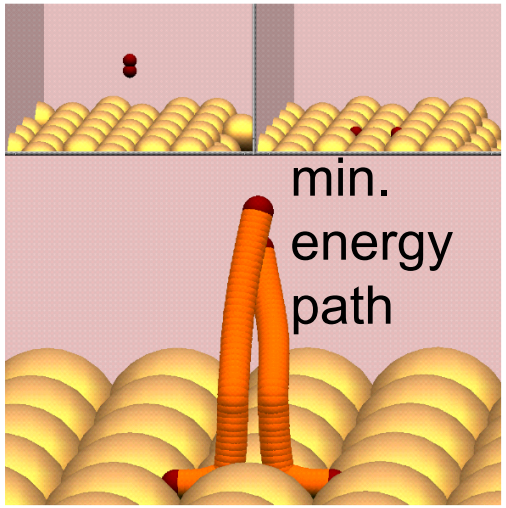


Various calculations for the Eckart barrier

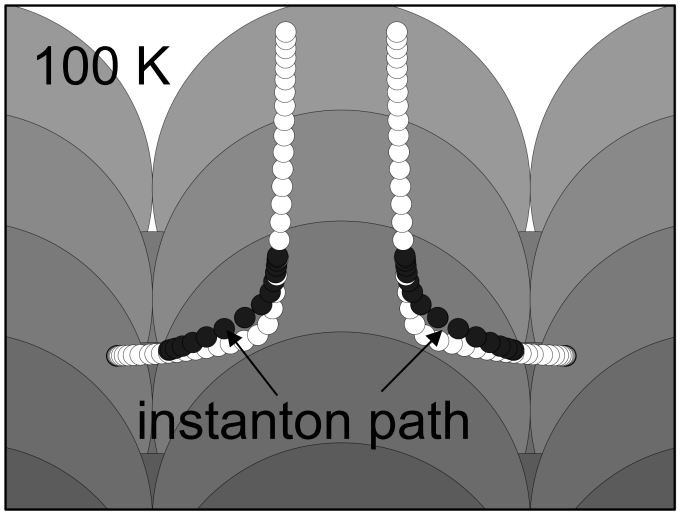


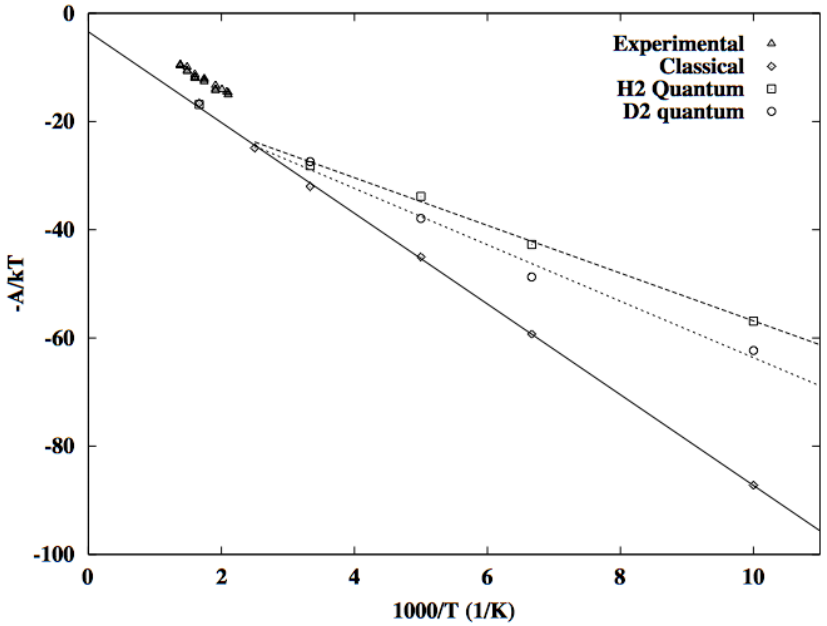
QTST calculations of H_2 adsorption/desorption on Cu(110)

Use EAM potential function for Cu-Cu and H-Cu interaction, dynamical surface atoms



NEB method

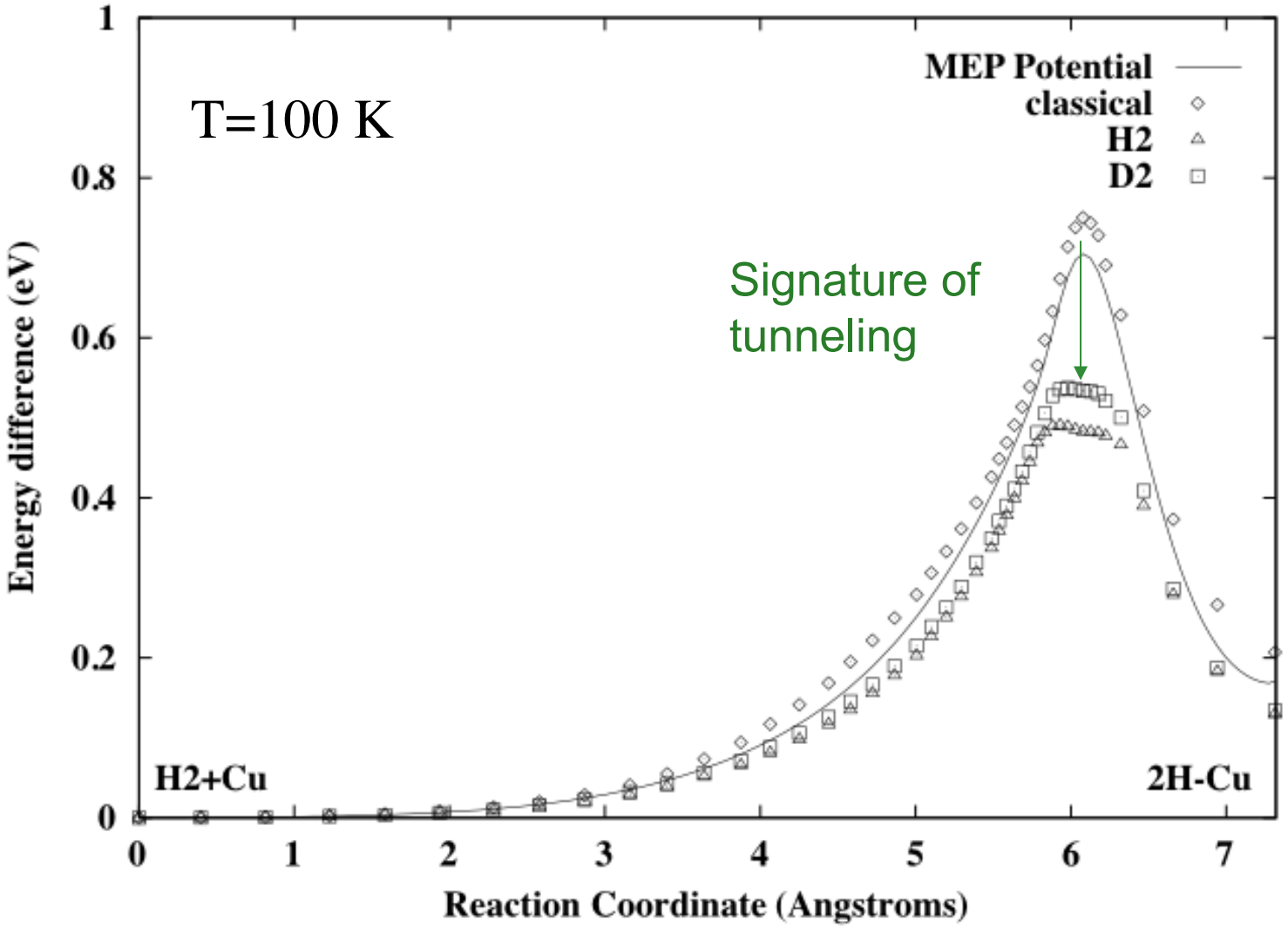




At T>300K the classical approximation to the thermally averaged rate constant agrees well with the quantum mechanical value, even though wave packet calculations show clear quantum effects in state-to-state cross sections.

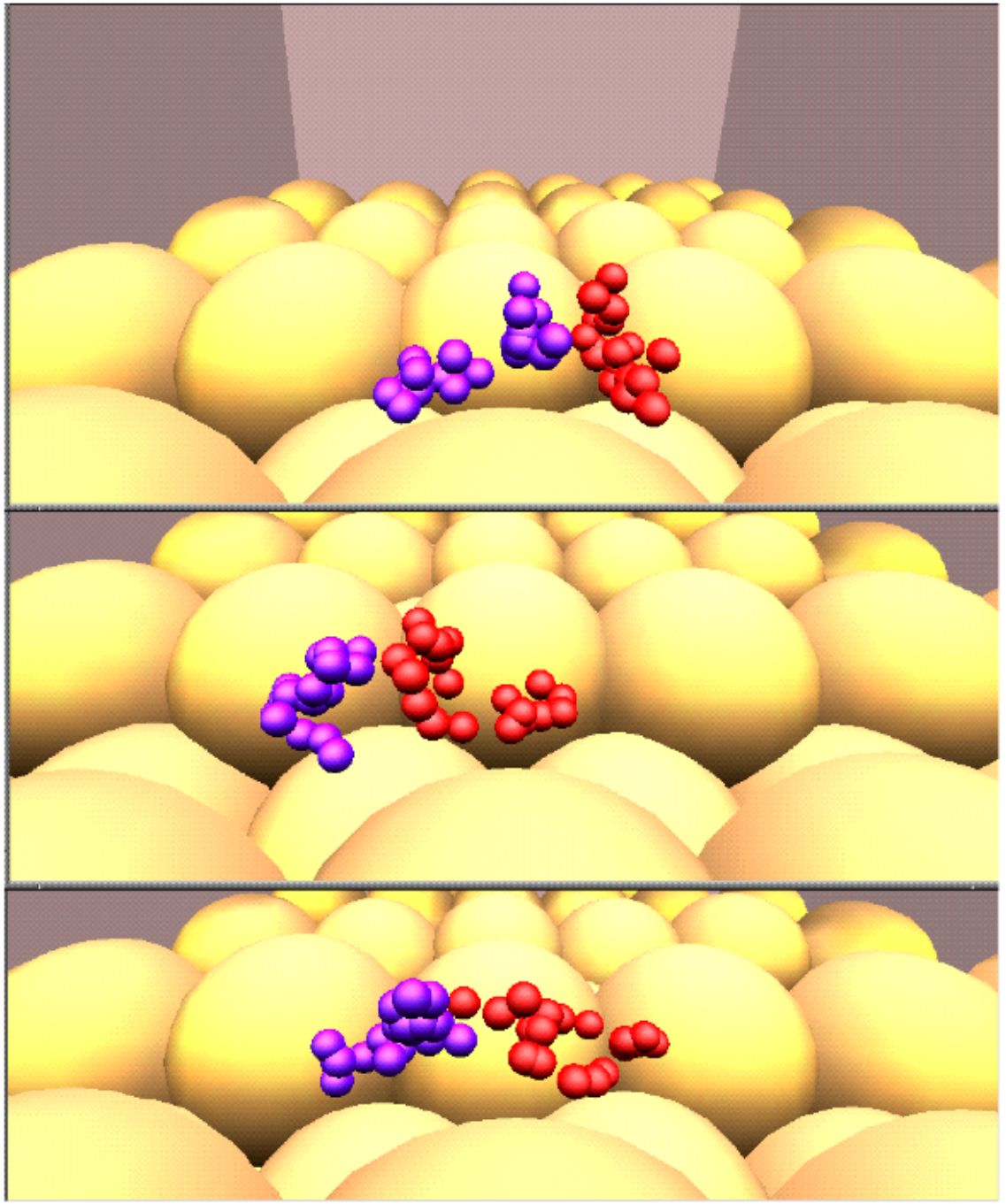
QTST calculations of H_2 adsorption/desorption on Cu(110)

Clear quantum effects at 100 K



Transition state at T=100 K shows clear quantum delocalization

Three snapshots from thermal sampling of TS (which includes 5 degrees of freedom)



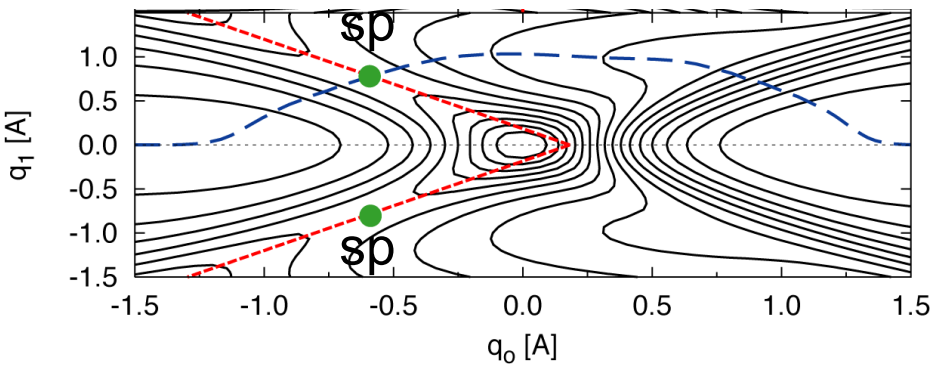
Harmonic QTST (instanton theory)

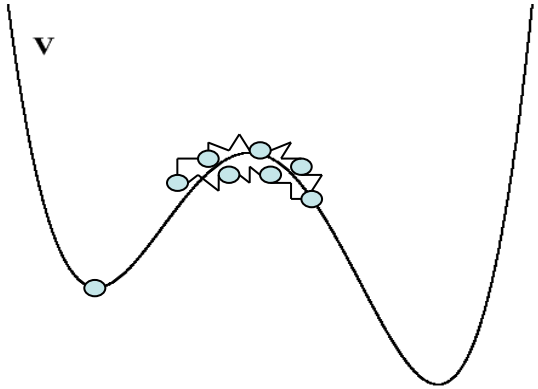
Again, use harmonic approximation to the effective potential, harmonic quantum TST. Expand V^{eff} around saddle points (instantons). Often referred to as 'instanton theory' (Miller, 1975, Callan and Coleman, 1977) or 'Im F' theory (Langer, 1969) .

$$Q^R \; k^{HQTST} \;=\; \sqrt{\frac{S_0}{2\pi\hbar}} \; \frac{1}{\Delta\tau |\Pi'_j \lambda_j|} \; e^{-(V_{sp}^{eff}(T,P) - V_{min})/k_B T}$$

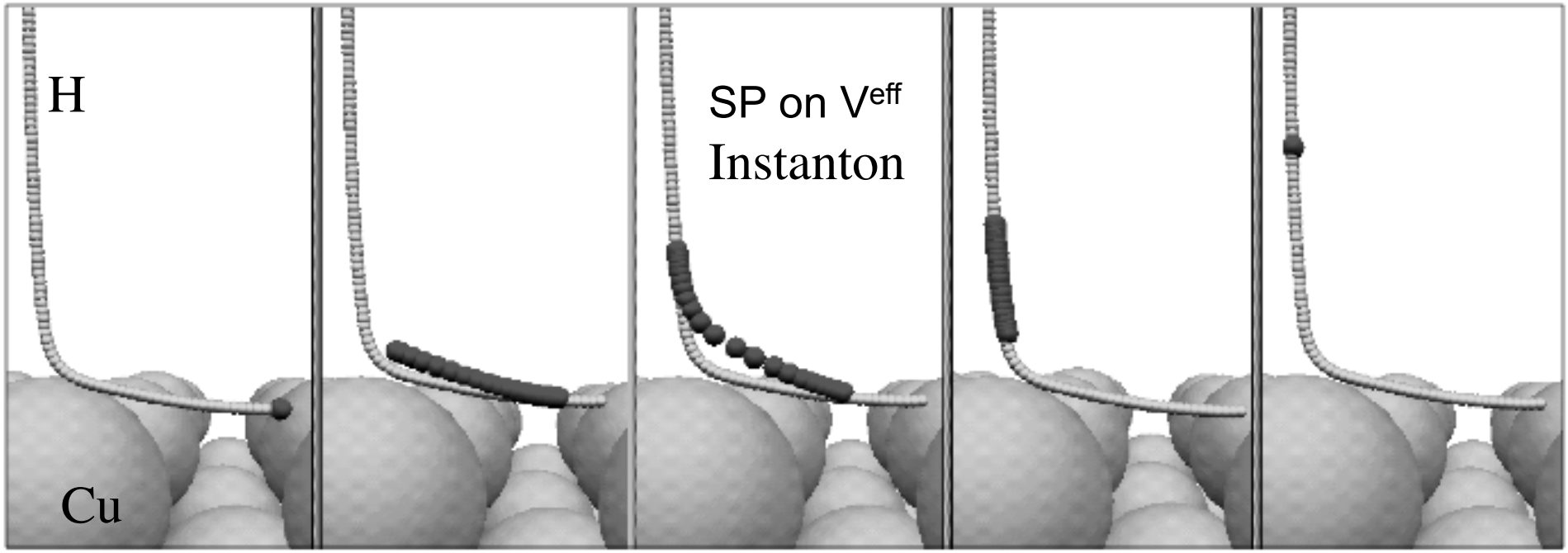
where $V^{eff}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_P) = \sum^{P} \left(k_s (\vec{r}_i - \vec{r}_{i-1})^2 + V(\vec{r}_i)/P \right)$

S_0 is the 'zero mode', replicas move along the path, no change in energy, but contributes to enropy





T = 100 K: Minimum action path for H_2 adsorption/desorption from Cu(110)

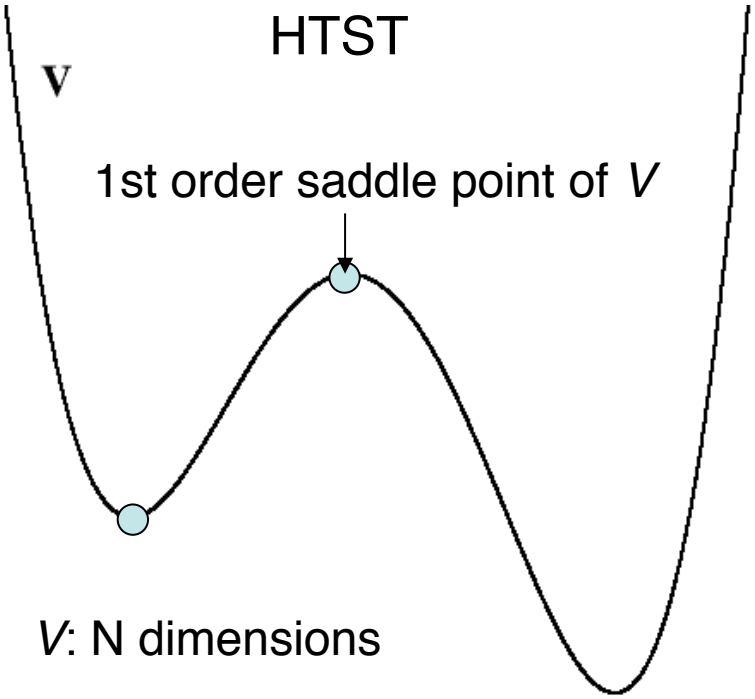


(only one of the two H-atoms is shown)

Instanton for a given temperature, T, is the same as a WKB *optimal tunneling path* for a certain energy, E.

Analogy between HTST and HQTST

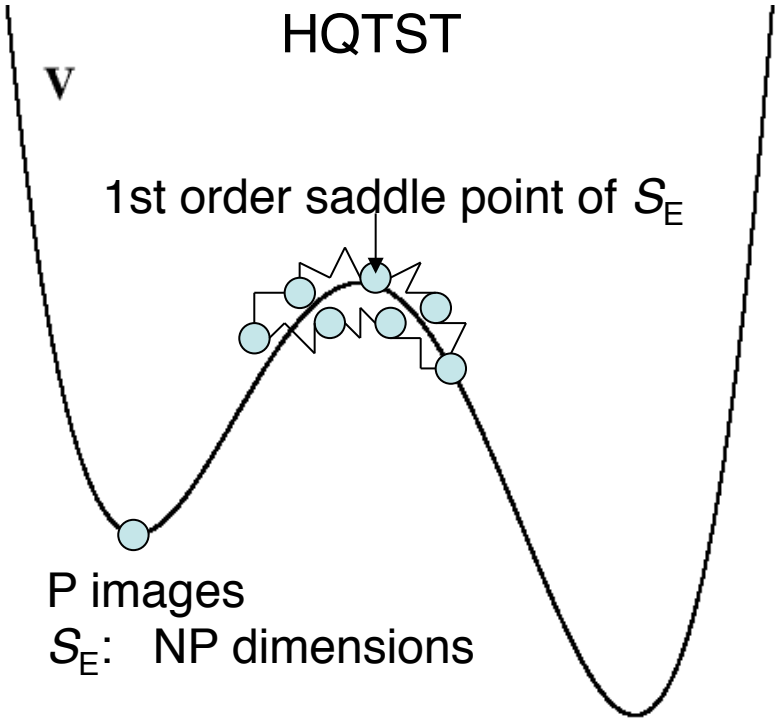
HTST



V: N dimensions

$$Q^R\ k^{HTST} = \frac{k_B T}{h} \frac{1}{\Pi_{j=1}^{N-1} \nu_j^{\ddagger}} \cdot e^{-(V_{sp} - V_{min})/k_B T}$$

HQTST



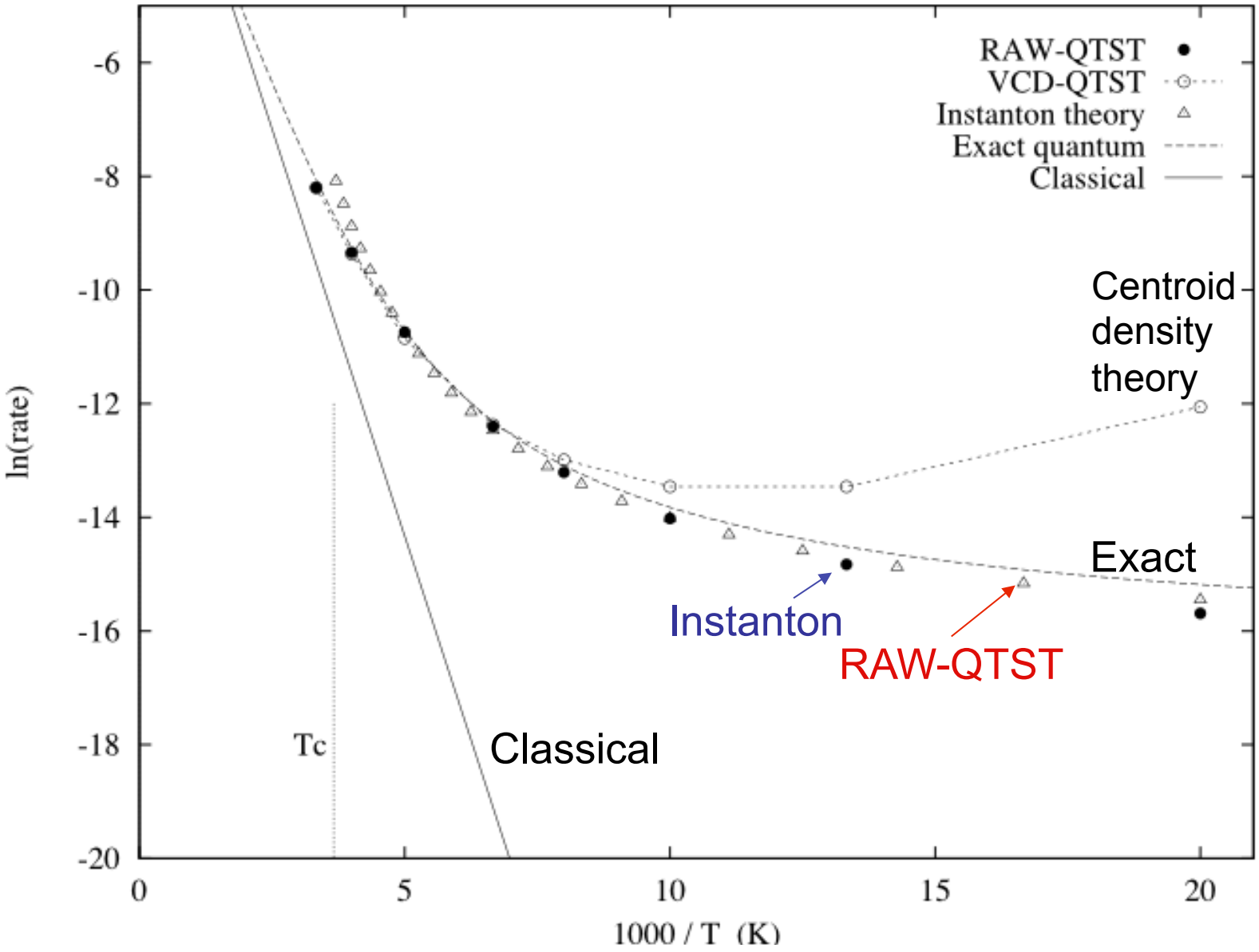
P images

S_E: NP dimensions

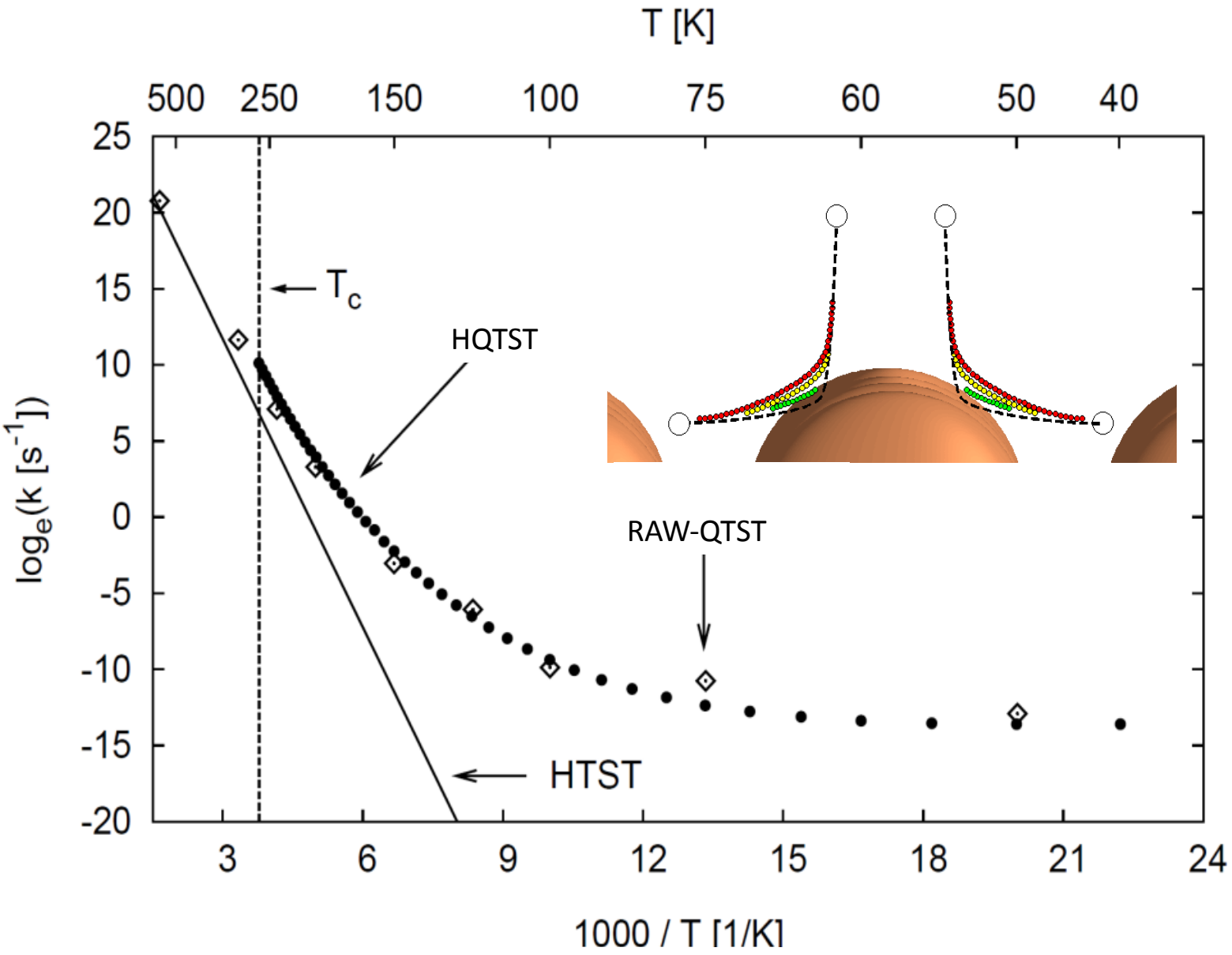
$$Q^R\ k^{HQTST} = \sqrt{\frac{S_0}{2\pi\hbar}} \frac{1}{\Delta\tau |\Pi_j' \lambda_j|} \cdot e^{-(V_{sp}^{eff}(T,P) - V_{min})/k_B T}$$

Spreading of images lowers the effective activation energy and accounts for tunneling!

Back to the Eckart barrier



Back to H_2 / Cu(110) problem



PNAS (2011)

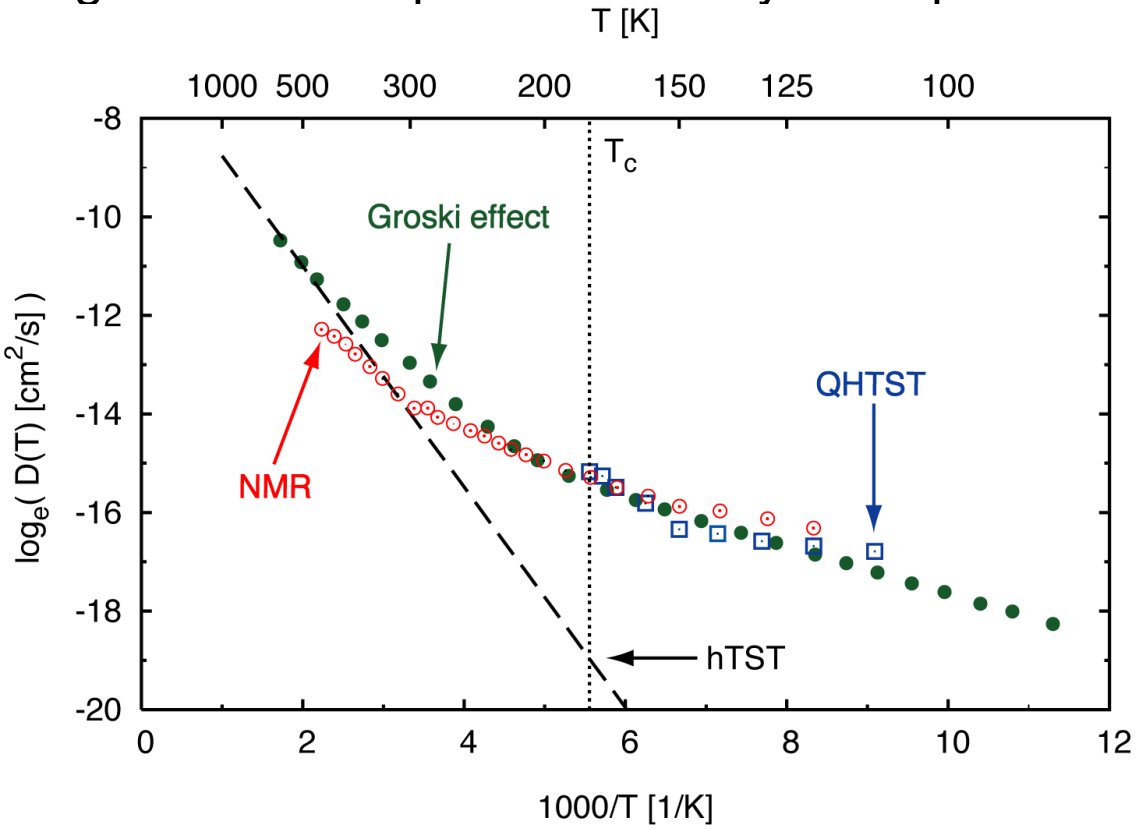
Application of HQTST: Hydrogen diffusion in Ta

DFT calculations using PAW, PW91 (VASP)

16 Ta atoms, 1 H atom.

Hops between adjacent tetrahedral holes.

Up to 58 images used to represent the Feynman paths.



Excellent agreement with experiments at low temperature *(no fitting!).*

Tunneling dominates below room temperature.

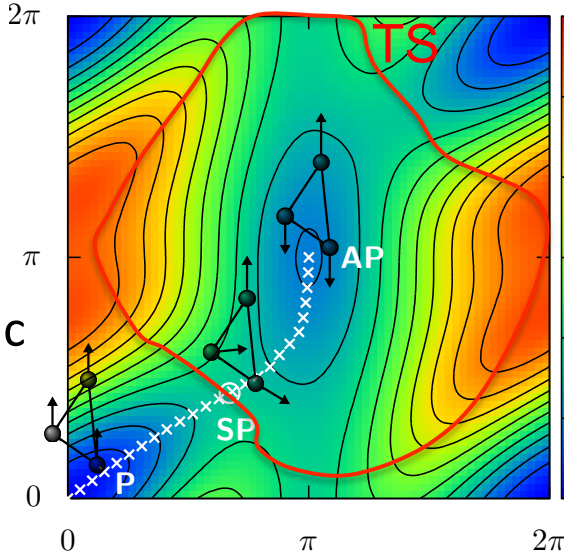
Magnetic Transitions

Landau-Lifshitz equation of motion:

$$\frac{dM_i}{dt} = \gamma\ M_i \times \frac{\partial E}{\partial M_i}$$

or $\dot{\phi}_i = \frac{\gamma}{M_i \sin\theta_i}\frac{\partial E}{\partial \theta_i}$ and $\dot{\theta}_i = -\frac{\gamma}{M_i \sin\theta_i}\frac{\partial E}{\partial \phi_i}$

Relies on an adiabatic approximation: length of the magnetic momentum vectors changes faster than orientation.



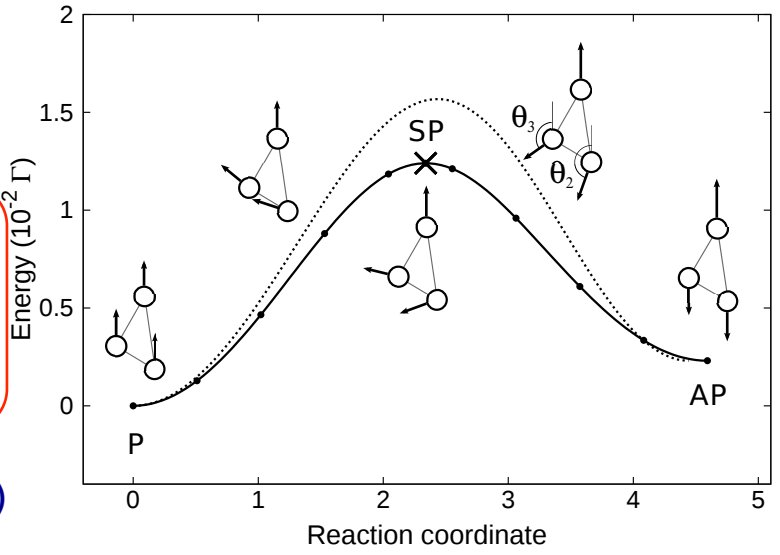
TST approximation of the rate constant:

$$k^{TST} = \frac{1}{C}\int \underbrace{e^{-E(\boldsymbol{x})/k_B T}}_{\text{Boltzmann}}\ \underbrace{\delta\left[f(\boldsymbol{x})\right]}_{\text{At TS}}\ \underbrace{v_\perp(\boldsymbol{x})}_{\text{flux}}\ \underbrace{h\left[v_\perp(\boldsymbol{x})\right]}_{\text{no recrossings}}\ d\boldsymbol{x}$$

Need to obtain $v_\perp$ from Landau-Lifshitz equation.

$$k^{HTST} = \frac{1}{2\pi}\frac{J_s}{J_m}\sqrt{\sum_{j=2}^{D}\frac{a_j^2}{\epsilon_{s,j}}\frac{\prod_{i=1}^{D}\sqrt{\epsilon_{m,i}}}{\prod_{i=2}^{D}\sqrt{\epsilon_{s,i}}}}\ e^{-(E^s-E^m)/k_B T}$$

(Pavel Bessarab, Valery Uzdin and HJ, *PRB* 2012)



Onset temperature for tunneling of magnetic moments

For a spin of length *s*, with orientation (θ, ϕ), the action is

$$S(\theta,\phi) = \int_{-\beta/2}^{\beta/2} d\tau \left[-is(1-\cos\theta)\dot{\phi} + U(\theta,\phi) \right]$$

where $U(\theta,\phi)$ is the potential energy surface.

$\delta S = 0$ gives classical eqns. of motion, Landau-Lifshitz eqns, in imaginary time.

At the first order saddle point of the energy surface, $\theta^\dagger, \phi^\dagger$

$$\delta^2 S = \int_{-\beta/2}^{\beta/2} d\tau \left[-2is\delta\theta\delta\dot{\phi}\sin\theta + \left(a\delta^2\theta + 2b\delta\theta\delta\phi + c\delta^2\phi \right) \right]$$

where

$$a \equiv \left.\frac{\partial^2 U(\theta^\dagger,\phi^\dagger)}{\partial\theta^2}\right|_{\theta^\dagger,\,\phi^\dagger},\; c \equiv \left.\frac{\partial^2 U(\theta^\dagger,\phi^\dagger)}{\partial\phi^2}\right|_{\theta^\dagger,\,\phi^\dagger},\; b \equiv \left.\frac{\partial^2 U(\theta^\dagger,\phi^\dagger)}{\partial\theta\partial\phi}\right|_{\theta^\dagger,\,\phi^\dagger}.$$

The onset temperature for tunneling is the temperature at which a second eigenvalue becomes negative. This gives

$$T_c = \frac{\sqrt{b^2 - ac}}{2\pi\, s\, k_B \sin\theta^\dagger}$$

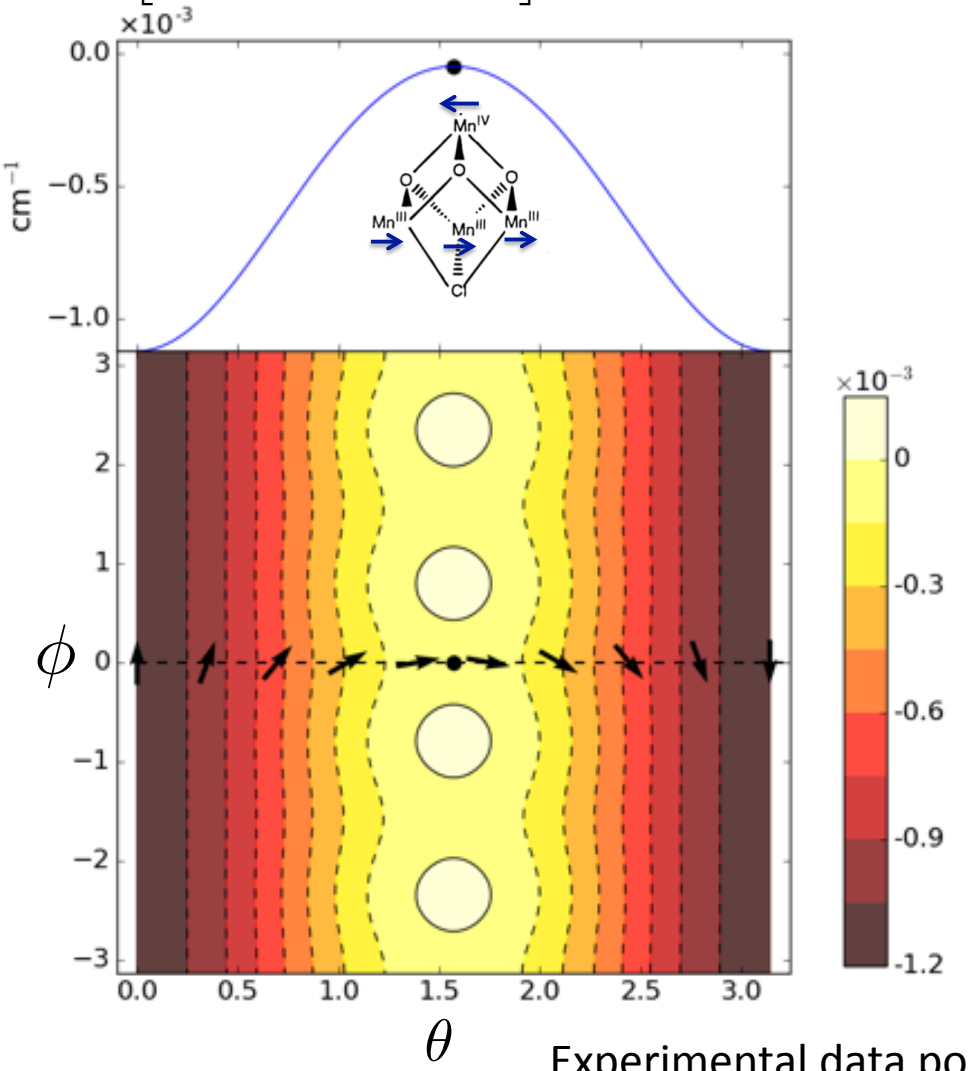
Can be applied to any system, described for example by DFT or Alexander-Anderson SCF model.

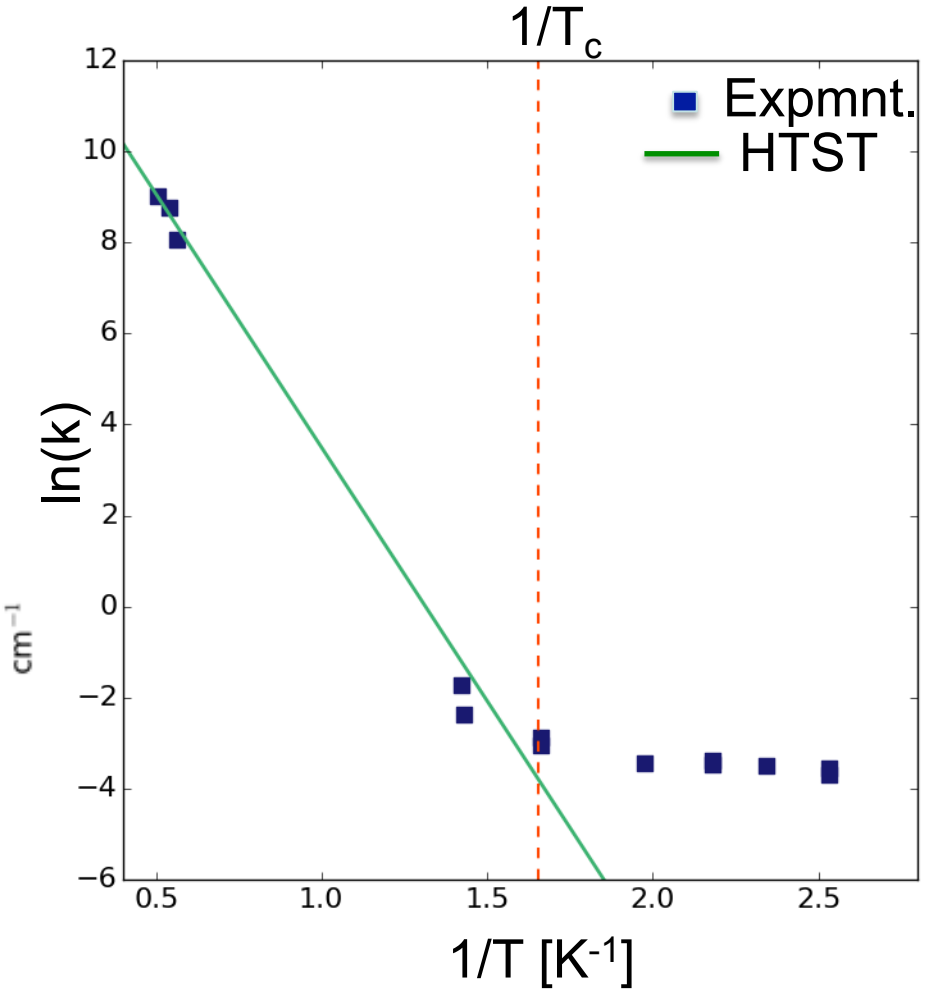
[Vlasov, Bessarab, Uzdin, Jónsson, *Farady Disc.* (2016)]

Application to a Mn_4 molecular magnet

$Mn_4O_3Cl(O_2CCH_3)_3(dbm)_3$ molecule with a total spin of s=9/2

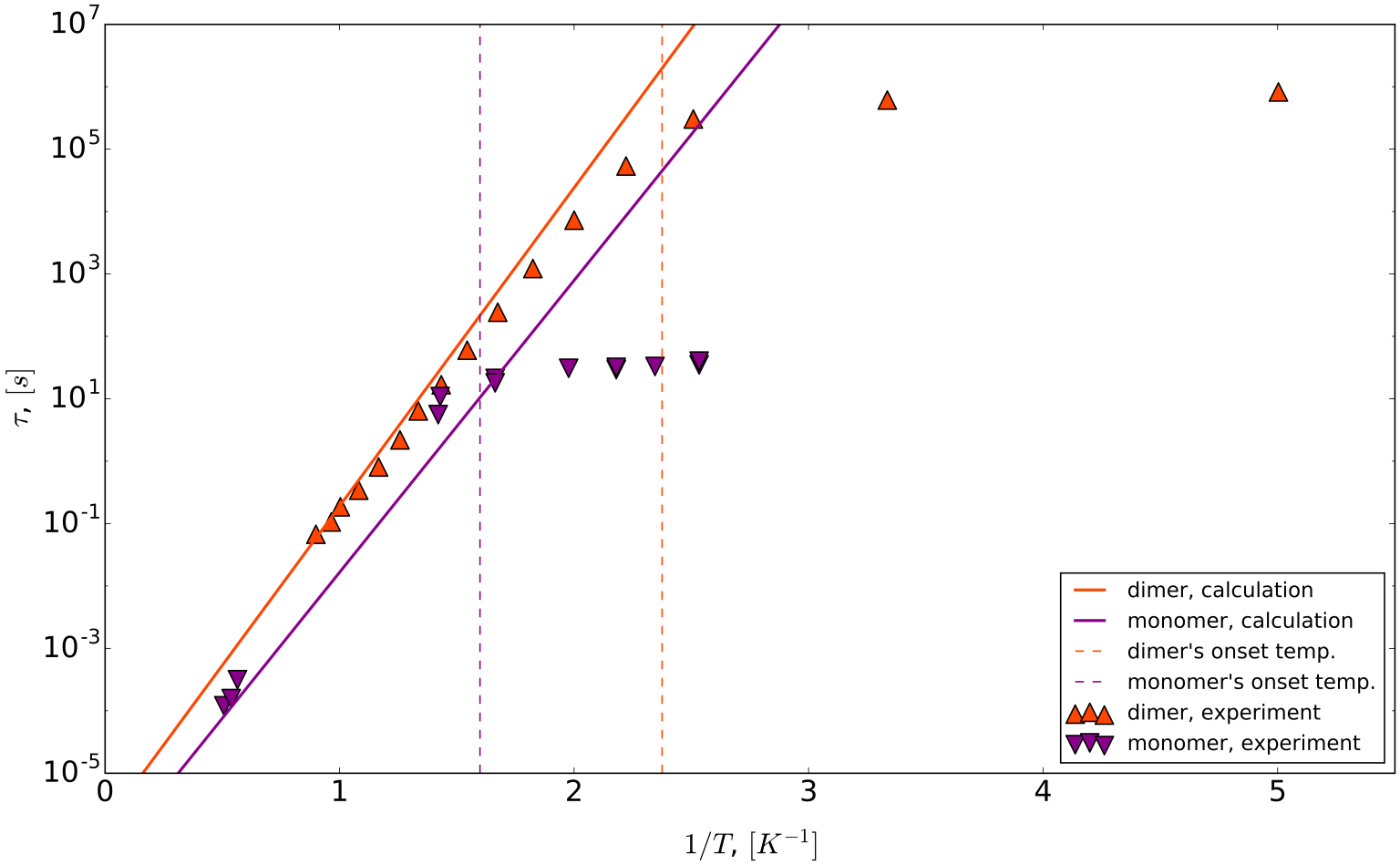
$$U = D\left[s^2\cos^2\theta - \frac{1}{3}s(s+1)\right] + B_4^0\left[35s^4\cos^4\theta - 5s^2\cos^2\theta(6s^2+6s-5) + 6s(s+1)\right] + B_4^4\left[\sin^4\theta\cos 4\phi\right]$$





Experimental data points: S.M.J. Aubin, *et al.*, *JACS* 120, 4991 (1998).
Calculations: Vlasov, Bessarab, Uzdin, Jónsson, *Farady Disc.* (2016).

Also, dimer of Mn_4 molecular magnets



Exp. Wernsdorfer, Aliaga-Alcalde, Tiron, Hendrickson and Christou, J. Magn. and Mag. Mat. (2004)

Summary:

- By using Feynman path integral representation of the quantum statistical mechanics (assuming rapid decoherence), the onset temperature for tunneling and the tunneling rate can be estimated for atomic systems - quantum extension of TST.
- Good agreement with exact calculations of model systems and expmntl. measurements H-atom diffusion.
- For magnetic systems, evaluate onset temperature for tunneling.

Ongoing work:

- Development of an expression for the thermally assisted tunneling rate using coherent state path integrals.
- Application to tunneling of skyrmions, domain walls, …

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