The Use of Newton Trajectories in MechanoChemistry and Catalysis

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Last year we detected that Newton trajectories are an important tool for Mechanochemistry.
Under a pull one has two anchor atoms where a force is added.
An enzyme acts by an electrostatic force.

Abstract

The talk starts with the definition of Newton trajectories (NT).[1]

On an NT, at every point the gradient of the potential energy surface (PES) points into the same direction.

Definitions of NTs and different calculation methods are reviewed.[2]

NTs connect stationary points of the PES, thus, they can be used to find saddle points.

Another important property of NTs is: they bifurcate at valley-ridge inflection points (VRI).

The problem to find unsymmetric VRIs is solved by a variational theory ansatz.[3]

Second part:

We apply NTs to Mechanochemistry and Catalysis:

NTs describe the movement of stationary points on an effective PES under an external force.[4]

It can be a mechanical pulling or an electrostatic force of an enzyme.

[1] W.Quapp, M.Hirsch, O.Imig, D.Heidrich, J.Computat.Chem. 19 (1998) 1087;

W.Quapp, M.Hirsch, D.Heidrich, Theor.Chem.Acc. 100 (1998) 285

[2] W.Quapp, J.Theoret.Computat.Chem. 2 (2003) 385, and 8 (2009) 101

[3] W.Quapp, Theor.Chem.Acc. 121 (2008) 227; and 128 (2011) 47, 132 (2012) 1305 (with B.Schmidt)

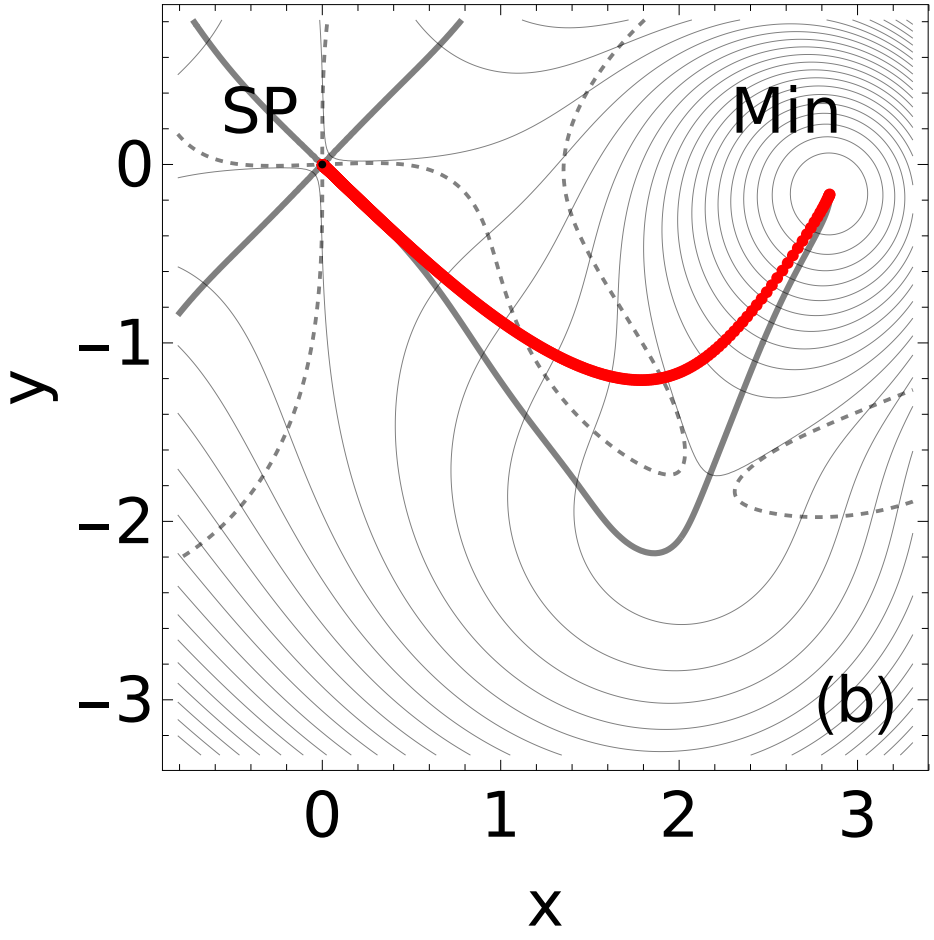
[4] W.Quapp, J.M.Bofill, J.Phys.Chem. B 120 (2016) 2644; Theor.Chem.Acc. 135 (2016) 113

and J. Computat. Chem. 37 (2016) 2467

In the next two slights I show for Your imagination three kinds of curves on a surface:
Gradient extremal and steepest descent, and Newton trajectories.
The surface has central a quasi-shoulder. The dashed curves are the convexity-border: The steepest descent crosses here a ridge; but the Gradient extremal follows the minimum energy pathway.

Example 1

Gradient extremal (black) and IRC (red)

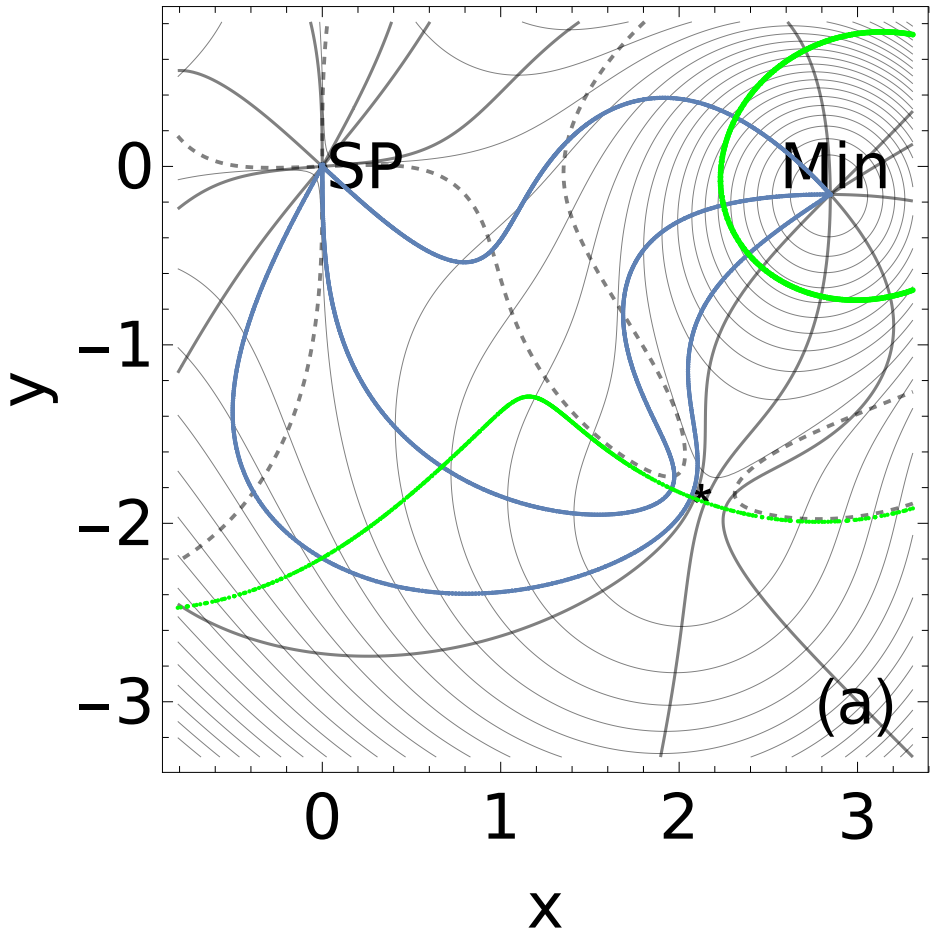


The IRC leaves the valley and goes over a ridge:
M.Hirsch, W.Quapp: Chem. Phys. Lett. 395 (2004) 150-156

On the next slight are some Newton trajectories. Along every NT, the gradient of the surface points into the same direction. Here, all the NTs have turning points of their energy. Thus they are not good reaction path models.
The green curve is discussed later.

Example 1

Some Newton Trajectories (blue)



Green is the BBP condition $det(\mathbf{H}) = 0$.

Definition

A Reaction Pathway (RP)

- Is a monotone way between Minimum and Transition State
- It looks nice if going through a valley of the PES
- It would be nice if indicating bifurcations of the valley

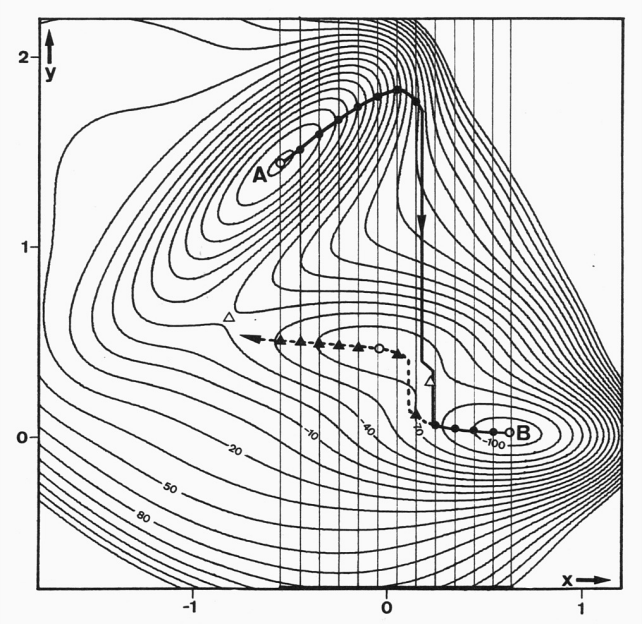
A synonyme for RP would be Minimum Energy Path.
From the point of view of practical calculations, it would also be helpful if we could calculate the RP beginning at the minimum.

Examples

- Steepest descent from SP, IRC
- Gradient Extremal
- Newton Trajectory

Note: none of the examples fulfills all properties, in all cases.
Thus, we can treat different RP-Examples on an equal footing.

- Historical Source: Distinguished Coordinate
  Choose a driving coordinate along the valley of the minimum, go a step in this direction, and perform an energy optimization of the residual coordinates.
  - This leads to problems if the valley ends . . .
  - The Distinguished Coordinate jumps



Alternative

- Use another definition: Newton Trajectory.

- Historical Source: Distinguished Coordinate
  Choose a driving coordinate along the valley of the minimum, go a step in this direction, and perform an energy optimization of the residual coordinates.
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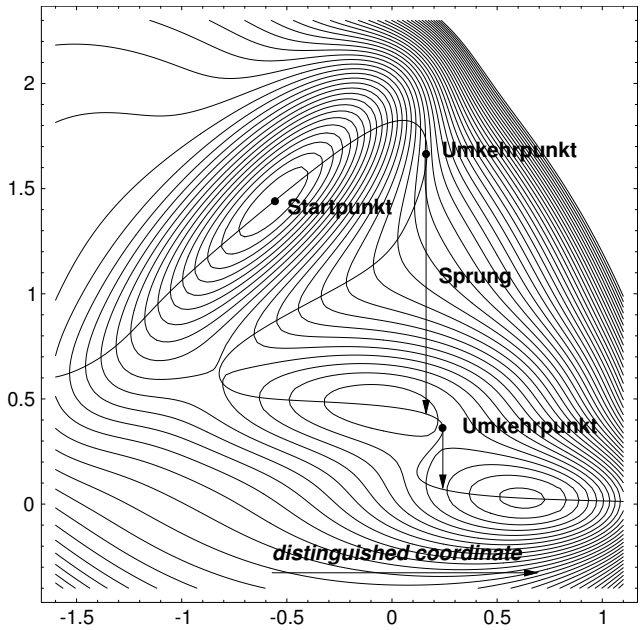


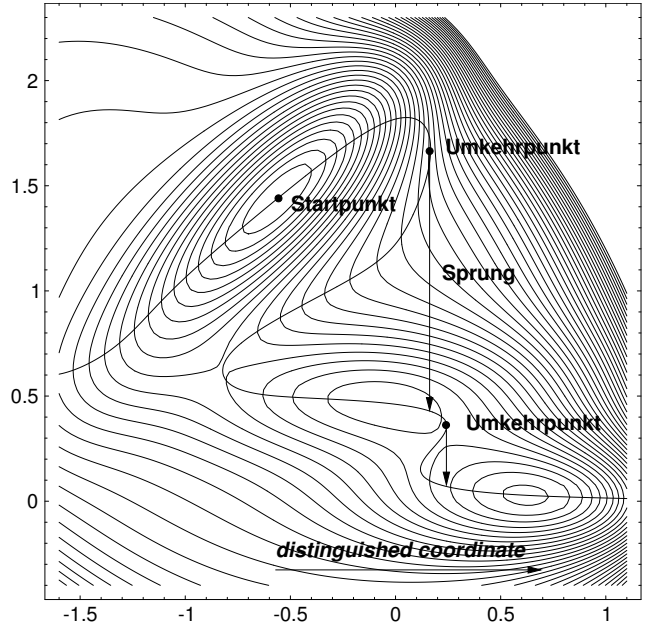
Alternative

- Use another definition: Newton Trajectory.

The first use of NTs in Chemistry was named distinguished coordinate.
The famous Müller-Brown surface was constructed to demonstrate the difficulties of this method.
The correct use of the NT-definition solves the jump-problem of the old distinguished coordinate method:
The jump point convertes into a turning point.

Definition of Newton Trajectory

- W. Quapp M. Hirsch O. Imig D. Heidrich, J Comput Chem **19** 1998, 1087-1100, "Searching for Saddle Points of Potential Energy Surfaces by Following a Reduced Gradient"
- W. Quapp M. Hirsch D. Heidrich, Theor Chem Acc **100** (1998) No 5/6, 285-299 "Following the streambed reaction on potential-energy surfaces: a new robust method"



- Chose a Search Direction **r**.
- Build the Projector Matrix $\mathbf{P}_r = \mathbf{I} - \mathbf{r}\,\mathbf{r}^T$ where **r** is a unit vector.
- Search the Curve $\mathbf{P}_r\,\mathbf{g} = 0$. It is the Newton Trajectory.

Predictor-Corrector Method I

Predictor

- Go along the tangent of the Newton trajectory

$$\mathbf{0} = \frac{d}{d\,s}[\mathbf{P_r}\,\mathbf{g}(\mathbf{x}(s))] = \mathbf{P_r}\,\frac{d\,\mathbf{g}(\mathbf{x}(s))}{d\,s} = \mathbf{P_r}\,\mathbf{H}(\mathbf{x}(s))\,\mathbf{x}'(s)$$

  the tangent is $\mathbf{x}'$; note: $\mathbf{P_r}$ is a constant $n \times n$ matrix.

Corrector

- Use the Newton-Method, jump back to the Curve

Both of the steps need the Hessian of the PES, or updates of it.

- The method was included in 3 top level quantum chemistry packets: in MOLPRO, COLUMBUS, and TURBOMOL.
- The method was accelerated by the TASC-method
  W.Quapp, M.Hirsch, D.Heidrich: TCA 105 (2000) 145-155;
  see also M.Hirsch, W.Quapp: JCC 23 (2002) 887

Predictor-Corrector Method II

TASC-method

- Use the tangent of the Newton trajectory for the next search direction **r**.

The result is a Gradient Extremal (GE).

- Quapp, Hirsch, Heidrich: Theor. Chem. Acc. 105 (2000) 145

Definition of a GE

- At every point the gradient of the PES is an eigenvector of the Hessian.

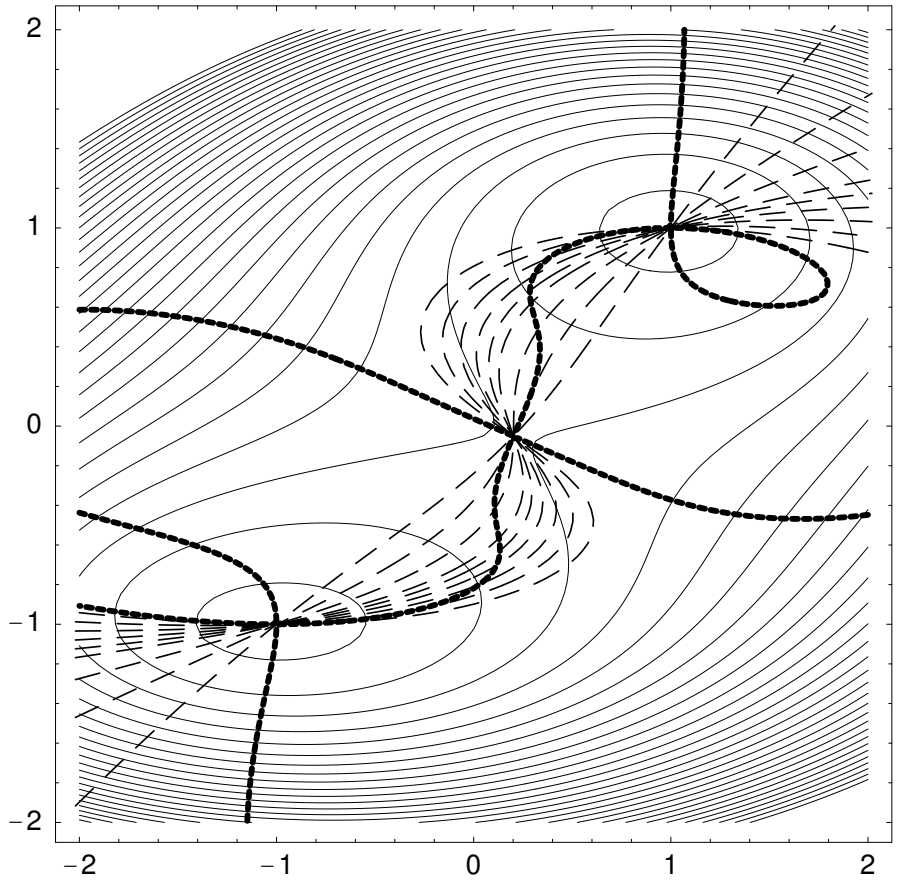
$$\mathbf{H}\,\mathbf{g} = \lambda \mathbf{g}$$

  and λ is the corresponding eigenvalue.

- D.K.Hoffman, R.S.Nord, K.Ruedenberg: TCA 69 (1986) 265-279.
  "Gradient Extremals"
- W.Quapp: TCA 75 (1989) 447-460.
  "Gradient Extremals and Valley Floor Bifurcations on PES"

Gradient Extremal (GE)

At every point the gradient of the PES is an eigenvector of the Hessian: $\mathbf{H}\,\mathbf{g} = \lambda\,\mathbf{g}$, and λ is the Eigenvalue.



The fat curves are the GEs,
they are fixed curves.
The thin dashes are NTs.
They form a field.

NTs indicate Bifurcations of the Valley

- NTs have a second definition by a differential equation

$$\frac{d\mathbf{x}(t)}{dt} = \pm\, \mathbf{A}(\mathbf{x}(t))\ \mathbf{g}(\mathbf{x}(t))$$

  named the Branin equation.
  It uses the adjoint matrix **A** of the Hessian **H**,
  which is $[(-1)^{i+j}\, m_{ij}]^T$, where m_{ij} is the minor of **H**.
  It is $\mathbf{A}\ \mathbf{H} = Det(\mathbf{H})\ \mathbf{I}$.

- The singular points of the equation are zeros of
  $\mathbf{A}(\mathbf{x})\ \mathbf{g}(\mathbf{x}) = 0$, thus
  (i) stationary points, if also $\mathbf{g}(\mathbf{x}) = 0$, or
  (ii) valley-ridge inflection points (VRI), if $\mathbf{g}(\mathbf{x}) \neq 0$

If $\mathbf{A}(\mathbf{x})\ \mathbf{g}(\mathbf{x}) = 0$ and $\mathbf{g}(\mathbf{x}) \neq 0$, then an eigenvector of the Hessian to eigenvalue zero is orthogonal to the gradient.

Branin is the desingularized, continuous Newton equation

- A Newton step is

$$\mathbf{x}_1 = \mathbf{x}_0 - \mathbf{H}^{-1}(\mathbf{x}_0)\, \mathbf{g}(\mathbf{x}_0)$$

- One may change this difference into a differential equation, the continuous Newton equation

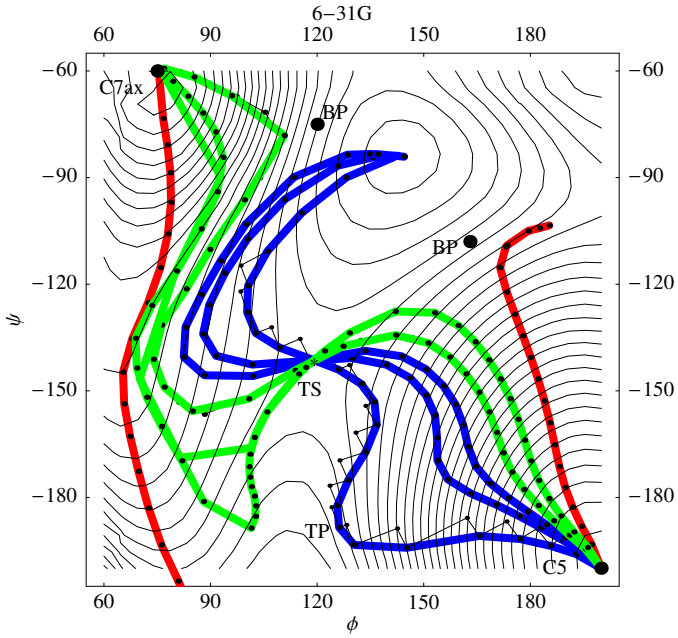
$$\frac{d\mathbf{x}(t)}{dt} = -\mathbf{H}^{-1}(\mathbf{x}(t))\, \mathbf{g}(\mathbf{x}(t)$$

- However, the inverse Hessian is singular, if the Hessian has a zero determinat. The way out is a desingularization of the differential equation

$$\frac{d\mathbf{x}(t)}{dt} = -Det(\mathbf{H}(\mathbf{x}(t))\, \mathbf{H}^{-1}(\mathbf{x}(t))\, \mathbf{g}(\mathbf{x}(t))$$

String Method

- Chose an initial Chain between two Minimums.
- Change the Chain by a controlled Newton-Method, step by step, back to the searched Newton Trajectory.



The colored curves are different NTs (W.Quapp, JTCC 8, (2009) 101-117

"The growing string method for flows of NTs by a second order corrector")

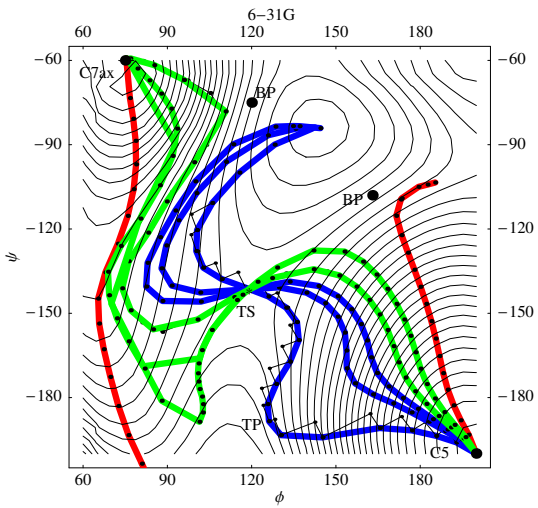
The PES concerns Alanine-Dipeptide: $CH_3CO\text{-}NHCHCH_3CO\text{-}NHCH_3$

The dimension is (3N-6)=60, N=22 atoms

One of the blue NTs shows Predictor- and Corrector steps

Effort for the String Method

- Example Alanine-Dipeptide, 60 internal coordinates, (2 dihedrals fixed, thus 58 coordinates optimized)
- Used: GamesUS on PC, DFT calculations B3LYP/6-31G basis set
- Number of chains calculated: 9
- Number of nodes per chain: 30
- Number of corrector steps per node: 2-3



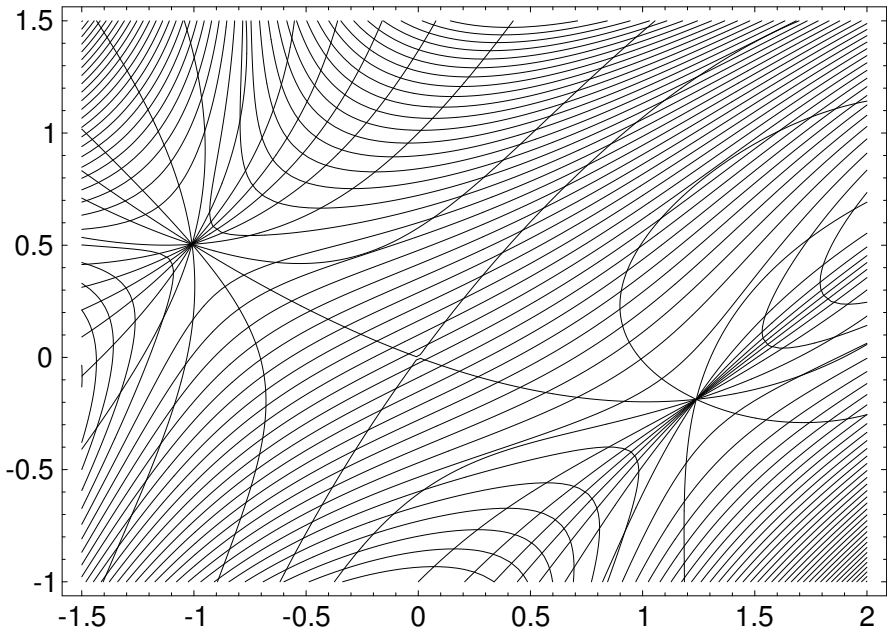
With such a nice convergence velocity, one can calculate many nodes per chain, and many NTs at all,
so to say, a flow of NTs.

The Index Theorem

Index Theorem: Let **a** and **b** be stationary points connected by a regular Newton trajectory. Then it holds

$$index(\mathbf{a}) \neq index(\mathbf{b}) ,$$

and the difference is one.



Regular NTs connect a SP (index 1) and a minimum (index 0).
The PES shows two adjacent SPs of index one.
There is no regular NT connecting the SPs.
Between the SPs a VRI point has to exist.
One singular NT leads to the VRI point and branches there.

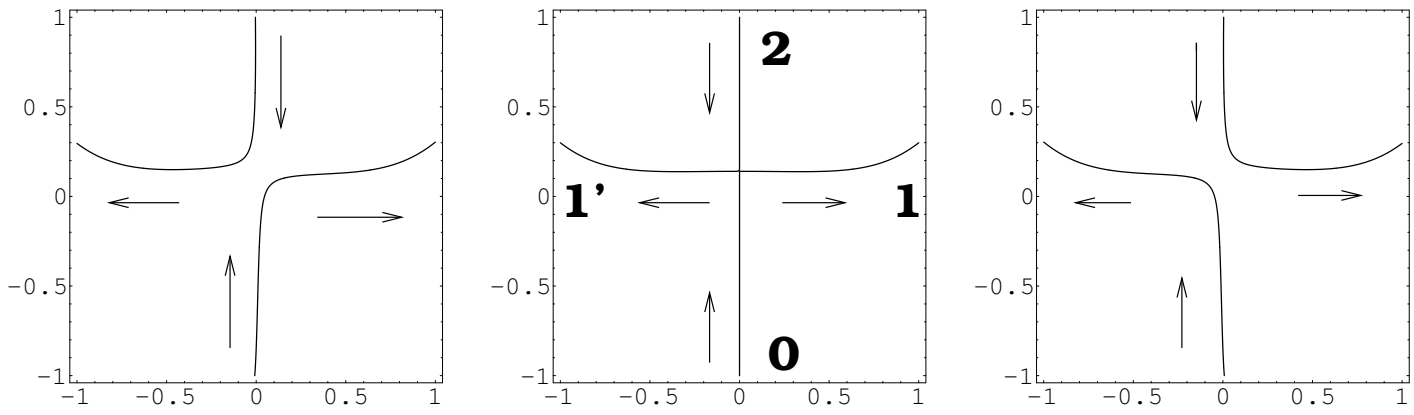
Hirsch, Quapp: JMSt THEOCHEM 683 (2004) 1

Two consecutive saddles can be connected only by a singular Newton trajectory which crosses a valley-ridge inflection (VRI) point.

Index Theorem: Let **a** and **b** be stationary points connected by a regular Newton trajectory. Then it holds

$$index(\mathbf{a}) \neq index(\mathbf{b}) ,$$

and the difference is one.



Regular NTs Singular NT Regular NTs

At the bottom may be a minimum, at the top an index-2 SP, and left and right may be an index-1 SP.

The VRI point divides the two families of NTs to the two index-1 SPs.

Mechanochemistry and Catalysis

Apply a pulling force **f** to the PES:
the generally accepted model consists in a first order perturbation on the PES of the unperturbed molecular system due to a catalytic or pulling force by

$$V_f(\mathbf{r}) = V(\mathbf{r}) - \mathbf{f}^T(\mathbf{r} - \mathbf{r}_o)$$

V_f is named the effective PES. The disarrangement of the stationary points of the new effective PES is described by NTs: The stationary points are given by the zero of the derivation

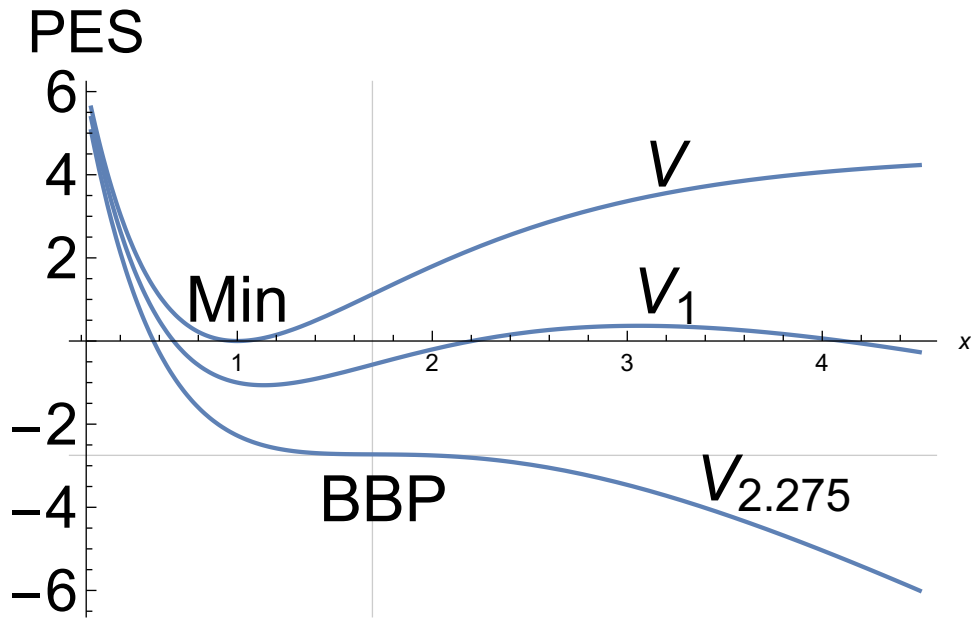
$$\nabla_{\mathbf{r}} V_f(\mathbf{r}) = \mathbf{0} = \mathbf{g} - \mathbf{f}$$

g is the gradient of the PES. One searches a point where the gradient of the original PES has to be equal to the force, **f**. If **f** points always into the same direction then the solution is an NT.

Apply a force to a molecule: it means apply the force also to the PES.

Example 1

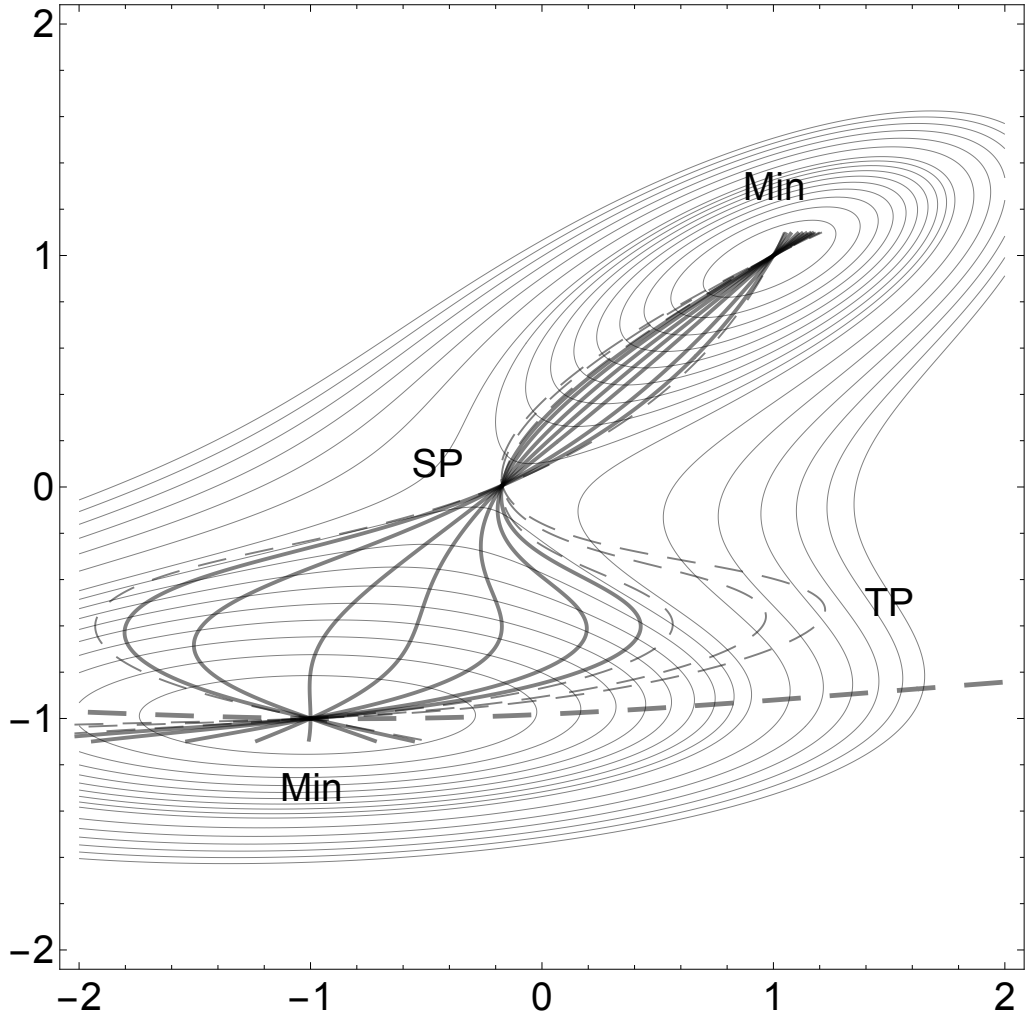
To start with we treat a one-dimensional case.



1D Morse potential over the *x*-axis: the upper curve. Below are two effective potential curves with increasing forces. The minimum moves to increasing *x*-values, where the SP moves to decreasing values. The lowest potential is the final case: minimum and SP coalesce to a shoulder. The former barrier is broken. The point is named barrier breckdown point (BBP).

Example 2

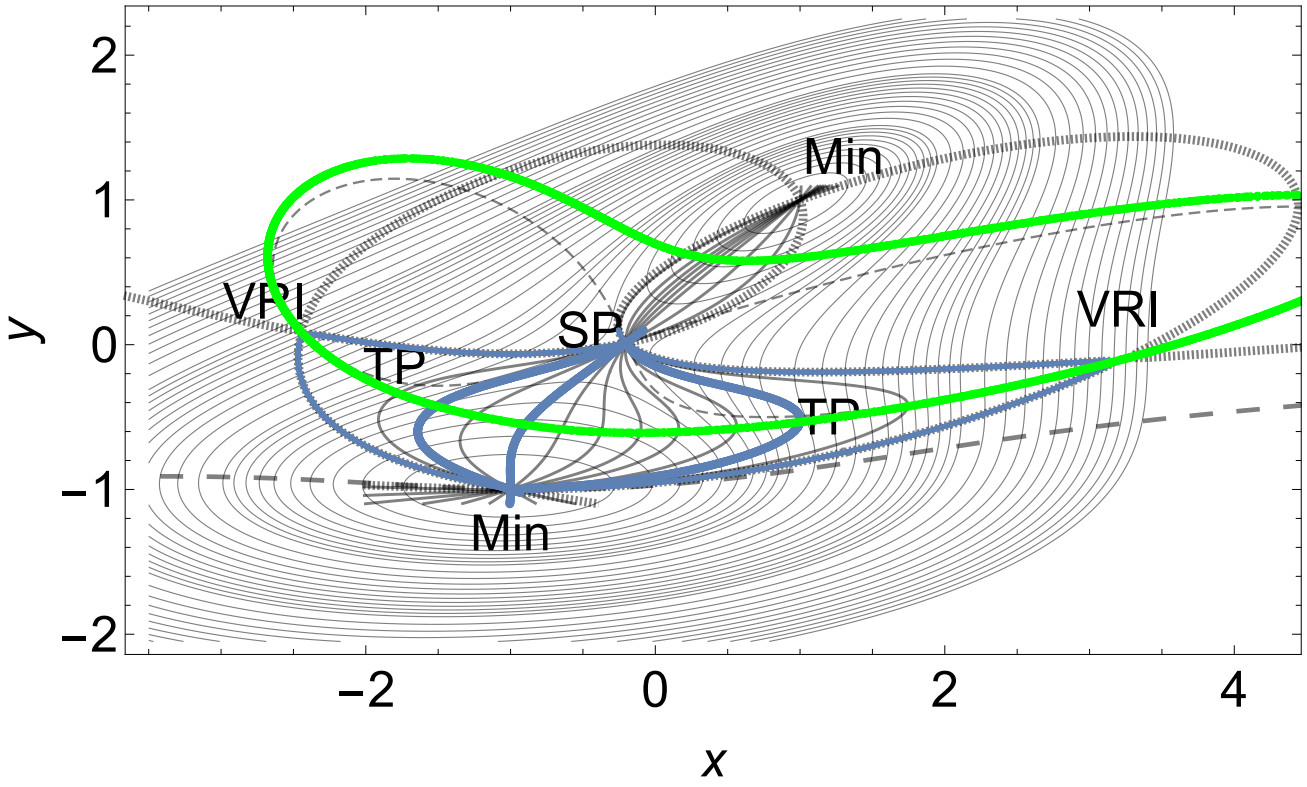
Let be two minimums connected by regular NTs over an SP.



Pulling into a defind direction uses a respective NT for the movement of minimum and SP. The arc of the NT can be of different length. Thin dashed NTs have a turning point (TP): pulling along such NTs is possible.

Example 2

We include a green BBP line whith Det(**H**)=0 (barrier break).[1]

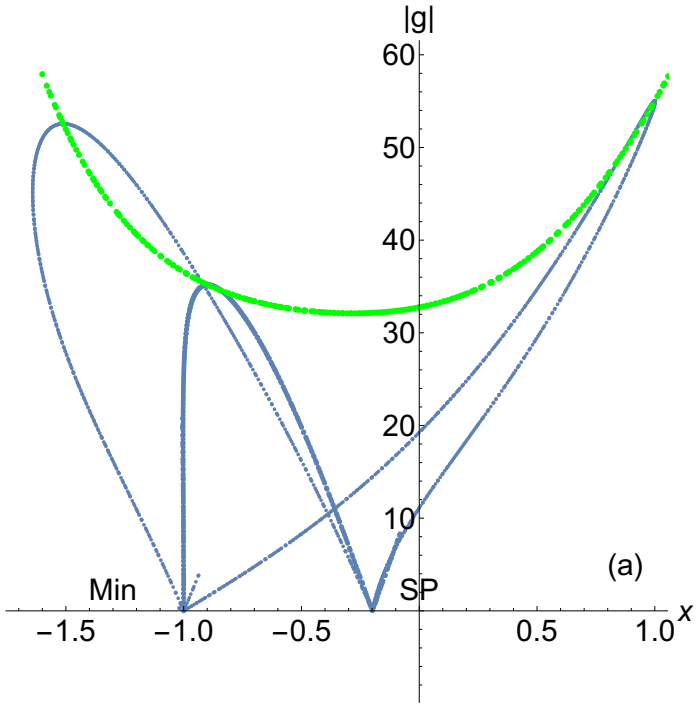


The energy, as well as the gradient norm variate on the green line.

[1] Konda, Avdoshenko, Makarov, J.Chem.Phys. **140** (2014) 927,
Quapp, Bofill, Theoret. Chem. Acc. **135** (2016) 113.

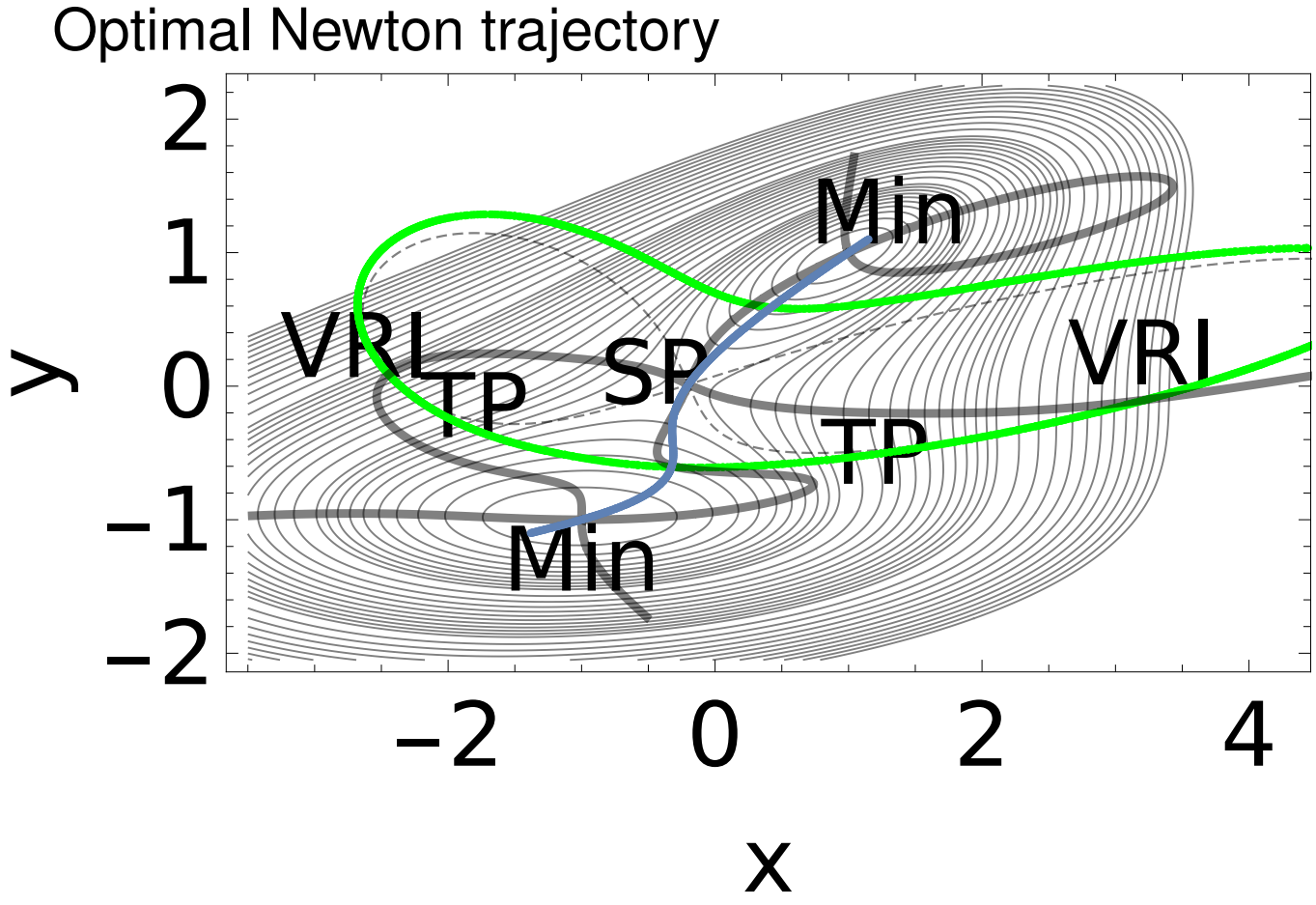
Example 2

Norm of the gradient over three inner NTs (thick blue curves).



The gradient norm variate with the crossing of the green line:
there must be a minimum: the optimal BBP.

Example 2

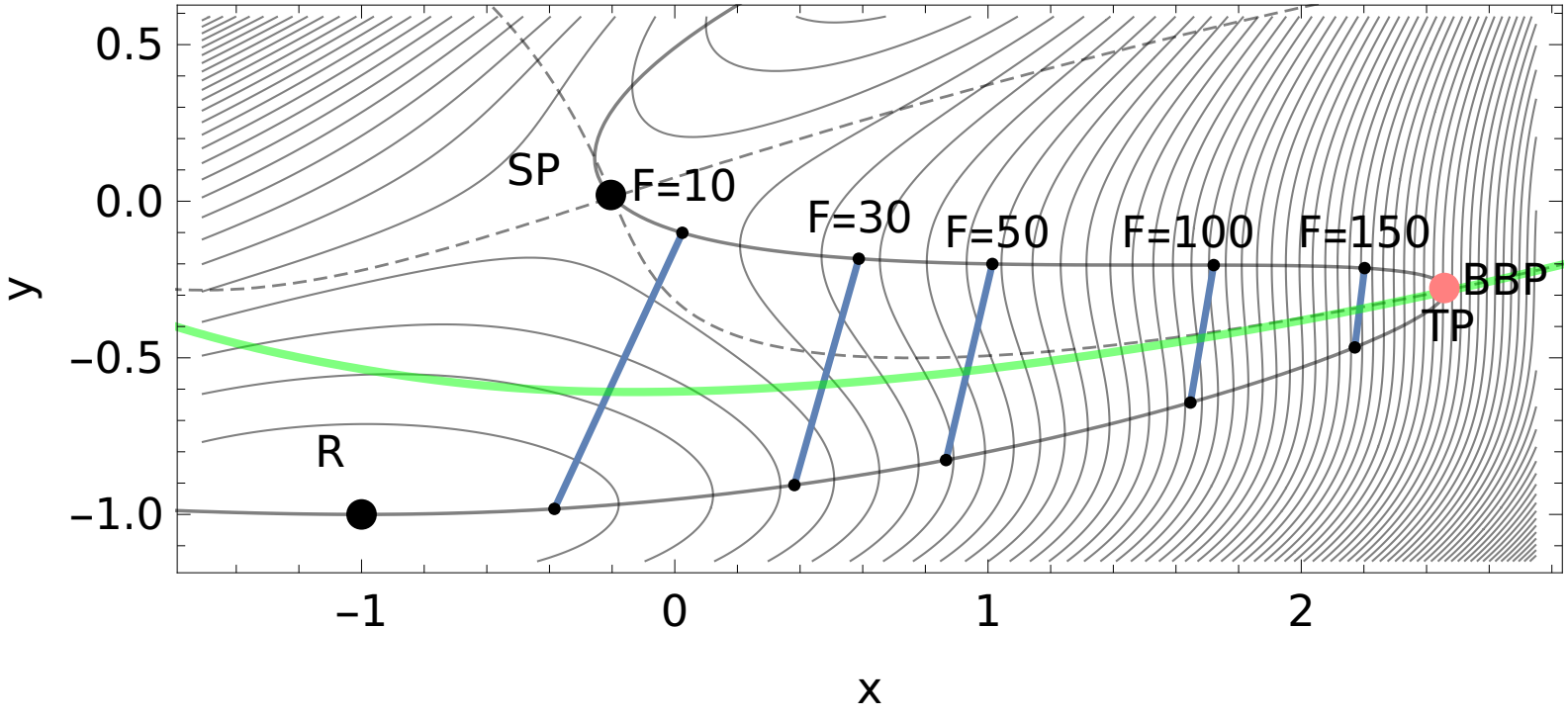


A special regular NT (blue) and a Gradient Extremal (thick black) cross the green line at the same point. This point is the BBP with lowest $|\mathbf{g}|$ with respect to the others NTs crossing the green line. The regular NT indicates the optimal pulling direction.

Proof: Quapp / Bofill, TCA **135** (2016) 113

Example 2

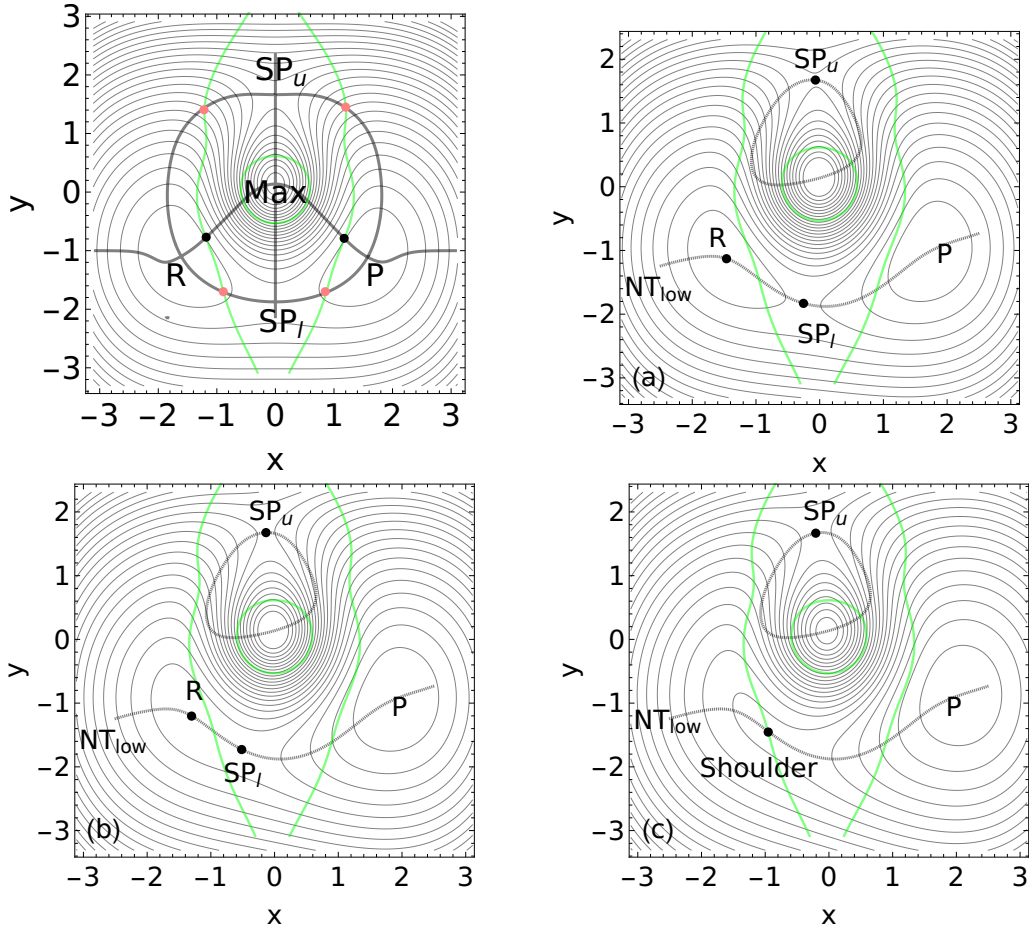
Extreme case of a regular NT with a turning point (TP).



The NT goes from minimum R over a TP and along a ridge back to the SP.
The red point is its BBP.
The effective stationary points are black points.
The sticks are the connections between the
effective SPs (above on the ridge) and the
effective minimums (below in the valley) at the forces, F.

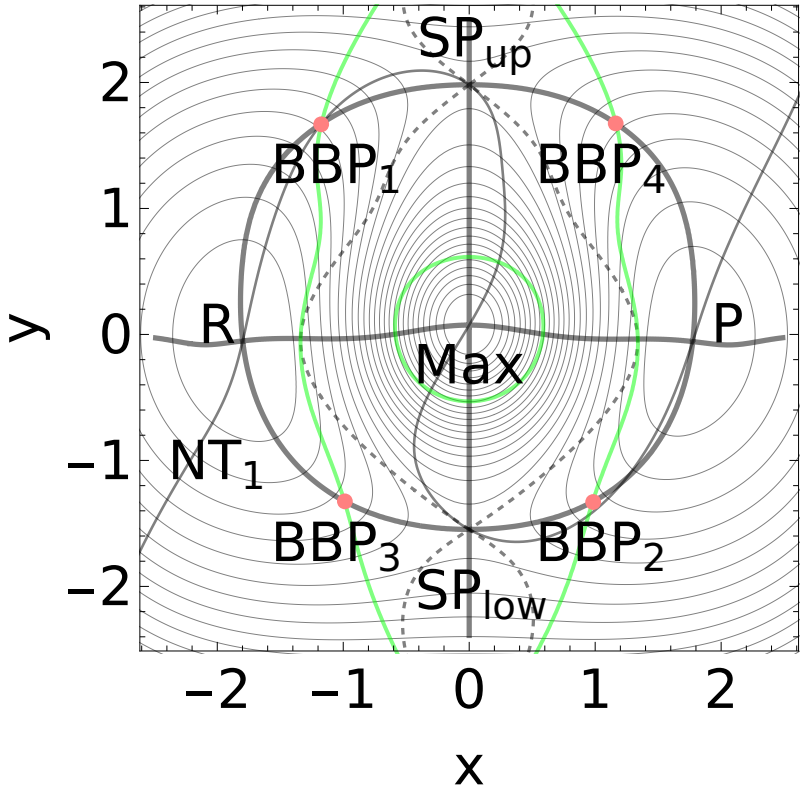
Example 3a

Development of effective PESs



Left above F=0.0, original PES with GE and optimal BBPs (red points).
(a)-(c): Effective PESs for **f**=F **l** with pull direction **l**=$(0.98,0.18)^T$ and
(a) F=1.4, (b) F=2.8, and (c) F=4.25 force along the same NT.
The R_{eff}, $SP_{l,eff}$ and $SP_{u,eff}$ are marked by black points.

Example 3b



GEs (fat) on a surface with 2 pathways. Crossings (red points) with the green lines are optimal BBPs. The optimal NT for a pulling over SP_{up} is NT_1. It intersects the left upper BBP_1. A pulling moves R and SP_{up} together, but it moves also Max and SP_{low} together. Thus, the hight of SP_{up} decreases, but of SP_{low} increases.

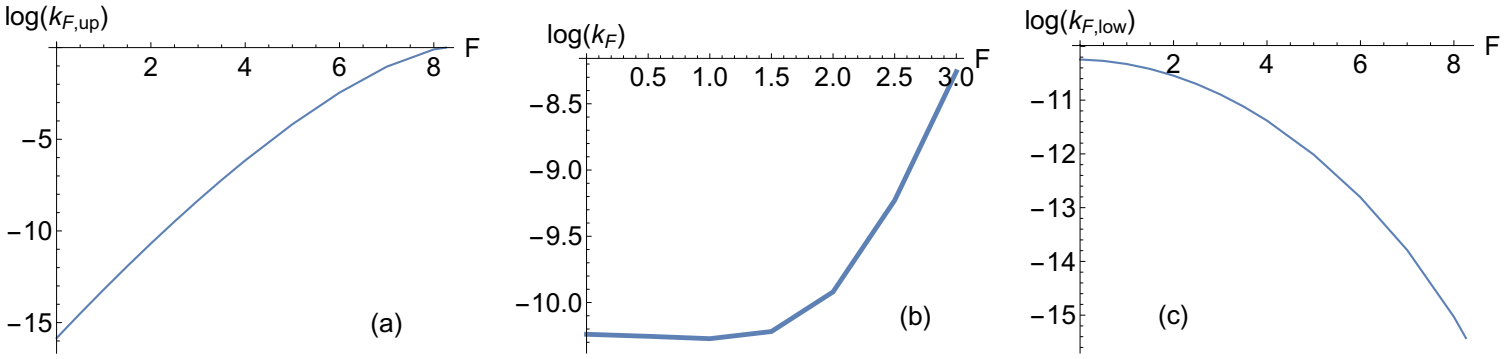
A pull to the upper saddle along NT_1 can circumvent the Woodward-Hoffman rules: it drives the reaction over the heigher saddle point.
NT_1 is here the optimal NT. On this NT, the minimum R and the SP_{up} move together.
However, the NT goes after the SP_{up} over the maximum to SP_{low}, and then to the product minimum, P.
This is allowed by the Index Theorem.
Inverting this pulling causes a hysteresis.
The pull along NT_1 makes that the height of SP_{up} decreases, however that of SP_{low} increases.
In the next slight are shown the reactivity consequences.

Example 3b

Reaction Rates:

$$k_{F,up} = k_{o,up}\, Exp[-(V_F(SP_{up}) - V_F(Min))/kT]$$

$$k_{F,low} = k_{o,low}\, Exp[-(V_F(SP_{low}) - V_F(Min))/kT]$$



Eyring rates for the pulling force in the direction of NT_1 uphill to the high SP_{up}.

Left (a): exit over SP_{up},

center (b) full rate of a reaction R→P, $k_F = k_{F,up} + k_{F,low}$

right (c): exit over SP_{low}.

See: Quapp / Bofill, JCC 37 (2016) 2467.

Summary: How to find a curve of Force Displaced Stationary Points, FDSPs?

- Describe the FDSPs by Newton Trajectories: it is tractable – in many practical cases.
- Find the BBP by Newton Trajectories: it is tractable.
- Find VRI-Bifurcations by special Newton Trajectories: it is tractable.

Acknowledgement

- I thank Prof. Josep Maria Bofill from Barcelona. The results presented here are born in discussions with him, and are published in the papers:
  WQ, JMB: J. Phys. Chem. B **120** (2016) 2644
  WQ, JMB: Theoret. Chem. Acc. **135** (2016) 113
  WQ, JMB: J. Computat. Chem. **37** (2016) 2467.

Thank You for Your interest !

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