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Computing Transition States and Mountain-Passes

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Transition States

Given a continuously differentiable function $f : \mathbb{R}^n \mapsto \mathbb{R}$ and two points $x_a$ and $x_b$, determine a critical point $x^*$ on a minimal energy path between $x_a$ and $x_b$.

- A fundamental problem in biology, chemistry, and mathematics

A critical value of $f$ is

$$
\gamma = \inf_{p \in \Gamma} \{ \max \{ f[p(t)] : t \in [0, 1] \} \}
$$

when $\Gamma$ is defined by

$$
\Gamma = \{ p \in C[0, 1] : p(0) = x_a, \ p(1) = x_b \}.
$$
Ingredients for a Mountain-Pass

diamond A closed set $S$ that separates points $x_a$ and $x_b$: The set $S$ does not contain $x_a$ or $x_b$ and every path from $x_a$ to $x_b$ meets $S$

diamond The value of $f$ on $S$ is sufficiently high:

$$\inf\{f(x) : x \in S\} > \max\{f(x_a), f(x_b)\},$$

Questions

diamond Is there a critical point $x^*$ between $x_a$ and $x_b$?

diamond What is the geometrical and eigenvalue structure of $x^*$?
Mountain-Pass Theorem

\[ \Gamma \equiv \{ p \in C[0, 1] : p(0) = x_a, \ p(1) = x_b \} \]

**Theorem.** Ambrosetti and Rabinowitz [1973]

Assume that there are points \( x_a \) and \( x_b \) and a separating set \( S \). If

\[ \inf \{ f(x) : x \in S \} > \max \{ f(x_a), f(x_b) \} \]

and \( f \) satisfies the Palais-Smale condition, then

\[ \gamma = \inf_{p \in \Gamma} \{ \max \{ f[p(t)] : t \in [0, 1] \} \} \]

is a minimax critical value of \( f \).
Palais-Smale Condition

The mapping $f$ satisfies the Palais-Smale condition on $C$ if the existence of a sequence $\{x_k\}$ in $C$ such that

$$\lim_{k \to \infty} f(x_k) = \gamma, \quad \lim_{k \to \infty} \nabla f(x_k) = 0,$$

implies that $\{x_k\}$ has a convergent subsequence.

- If $f$ has compact level sets then $f$ satisfies the PS condition.
- If $f$ is bounded below and satisfies the PS condition, then $f$ achieves its minimum.

Note. The PS condition rules out critical points at infinity.
Definition. Hofer [1985]

A critical point $x^*$ is a mountain pass if for any sufficiently small neighborhood $N$ of $x^*$ the set

$$\mathcal{L}(x^*) = \{x \in N : f(x) < f(x^*)\}$$

is non-empty and not path-connected.

$\diamond$ $\mathcal{L}(x^*)$ is empty if and only if $x^*$ is a minimizer.
Minimax Critical Points and Mountain-Passes

**Conjecture.** If \( x^* \) is a minimax critical point then either

- \( x^* \) is a limit point of minimizers, or
- \( x^* \) is a mountain-pass

**Example:** Each point in \([1, 2]\) is a minimax critical point and a limit point of minimizers, but not a mountain-pass.
Geometry of Mountain-Passes: A non-degenerate case

\[ f(x) = \gamma \]
Geometry of Mountain-Passes: A degenerate case
Eigenvalue Structure of Mountain-Passes: Quadratics

**Theorem.** The quadratic function $q : \mathbb{R}^n \mapsto \mathbb{R}$ defined by

$$q(x) = \sum_{k=1}^{n} \lambda_i x_i^2, \quad \lambda_1 \leq \ldots \leq \lambda_n,$$

has a mountain pass at $x^* = 0$ if and only if

$$\lambda_1 < 0 < \lambda_2.$$
Transition States and Mountain Passes

**Theorem.** Assume that $f : \mathbb{R}^n \to \mathbb{R}$ is twice continuously differentiable in a neighborhood of the critical point $x^*$. If the Hessian matrix $\nabla^2 f(x^*)$ is nonsingular, then $x^*$ is a mountain pass if and only if $\nabla^2 f(x^*)$ has precisely one negative eigenvalue.

**Question.** Are transition states of other types desirable?

The number of negative eigenvalues of the Hessian $\nabla^2 f(x^*)$ is the Morse index of the critical point.
The Elastic String Algorithm

Compute

\[
\min_{p \in \Gamma_{\pi}} \{ \max \{ f[p(t_k)] : 0 \leq k \leq m \} \},
\]

where \( \pi = \{t_0, \ldots, t_{m+1}\} \) is a partition of \([0, 1]\), and \( \Gamma_{\pi} \) is the set of piecewise linear paths that connect \( x_a \) with \( x_b \) with

\[
\int_0^1 \|p'(t)\| \, dt \leq L.
\]

\( \diamond \) We only need to determine the breakpoints \( x_k = p(t_k) \).

\( \diamond \) The constraint on the length of the path requires that

\[
\|x_{k+1} - x_k\| \leq h_k, \quad \sum_{k=0}^{m} h_k = L.
\]
Determining Breakpoints

Version 1.

$$\min \{ \nu(x) : \|x_{k+1} - x_k\| \leq h_k, \ 0 \leq k \leq m \},$$

where

$$\nu(x) = \max \{ f(x_1), \ldots, f(x_m) \}.$$ 

Version 2.

$$\min \{ \nu : f(x_k) \leq \nu, \ 1 \leq k \leq m, \ \|x_{k+1} - x_k\| \leq h_k, \ 0 \leq k \leq m \},$$
The Elastic String Algorithms

- Choose the number $m$ of breakpoints.
- Choose the bounds $L$ and $h_k$.
- Determine the breakpoints $x_1, \ldots, x_m$ for the path $p_m$.
- Let $x^*_m = \max\{f(x_k) : 1 \leq k \leq m\}$.
- Increase $m$ and update $L$.

**Remark.** In the computational experiments we used $m \in [10, 30]$, and set $L = 2\|x_b - x_a\|$ and $h_k = L/(m+1)$. In most cases, $m = 10$. 
Convergence of the Elastic String Algorithm

**Theorem.** Any limit point of the paths \( \{p_m\} \) is a path \( p^* \) that crosses a critical point \( x^* \) of \( f \).

- We consider functions that are unbounded below, and those with compact level sets
- There is no need to assume that the constraint \( L \) on the length of the path is sufficiently large
- The main technical (nondegeneracy) assumption is that

\[
f(x_k) = \nu = \max \{ f(x_j) : 1 \leq j \leq m \}, \quad k = k_1, \ldots, k_l,
\]

where \( l \) is bounded independent of \( m \)
Convergence of the Piecewise Linear Paths

Six-hump camel back function contours for $m = 5, 10$.  

Convergence of the Piecewise Linear Paths

Six-hump camel back function contours for $m = 15, 20$. 
Computational Experiments

Transition states

- Highly nonlinear
- \( f \) is bounded below and coercive
- A finite number of critical points

Henkelman, Jóhannesson, and Jónsson [2000].

Variational problems

- Mildly nonlinear
- \( f \) is unbounded below and \(|f|\) is coercive
- An infinite number of critical points

Chen, Zhou, and Ni [2000], Li and Zhou [2001,2002]
Transition States: LEPS Potential

Typical results for $m = 20$ breakpoints
Mountain-Passes: The Henon Problem (Structured Mesh)

\[
\int_{\mathcal{D}} \left( \frac{1}{2} \| \nabla u(s) \|^2 - \frac{1}{4} \| s \| u(s)^4 \right) ds
\]
Mountain-Passes: The Henon Problem (Un-Structured Mesh)

\[
\int_D \left( \frac{1}{2} \| \nabla u(s) \|^2 - \frac{1}{4} \| s \|^4 \right) ds
\]
Research Issues

- Eliminate nondegeneracy assumption in convergence result
- Investigate the relationship to other minimax algorithms
- Improvements to the optimization formulation
- Develop multilevel techniques
- Benchmark algorithms on applications: PNNL, SNL, …
- Transition states: Julius Jellinek and Al Wagner
- Nanoscale modelling: Larry Curtiss
- Investigate other areas of applicability: biology, …