## Finding transition mechanisms and estimating rates

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#### **Overview:**

- Motivation: Find mechanism and rate of thermally activated transitions
- Transition state theory (TST)

and harmonic approximation to TST (HTST)

- Calculations of minimum energy paths and saddle points
  - two point problem: when both initial and final states specified
  - single point problem: when only initial configuration is specified





## **Conventional approach to atomic simulations**

### **Born-Oppenheimer** (adiabatic) approximation:

- Solve for the electronic degrees of freedom, r, while keeping the nuclei fixed at coordinates x. Usually done with Kohn-Sham density functional theory (DFT) using approximate functionals such as PW91, PBE, RPBE, ... Gives energy surface, V(x).
- 2. Solve for the motion of the nuclei, usually within the classical approximation, F=ma, and often using a harmonic approximation (----)  $V(\mathbf{x}) \sim -\frac{1}{2} k_{sp} (\mathbf{x} - \mathbf{x}_{min})^2$ .



## A direct *dynamical* simulation of a thermally activated process is typically impossible

### Time scale problem:

Most interesting transitions are *rare events* (much slower than vibrations).

 A transition with an energy barrier of 0.5 eV and a typical pre-exponential factor occurs 1000 times per second at room temperature

- fast on laboratory scale!



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### Time scale problem:

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- A transition with an energy barrier of 0.5 eV and a typical pre-exponential factor occurs 1000 times per second at room temperature – fast on laboratory scale!
- A video of a direct classical dynamics simulation where each vibration spans a second in the video would go on for more than 100 years in between such reactive events – *slow on atomic scale!*



Typically there is a clear separation of time scales, and a *statistical* approach can be used

#### Note:

Should not simply heat up the system to speed up the transition



A cross-over from one mechanism to another can occur as the temperature is increased.

*Example:* Diffusion of H<sub>2</sub>O admolecule on an ice surface vs. melting of the ice crystal ...

#### **Overview:**

The *rare event* problem and transition state theory (TST)

- Transition states, dividing surfaces and reaction coordinates
- Recrossing corrections and the variational principle
- The WKE two step procedure for finding the mechanism and 'exact' rate

Harmonic approximation and first order saddle points (SPs)

- A. Mininum energy path calculations
  - Initial path generation
  - NEB and CI-NEB
  - Variants: energy weighted springs, symmetry, remove zero modes
- B. Finding saddle points given only initial state, not final states
  - Transformation of the force field from SP to minimum
  - Escaping the convex region

Adaptive kinetic Monte Carlo (AKMC)

- Long time scale simulations using saddle points searches and HTST
- Coarse graining, recycling, symmetry operations
- Acceleration using Gaussian process regression
- Applications: Simulations of grain boundaries, diffusion, island growth, ...

## **Rate Theory Methods**

Characterize transitions that occur due to thermal energy in the system, for example diffusion events, defect formation/migration, chemical reactions ... Want to be able to:

- 1. predict the mechanism and rate of transitions given information about the atomic structure and interaction between the atoms (such as DFT).
- 2. interpret measurements of rates in terms of the atomic interactions and transition mechanism, typically Arrhenius plots
- 3. Carry out simulations of long timescale evolution of a system



# **Transition State Theory (TST)**

Also known as "Absolute Rate Theory" or "Activated Complex Theory"

Early pioneers:

Pelzer & Wigner, Z. Phys. Chem. B15, 445 (1932);
Wigner, Trans. Faraday Soc. 34, 29, (1937).
Eyring, J. Chem. Phys. 3, 105 (1935).
Evans & Polyani, Trans. Faraday Soc. 31, 857 (1935).

**TST** is a method for estimating the rate of **slow** transitions between states of a system due to thermal energy:

- 1. Gives an **approximation** to the rate constant, and
- 2. can later calculate a correction to the TST estimate
  - to obtain the exact rate using just short timescale simulations.

# Transition State Theory (Wigner, Eyring 1930s)

Identify a 3*N*-1 dimensional dividing surface, a **bottleneck** for going from the initial to a final state:



The bottleneck can be due to an energy barrier and/or *entropy barrier* 

 $k^{TST} = (probability of being in TS) \cdot (flux out of TS)$ 

# **Transition State Theory** the basic assumptions

- 1. Born-Oppenheimer
- 2. Classical dynamics of nuclei (can be extended to quantum systems ...)
- 3. Boltzmann distribution in initial state (*OK if slow enough*,  $k_{B}T < \Delta E/5$ )
- 4. No recrossings of TS, (often most serious, but can be fixed using trajectories)

## Note:

- TST gives the lifetime,  $\tau=1/k$ , of a given initial state
- No knowledge of final state(s).



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## Note:

- TST gives the lifetime,  $\tau=1/k$ , of a given initial state
- No knowledge of final state(s).
- Can run short time scale dynamics starting from TS to find the final state(s).
- Such trajectories can be used to take recrossings into account dynamical correction

$$k^{exact} = \kappa k^{TST}$$
where  $0 < \kappa <$ 



Recrossings and variational principle for TST

The neglect of recrossings, approximation 4, results in an overestimate of the transition rate in TST: kTST > k



Should not contribute to k, but counts as one reactive event in TST.

Should only count once, but gives two reactive events in TST.

The optimal TS is the one that gives smallest estimate for  $k^{TST}$ This gives a **variational principle** that can be used to find the dividing surface that provides the **optimal** transition state.

Keck, J. Chem. Phys. 32, 1035 (1960)

First, review a bit of classical statistical statistical mechanics:

Total energy of a conservative system:  $E(x, v) = E_{kin} + E_{pot} = \sum_{i} \frac{1}{2}m_i v_i^2 + V(x)$ 

Boltzmann distribution:

probability that (x, v) is in the range  $\{x, x+dx\}$  and  $\{v, v+dv\}$  is:

 $P(x, v)dxdv = Ae^{-E(x, v)/k_BT}dxdv$  (A is a normalization constant)

 $\underbrace{A_{v} e^{-\sum_{i} \frac{1}{2} m_{i} v_{i}^{2} / k_{B} T}}_{p_{v}(\mathbf{v})} d\mathbf{v} \underbrace{A_{c} e^{-V(\mathbf{x}) / k_{B} T}}_{p_{c}(\mathbf{x})} d\mathbf{x}$ Initial

state

This factorizes into:

Given that the system is initially somewhere in *R*:

$$A_c = \frac{1}{\int_R e^{-V(x)/k_B T} dx}$$

The probability of being in some subspace, S, of R is:

$$P_{S} = \frac{\int_{S} e^{-V(x)/k_{B}T} dx}{\int_{R} e^{-V(x)/k_{B}T} dx} \equiv \frac{Z_{S}}{Z_{R}} \longrightarrow \text{configuration integrals}$$

Final

state

 $k^{TST}$  = (probability of getting to TS) • (flux across TS)

Choose the dividing surface to be a *hyperplane* ax+b=0. This is particularly simple (but, may not be good enough ...)

$$k^{TST} = P_{\ddagger} \frac{\langle v_{\perp} \rangle}{\sigma}$$

$$= \frac{\sigma \int_{\ddagger} e^{-V(\mathbf{x})/k_B T} d\mathbf{x}}{\int_R e^{-V(\mathbf{x})/k_B T}} d\mathbf{x} \ \frac{\langle v_{\perp} \rangle}{\sigma}$$



where  $\mu_{\perp}$  is reduced mass corresponding to motion perpendicular to the hyperplane.

So 
$$k^{TST} = \sqrt{\frac{k_B T}{2\pi\mu_{\perp}}} \frac{Z_{\ddagger}}{Z_R}$$



### A simple example: Effusion of gas atoms through a small hole

Use 
$$k^{TST} = \sqrt{\frac{k_B T}{2\pi\mu_{\perp}}} \frac{Z_{\ddagger}}{Z_R}$$

where 
$$Z_s \equiv \int_S e^{-V(x)/k_B T} dx$$



No energy barrier here,

just an entropic bottle neck

Notation: V is volume of the box, A is area of the hole  $Z_R = V$  and  $Z_{\ddagger} = A$ So  $k^{TST} = \sqrt{\frac{k_B T}{2\pi m}} \frac{A}{V}$ ideal gas eqn.  $PV = Nk_B T$ gives  $k^{TST} = \frac{PA}{\sqrt{2\pi m k_B T}N}$ 

Rate of effusion obtained from TST  $r = Nk^{TST} = \frac{PA}{\sqrt{2\pi mk_B T}}$ 

Same result as is obtained from kinetic theory of gases.

TST is exact in this case, since there are no recrossings in the hole. 16

# Both good and bad choices for the transition state can work, *in principle* ....



Less than optimal TS dividing surface. Many recrossings, K<<1, need many short trajectories to identify product states and correct k<sup>TST</sup> Optimal TS
dividing surface.
Few recrossings,
κ~1, only need a few
short trajectories to identify
product states and correct k<sup>TST</sup>

### Note: systems of interest typically involve many degrees of freedom!



Maxima: filled circles First order saddle points: x Energy Ridge: dotted line Solid straight lines: go through x

Need to take a long stroll on a 3Ndimensional **potential energy surface**,  $V(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ , where N is the number of atoms.

Given some initial state,  $\mathbf{R}$ , want to find the rate of transitions and possible final states,  $\mathbf{P}_1, \mathbf{P}_2$ ...

Also, want to find the mechanism of the transitions (*how do the atoms move during a transition?*).

# Use Wigner-Keck-Eyring (WKE) to generate reactive trajectories with much smaller computational effort than direct dynamics

- 1. Find optimized transition state dividing surface using  $k^{TST} > k^{exact}$ For a hyperplane  $k^{TST} = \sqrt{\frac{k_B T}{2\pi\mu_{\perp}}} \frac{Z_{\ddagger}}{Z_R}$  where  $Z_S \equiv \int_S e^{-V(\mathbf{x})/k_B T} d\mathbf{x}$
- 2. Run (short time) dynamics trajectories from the transition state to find product states and dynamical correction,  $k^{exact} = \kappa k^{TST}$

Note: Step 2 is hard unless a good job has been done in 1, need to optimize the dividing surface.

WKE procedure generates (pseudo) trajectories over long time scale



time





A first order saddle point

designed by Ivan Tambovtsev using a chatbot



At a 1st order saddle point, the Hessian (matrix of second derivatives) has one and only one negative eigenvalue.

# HTST: Harmonic approximation to transition state theory for particle rearrangements

Good approximation when

- energy of second order saddle points is significantly higher than k<sub>B</sub>T over the energy of *first* order saddle points and
- the energy surface is smooth enough that a second order Taylor approximation is good enough in the region that has significant statistical weight.

A good approximation for processes in and on the surface of solids at not too high temperature.



#### **Derivation of HTST:** Expand PES around minimum in *normal mode* coordinates

∮SP

Taylor expand PES around minimum and saddle point, use vibrational normal modes, q

$$V_{R}(\mathbf{q}) \approx V_{min} + \sum_{i=1}^{3N} \frac{1}{2} k_{R,i} q_{R,i}^{2}$$
$$V_{\ddagger}(\mathbf{q}) \approx V_{SP} + \sum_{i=1}^{3N-1} \frac{1}{2} k_{\ddagger,i} q_{\ddagger,i}^{2}$$

Plug into the expression for the rate constant

$$k^{TST} = \sqrt{\frac{k_BT}{2\pi\mu_{\perp}}} \frac{Z_{\ddagger}}{Z_R}$$

$$= \sqrt{\frac{k_BT}{2\pi\mu_{\perp}}} \frac{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\left(V_{SP} + \sum_{i=1}^{3N-1} \frac{1}{2} k_{\ddagger,i} q_{\ddagger,i}^2\right)/k_B T} d\mathbf{q}_{\ddagger}}{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\left(V_{min} + \sum_{i=1}^{3N} \frac{1}{2} k_{R,i} q_{R,i}^2\right)/k_B T} d\mathbf{q}_R}$$
Define  $\nu_i = \frac{\omega_i}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k_i}{\mu_{\perp}}}$ 
which gives  $k^{HTST} = \frac{\prod_{i=1}^{3N} \nu_{R,i}}{\prod_{i=1}^{3N-1} \nu_{\ddagger,i}} e^{-(V_{SP} - V_{min})/k_B T}$  Agrees with the empirical Arrhenius law  $k(T) = \nu e^{-E_a/k_B T}$ 

## Interpretation of the expression for $k^{HTST}$



If the width of the energy valley is the same at the minimum and saddle point in all directions,



# A first order saddle point gives an estimate for a transition state within HTST,

### provides information about mechanism and rate of a transition

Initial state corresponds to a local minimum on the surface that describes how the energy depends on atom coordinates.

Want to find adjacent first order saddle points

(here labeled 1, 2, 3 and 4).

Each saddle point represents a mechanism for atomic rearrangement, can estimate transition rate within harmonic transition state theory.



26

- Need to find **all relevant saddle points** on the potential energy rim surrounding the energy basin corresponding to the initial state.
- The transition state is approximated as a set of hyperplanes going through the saddle points with the unstable mode normal to the hyperplane.
- For each hyperplanar segment:  $k^{\text{HTST}} = \frac{\prod_{i=1}^{D} v_{R,i}}{\prod_{i=1}^{D-1} v_{*,i}^{*}} e^{-(V_{\mathcal{SP}} - V_{\min})/k_{B}T}$

Temperature and entropy are taken into account within the normal mode harmonic approximation



HTST is typically more than 10<sup>3</sup> faster than full TST! But, need to find the saddle pts.

How to find the saddle point(s)?

Two categories:

➡ A. Two point problem – both initial and final state minima

are known.

Easier, since info about final state minimum can guide the search



B. Single point problem – only initial state minimum is known.

Harder, can only use local info about the energy surface



## Drag method:

Given some (presumed) reaction coordinate (here linear interpolation between R and P, \_\_\_\_\_), drag the system along that direction while relaxing all other degrees of freedom.

Can work, but fails when the reaction coordinate differs significantly from the drag path.

Can lead to a discontinuous path and hysteresis (P to R gives different estimate than R to P).

See Figure: Even when the constraint hyperplane goes right through the SP, the relaxed position of the system is far from the saddle point!



# Nudged Elastic Band (NEB) Method



Create several replicas of the system, 'images' (discretization points for the path) Estimate the tangent at each image,  $\hat{\tau}_{\parallel}$ , using line segment to adjacent image with higher energy.

Only the perpendicular component of the force acts on each image

$$\nabla V(\mathbf{x}_i)|_{\perp} = \nabla V(\mathbf{x}_i) - \left(\nabla V(\mathbf{x}_i) \cdot \hat{\tau}_{\parallel}\right) \hat{\tau}_{\parallel}$$

and the distribution of the images along the path is controlled by adding a spring force

$$\mathbf{F}_{i}^{s} = k_{i+1} \left( \mathbf{x}_{i+1} - \mathbf{x}_{i} \right) - k_{i} \left( \mathbf{x}_{i} - \mathbf{x}_{i-1} \right)$$

So the net force on an image becomes

$$\mathbf{F}_{i}^{NEB} = -\nabla V(\mathbf{x}_{i})|_{\perp} + \left(\mathbf{F}_{i}^{s} \cdot \hat{\tau}_{\parallel}\right) \hat{\tau}_{\parallel}$$

Adjust all images simultaneously, parallel computing.

(Mills, Jónsson & Schenter, Surf. Sci. **324**, 305 (1995); Jónsson, Mills, Jakobsen, 1998). Review: V. Ásgeirsson and H. Jónsson, "Handbook of Materials Modeling. 1 Methods: Theory and Modeling" (Springer, 2018).

## Climbing image NEB (CI-NEB): Push the highest energy image up to converge on saddle point



The highest energy image is pushed up to the saddle point to give accurate estimate of the barrier height (activation energy)

$$F_{CI} = \nabla V(R_{CI}) - 2\nabla V(R_{CI}) \cdot \tau_{\parallel} \tau_{\parallel}$$



(G. Henkelman, B.P. Uberuaga and HJ, J. Chem. Phys. 113, 9902 (2000))

## Example 1: $H_2$ adsorption/desorption from Cu(110)

G. Mills and HJ, Phys. Rev. Letters 1994 (first paper using NEB method)

PES: Empirical potential of the EAM type where the H-Cu interaction is fitted to the LEPS potential of Depristo *et al*.



Evaluate the reversible work required to shift the system from reactants towards products to get  $\Delta F$ 

If H<sub>2</sub> comes from a gas with temperature equal to that of the surface, then TST applies!



## Example 2: $H_2$ adsorption/desorption from Ni(111)

Energy [eV]

Use DFT/PBE to estimate energy and atomic forces.

One of the H-atoms starts in a subsurface site.

Start up NEB assuming direct path for subsurface H-atom to attach to a surface H-atom

But, the MEP found shows that surface H-atom hops away. So, not direct H-H binding

G. Henkelman, A. Arnaldsson and HJ, JCP 2006



#### Example 3: Chemical Reaction of gas phase molecules



V. Ásgeirsson, B. O. Birgisson, R. Bjornsson, U. Becker, F. Neese, C. Riplinger and H. Jónsson, J. Chem. Theory Comput. 17, 4929 (2021).

## A good initial path for NEB calculations: IDPP and, more recently, S-IDPP

Interpolate pairwise distances in images between initial and " final configurations, then fit coordinates of intermediate images to best satisfy the interpolated distances. This generates **IDPP** - image dependent pair potential. Can reduce SCF iterations since very close proximity of atoms is avoided, and saves atomic displacement iterations because the path is closer to MEP.



IDPP: S. Smidstrup, A. Pedersen, K. Stokbro and HJ, *JCP 140*, 214106 (2014) S-IDPP: Y. L. A. Schmerwitz, V. Ásgeirsson and H. Jónsson, JCTC 20, 155 (2024)

#### Locally optimal MEP:

The NEB optimization usually brings the images to the MEP that is nearest to the initial path. But, this may not be the best path (i.e. the one with lowest activation energy).

#### **Globally** optimal MEP:

Genetic algorithm to search for the best MEP. New intermediate configurations generated from two parent configurations using a heredity transformation. Each intermediate local minimum found in NEB calculations added to the set.



NEB

C⊡na'

## **Remarks on using the NEB Method**

#### Cubic interpolation of the energy:

Important to use the force in the direction of the path as well as the energy at each image in the interpolation, gives a lot of info, in particular indications of intermediate minima (see appendix in *JCP* **113**, 9978 (2000)).

#### Divide and conquer:

If there is a hint of an intermediate minimum, then release the nearest Image and relax to converge to that minimum (if it exists). Then break up the path and calculate separately the two segments of the MEP.

#### Rotation and translation:

Six degrees of the system (at least) need to be frozen out. Otherwise, the system will do whatever it can to avoid the saddle point region.

In materials simulations with periodic boundary conditions, rotation is not a problem, but translation of the center of mass may need to be removed.

For clusters, remove also rotation using quaternions, see

(Melander, Lasonen and Jónsson, J. Chem. Theo. Comput. 11, 1055 (2015)).

## Two categories:

A. Two point problem – both initial and final state minima

are known.

Easier, since info about final state minimum can guide the search



→ B. Single point problem – only initial state minimum is known.

Harder, can only use local info about the energy surface



## Methodology: Simple method for converging on a first order saddle point

Make a transformation of the force (negative gradient):

The force field around a first order saddle point, **F**<sub>i</sub>

After inverting the component along the eigenvector corresponding to the lowest eigenvalue of the Hessian,  $\hat{\mathbf{v}}_{i,min}$ , so-called "minimum mode"

$$\mathbf{F}_{i,eff} = \mathbf{F}_i - 2\left(\mathbf{F}_i \cdot \hat{\mathbf{v}}_{i,min}\right) \hat{\mathbf{v}}_{i,min}$$

the transformed force field corresponds to a minimum



The force projection locally transforms a first order saddle point into a minimum



designed by Ivan Tambovtsev using a chatbot

**Dimer method** 



create two replicas of the system with fixed distance,

minimise energy

converge on minimum mode using only first derivatives Minimum mode:

Found using dimer method, or Lanczos, or Davidson algorithms.

Use only first derivatives of the energy.

No need to even construct the Hessian matrix!

Then, transform the force by inverting the component along the minimum mode,  $\hat{\bm{v}}_{i\,\text{min}}$ 

 $\mathbf{F}_{i,eff} = \mathbf{F}_{i} - 2(\mathbf{F}_{i} \cdot \hat{\mathbf{v}}_{i,min}) \hat{\mathbf{v}}_{i,min} \quad \text{if min eigenvalue} < 0$  $= -(\mathbf{F}_{i} \cdot \hat{\mathbf{v}}_{i,min}) \hat{\mathbf{v}}_{i,min} \quad \text{else}$ 



G. Henkelman and HJ, *J. Chem. Phys.* (1999)

Then can use any force based minimisation to converge on the saddle point.







basins of attraction

## Minimum mode following method

Within HTST, need to find all the relevant saddle points on the energy rim surrounding the current state minimum.



Make Gaussian random displacement from the minimum.

Transform the force by inverting the component along the minimum mode,  $\hat{\mathbf{v}}_{i,min}$ , of the Hessian (matrix of second derivatives)  $\mathbf{F}_{i,eff} = \mathbf{F}_i - 2(\mathbf{F}_i \cdot \hat{\mathbf{v}}_{i,min})\hat{\mathbf{v}}_{i,min}$ 

The direction along the minimum mode is found by minimizing the energy of a **dimer** (two replicas of the system, **O**) or by using the **Davidson** algorithm. No need to construct the Hessian matrix.



Use some minimization algorithm that only requires forces to move the system along the effective force and converge on first order saddle point. The force projection locally transforms a first order saddle point to a minimum.

# Important to find rather than to specify a priori the mechanism of transitions

Classical example of a surprise mechanism: Al adatom diffusion on Al(100) (see: Feibelman, *Phys. Rev. Lett.* **65**, 729 (1990)).

> Al(100) surface with Al adatom



Another example of a surprise (explains re-entrant layer-by-layer growth):
Pt adatom descent from atop islands on Pt(111) near but not at kinks.
(see: Jónsson, Annual Review of Physical Chemistry 51, 623 (2000))

It is important not to impose a preconceived notion of the mechanism of a transition, rather **learn about the mechanism from the calculation**!

## Warning: The mechanism can be unexpected!



## Satistics on saddle point searches

![](_page_42_Figure_1.jpeg)

Two categories:

A. Two point problem – both initial and final state minima

are known.

Easier, since info about final state minimum can guide the search

![](_page_43_Figure_5.jpeg)

B. Single point problem – only initial state minimum is known.

Harder, can only use local info about the energy surface

![](_page_43_Figure_8.jpeg)

## Optimal strategy: First CI-NEB with loose tolerance, then MMF to converge on saddle point

![](_page_44_Picture_1.jpeg)

#### Red:

NEB calculation with a rather large convergence tolerance

#### Blue:

MMF calculation to converge well on saddle point.

V. Ásgeirsson, B. O. Birgisson, R. Bjornsson, U. Becker, F. Neese, C. Riplinger and H. Jónsson, J. Chem. Theory Comput. 17, 4929 (2021).

![](_page_45_Picture_0.jpeg)

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![](_page_45_Picture_4.jpeg)

![](_page_46_Picture_0.jpeg)

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![](_page_47_Picture_0.jpeg)

- Calculations based on rate theory can be used to identify the mechanism and estimate the rate of thermally activated transitions such as chemical reactions, diffusion events, configurational changes ...
- The NEB method can be used to find the minimum energy path of a transition when the final state is known.
- The minimum mode following method (MMF) can be used to find saddle points without preconceived notion of the final state (the basis of long time scale simulations).
- Has been extended to magnetic transitions and tunneling mechanism.