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Computing Transition States and Mountain Passes

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Joint work with Todd Munson

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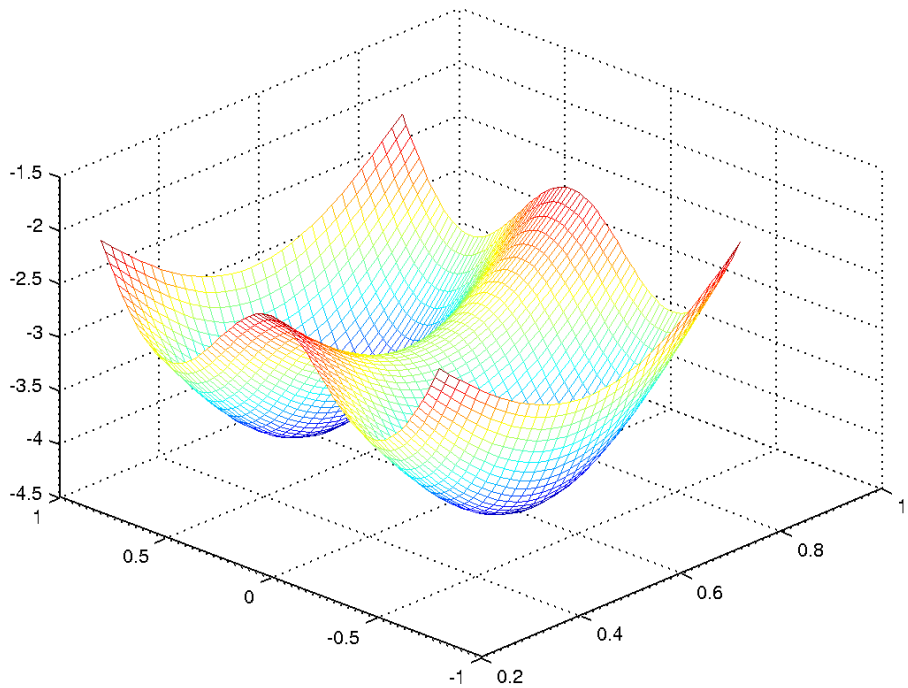
Motivation

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
- Collaborations with MPQC (SNL) and NWChem (PNNL)

Mountain-Passes: Motivation



Minimax Characterization of a Mountain-Pass

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

Ingredients for a Mountain-Pass

- 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
- The value of f on S is sufficiently high:

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

Questions

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

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

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.

Mountain-Passes

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.

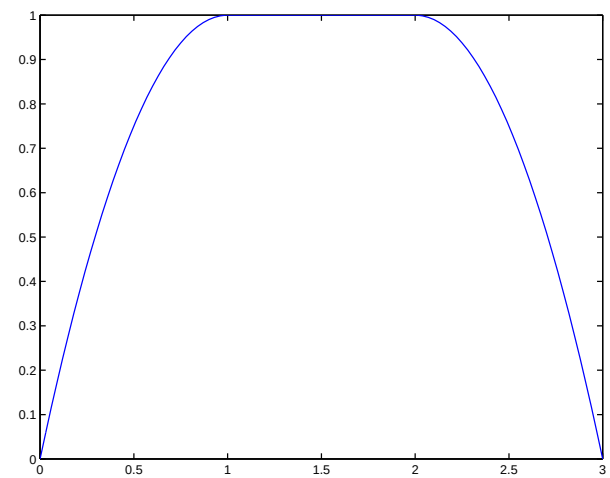
- $\mathcal{L}(x^*)$ is empty if and only if x^* is a minimizer.

Minimax Critical Points and Mountain-Passes

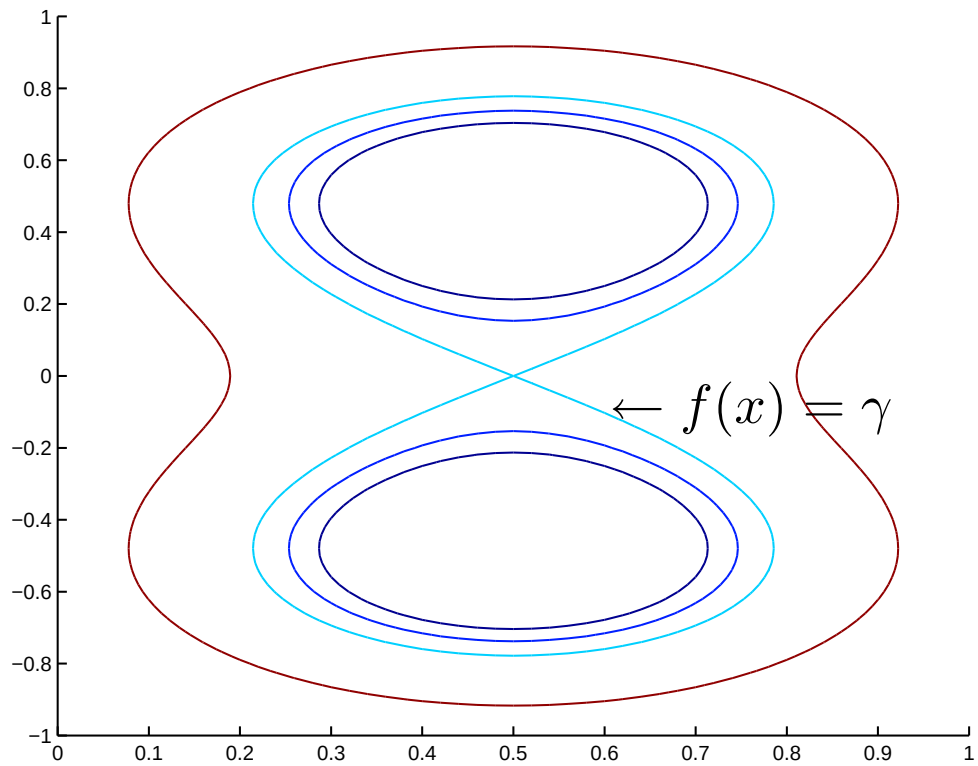
Conjecture. If x^* is a minimax critical point then either

- x^* is a limit point of minimizers, or
- x^* is a mountain-pass with $\mathcal{L}(x^*)$ not path-connected

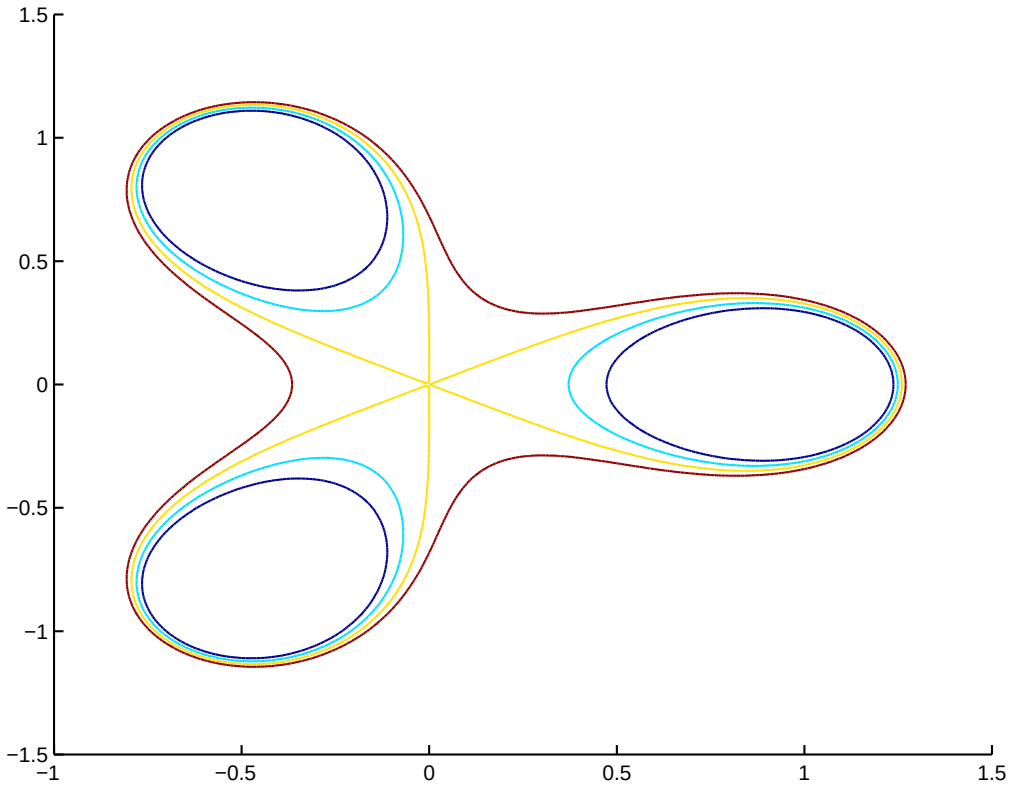
For this function each minimax critical point is a limit point of minimizers.



Geometry of Mountain-Passes: A non-degenerate case



Geometry of Mountain-Passes: A degenerate case



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Eigenvalue Structure of Mountain-Passes: Quadratics

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

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

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

$$\lambda_1 < 0 < \lambda_2.$$

Transition States and Mountain Passes

Theorem. Assume that $f : \mathbb{R}^n \mapsto \mathbb{R}$ 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

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

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

$$\int_0^1 \|p'(t)\| \, dt \le L.$$

- We only need to determine the breakpoints $x_k = p(t_k)$.
- The constraint on the length of the path requires that

$$\|x_{k+1} - x_k\| \le h_k, \qquad \sum_{k=0}^{m} h_k = L.$$

Determining Breakpoints

Version 1.

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

where

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

Version 2.

$$\min\left\{\nu : f(x_k) \le \nu,\ 1 \le k \le m,\quad \|x_{k+1} - x_k\| \le h_k,\ 0 \le k \le m\right\},$$

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

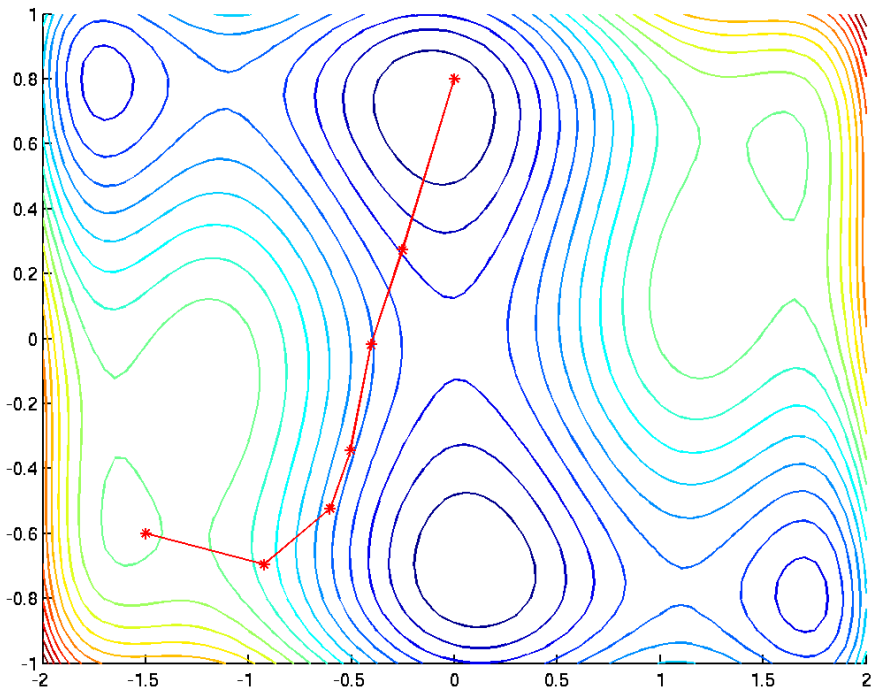
Theorem. Any limit point of the paths $\{p_m\}$ is a path p^* that crosses a critical point x^* of f.

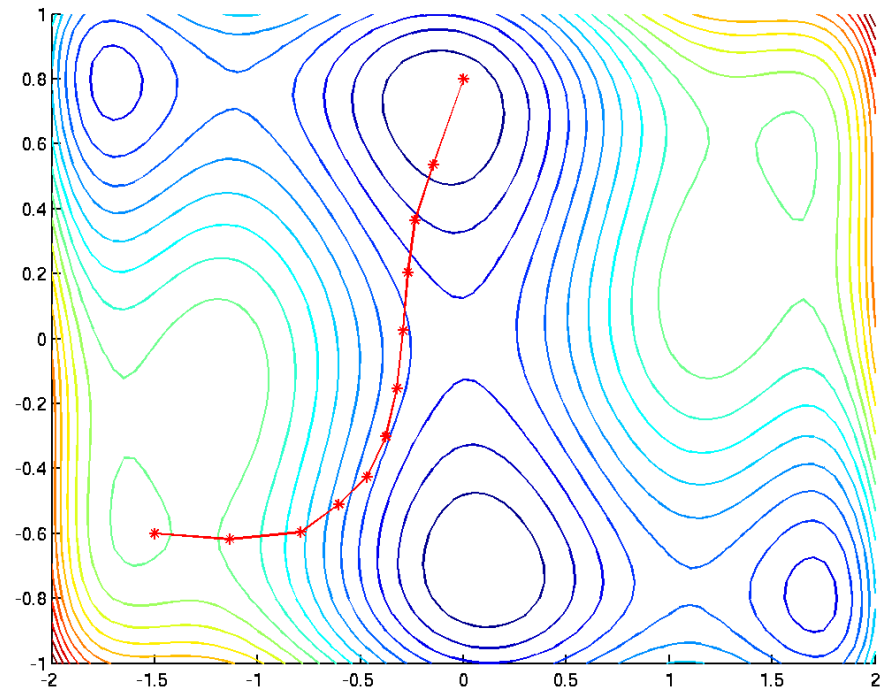
- We consider functions that are unbounded below, and those with compact level sets
- There is no need to assume that the constraint L on the length of the path is sufficiently large
- The main technical (nondegeneracy) assumption is that

$$f(x_k) = \nu = \max\{f(x_j) : 1 \le j \le m\}, \qquad k = k_1, \ldots, k_l,$$

where l is bounded independent of m

Convergence of the Piecewise Linear Paths





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

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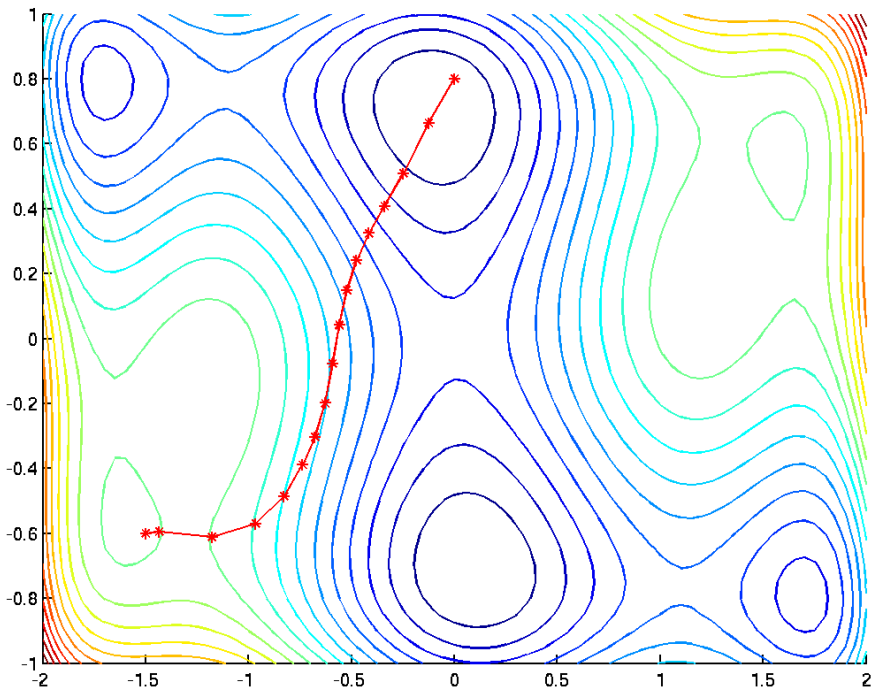
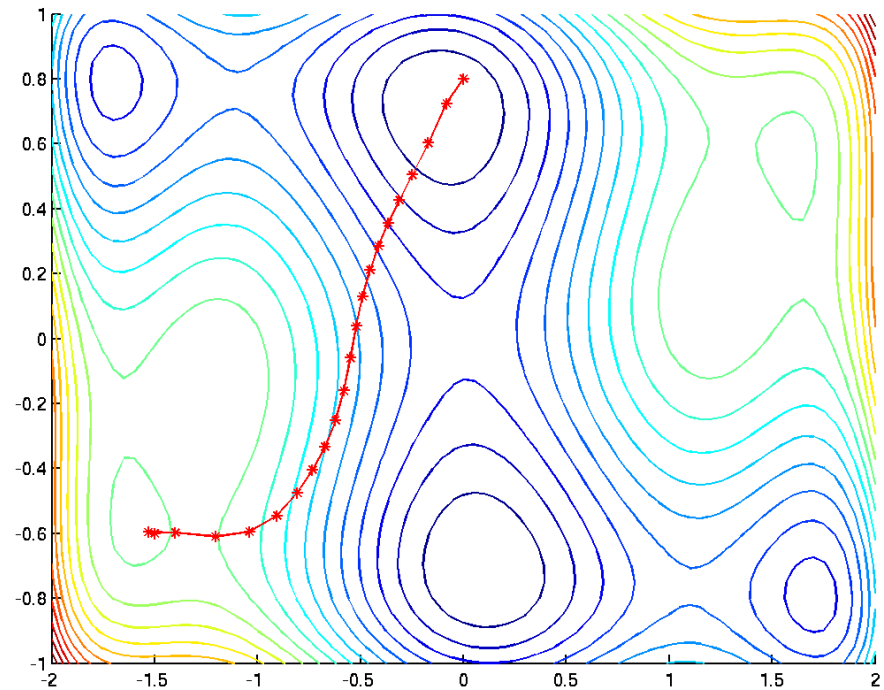
Convergence of the Piecewise Linear Paths





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].

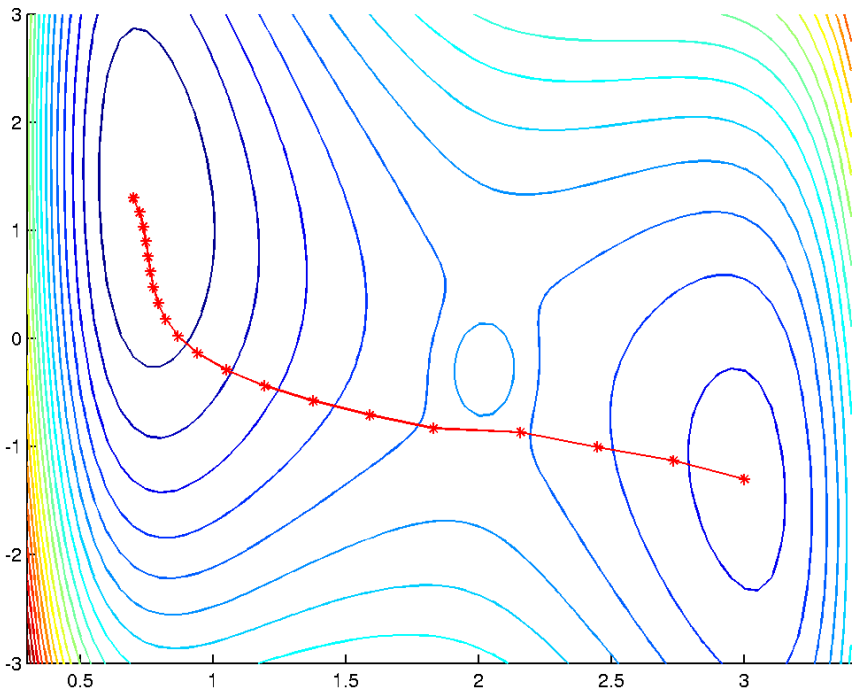
Variational problems

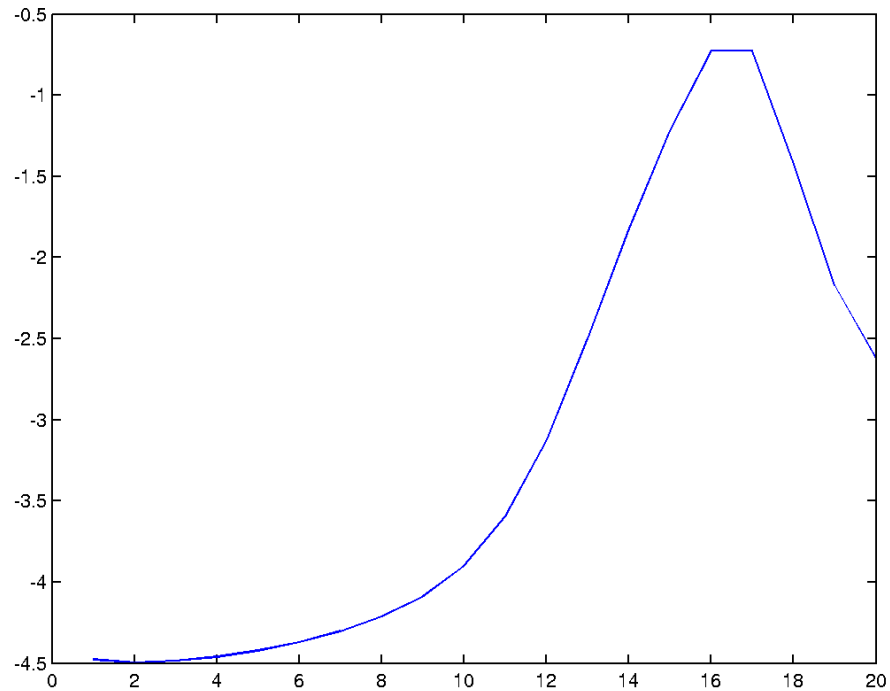
- Mildly nonlinear
- f is unbounded below and $|f|$ is coercive
- An infinite number of critical points

Chen, Zhou, and Ni [2000], Li and Zhou [2001,2002]

Transition States: LEPS Potential

Typical results for $m = 20$ breakpoints





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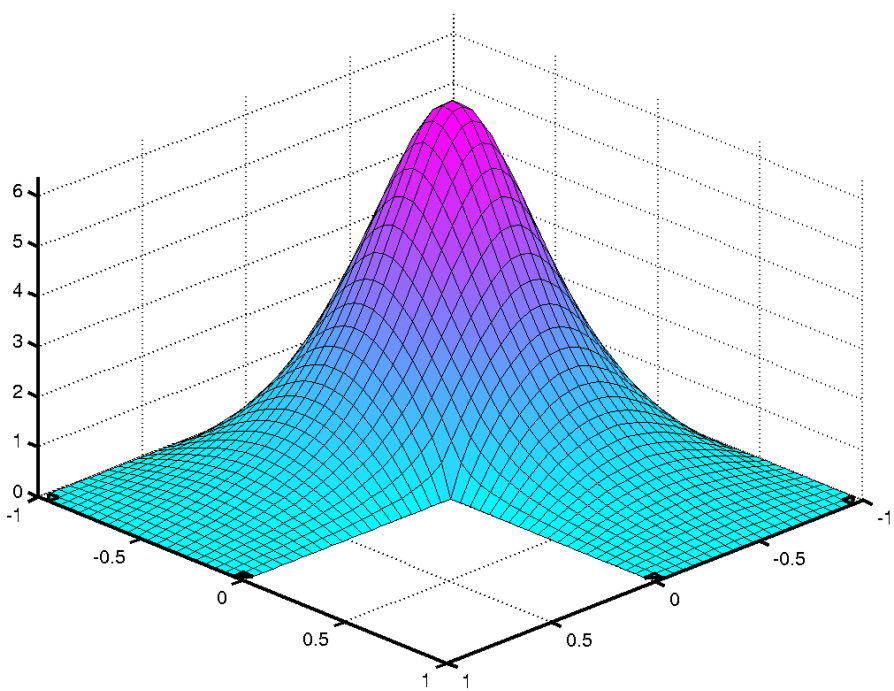
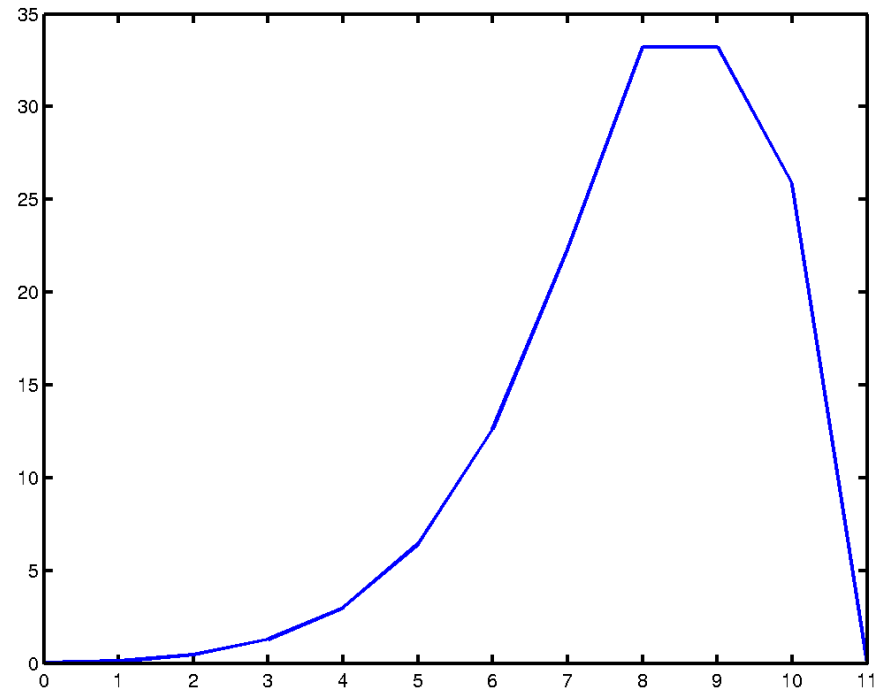
Mountain-Passes: The Henon Problem (Structured Mesh)

$$\int_{\mathcal{D}} \left(\frac{1}{2} \|\nabla u(s)\|^2 - \frac{1}{4} \|s\| u(s)^4 \right) ds$$





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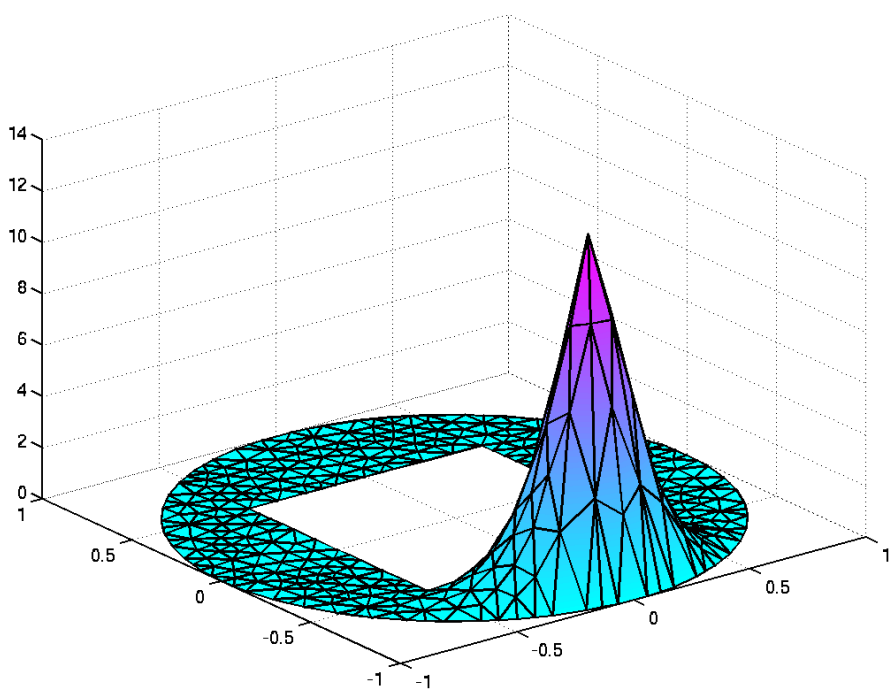
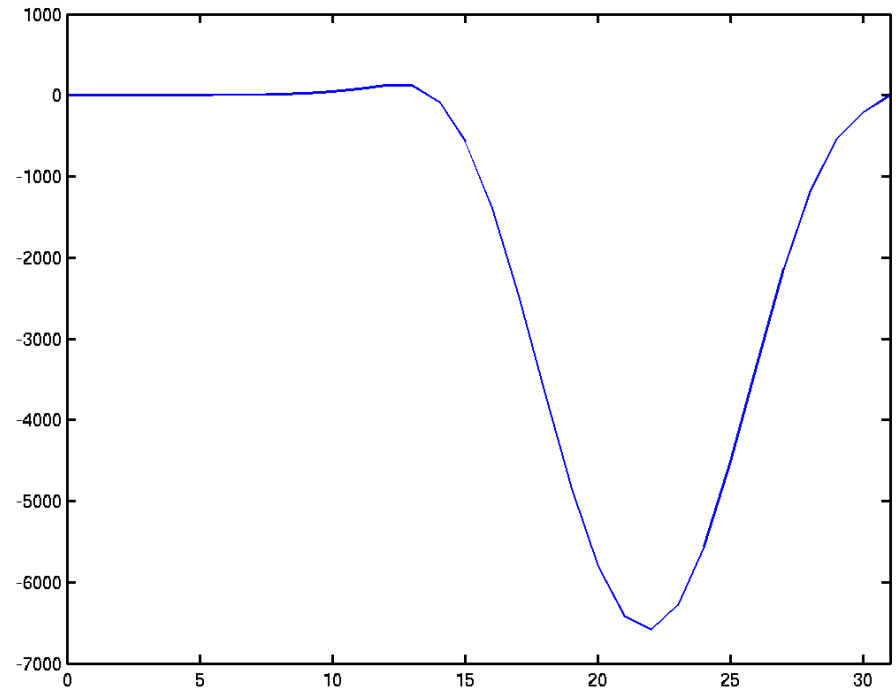
Mountain-Passes: The Henon Problem (Un-Structured Mesh)

$$\int_{\mathcal{D}} \left(\frac{1}{2} \|\nabla u(s)\|^2 - \frac{1}{4} \|s\| u(s)^4 \right) ds$$





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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, ...