Chimica Computazionale

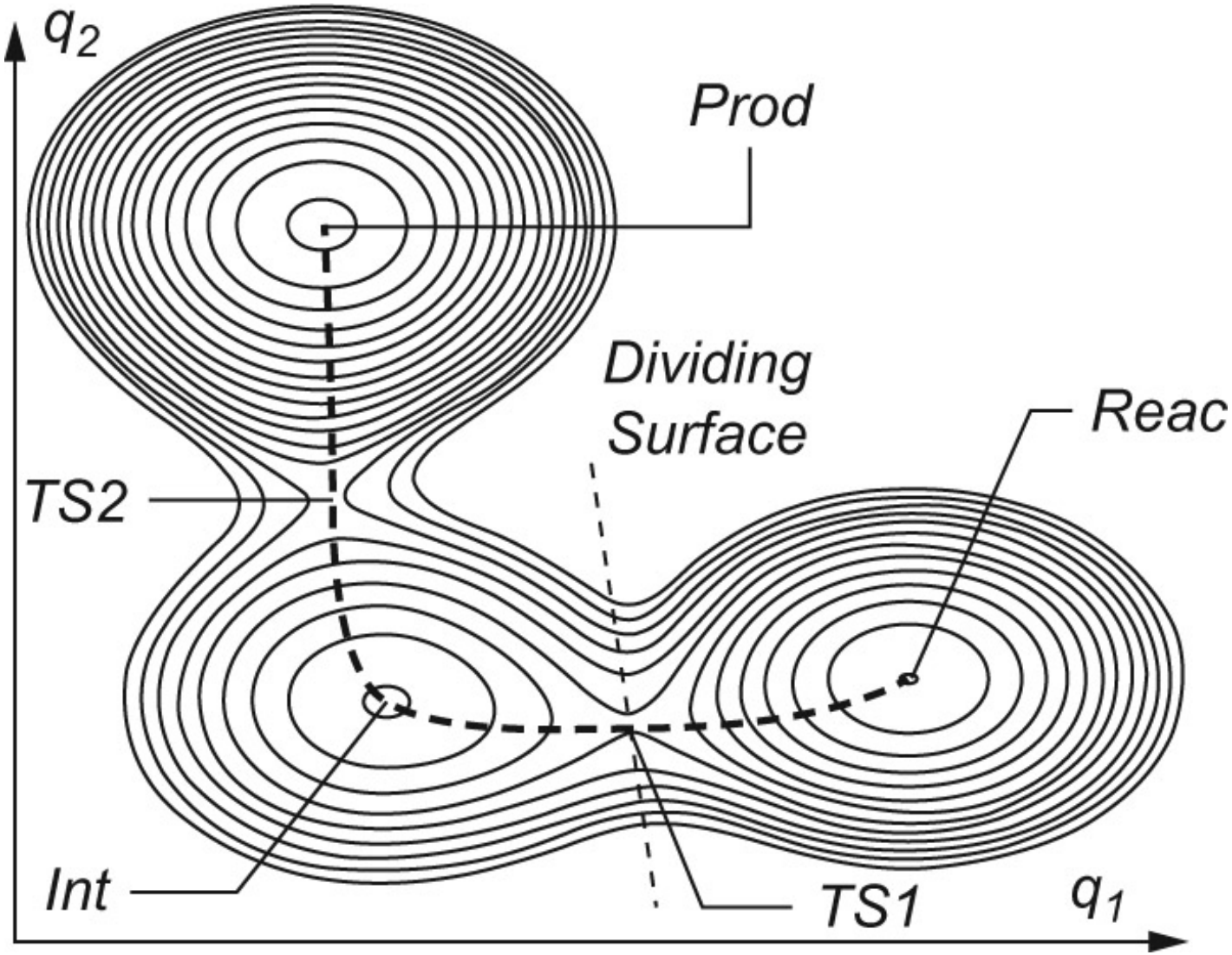
Geometry optimization and reaction profile

Emanuele Coccia

PhotoInduced Quantum Dynamics (PIQD) Group

Characterizing a PES

Stationary points in a PES



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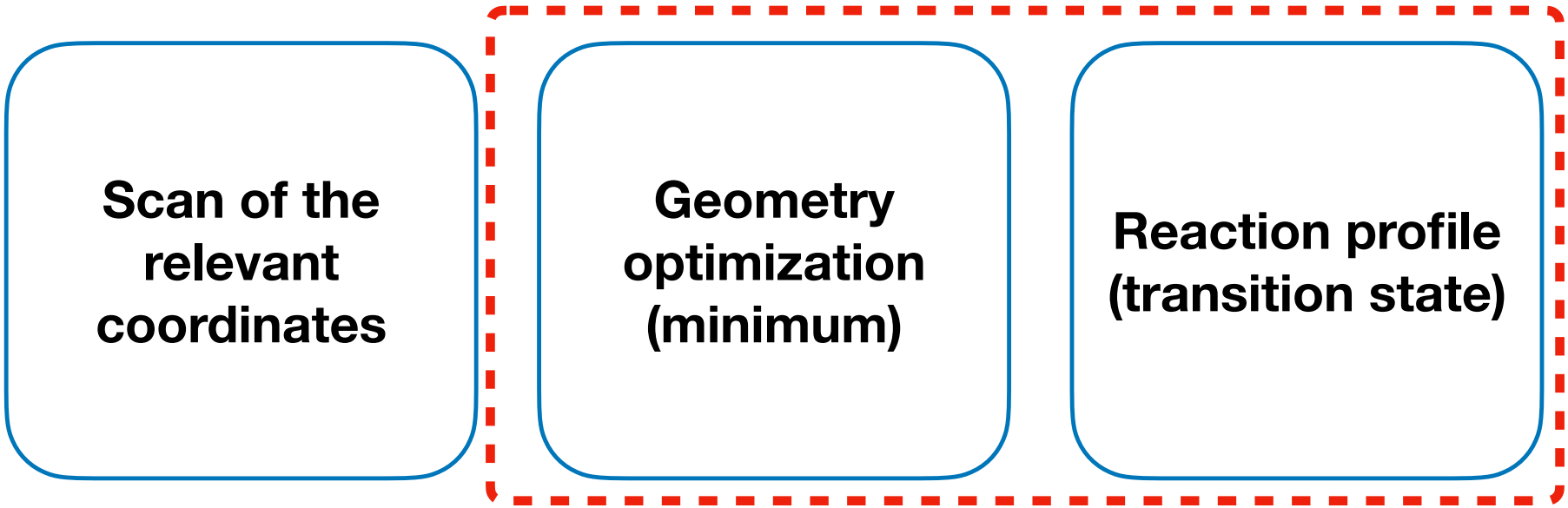
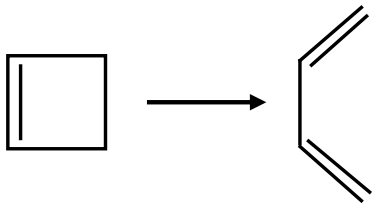


Computing a PES

- Unimolecular reactions



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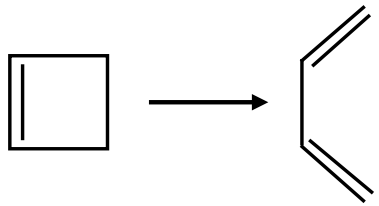
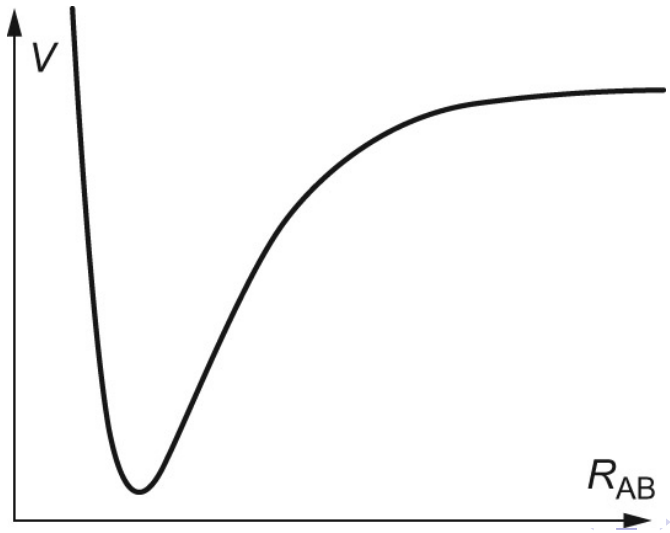


- Bimolecular reactions (atom- or radical-recombination process)

$$\mathrm{H} + \mathrm{F} \rightarrow \mathrm{HF}$$

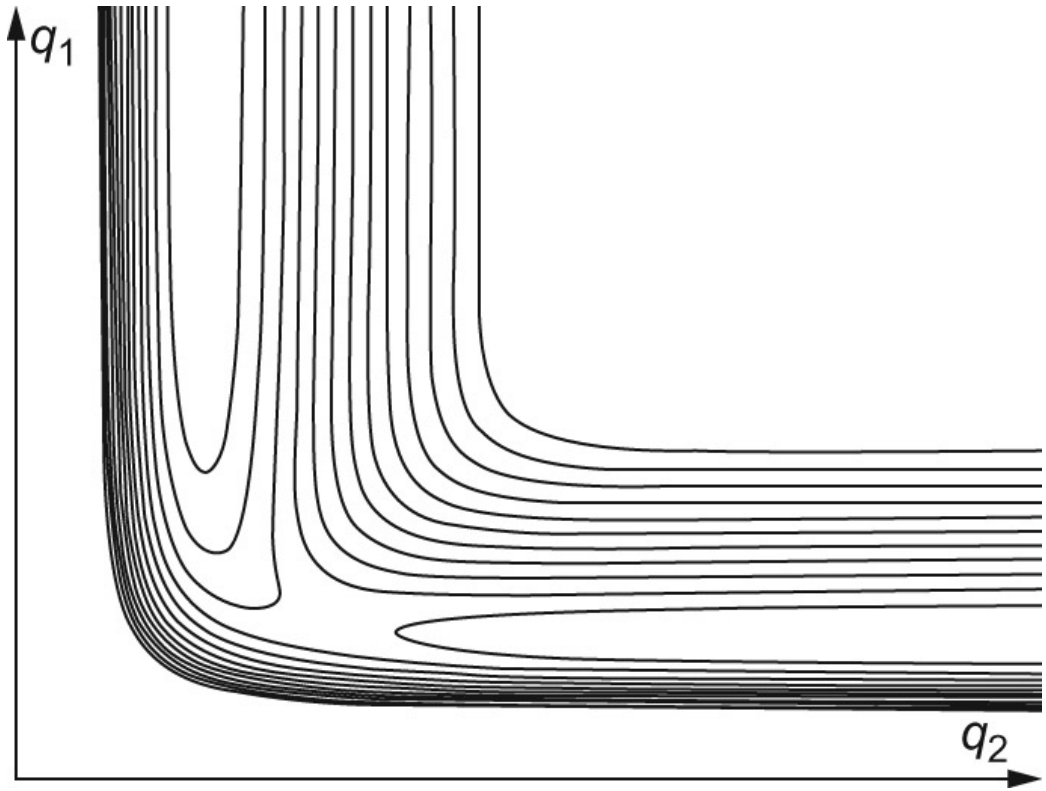
$$\mathrm{CH_3} + \mathrm{OH} \rightarrow \mathrm{CH_3OH}$$



Computing a PES

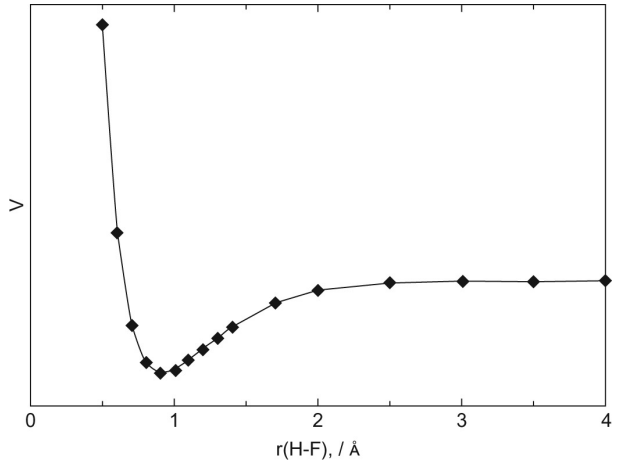
- Bimolecular reactions (bond breaking)

$$CH_4 + OH \rightarrow H_2O + CH_3$$
$$CH_2 = CH_2 + CH_2 \rightarrow CH_2 = CH - CH = CH_2 \rightarrow \text{cyclohexene}$$



Computing the PES

- Scan on the coordinate for small molecules:
  - HF molecule: 13 structures from 0.5 to 4 Å)



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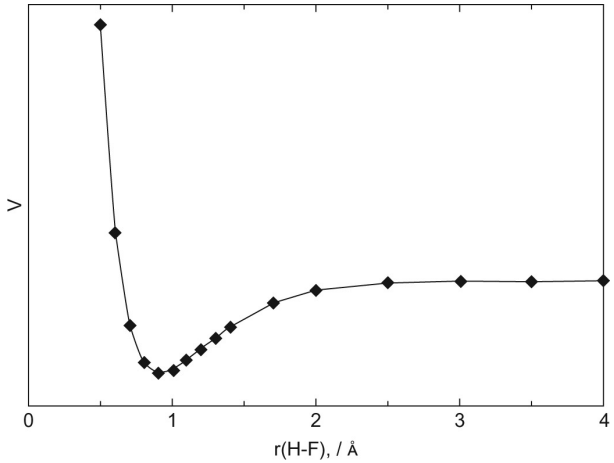
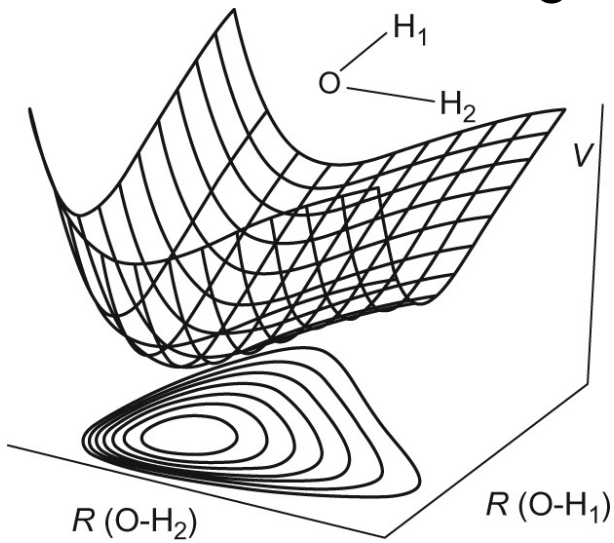


  - H_2O: 11x11 = 121 structures at frozen angle



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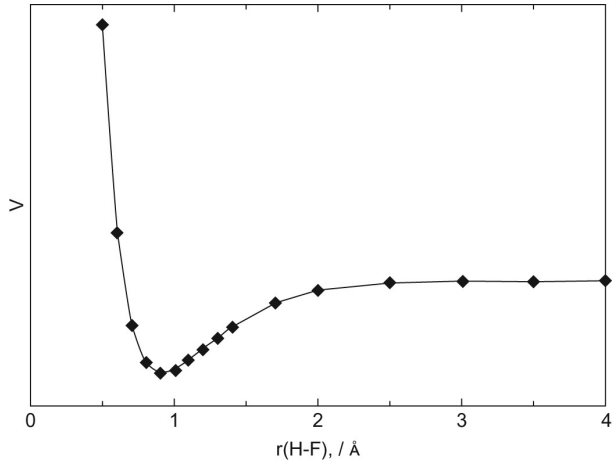

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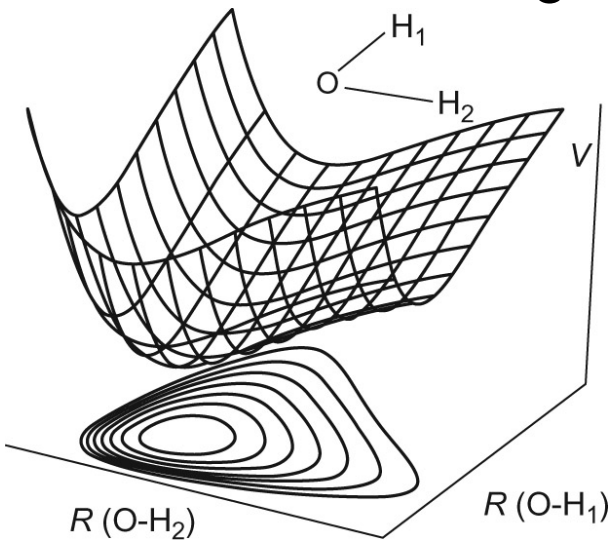
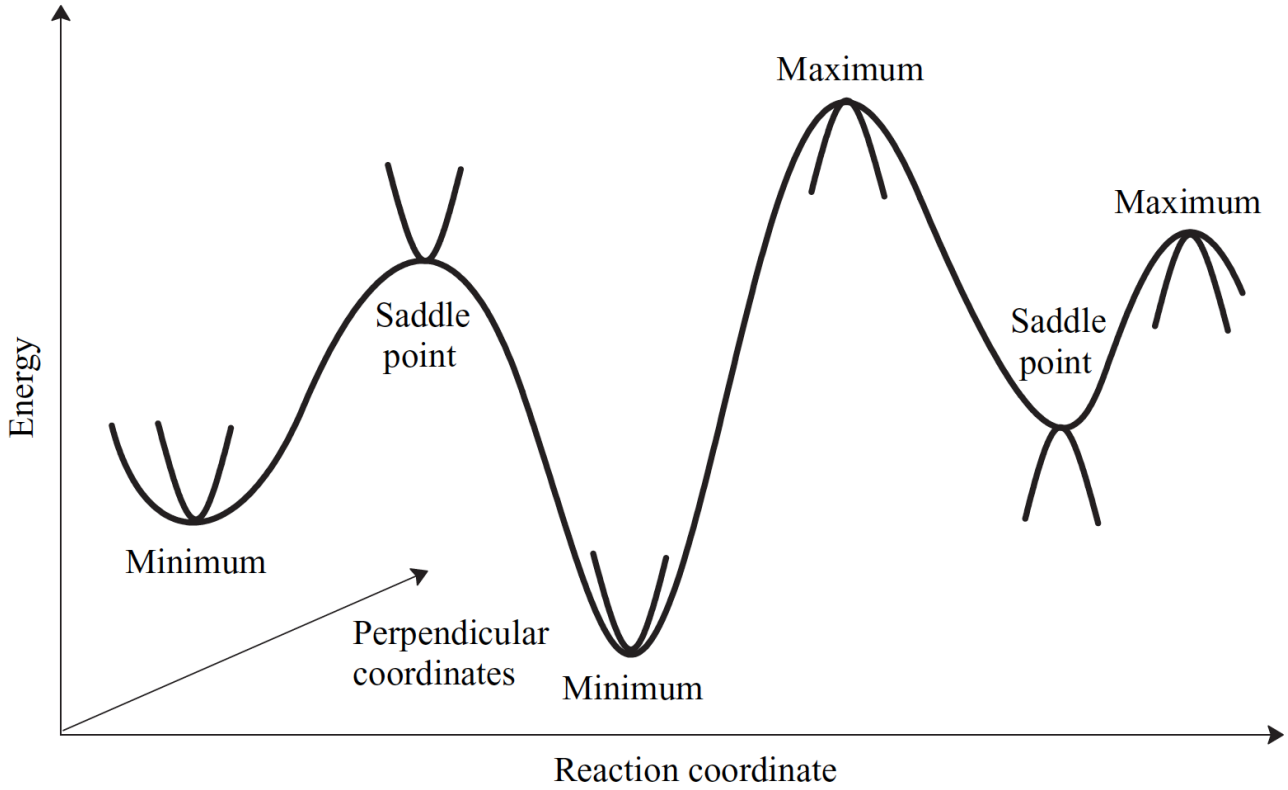


- Impractical approach for large molecules (10^n points!)

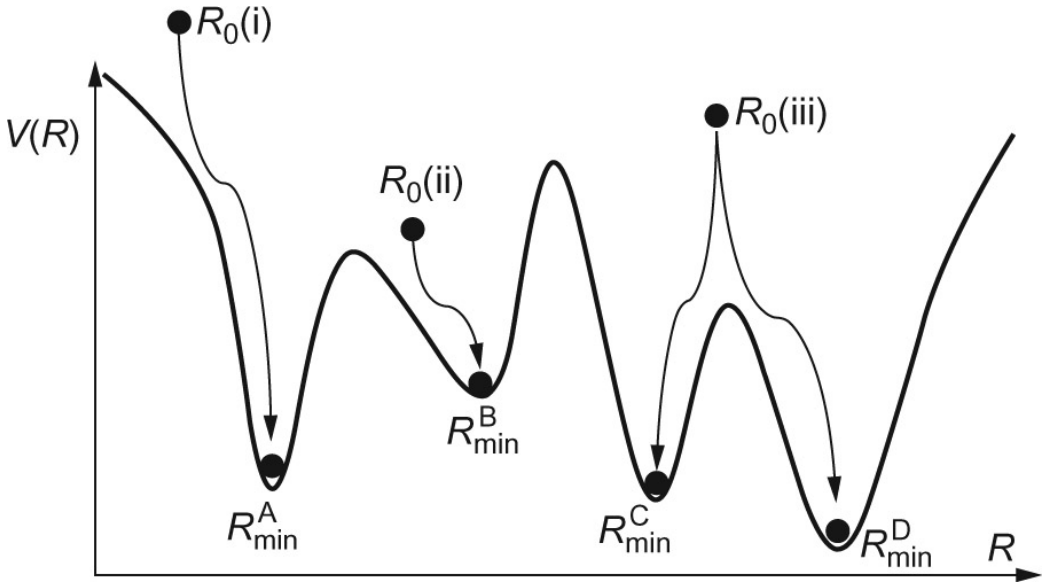
Optimization problem

- Goal: find stationary points of a PES
- Stationary points = first derivative is zero
- Minimum = second derivatives are positive
- Saddle point = second derivative negative along one direction



Optimization problem

- Global and local minima



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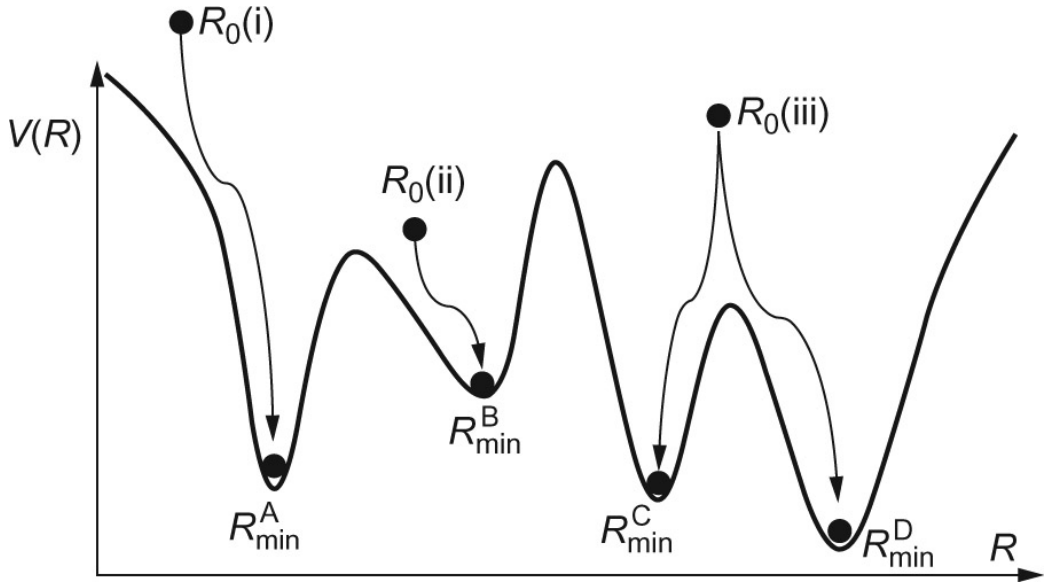
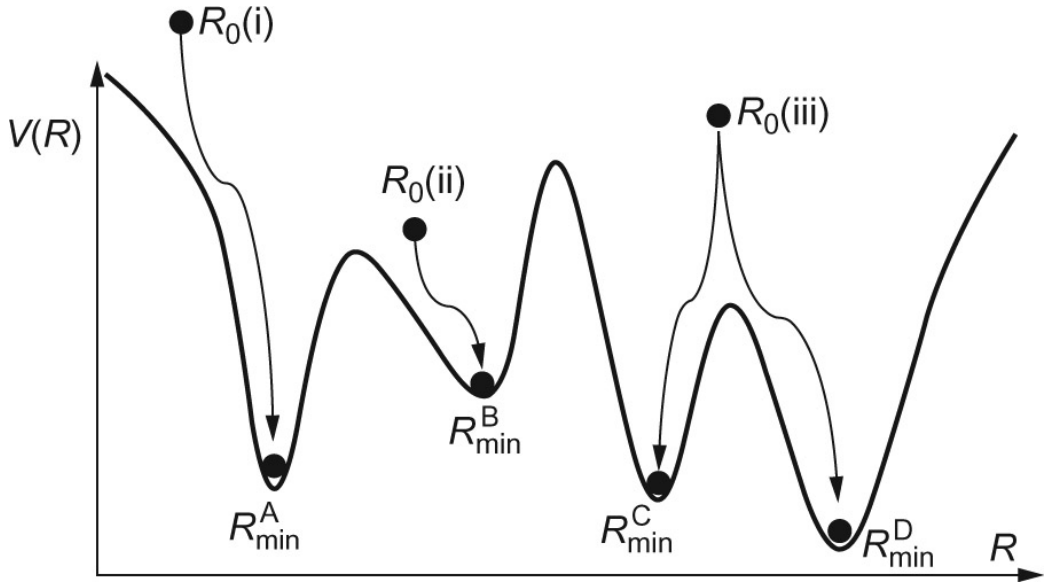


- Energy as a function of nuclear coordinates:
  - Minima
  - Transition-state structures (saddle points)

Optimization problem

- Global and local minima



- Energy as a function of nuclear coordinates:
  - Minima
  - Transition-state structures (saddle points)
- Energy as a function of variational wavefunction parameters:
  - Molecular orbital coefficients
  - Slater determinant coefficients
  - Basis function exponents

Minimum search

Finding a minimum

- Goal: determine the nearest stationary point
- Many local minima

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- Many local minima
- At least, the first derivative of the energy $E(\mathbf{q}_1, \mathbf{q}_2, ...)$ with respect to all variables is needed (gradient $\mathbf{g}$)

$$\mathbf{g} = \nabla E = \left(\frac{\partial E}{\partial \mathbf{q}_1}; \frac{\partial E}{\partial \mathbf{q}_2}; ... \right)$$

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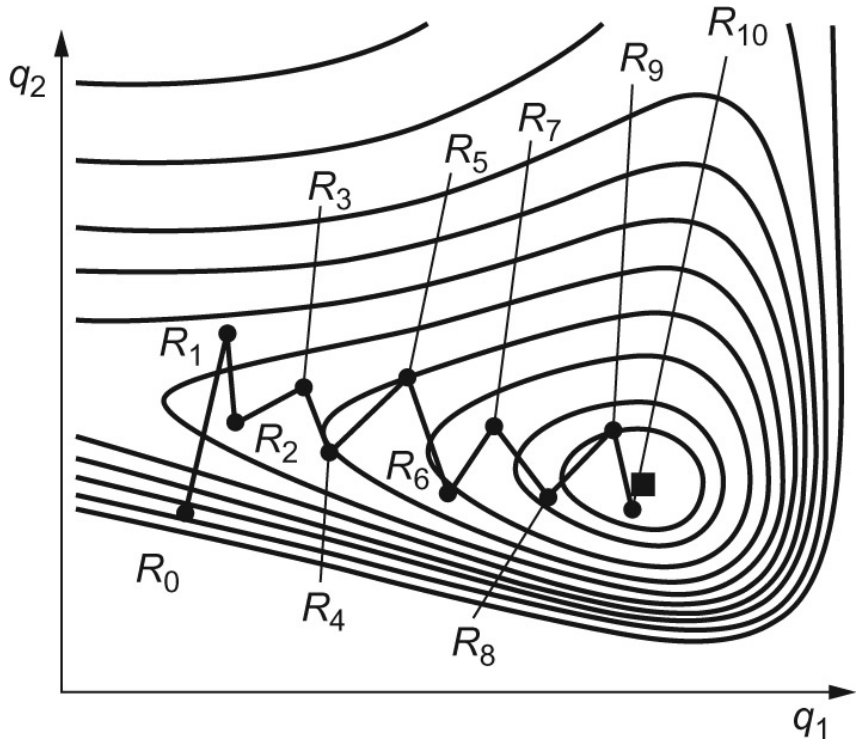
- Convergence achieved:
  - $\mathbf{g}$ reduced below a threshold
  - $\Delta E = E(\mathbf{q}_1^{i+1}, \mathbf{q}_2^{i+1}, ...) - E(\mathbf{q}_1^{i}, \mathbf{q}_2^{i}, ...) < \epsilon$

Steepest descent method

- Exploring the configurational space along a direction $\mathbf{d}$

$$\mathbf{d} = -\mathbf{g}$$

- Finding a minimum is guaranteed
- Simple algorithm



- Slow convergence
- Hard to converge for narrow valleys

Newton-Raphson method

- Second-order expansion of E around the current point $\mathbf{q}^0$
- $\mathbf{q}^0 = \mathbf{q}^0_1, \mathbf{q}^0_2, \mathbf{q}^0_3 \ldots$
  $\mathbf{q} = \mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3 \ldots$

$$E(\mathbf{q}) \sim E(\mathbf{q}^0) + \mathbf{g}^T(\mathbf{q} - \mathbf{q}^0) + \frac{1}{2}(\mathbf{q} - \mathbf{q}^0)^T\mathbf{H}(\mathbf{q} - \mathbf{q}^0)$$

$$\mathbf{H}_{ij} = \frac{\partial^2 E}{\partial \mathbf{q}_i \partial \mathbf{q}_j}$$

- $\mathbf{g} = 0$ if

$$(\mathbf{q} - \mathbf{q}^0) = -\mathbf{H}^{-1}\mathbf{g}$$

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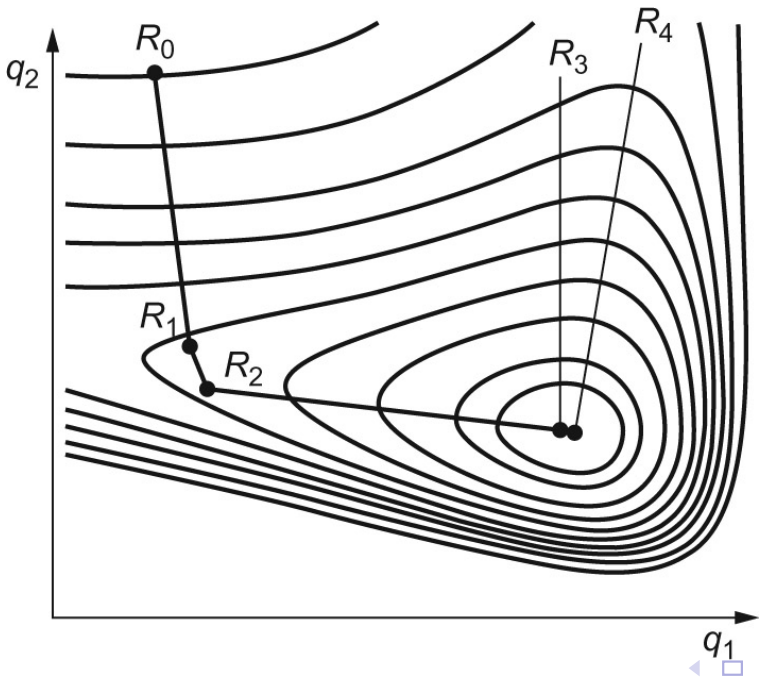
- Method converges to a stationary point (minimum or saddle point)
- Computing the Hessian demanding or impossible
- Storage issue

Computing the Hessian

- One order of magnitude more demanding than the gradient
- Approximation for computing the Hessian:
  1. Initial guess
  2. First step: steepest descent
  3. Iterative estimation of the Hessian

$$\mathbf{H}_n = \mathbf{H}_{n-1} + \Delta\mathbf{H}$$

$$\Delta\mathbf{H} = \frac{\Delta\mathbf{g}\Delta\mathbf{g}^T}{\Delta\mathbf{g}^T\Delta\mathbf{q}} - \frac{\mathbf{H}\Delta\mathbf{q}\Delta\mathbf{q}^T\mathbf{H}}{\Delta\mathbf{q}^T\mathbf{H}\Delta\mathbf{q}}$$



Geometry optimization with quantum chemistry

- Methods applied to any level of theory (focus here on quantum chemistry)

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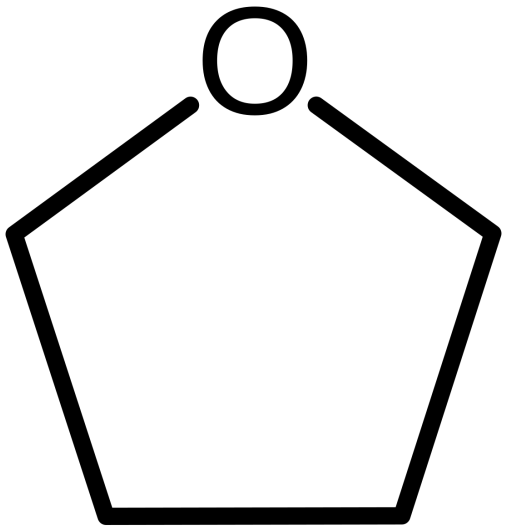
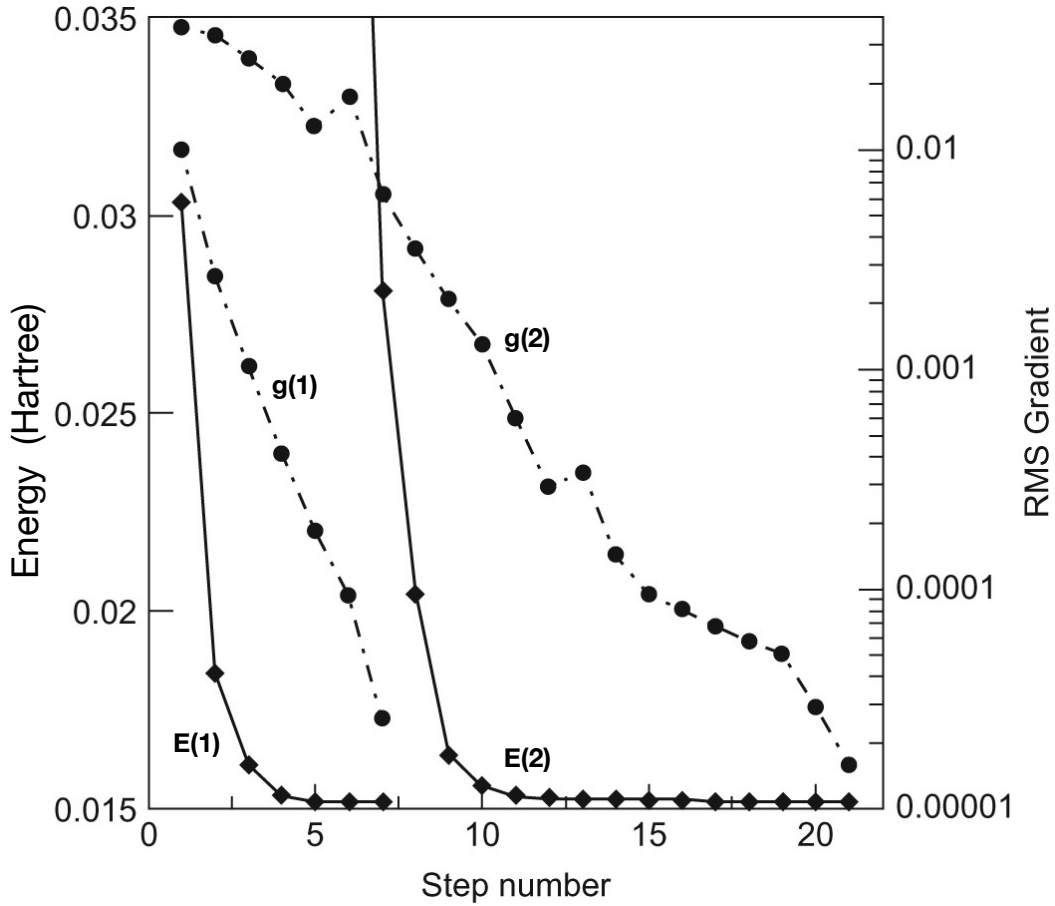
Geometry optimization with quantum chemistry

- Methods applied to any level of theory (focus here on quantum chemistry)
- Approximated Hessian for molecules up to few hundred atoms
- Convergence improved with choice of the set of coordinates **q**:
  - Cartesian coordinates: simple algorithms, possible slow convergence
  - Internal coordinates: bond lengths and angles..., "natural" set, redundant

Geometry optimization: examples

- Tetrahydrofuran (THF): 39 Cartesian and 71 internal coordinates
- Optimization with Hartree-Fock and 6-31G basis set
  - First method (1): initial structure optimized with MM
  - Second method (2): "random" initial structure





Geometry optimization: examples

H_2O ground-state geometry

- HF

L_{max}	Basis	R_{OH} (Å)	θ_{HOH} (°)
1			
2	cc-pVDZ	0.9463	104.61
3	cc-pVTZ	0.9406	106.00
4	cc-pVQZ	0.9396	106.22
5	cc-pV5Z	0.9396	106.33
6	cc-pV6Z	0.9396	106.33

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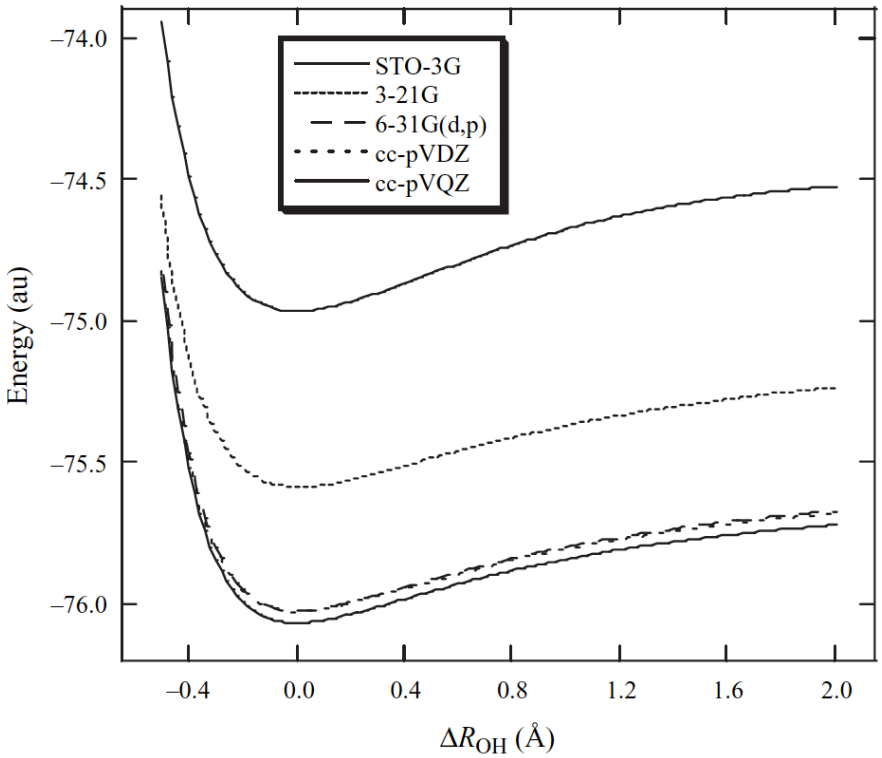
- DFT

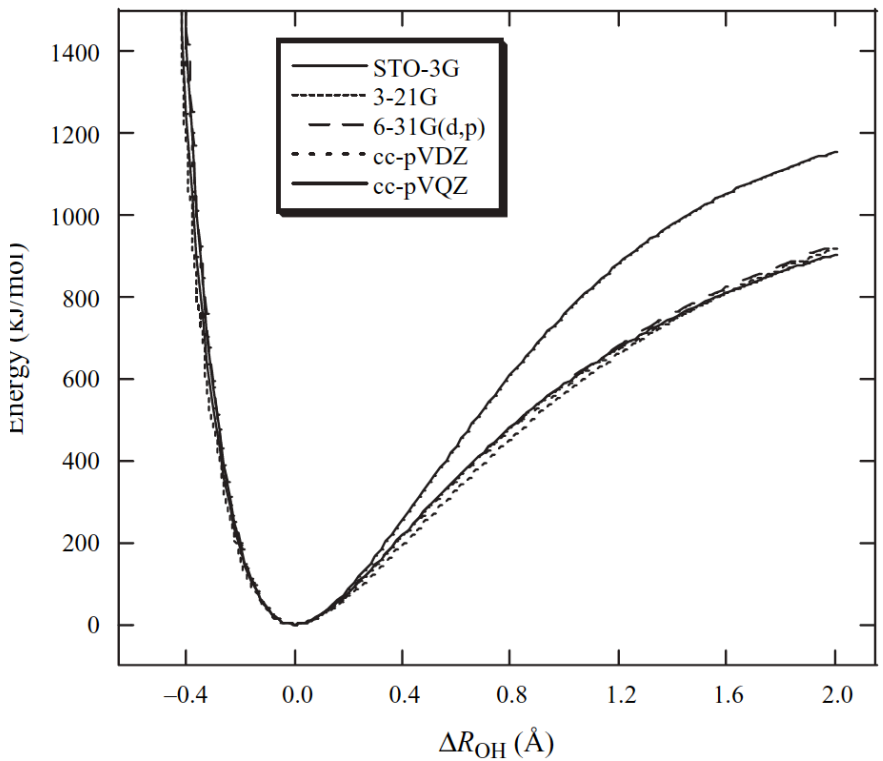
Basis	LSDA	BLYP	PBE	HCTH	B3LYP	PBE0
pc-0	0.9878	0.9962	0.9936	0.9854	0.9841	0.9806
pc-1	0.9764	0.9791	0.9763	0.9656	0.9683	0.9645
pc-2	0.9696	0.9706	0.9689	0.9589	0.9604	0.9574
pc-3	0.9700	0.9704	0.9689	0.9589	0.9604	0.9576
pc-4	0.9700	0.9704	0.9689	0.9590	0.9604	0.9576

Basis	LSDA	BLYP	PBE	HCTH	B3LYP	PBE0
pc-0	111.82	109.27	109.40	109.43	110.72	110.93
pc-1	104.15	103.24	103.09	103.22	104.06	103.99
pc-2	105.10	104.56	104.27	104.52	105.19	104.98
pc-3	104.98	104.52	104.21	104.44	105.13	104.90
pc-4	104.98	104.52	104.21	104.42	105.13	104.90

Geometry optimization: examples

H_2O dissociation energy at HF level





Transiton state search

Transition-state theory

- Born-Oppenheimer approximation: chemical reaction as nuclei moving on a PES

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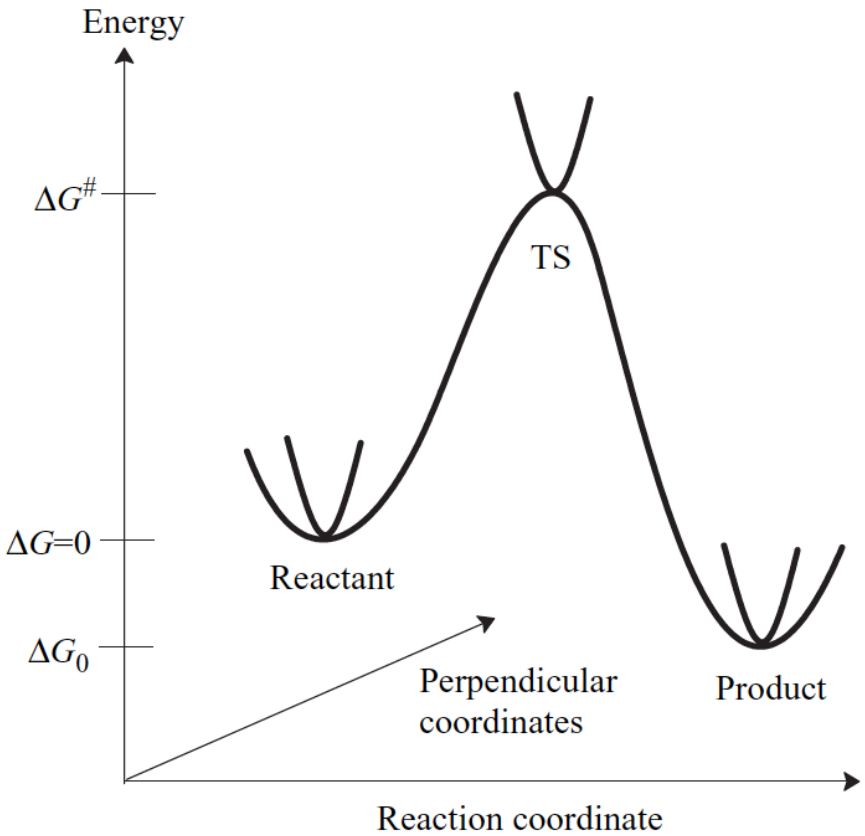
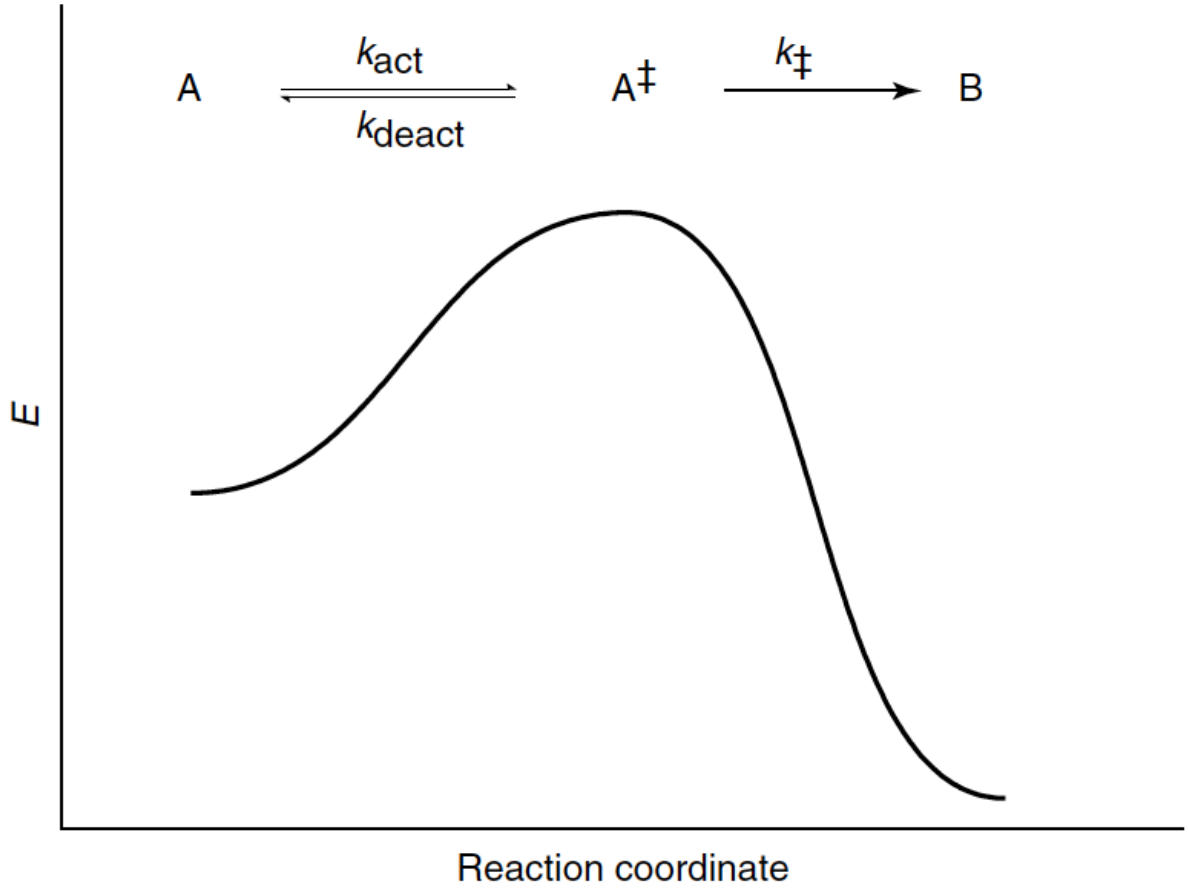
- From reactant to products: path with lowest energy, minimum energy path (MEP)
- The highest point in energy is the transition state



Transition-state theory

- Unimolecular reaction A $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ B



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- Semi-classical theory:
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  - Quantization of vibrational and rotational degrees of freedom

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- Production B rate

$$\begin{aligned} k_1 &= \frac{k_B T}{h} e^{-\Delta G_\ddagger / k_B T} \\ \Delta G_\ddagger &= G_\ddagger - G_A \end{aligned}$$

- $\Delta G_\ddagger$: activation free energy

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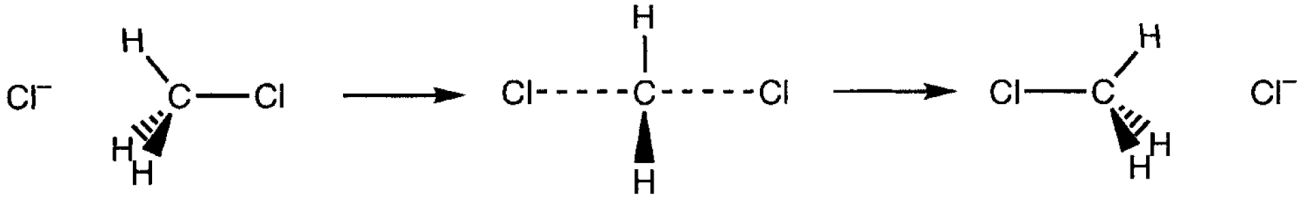
- No re-crossing assumed in the model
- Single PES, i.e. thermal reaction

Finding transition-state structures



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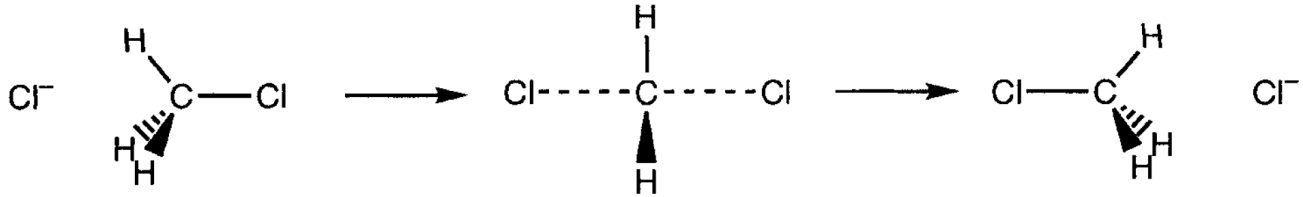

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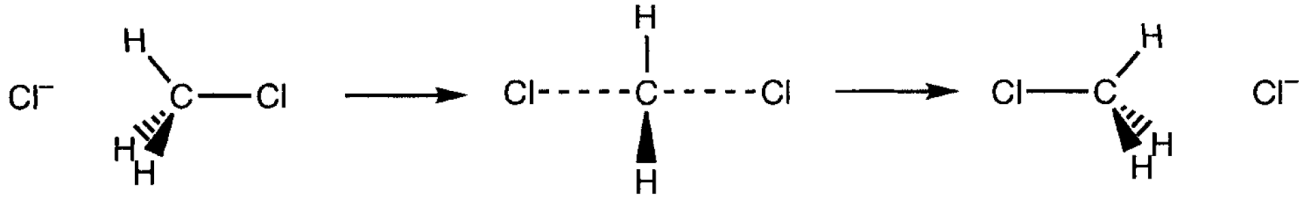


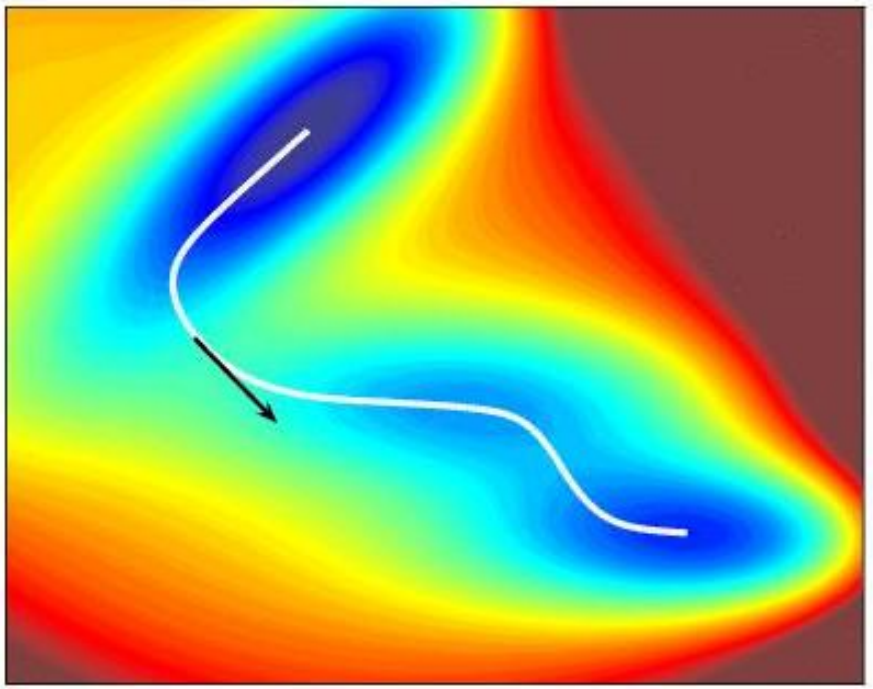
- Two main approaches for locating transition-state (TS) structures:
  - Interpolation methods
  - Local methods
- Interpolation: TS located in between two end-points (minima)
- Local: propagating from an optimized geometry, gradient and (possibly) Hessian known

Computing energy barriers

Minimum energy path

- Path lying on the PES between the reactants (R) and products (P), offering least resistance to the atomic motion
- Going through the saddle point, i.e. the TS
- From the TS, MEP is the union of steepest descent paths to the minima
- MEP is a smooth curve ϕ satisfying

$$(\nabla E)^{\perp}(\phi) = 0$$



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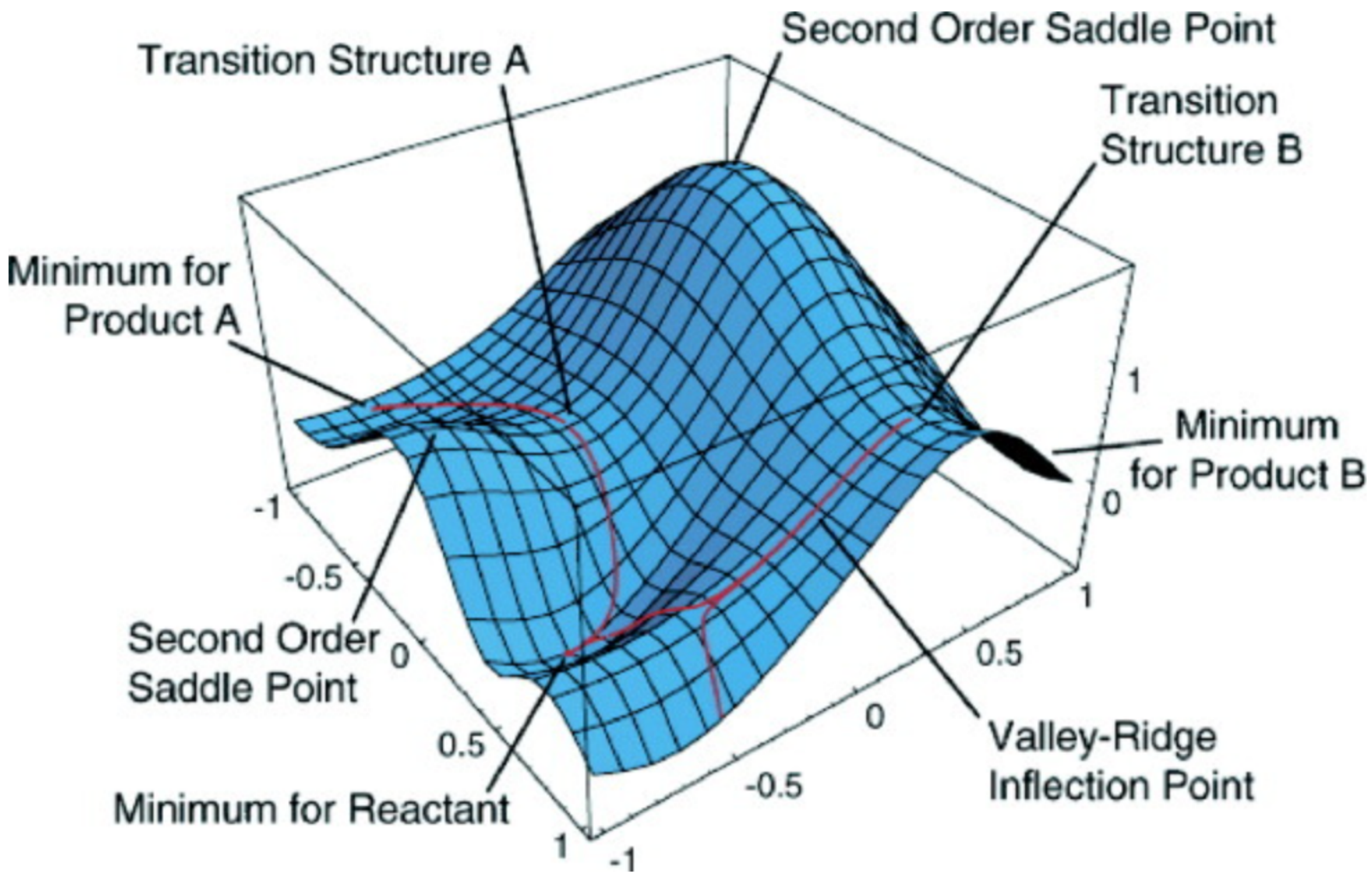
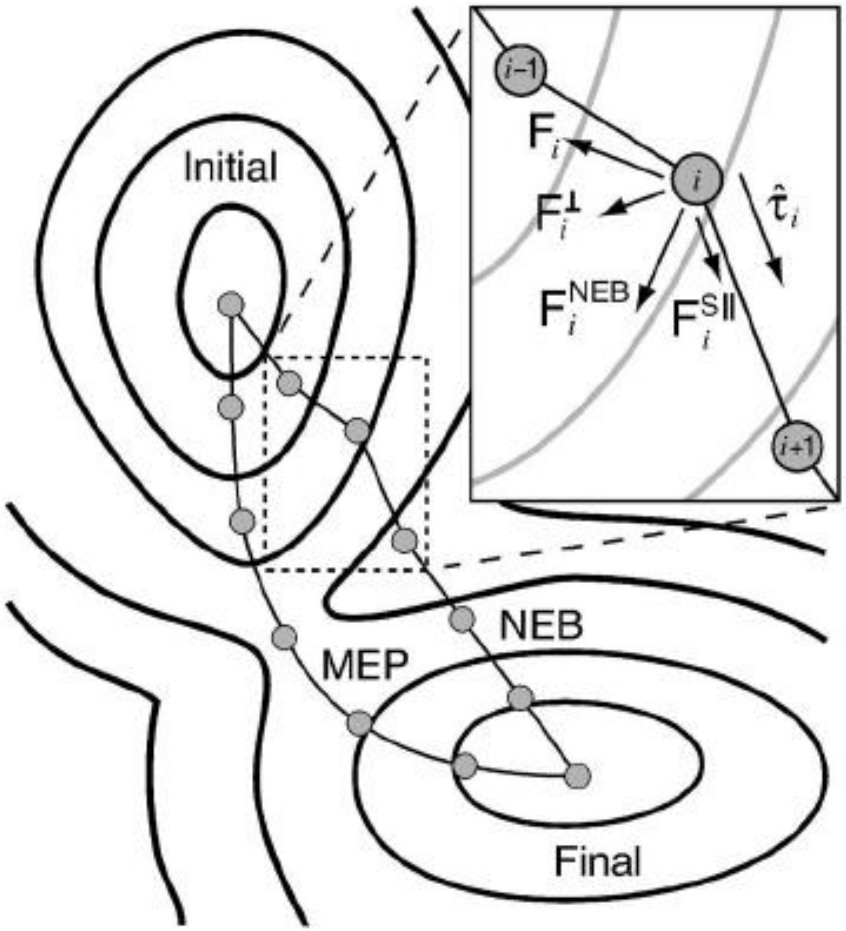


Nudged elastic band (NEB) method

- Chain method: a string of replicas (images) of the system between R and P is created
- Images are connected with springs
- Optimization algorithm is applied to relax the images down towards the MEP
- Interpolation between images to get TS

NEB method

(Numerical) NEB convergence to the MEP

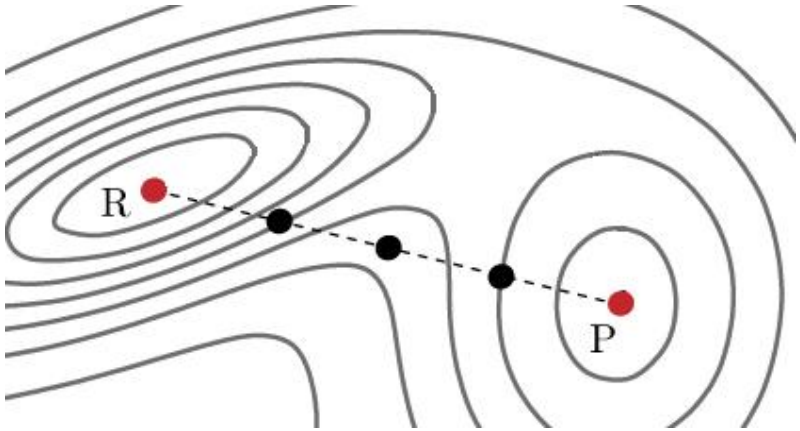


NEB method: initialization

- Reactant $\vec{R}$ and product $\vec{P}$ structures known
- Possible guess of intermediates and/or TS (not needed)

$$\begin{aligned} \text{path} &= \left[\vec{R}_0, \vec{R}_1, \vec{R}_2, ..., \vec{R}_N\right] \\ \vec{R}_0 &= \vec{R} \\ \vec{R}_N &= \vec{P} \end{aligned}$$

- Linear interpolation for initial chain

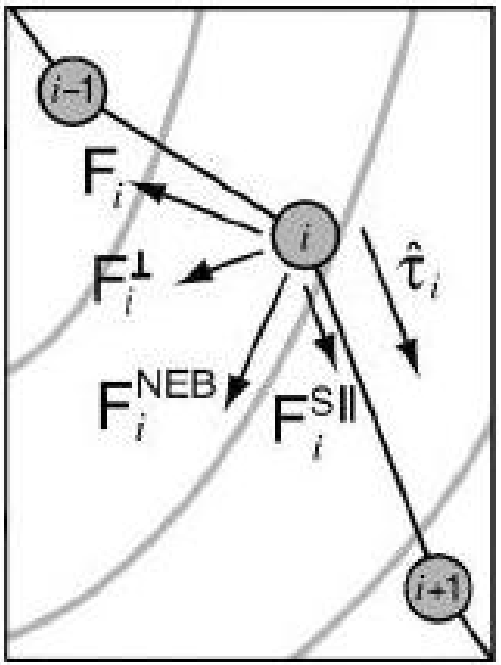


NEB method: forces

- Intermediate images $[..., \vec{R}_{i-1}, \vec{R}_i, \vec{R}_{i+1}, ...]$ with a NEB force

$$\vec{F}_i^{NEB} = \vec{F}_i^{\perp} + \vec{F}_i^{S\parallel}$$

- Parallel spring force ($\vec{F}_i^{S\parallel}$)
- Perpendicular component of the true force ($\vec{F}_i^{\perp}$)



NEB method: forces

- Perpendicular force $\vec{F}_i^{\perp}$

$$\vec{F}_i^{\perp} = -\nabla V(\vec{R}_i)|_{\perp} = -\nabla V(\vec{R}_i) + \nabla V(\vec{R}_i) \cdot \hat{\vec{\tau}}_i \hat{\vec{\tau}}_i$$

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- Spring force $\vec{F}_i^{S\parallel}$

$$\vec{F}_i^{S\parallel} = k \left(|\vec{R}_{i+1} - \vec{R}_i| - |\vec{R}_i - \vec{R}_{i-1}| \right) \hat{\vec{\tau}}_i$$

- k is a parameter given by input

Climbing-image NEB method

- After a few iterations, the spring force is not applied to the highest energy image /

Climbing-image NEB method

- After a few iterations, the spring force is not applied to the highest energy image I
- Climbs to the saddle point via a reflection of the true force

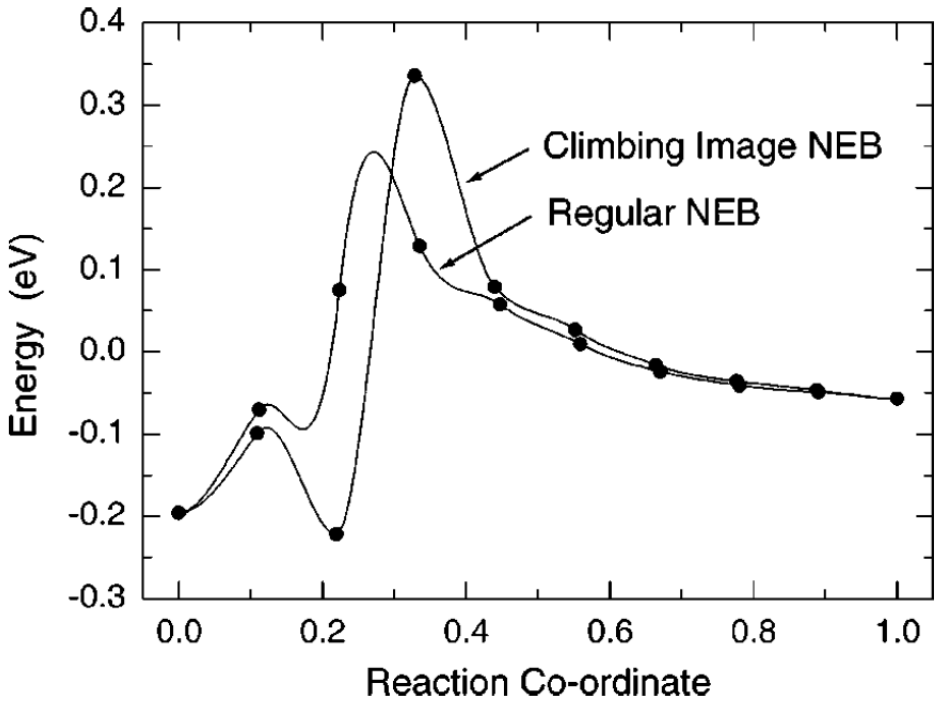
$$\vec{F}_I^{CI} = \vec{F}_I - 2\vec{F}_I \cdot \hat{\vec{\tau}}_I \hat{\vec{\tau}}_I$$

Climbing-image NEB method

- After a few iterations, the spring force is not applied to the highest energy image *I*
- Climbs to the saddle point via a reflection of the true force

$$\vec{F}_I^{CI} = \vec{F}_I - 2\vec{F}_I \cdot \hat{\vec{\tau}}_I \hat{\vec{\tau}}_I$$

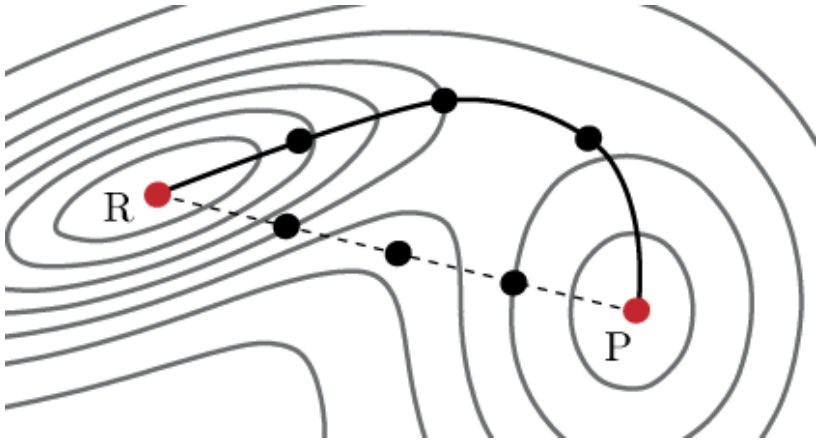
- $\hat{\vec{\tau}}_I$ is the tangent vector to the path, referred to the image *I*



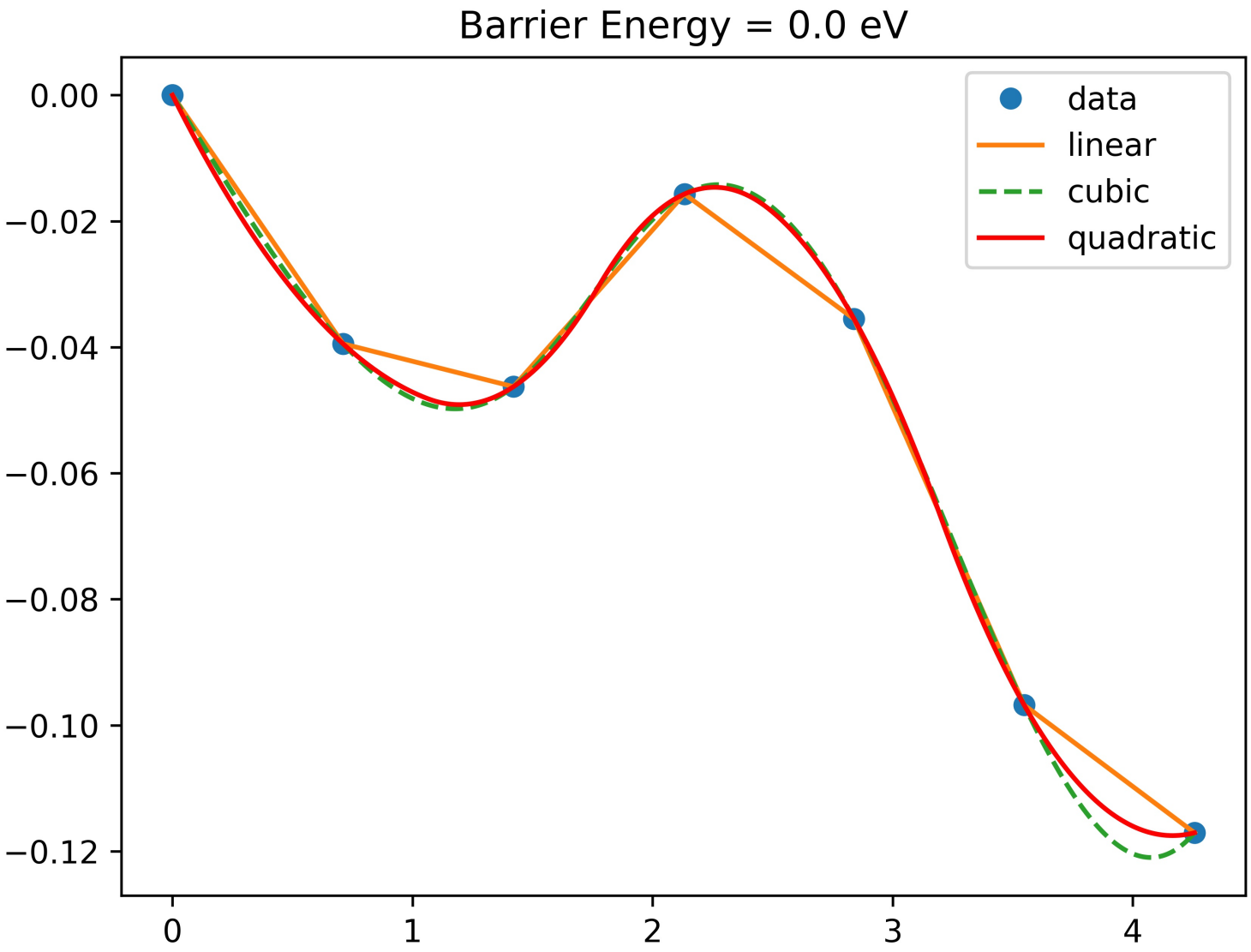
NEB method: convergence

- Spring force on each image fully determined
- Minimization algorithm to compute energy and gradients (true force)
- Iterate until absolute value of the maximum component of the NEB force at every image is less than a given threshold

$$|\vec{F}^{NEB}_{max,i}| < \varepsilon \quad \forall i$$



NEB method: interpolation



NEB method: algorithm

1. Set $\vec{R}$ and $\vec{P}$

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5. Connect each pair of images with a spring, yielding a force on each image of

$$\vec{F}_i^{S\parallel} = k\left(|\vec{R}_{i+1} - \vec{R}_i| - |\vec{R}_i - \vec{R}_{i-1}|\right)\widehat{\tau}_i$$

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$$\vec{F}_i^{S\parallel} = k\left(|\vec{R}_{i+1} - \vec{R}_i| - |\vec{R}_i - \vec{R}_{i-1}|\right)\widehat{\tau}_i$$
6. Project out the component of the interatomic force parallel to the tangent at each image i, $\vec{F}_i^{\perp} = -\nabla E(\vec{R}_i) + \nabla E(\vec{R}_i)\cdot\widehat{\vec{\tau}}_i\widehat{\vec{\tau}}_i$

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7. Minimize the energy for each image using $\vec{F}_i^{NEB} = \vec{F}_i^{\perp} + \vec{F}_i^{S\parallel}$

Steps from 3 to 7 will be repeated until getting a NEB force smaller than a tolerance

NEB method: algorithm

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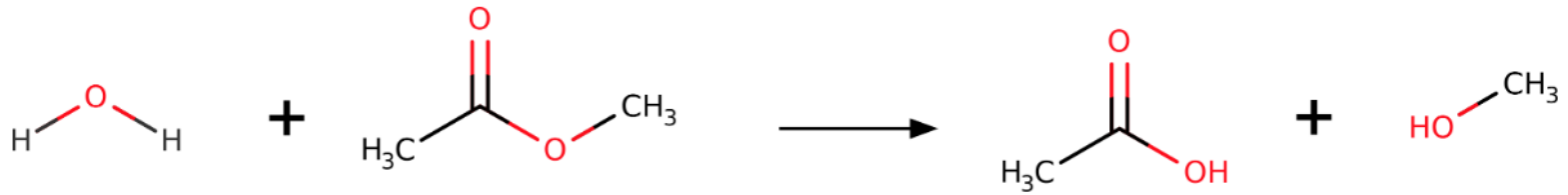
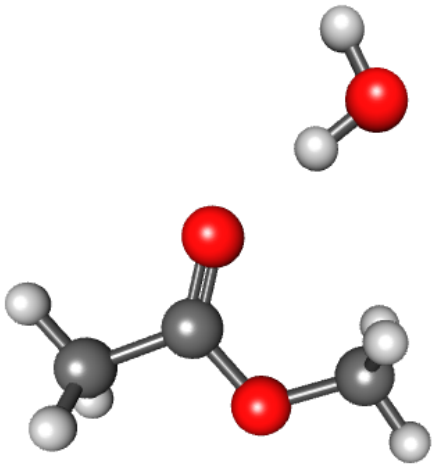
   Steps from 3 to 7 will be repeated until getting a NEB force smaller than a tolerance
8. Cubic polynomial piecewise interpolation of the final images

NEB method: example

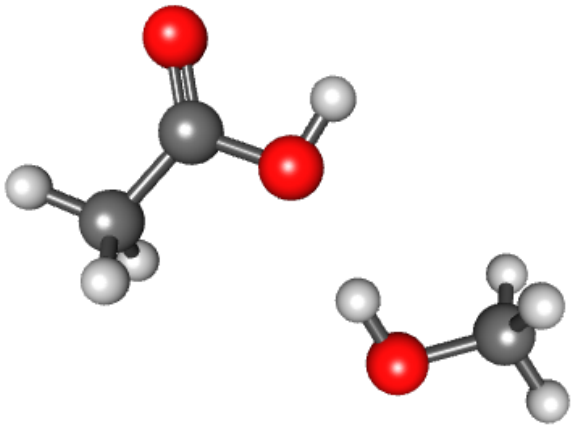
Hydrolysis of methyl-acetate into acetic acid and methanol



REACTANTS



PRODUCTS



NEB method: example

- Level of theory: DFT with B3LYP functional and DEF2-SVP basis set
- Eight intermediate images
- Final interpolation