中国科学技术大学本科生课程

应用量子化学(H)

Applied Quantum Chemistry

李震宇

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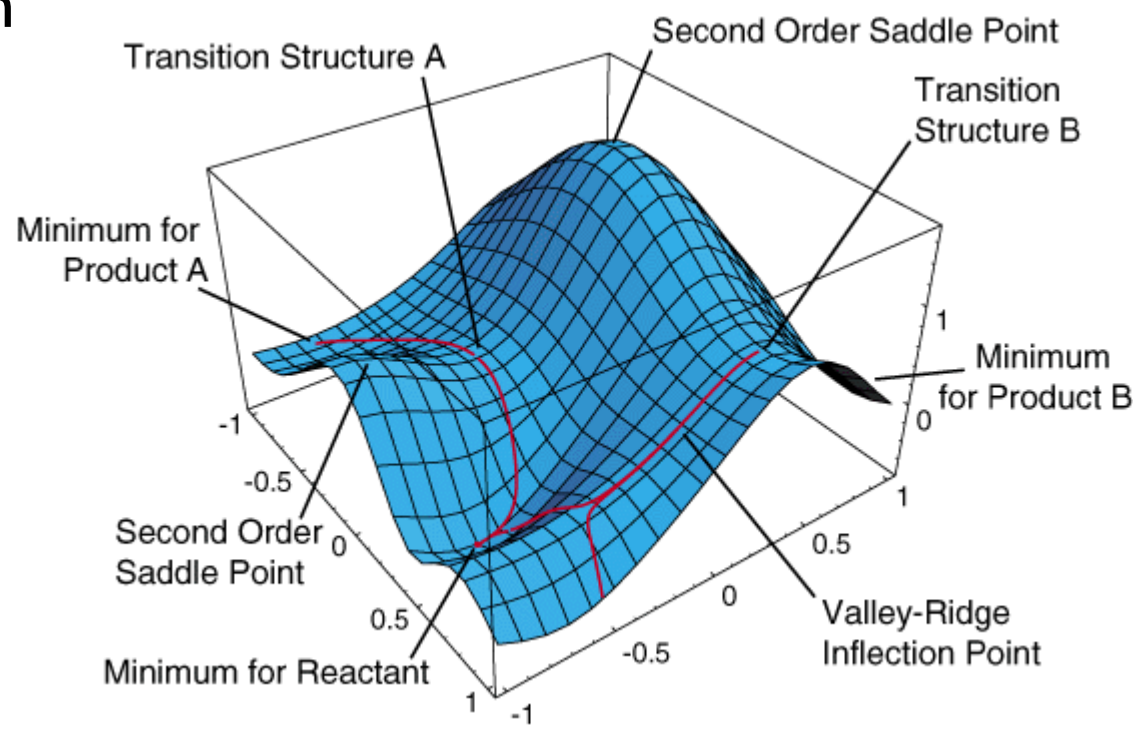
第五章 量子化学的应用

主要内容

- 势能面相关应用
- …

Introduction

- Geometry optimization (local minimum)
- Global optimization (global minimum)
- Minimum energy path
- PES representation



Geometry Optimization

- Find a local minimum on PES

$$f(\vec{x}) = a + \vec{b}\vec{x} + \frac{1}{2}\vec{x}\mathbf{B}\vec{x} = \bar{a} + \frac{1}{2}(\vec{x} - \vec{x}^0)\mathbf{B}(\vec{x} - \vec{x}^0) \qquad \mathbf{B}_{ij} = \frac{\partial^2 f}{\partial x_i \partial x_j}$$

quadratic function

- Gradient

$$\vec{g}(\vec{x}) = \frac{\partial f}{\partial \vec{x}} = \mathbf{B}(\vec{x} - \vec{x}^0)$$

- Newton's method (find the root of the derivative)

$$\vec{x} = \vec{x}^1 - \mathbf{B}^{-1}\vec{g}(\vec{x}^1)$$

Force

- Force

$$\mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I}$$

- Hellmann-Feynman theorem

$$\frac{dE}{d\lambda} = \left\langle \Psi \left| \frac{\partial H}{\partial \lambda} \right| \Psi \right\rangle / \langle \Psi | \Psi \rangle + \left[\left\langle \Psi \left| H - E \right| \frac{\partial \Psi}{\partial \lambda} \right\rangle + \left\langle \frac{\partial \Psi}{\partial \lambda} \left| H - E \right| \Psi \right\rangle \right] / \langle \Psi | \Psi \rangle$$

$$= \left\langle \Psi \left| \frac{\partial H}{\partial \lambda} \right| \Psi \right\rangle / \langle \Psi | \Psi \rangle \qquad H\Psi = E\Psi$$

- Pulay forces

$\langle \Psi | H - E | \Psi \rangle = 0,$ Hurley's condition

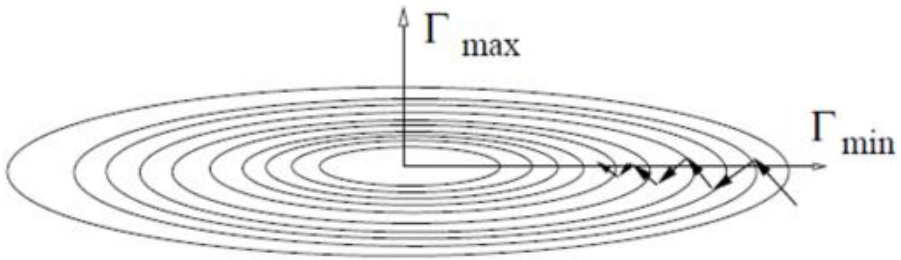
$\Psi = C\chi$ $\delta E / \delta \Psi = 0$ $d\chi / d\lambda$

Steepest Descent

- Guess $\vec{x}^1$
- Calculate $\vec{g}(\vec{x}^1)$
- Step along the steepest descent direction

$$\vec{x}^2 = \vec{x}^1 - \frac{1}{\Gamma_{\max}}\vec{g}(\vec{x}^1)$$

- Repeat to get converged geometry



Speed of Convergence

- Assume B is diagonal, and start from $\vec{x}^1 = \vec{x}^0 + \mathbf{1}$
- After a SD step

$$\vec{g}(\vec{x}^1) = \mathbf{B}(\vec{x}^1 - \vec{x}^0) = \begin{pmatrix} \Gamma_1 \\ \cdots \\ \Gamma_n \end{pmatrix} \qquad \vec{x}^2 = \vec{x}^1 - \frac{1}{\Gamma_n}\vec{g}(\vec{x}^1) = \vec{x}^0 + \begin{pmatrix} 1 - \Gamma_1/\Gamma_n \\ \cdots \\ 1 - \Gamma_n/\Gamma_n \end{pmatrix}$$

- The highest frequency mode determines the maximum stable step-width, but the soft modes converge slowest
- Asymptotic convergence rate: number of iterations

$$\left(1 - \frac{\Gamma_{\min}}{\Gamma_{\max}}\right)^k \approx \varepsilon$$

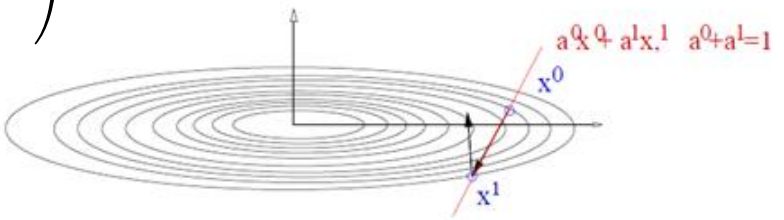
$$k \ln\left(1 - \frac{\Gamma_{\min}}{\Gamma_{\max}}\right) \approx \ln\varepsilon$$

$$-k\frac{\Gamma_{\min}}{\Gamma_{\max}} \approx \ln\varepsilon \implies k \approx -(\ln\varepsilon)\frac{\Gamma_{\max}}{\Gamma_{\min}} \qquad k \propto \frac{\Gamma_{\max}}{\Gamma_{\min}}$$

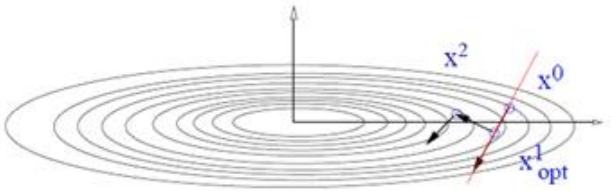
DIIS

- Find a linear combination of $\vec{x}^i$ which minimizes $\vec{g}^i$
- Gradient is linear in it's arguments for a quadratic function

$$\vec{g}\left(\sum_i \alpha^i \vec{x}^i\right) = \mathbf{B}\left(\sum_i \alpha^i \vec{x}^i - \vec{x}^0\right) = \mathbf{B}\left(\sum_i \alpha^i \vec{x}^i - \sum_i \alpha^i \vec{x}^0\right)$$
$$= \sum_i \alpha_i \mathbf{B}\left(\vec{x}^i - \vec{x}^0\right) = \sum_i \alpha_i \vec{g}^i$$

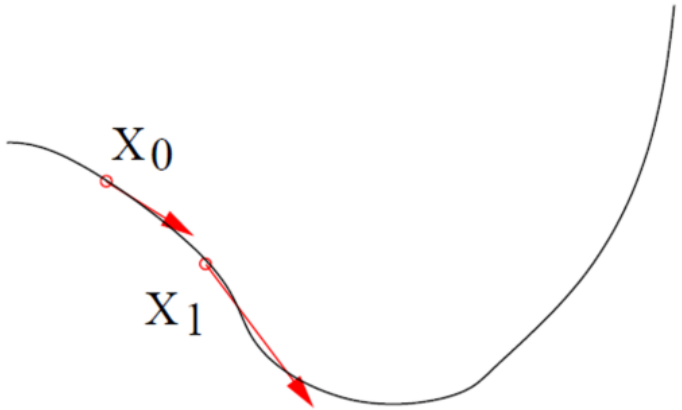


- Full DIIS algorithm
  - Start with a single initial point $\vec{x}^i$
  - SD along gradient $\vec{g}(\vec{x}^1)$: $\vec{x}^2 = \vec{x}^1 - \lambda \vec{g}^1$
  - →new gradient $\vec{g}^2 = \vec{g}(\vec{x}^1)$
  - Search for the minimal gradient in the subspace $\vec{g}^i$: $\longrightarrow \vec{g}_{\text{opt}} = \sum_i \alpha^i \vec{g}^i$
  - Calculate the corresponding position $\vec{x}_{\text{opt}} = \sum_i \alpha^i \vec{x}^i$
  - → $\vec{x}^3 = \vec{x}_{\text{opt}} - \lambda \vec{g}_{\text{opt}}$



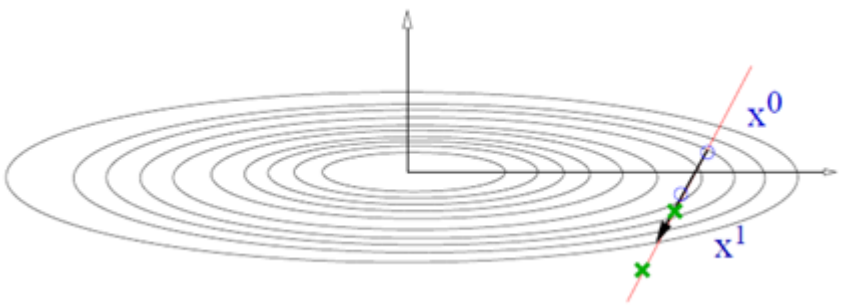
DIIS

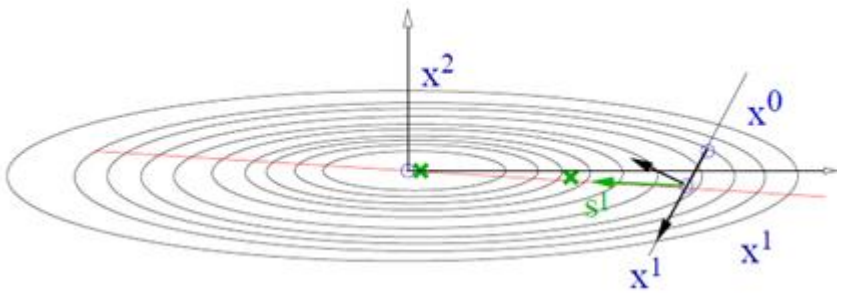
- Number of iterations $\propto \sqrt{\Gamma_{max}/\Gamma_{min}}$
- POTIM determines the step size in SD steps, no line minimization is performed.
- NFREE determines how many ionic steps are stored in the iteration history.
- Since it consider forces only, DIIS will move uphill when force increases along the search direction.



CG

- The CG Algorithm
  - SD from $\vec{x}^0$ along $\vec{g}^0$
  - Line minimization to $\vec{x}^1$
  - New gradient $\vec{g}^1 = \vec{g}(\vec{x}^1)$ and conjugated gradient $\vec{s}^1$
  - Points directly towards the minimum
- Line minimization is done using a variant of Brent algorithm
  - trial step along search direction (conjg. gradient scaled by POTIM)
  - quadratic or cubic interpolation using energies and forces at x_0 and x_1 allows to determine the approximate minimum
  - continue minimization as long as approximate minimum is not accurate enough





Damped MD

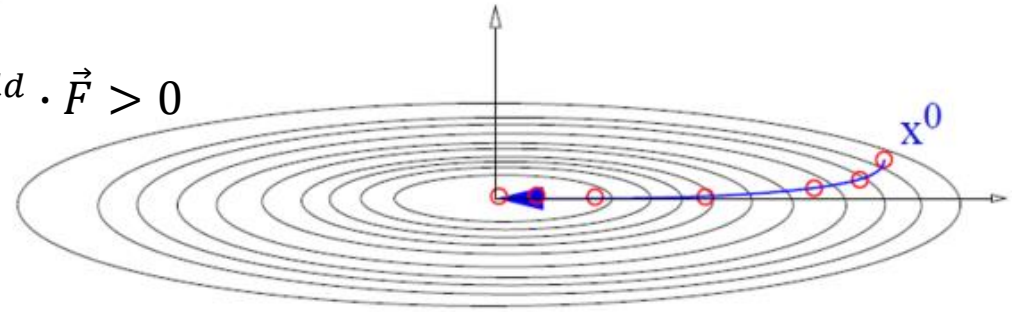
- equation of motion

$$\ddot{\vec{x}} = -2 * \alpha \vec{g}(\vec{x}) - \mu \dot{\vec{x}}$$

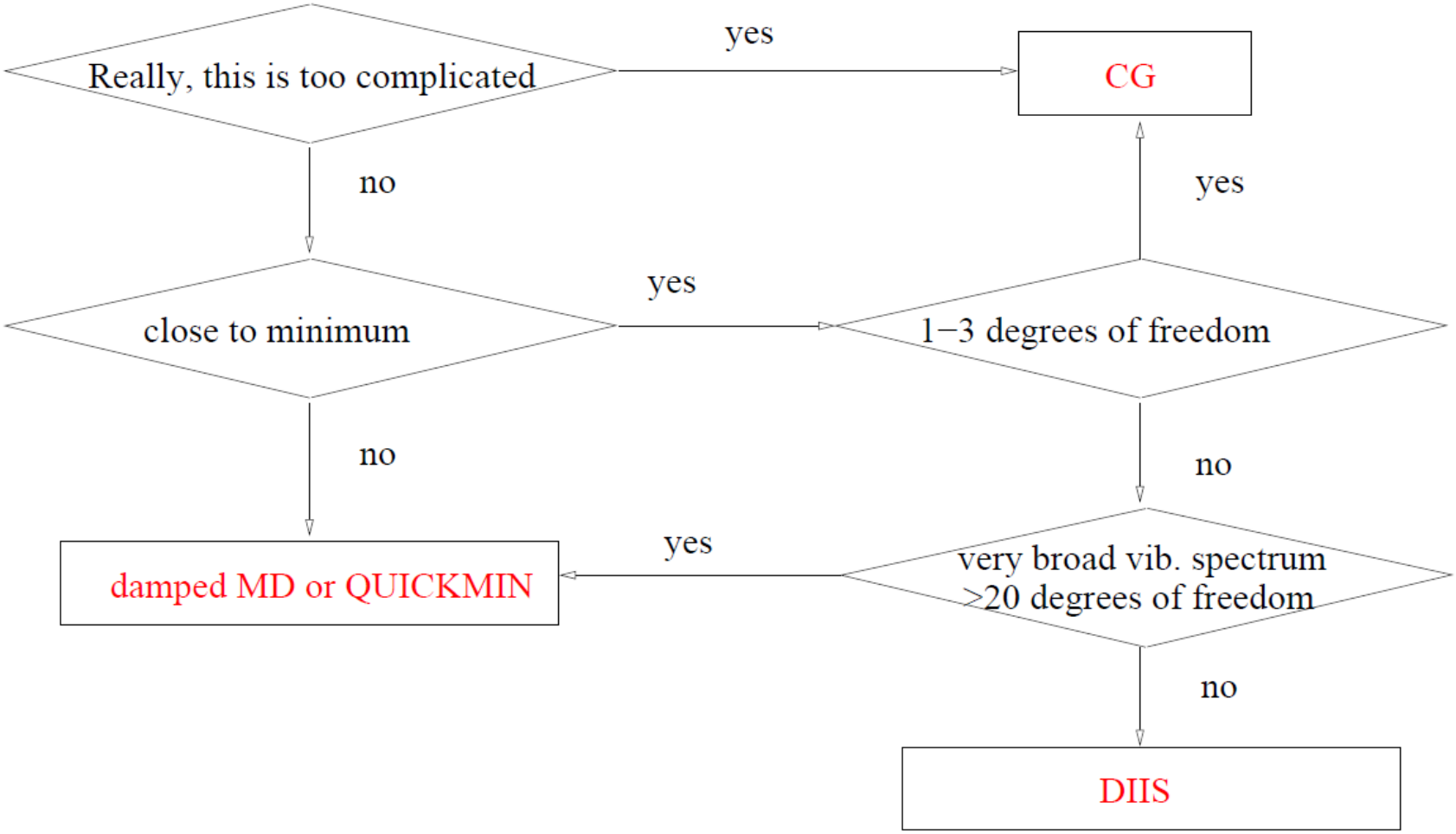
$$\vec{v}_{N+1/2} = \left((1-\mu/2)\vec{v}_{N-1/2} - 2 * \alpha \vec{F}_N\right)/(1+\mu/2) \qquad \vec{x}_{N+1} = \vec{x}_N + \vec{v}_{N+1/2}$$

- α(POTIM) must be as large as possible (for example, 0.15 < POTIM < 0.4), but without leading to divergence
- For a too small friction, it will overshoot the minimum and accelerate back; for a too large friction, relaxation will also slow down (μ=2 recovers SD). A reasonable estimation of μ (SMASS) is $\mu \approx 2\sqrt{\Gamma_{\min}/\Gamma_{\max}}$
- QUICKMIN

$$\vec{v}^{new} = \begin{cases} \alpha\vec{F} + \dfrac{\vec{F}\left(\vec{v}^{old} \cdot \vec{F}\right)}{\left\|\vec{F}\right\|} & \text{for } \vec{v}^{old} \cdot \vec{F} > 0 \\ \alpha\vec{F} & \text{else} \end{cases}$$

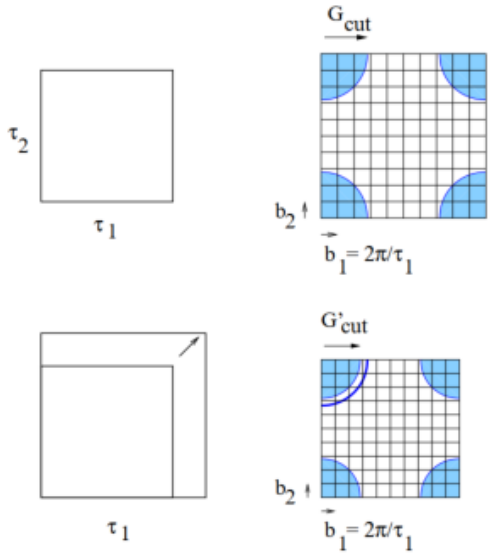


How to Choose an Opt Algorithm



Lattice Relaxation

- Optimization by hand: do a series of calculations at different volumes
- Optimization by hand: fit to thermodynamics equations
- Automatic optimizations based on Hellmann-Feynman stresses
  - The basis set changes discontinuously when the cell volume and shape are changed
  - When using fixed basis sets, quality of the basis set becomes worse with increasing V, and min(E(V) is shifted
  - increase ENCUT (by 30%) to perform lattice relaxations



- lattice expanded $\tau_1 \longrightarrow \tau_1'$
- cutoff decreases by a factor τ_1/τ_1'
- effective cutoff G_{cut}' is lower
- E is overestimated for large V
- The apparent V_{eq} is too small

Harmonic Region Thermodynamics

- Free energy at a finite temperature

$$G = E_0 + E_{\mathrm{ZPE}} + k_B T \sum_i \ln\left(1 - e^{-\hbar\omega_i / k_B T}\right)$$

- Phonon frequency

$$C_{ij} = -\frac{\partial F_i}{\partial \boldsymbol{R_j}} = \frac{\partial^2 E}{\partial \boldsymbol{R_i} \partial \boldsymbol{R_j}} \qquad \frac{C_{ij}}{\sqrt{M_I M_J}}$$

  - Frozen phonon (finite difference)
  - Density functional perturbation theory

$$\frac{\partial n(\boldsymbol{r})}{\partial R_{\boldsymbol{i}}} = \frac{\partial n(\boldsymbol{r})}{\partial v_{ext}} \frac{\partial v_{ext}}{\partial R_{\boldsymbol{i}}} \qquad \chi = \frac{\partial n(\boldsymbol{r})}{\partial V_{ext}}$$

Global Optimization

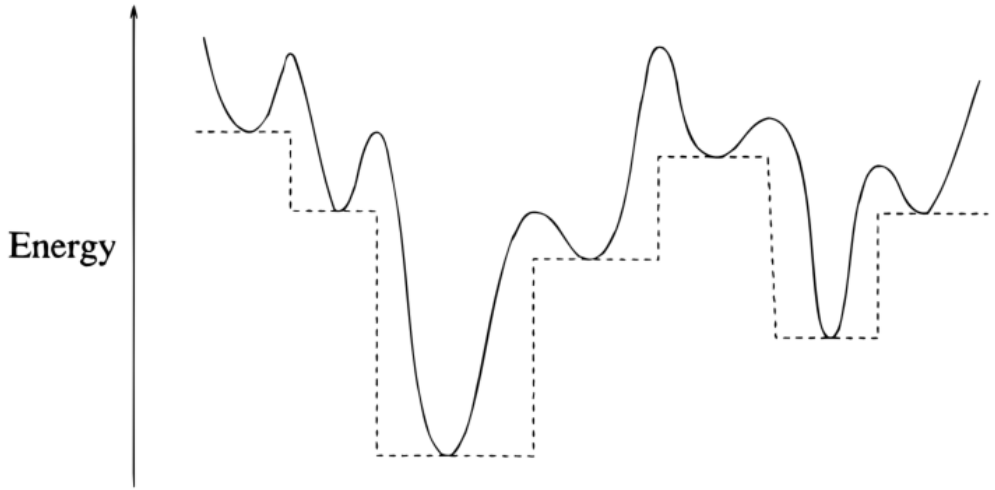
- Deterministic methods
- Stochastic methods
  - Basin hopping, stochastic surface walking, …
- Heuristics and metaheuristics
  - Simulated annealing, genetic algorithms, particle swarm optimization, ant colony optimization, artificial bee colony algorithm, …

Basin Hopping

- PES transformation

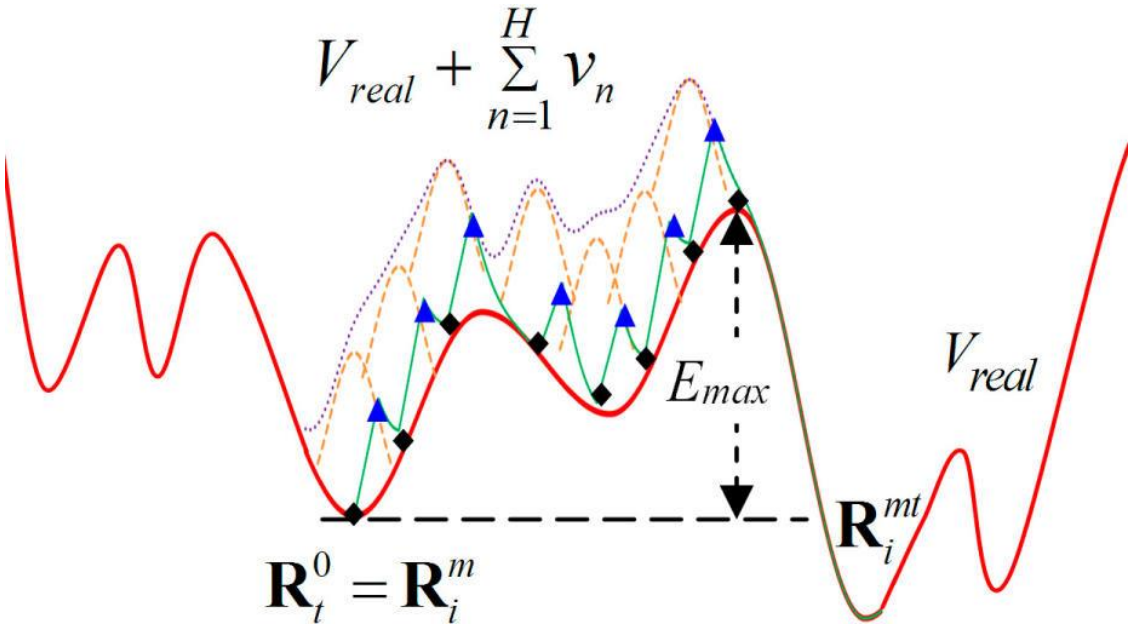
$$\tilde{E}(X) = \min\{\tilde{E}(X)\}$$

- Energy landscape exploration via MC



Stochastic Surface Walking

- Combine bias-potential-driven dynamics and Metropolis Monte Carlo to manipulate smoothly the structural configuration from one minimum to another on PES.



Simulated Annealing

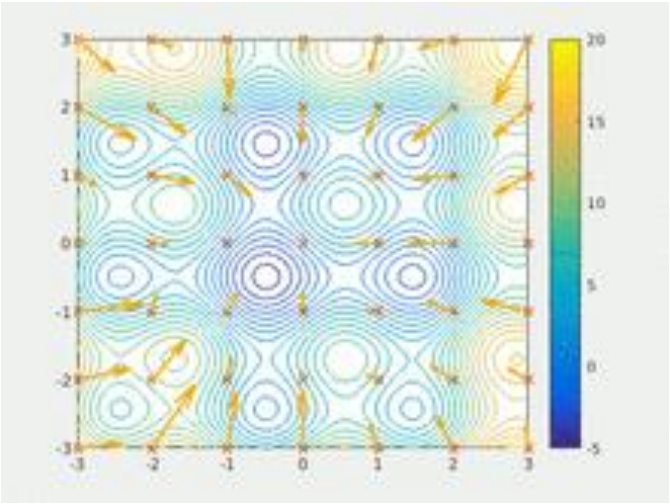
- Annealing: a technique involving heating and controlled cooling of a material to increase the size of its crystals and reduce their defects.
- Pseudocode
  - Let $s = s_0$
  - For $k = 0$ through k_{max}:
    - $T \leftarrow$ temperature(k / k_{max})
    - Pick a random neighbor, $s_{new} \leftarrow$ neighbor(s)
    - If $P(E(s), E(s_{new}), T) \geq$ random(0, 1):
      - $s \leftarrow s_{new}$
  - Output: the final state s

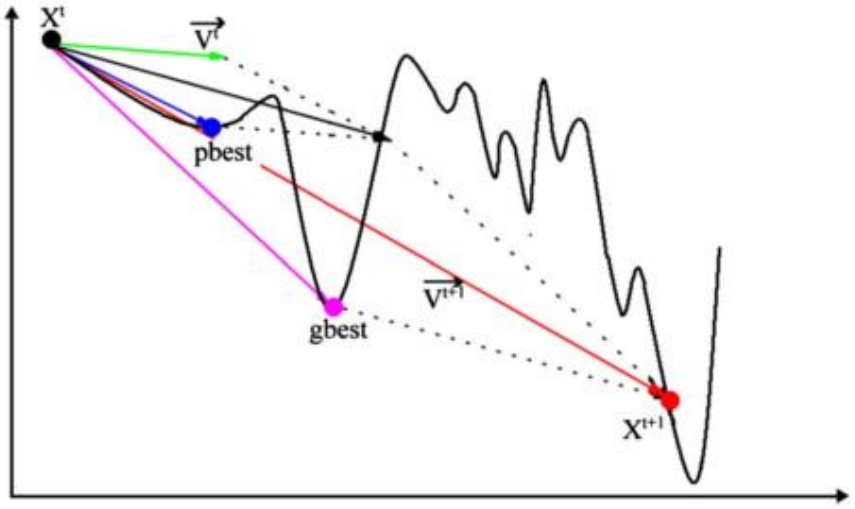
Genetic Algorithms

- A metaheuristic inspired by the process of natural selection that belongs to the larger class of evolutionary algorithms
- It requires
  - a genetic representation of the solution domain (mutation, crossover, and selection)
  - a fitness function to evaluate the solution domain

Particle Swarm Optimization

- Update particle's position and velocity based on the local and global best position.





Artificial Bee Colony Algorithm

- Employed bee, onlooker, and scout
- Main steps
  - Initial food sources are produced for all employed bees

$$X_i = \{x_{i,1}, x_{i,2}, \cdots, x_{i,n}\}$$

  - REPEAT
    - Each employed bee goes to a food source in her memory and determines a closest source, then evaluates its nectar amount and dances in the hive

$$V_{i_k} = X_{i_k} + \Phi_{i_k} \times \left(X_{i_k} - X_{j_k}\right)$$

    - Each onlooker watches the dance of employed bees and chooses one of their sources depending on the dances, and then goes to that source. After choosing a neighbour around that, she evaluates its nectar amount.

$$P_i = \frac{fit_i}{\sum_j fit_j}$$

Artificial Bee Colony Algorithm

- Abandoned food sources are determined and are replaced with the new food sources discovered by scouts. $X_{i_k} = lb_j + rand(0,1) \times (ub_j - lb_j)$
- The best food source found so far is registered.

- UNTIL (requirements are met)

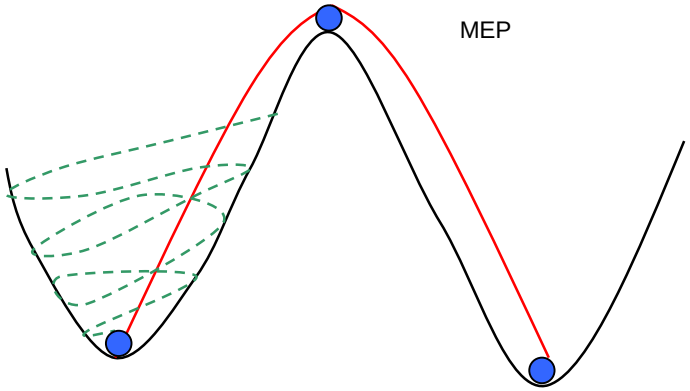
- Algorithm properties
  - Positive feedback: As the nectar amount of food sources increases, the number of onlookers visiting them increases, too.
  - Negative feedback: The exploration process of a food source abandoned by bees is stopped.
  - Fluctuations: The scouts carry out a random search process for discovering new food sources.
  - Multiple interactions: Bees share their information about food source positions with their nest mates on the dance area.

Transition State Theory

- Assume a special type of chemical equilibrium (quasi-equilibrium) between reactants and activated transition state complexes

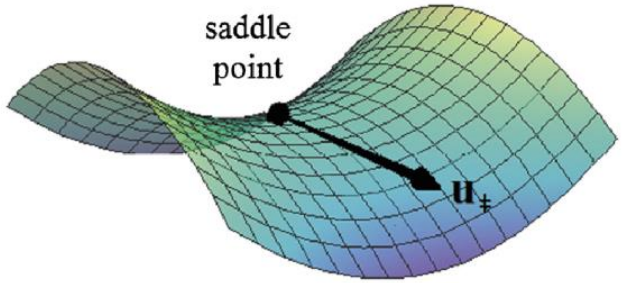
$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB$$

$$A + B \leftrightharpoons AB^{\neq} \xrightarrow{k_{\neq}} AB$$



- Reaction rate

$$k_1 = k^{\neq} \frac{[AB^{\neq}]}{[A][B]} = k^{\neq} e^{-(\Delta G^{\neq})/k_B T}$$

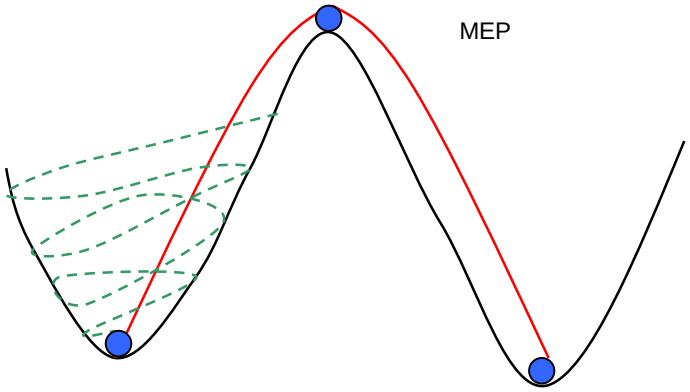


Harmonic Transition State Theory

- Reaction rate

$$\frac{d[P]}{dt} = k^{\neq}[AB]^{\neq} = k^{\neq}K^{\neq}[A][B] = k[A][B]$$

$$k = k^{\neq}\, K^{\neq}$$



- Harmonic TST

$$k^{\neq} = \frac{1}{2\delta q}\langle|\dot{q}|\rangle_{\neq} \qquad \langle|\dot{q}|\rangle_{\neq} = \frac{\int_{-\infty}^{\infty} d\dot{q} exp\left[-\beta\mu_q\,\dot{q}^2/2\right]\cdot|\dot{q}|}{\int_{-\infty}^{\infty} d\dot{q} exp\left[-\beta\mu_q\,\dot{q}^2/2\right]} = \sqrt{\frac{2k_BT}{\pi\mu_q}}$$

$$K^{\neq} = \frac{\delta q}{\lambda_{T,q}}K^{\neq\prime} \qquad \lambda_{T,q} = \frac{h}{\sqrt{2\pi\mu_q k_B T}} \qquad K^{\neq\prime} = e^{-\frac{\Delta G^{\neq}}{RT}}$$

$$k = \frac{k_B T}{h}e^{-\frac{\Delta G^{\neq}}{RT}}$$

Transition State Location

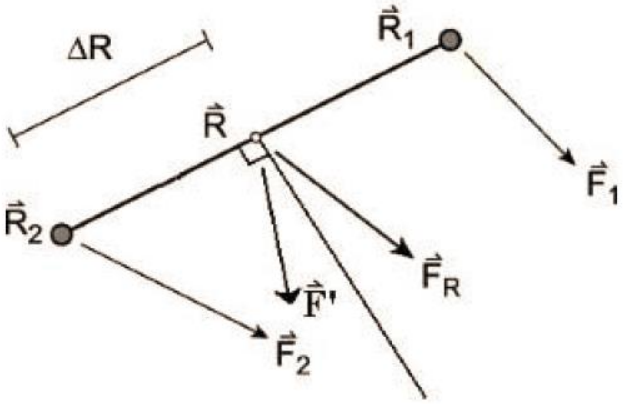
- From the reactant or an initial guess
  - Constrained minimization: fix reaction coordinate R and optimize other degrees of freedom.
  - Eigenvector following: when Hessian or its approximation is obtained, follow the eigenvector corresponding to the most negative (largest) eigenvalue.
  - Dimer method: form a dimer by two images very close to each other on the PES and move the dimer uphill from the starting position whilst rotating the dimer to find the direction of lowest curvature (ultimately negative).

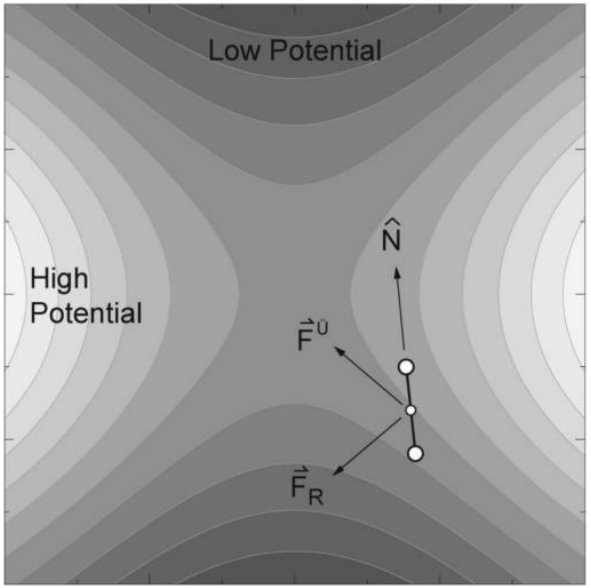
Transition State Location

- From a reactant-product pair
  - Linear synchronous transit (LST): taking interpolated points between the reactant and product geometries and choosing the one with the highest energy for subsequent refinement via a local search.
  - Quadratic synchronous transit (QST): extends LST by allowing a parabolic reaction path, with optimization of the highest energy point orthogonally to the parabola.
  - Nudged elastic band: beads along the reaction pathway have simulated spring forces in addition to the chemical forces.

Dimer Method

- At each step
  - Rotating the dimer towards the minimum energy configuration to orient it along the lowest curvature mode.
  - Translating the dimer with a modified force where the component along the dimer is inverted.





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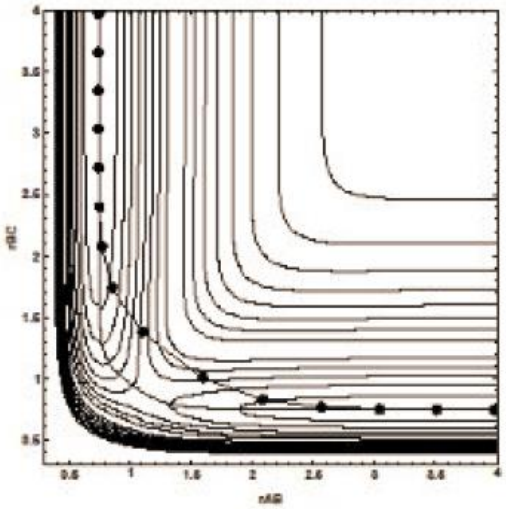
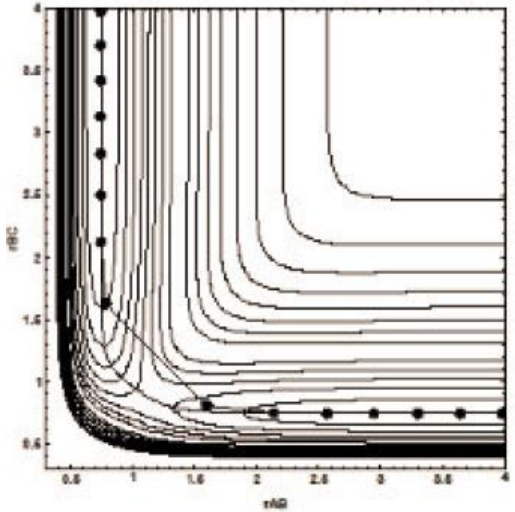
NEB

- Plain elastic band



Corner Cutting



Sliding Down

- Nudged elastic band
  - The total force acting on an image is the sum of the spring force along the tangent and the true force perpendicular to the tangent.

CI-NEB

- The highest energy image does not feel the spring forces along the band. Instead, the true force at this image along the tangent is inverted.