

# Introduction to Chemical Reaction Dynamics

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# We make many assumptions (Ansatz) in our computations

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- Time Independent Schrodinger Equation is all you need

$$i\hbar \frac{\partial \Psi(\mathbf{N}, \mathbf{n}, t)}{\partial t} = H\Psi(\mathbf{N}, \mathbf{n}, t)$$

- But it is prohibitively expensive, let's separate nuclear motion and electronic motion (**Bohn-Oppenheimer Approximation** or **Adiabatic Approximation**)

$$\Psi(\mathbf{N}, \mathbf{n}, t) = \Psi(\mathbf{N}, t)\Psi(\mathbf{n}, t) = \Psi(\mathbf{N}, t)\Psi(\mathbf{n})e^{-i\omega t}$$

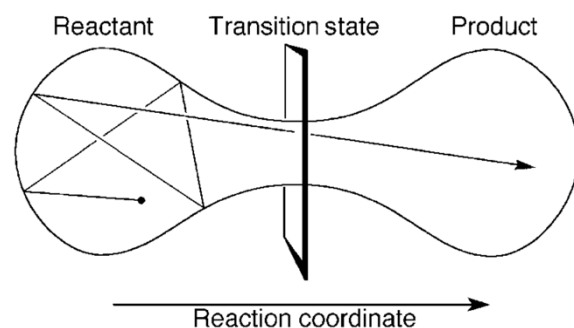
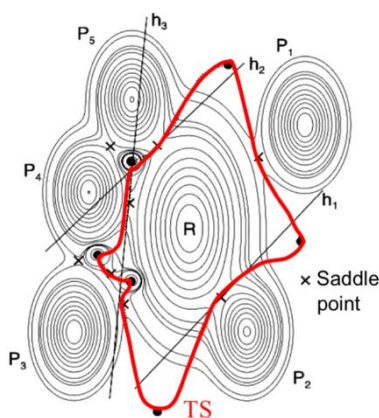
- We can separate out **time** in our electronic wavefunction through a phase factor. Dynamic of the electronic wavefunction is in **Berry phase** (evolution of coefficients of eigenstates), we will not discuss it here.
- We assume nuclei are **classical particles**, and they obey Newton's second Law of motion. For an adiabatic reaction, the system is governed by two equations.

$$H\Psi(\mathbf{n}) = E\Psi(\mathbf{n})$$
$$F(\mathbf{N}, t) = \frac{d\mathbf{p}}{dt}$$

- A chemical system is a collection of all the geometrical configurations (**q**) and momentum coordinate (**p**). It is called a **phase space**. A mechanistic study is generally exploring the phase space of the reaction.

# We live in the Phase Space – Statistical Model

- But keeping track of the momentum of all atoms is very difficult, we need more assumptions. Can we apply statistical techniques to derive a kinetic model?
- Two main assumptions for **Conventional Transition-State Theory**
  - **Local Equilibrium Assumption:** There must be thermal equilibrium in the reactant valley. In other words, for microcanonical ensemble, all states of reactants with the same total energy are equally likely to be populated. Or the reactant-molecule trajectories is **ergodic**.
  - **No recrossing Assumption:** Any trajectory crossing the TS dividing surface from the reactant state is on a path towards the product state and will reach it without recrossing the dividing surface prior to the product being reached



- **Dividing Surface:** A  $3N-1$  surface that enclose the reactants to separate them from products.
- TST gives the rate of loss of reactants, but not knowledge of products.

# Conventional Transition State Theory

## Thermal Average of the Flux through a Dividing Surface

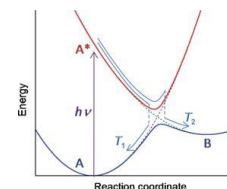
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$$k^{TST} = Q_R^{-1} \int \frac{d^{3N}p d^{3N}q}{h^{3N}} e^{-H(\mathbf{p},\mathbf{q})/kT} \delta[f(\mathbf{q})] \frac{\partial f(\mathbf{q})}{\partial \mathbf{q}} \cdot \left(\frac{\mathbf{p}}{\mathbf{m}}\right) \Theta\left(\frac{\partial f(\mathbf{q})}{\partial \mathbf{q}} \cdot \mathbf{p}\right)$$

- $Q$ : partition function in the reactant region
- $H(\mathbf{p},\mathbf{q})$  is the classical Hamiltonian of the system
- The delta function  $f(\mathbf{q})$  defines the dividing surface via the condition  $f(\mathbf{q}) = 0$  so we are integrating on the  $3N-1$  dividing surface
- $\frac{\partial f(\mathbf{q})}{\partial \mathbf{q}} \cdot \left(\frac{\mathbf{p}}{\mathbf{m}}\right)$  is the inner product between the surface normal in the direction of products, and the momentum when the reactive flux passes through the dividing surface
- The heavy-side function selects momenta in the direction of products at the dividing surface

# When do the assumptions break down?

- **Bohn-Oppenheimer Approximation:** when the system approaches intersection points between electronic states that the motion of the nuclei is drastic. The coupling between electron and nuclei motion is not negligible.
- **Classical Assumption:** Quantum Effect of the nuclei
- **Local equilibrium Assumption:** The reactant state and TS is **NOT** in thermal equilibrium. The energy distribution in the molecule is not fully equilibrated (slow IVR). Excess kinetic energy influences the reaction outcome
- **No recrossing Assumption:** TS has the maximum electronic energy along the MEP, but not necessarily the maximum free energy (bottleneck); or there is a hidden dynamic bottleneck (entropic or ZPE intermediate).
- **Non-adiabatic effect in excited states.** Usually around conical intersections (CI)
- **Tunnelling:** Hydrogen tunnelling, Heavy-atom tunnelling (HAT)
- **Dynamic effects:** Dynamic matching, Avoiding Minima; Bifurcation(?);
- **Dynamic effects:** Hidden dynamic bottleneck



# We need details of the phase space

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- When we apply statistical model (TST), we ignore the  $\mathbf{p}$  dimension of the phase space. To study the phase space, we need to investigate how the chemical system evolve with time – **Molecular Dynamics!**
- The evolution of the chemical system is a trajectory. It requires solving the the equation of motion in classical mechanics. In other words, we use the forces on atoms to propagate (integrate) the system.

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}} \right) = \frac{\partial L}{\partial q_j}$$

- In ab initio MD, we obtain the forces (gradient) through QM calculations. Any calculation method that can output gradient (first-order derivative of electronic energy) can be used for AIMD.

$$F = -\nabla U$$

- However, the equation of motion is not analytically solvable. We need numerical integration method to solve it. For simplification we try to integrate the Newton's Laws through Tylor expansion.

$$m\ddot{\vec{x}} = m\vec{a} = \vec{F}$$
$$x(t) = x(0) + \dot{x}(0)t + \frac{1}{2}\ddot{x}(0)t^2 + \frac{1}{3!}\dddot{x}(0)t^3 + \frac{1}{4!}\cdot\ddot{x}(0)t^4$$

# Euler Integration Algorithm

## A first-order integration algorithm

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1. Set initial positions  $\vec{x}(t = 0)$
2. Set initial velocities  $\vec{v}(t = 0)$
3. Compute force  $\vec{F}(t)$  from  $-\vec{\nabla}U(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N)$
4. From  $\frac{\vec{F}(t)}{m}$  obtain  $\vec{a}(t)$
5. propagate  $\vec{x}(t)$  and  $\vec{v}(t)$  for small timestep  $h$ :

$$\vec{x}(t + h) = \vec{x}(t) + h\vec{v}(t) + \frac{1}{2}h^2\vec{a}(t) + O(h^3)$$

$$\vec{v}(t + h) = \vec{v}(t) + \vec{a}(t)h + O(h^2)$$

$t + h$  is now  $t$  return to **Step 3**

The error comes from the approximation that the acceleration is constant during the time step. But it is often not the case. We can circumvent it by reducing the timestep, but it will significantly increase the cost. It is generally not used in MD

- **Practical hint on choosing time step in MD simulations.**

General principle: Take time steps that are several times faster (smaller) than the fastest degree of freedom in the system.

Usually, the fastest DoF is the stretching of a bond. We want to make a balance between cost and accuracy. For normal AIMD, 1 fs timestep is in general decent. Reduce the timestep to 0.5 fs if the chemical reaction is very fast (<100 fs). For non-adiabatic MD, smaller time step of 0.25-0.5 fs is required. For less accurate semi-empirical or force-field MD, sometimes 2 fs timestep is reasonable.

# Velocity Verlet Integration Algorithm

## A second-order integration algorithm

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- We expand the expression for velocity to second-order to be more accurate (we expand on velocity because the error in velocity is larger than the error in position)

$$v(t + h) = v(t) + hv(t) + \frac{h^2}{2}\ddot{v}(t) + O(h^3)$$

- However, we need to estimate the second-order derivative of velocity

$$\dot{v}(t + h) = \dot{v}(t) + h\ddot{v}(t) + O(h^2)$$

$$\begin{aligned} h\ddot{v}(t) &= \dot{v}(t + h) - \dot{v}(t) + O(h^2) \\ &= \frac{1}{m}(F(t + h) - F(t)) + O(h^2) \end{aligned}$$

- The velocity at  $t+h$  is:

$$v(t + h) = v(t) + h\frac{F(t)}{m} + \frac{h}{2m}(F(t + h) - F(t)) + O(h^3)$$

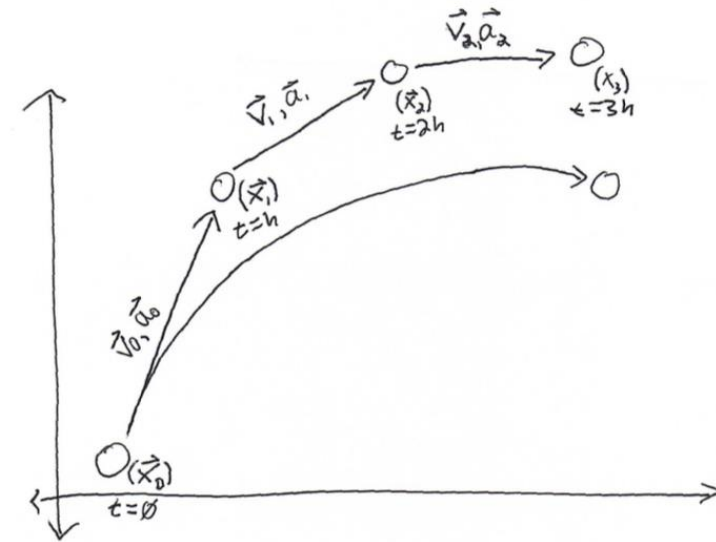
$$v(t + h) = v(t) + \frac{h}{2m}(F(t + h) + F(t)) + O(h^3)$$

# Velocity Verlet Integration Algorithm

## Implementation

1. Set initial parameters:  $x(t = 0), v(t = 0)$
2. Calculate  $x(t + h)$  as:  $x(t + h) = x(t) + hv(t) + \frac{h^2}{2} \frac{F(t)}{m} + O(h^3)$
3. Calculate  $F(t + h)$  as:  $F(t + h) = -U(x(t + h))$
4. Calculate  $v(t + h)$  as:  $v(t + h) = v(t) + \frac{h}{2m}(F(t + h) + F(t))$
5.  $t + h$  is now  $t$  return to **Step 2**

- Other integration methods also exist, such as leapfrog algorithm (2<sup>nd</sup> order), Runge-Kutta method (4<sup>th</sup> order)



The error of Euler algorithm accumulate fast. Velocity Verlet provide a much more accurate and an easy implementation of propagator.

# Initialization of AIMD

## Quasi-classical vs classical AIMD

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### ■ Initialize momentum ( $v_0$ )

**Classical:** randomly assign momentum to atoms base on Boltzmann distribution

$$P(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left[-\beta \frac{mv^2}{2}\right]$$

**Quasi-classical:** Assign momentum base on quantized vibrational mode and random vibration phases.

(High frequency mode has zero-point energy ( $0.5h\nu$ ), low frequency mode can be excited above  $v=0$ )

### ■ Initialize displacement (Progdyn as example)

**No displacement:** All trajectories start from the same point

**Flat displacement:** All possible displacements of a harmonic oscillator are equally likely

**Gaussian displacement:** Gaussian distribution of displacements, so that displacements in the middle are more likely.

### ■ Initialize Geometry ( $x_0$ )

**Uphill:** Initialize from minima

**Downhill:** Initialize from vicinity of TS. (Chemical reaction is a rare event)

# Caveats of quasi-classical AIMD

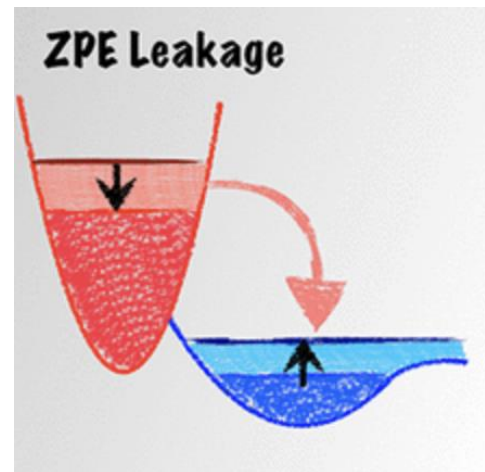
## Zero-point energy leakage (kinetic energy spilling problem)

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- Zero-point energy leakage (kinetic energy spilling problem)

Definition: Artificial transfer of kinetic energy between vibrational modes.

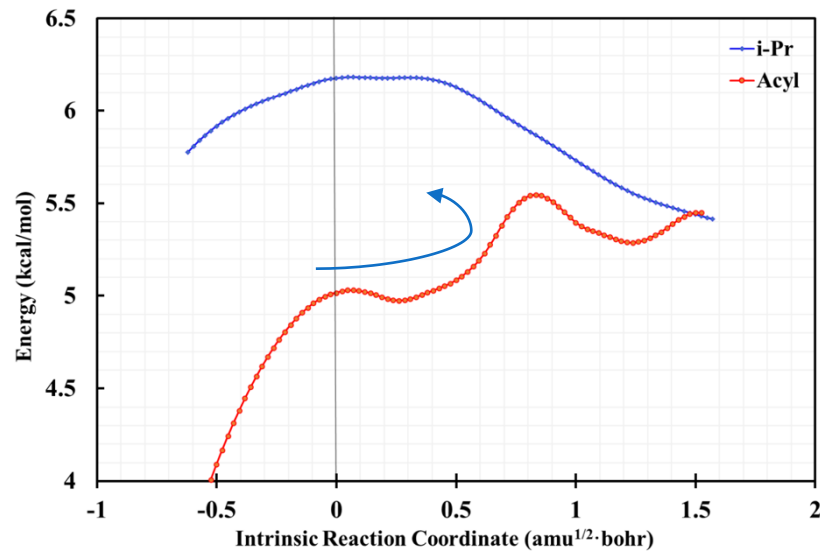
In quasi-classical MD, the momentum is initialized based on **quantum HO**, which does not allow energy transfer between vibrational modes. This causes the high frequency vibrational modes to have larger kinetic energy than classical HO due to ZPE. However, the propagation of a trajectory is classical, meaning that its ZPE energy can gradually transfer to lower frequency vibrational modes and causes unphysically hot low-lying vibrational states, especially for long trajectories.



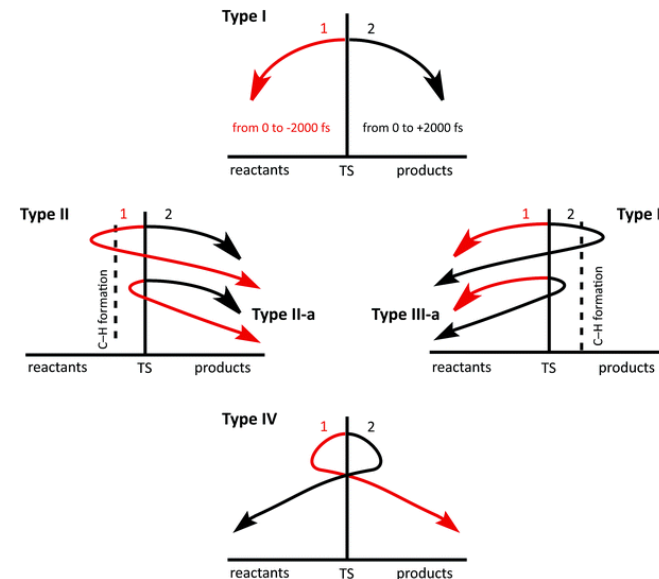
# Caveats of quasi-classical MD

## Minimizing Recrossing

- Recrossing trajectory is a trajectory that does not connect the reactant and the product. Usually it implies that you are not starting from the true free energy maxima.



Free energy plot

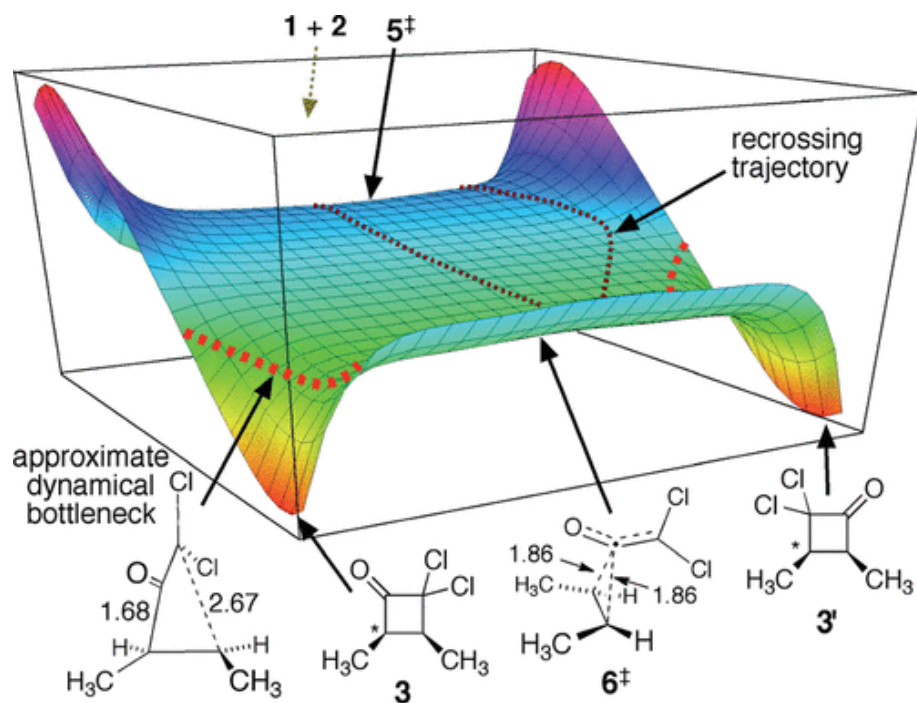


- Substantial amount of recrossing does not mean that the AIMD simulation is wrong. It may be an implication that we have a very flat surface around the TS.

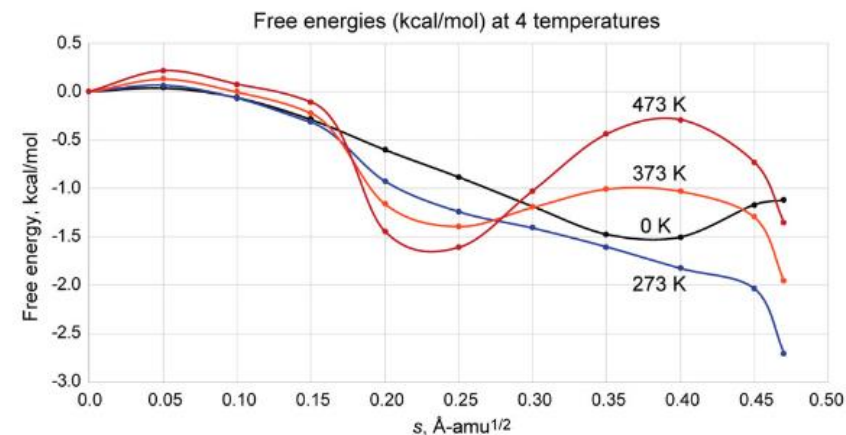
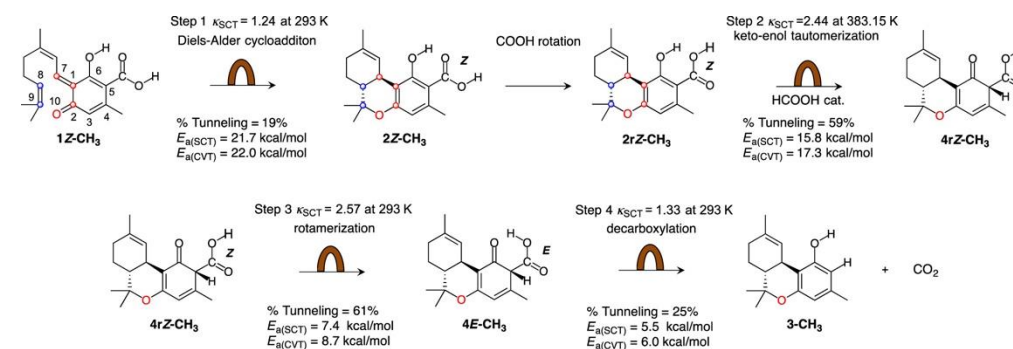
# Entropic/ZPE intermediate

## Dynamical Bottleneck

- Presence of entropic intermediate changes the bottleneck from the TS to the entropic barrier

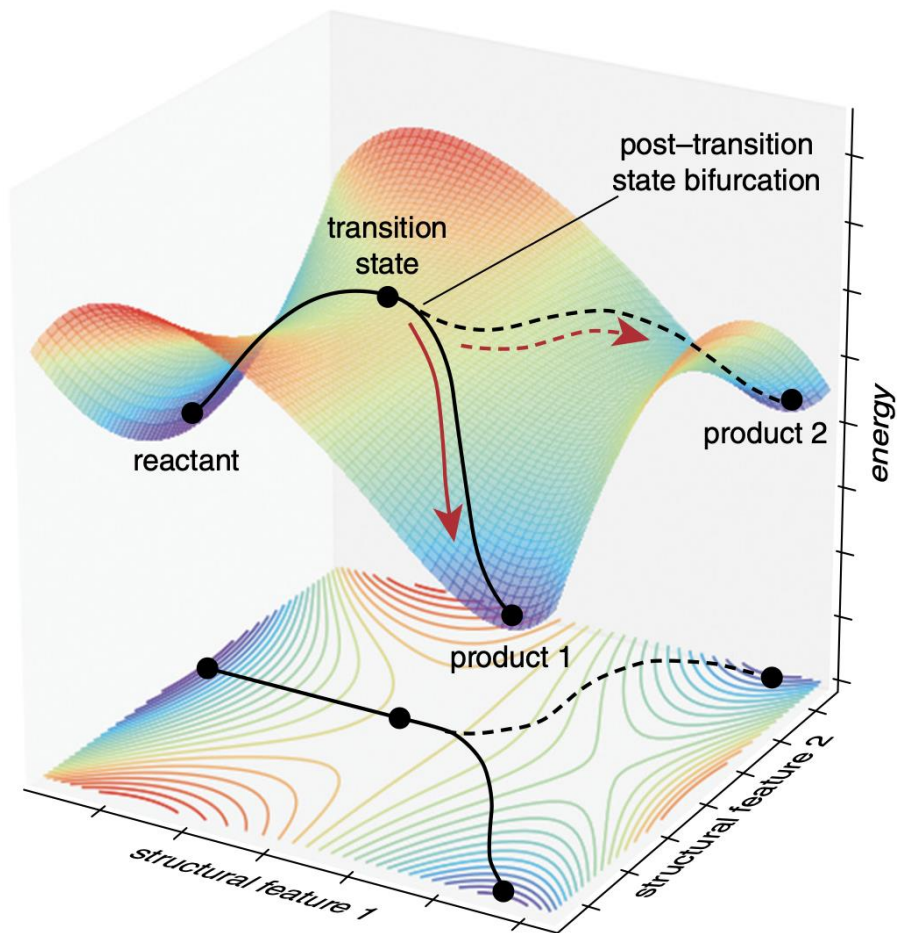


- Evidence of zero-point energy intermediate in keto-enol tautomerization



# Post-Transition State Bifurcation

A single TSS leads to multiple products without minima



- Bifurcation is a 2D dynamic effect that is not captured in 1D reaction coordinate.

- Valley-Ridge Inflection **point** (VRI)

Definition: A point that the lowest eigenvalue of a Hessian becomes 0 and the gradient vector is perpendicular to the corresponding vector

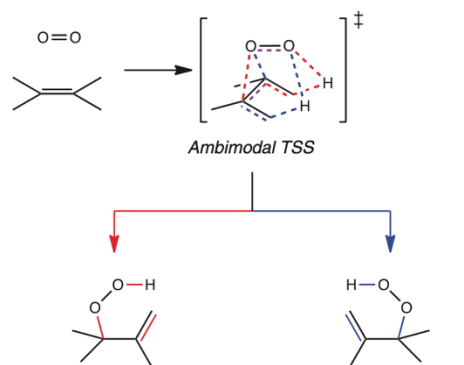
Roughly, it is where the trajectory decides which way to take

- Bifurcation ratio is influenced by the shape of the PES (gradient), and is very sensitive to the environment.

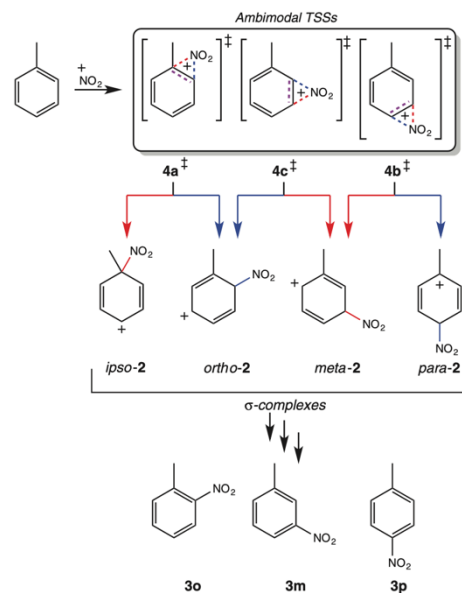
# Post-Transition State Bifurcation

## Examples

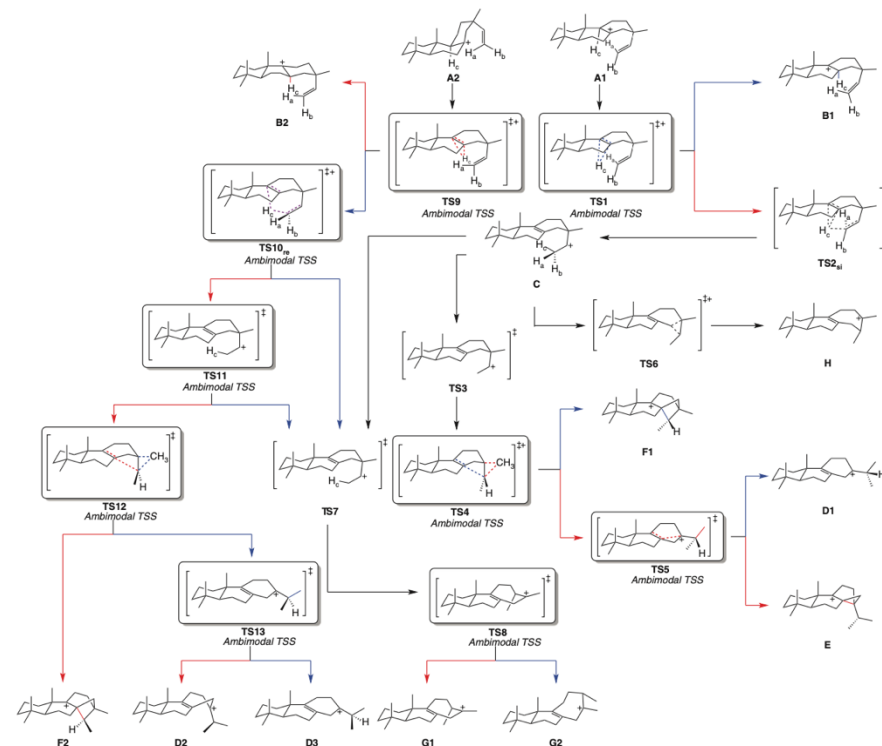
- Bifurcation arises when a proposed intermediate disappears on the PES, usually due to lack of some kind of stabilization (e.g, secondary carbocations).



Addition of singlet oxygen to ethylene



Nitration of Toluene

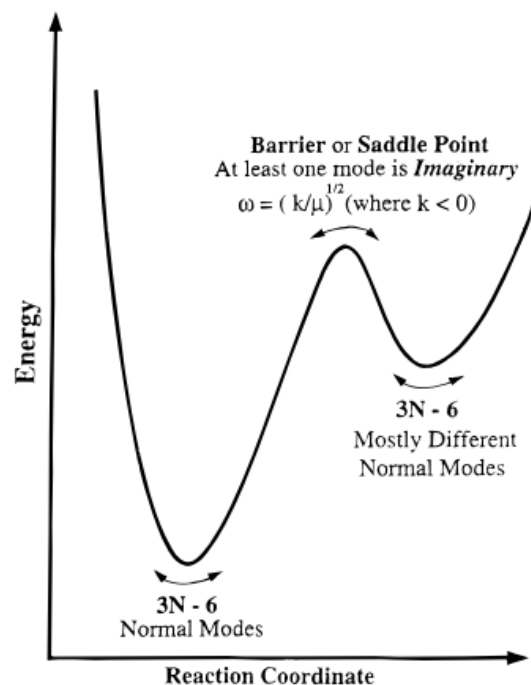


Carbocation rearrangement of Terpenes

# Dynamic Matching

## Intramolecular Vibrational Energy Redistribution (IVR)

- Under Harmonic Oscillator Approximation, the vibrational modes are orthogonal and not coupled. But when bonds break/form, it breaks down.
- The energy will flow from one mode to another through anharmonic coupling between modes and the excess energy will spread out to all degrees of freedom. The excess energy decays exponentially.

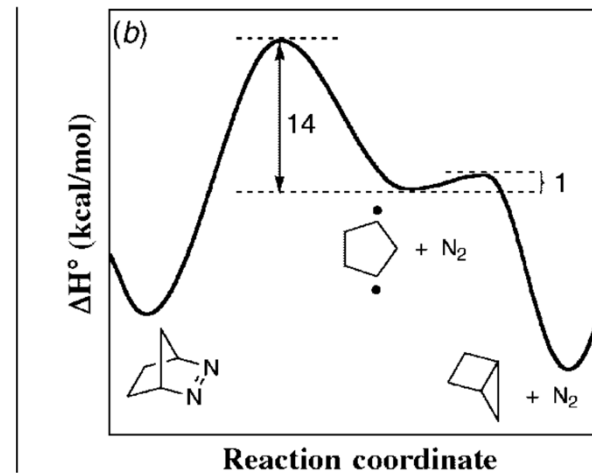
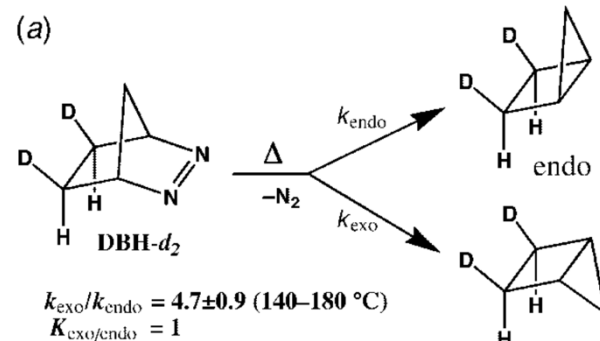
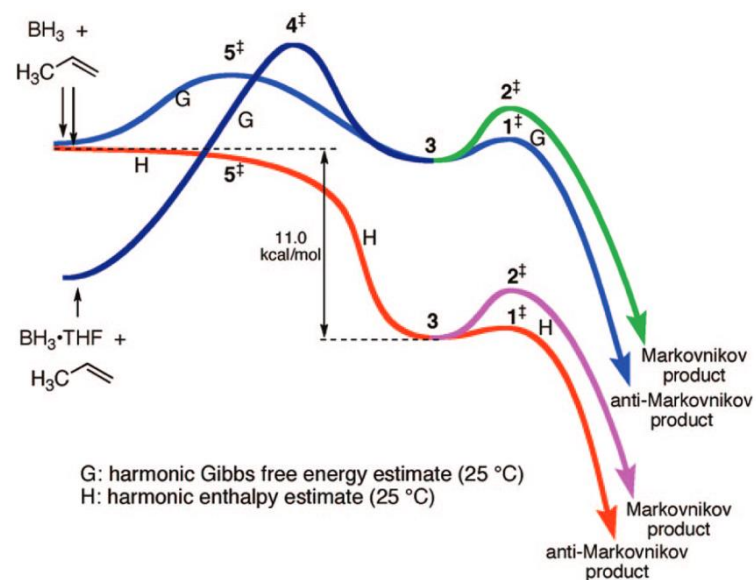


- TST assumes that IVR is much faster than the rate of passing through the TS
- The rate of IVR is effectively around  $10^{-12} \text{ s}^{-1}$ , meaning that in 1 ps, half of the vibrational states are statistically distributed.
- However, if we have a very shallow intermediate followed by a very exergonic process, there is no time for IVR to be complete before the next reaction event occur – **Dynamic Matching**

# Dynamic Matching

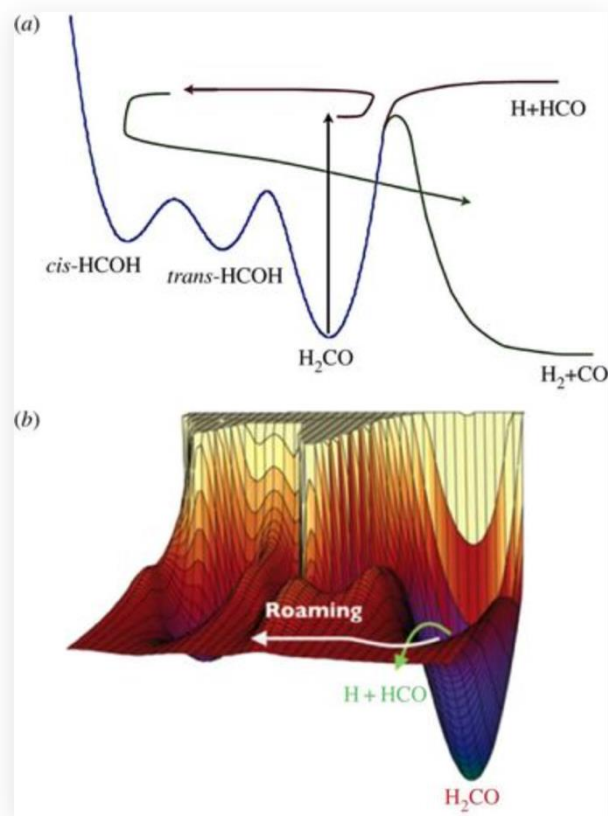
## Examples

- When dynamic matching occurs, the reaction keeps the memory of the previous step. The excess momentum steers the reaction outcome.

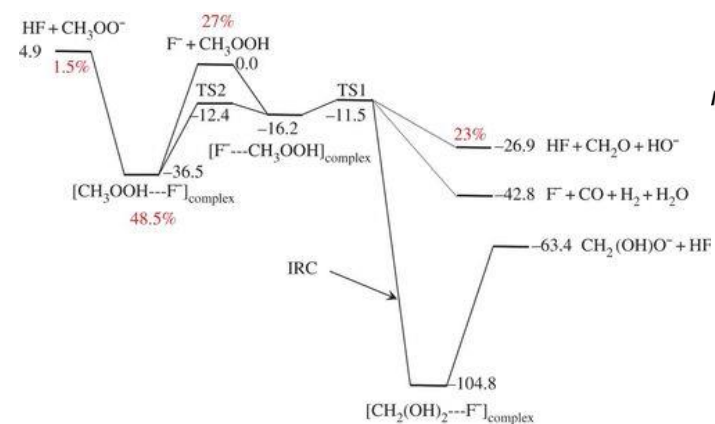
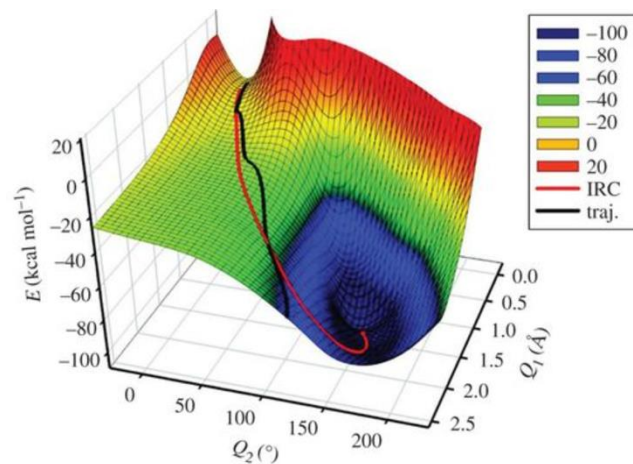


# Other dynamic effects

## Roaming Dynamics



## Avoiding Minima



## Caldera PES Dynamics

