The Use of Newton Trajectories in Theoretical Chemistry

Wolfgang Quapp

Mathematical Institute, University Leipzig, Germany

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Abstract

The talk starts with a discussion of problems of the definition of a reaction pathway, especially of the intrinsic reaction coordinate (IRC). We propose Newton trajectories (NT) for an alternative.[1]

An NT is a curve where at every point the gradient of the PES points into the same direction.

Definitions of NTs and different calculation methods are reported.[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). By simple 2D schemes we explain some methods used to find VRIs.

A further step are some theoretical extensions: NTs allow to explore the PES in relation to convex regions (valleys), or concave regions (ridges), as well as statements about the index of connected stationary points.

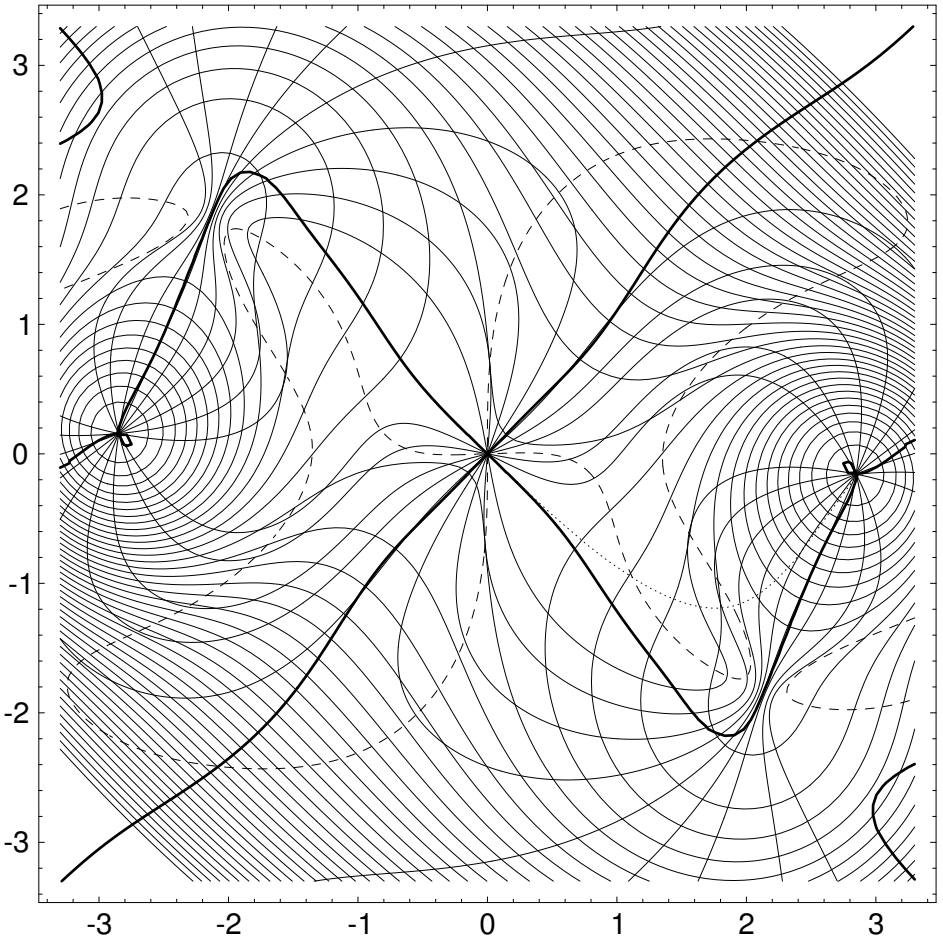
An outlook on future research concerns the problem to find unsymmetric VRIs by a variational theory ansatz.[3]

[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.

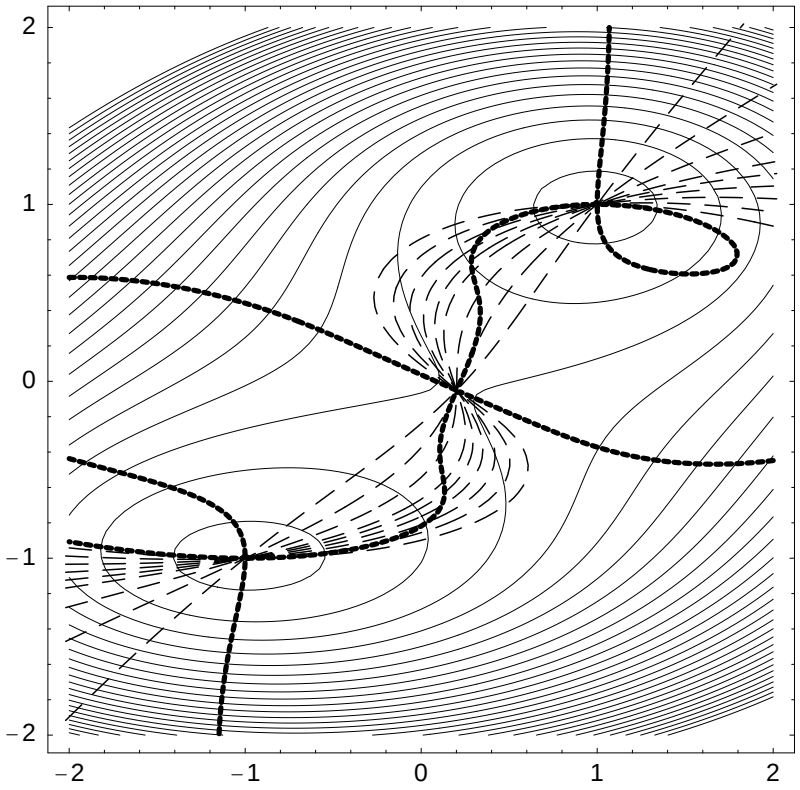
[3] W.Quapp, Theor.Chem.Acc. 121 (2008) 227.

Figure: Gradient extremal, IRC, and Newton Trajectories



What is a Reaction Path?

1. You hopefully know this after the talk. . .



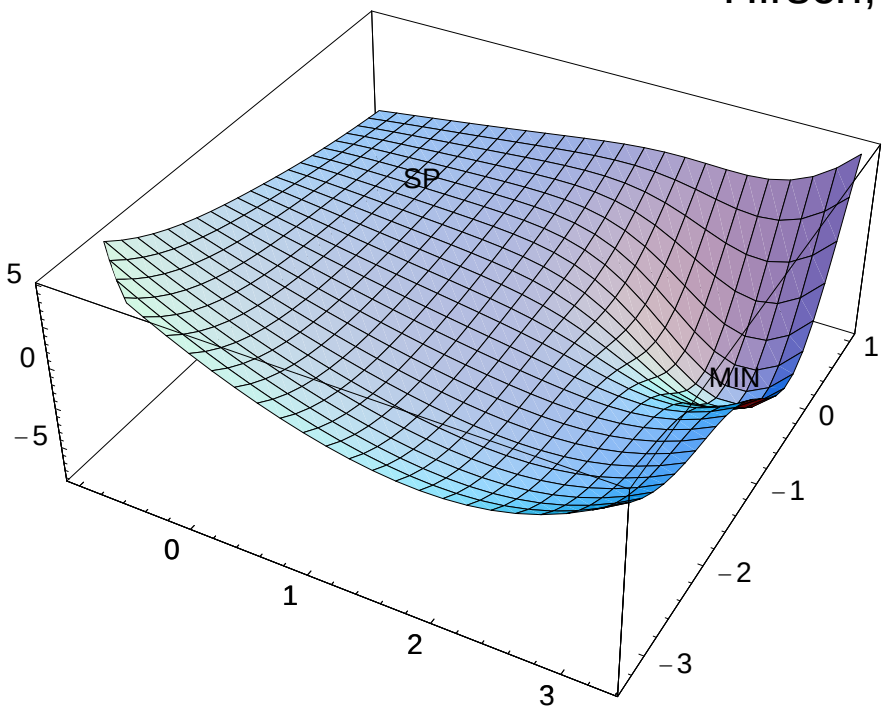
... a little better.

General problems of the steepest descent

IRC I

- $\frac{d\mathbf{x}(s)}{ds} = -\frac{\mathbf{g}(\mathbf{x}(s))}{|\mathbf{g}(\mathbf{x}(s))|}$, $\mathbf{g}$ is gradient, Start at SP
- Does not always follow the valley of the PES

Hirsch, Quapp, CPL 395 (2004) 150



(2D modified PES using the Neria, Fischer, Karplus-surface, see JCP 105 (1996) 1902)

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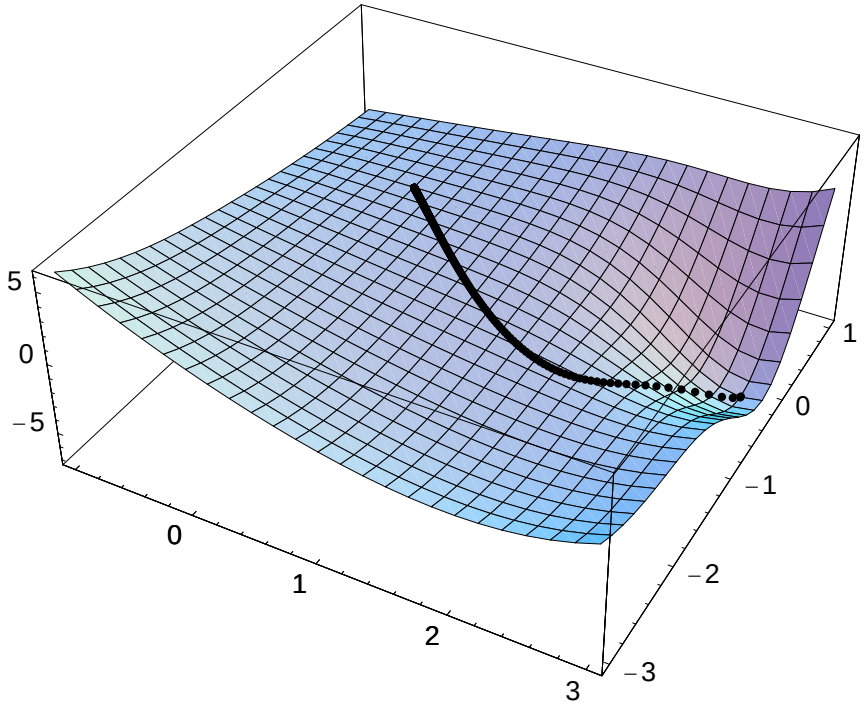

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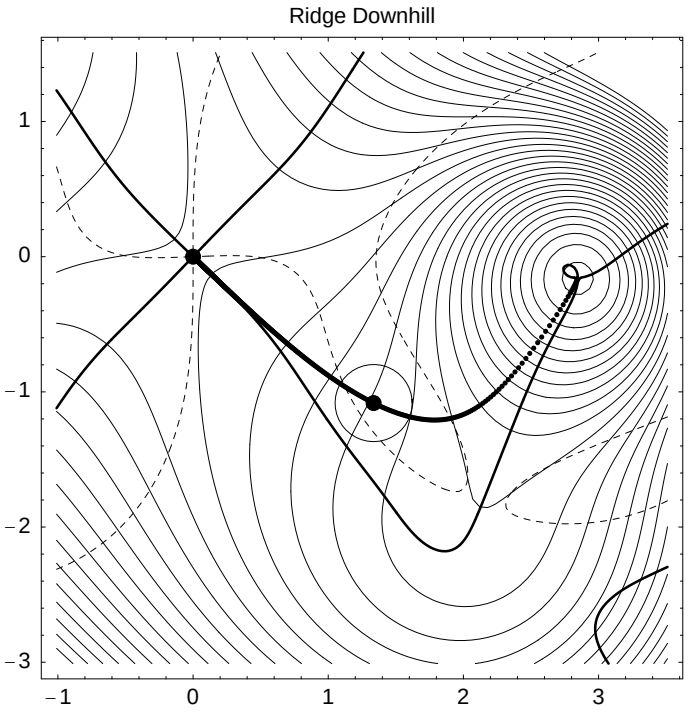

Hirsch, Quapp, CPL 395 (2004) 150

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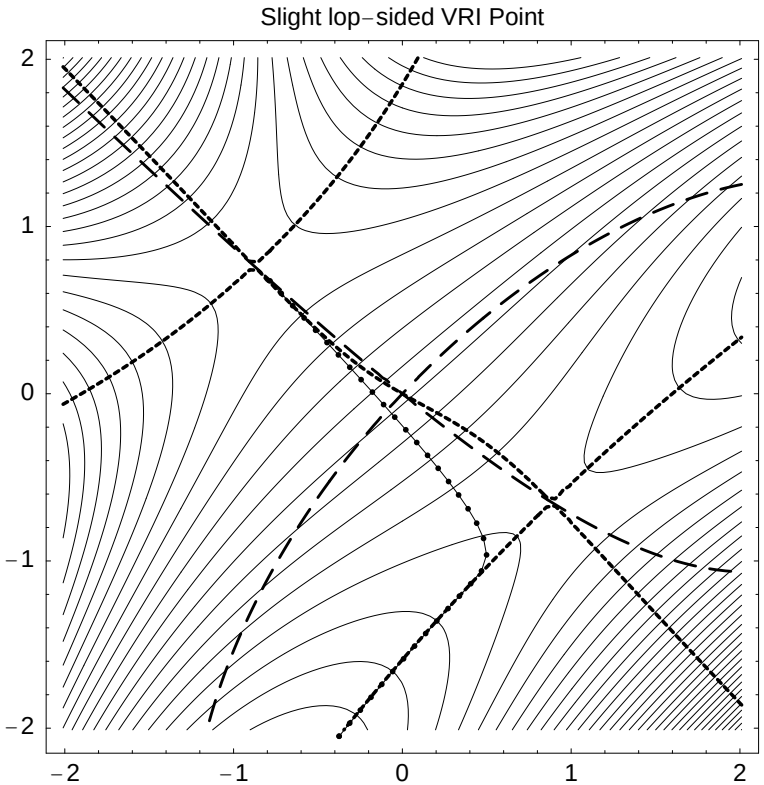
General problems of the steepest descent

IRC II

- IRC does not indicate bifurcations of a valley

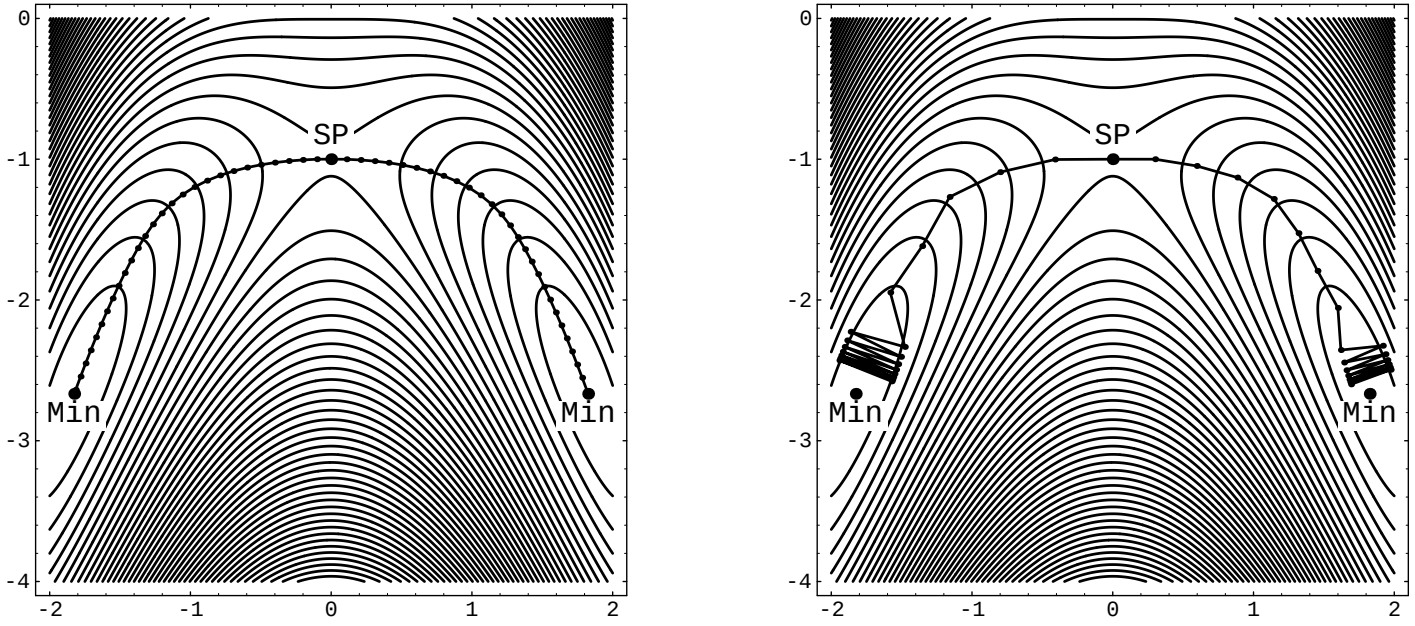


The dotted curve is the IRC.
It does not see the valle-ridge inflection point.

General problems of the steepest descent

IRC III

- $\mathbf{x}_{k+1} = \mathbf{x}_k - \lambda \frac{\mathbf{g}(\mathbf{x}_k)}{|\mathbf{g}(\mathbf{x}_k)|}$, λ any steplength
- Shows numerical zigzagging



Left: exact IRC, right: numerically determined IRC

(Fig. by Benjamin Schmidt)

Definition of 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.

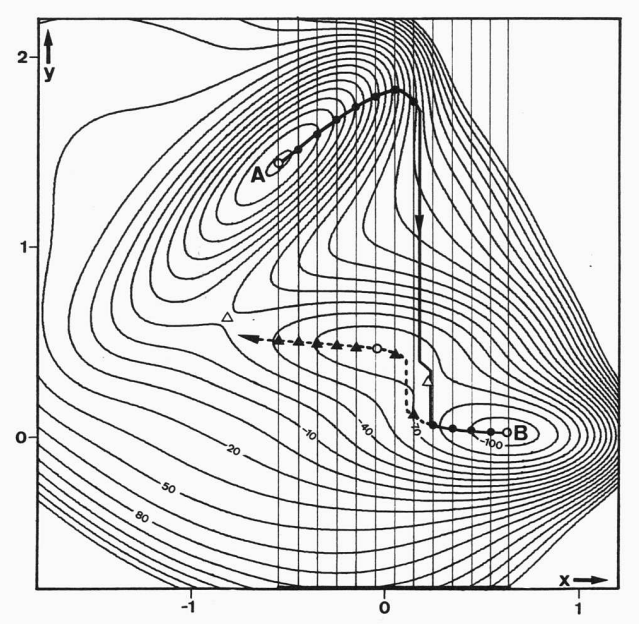
Examples

- 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.

Distinguished Coordinate

- 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.

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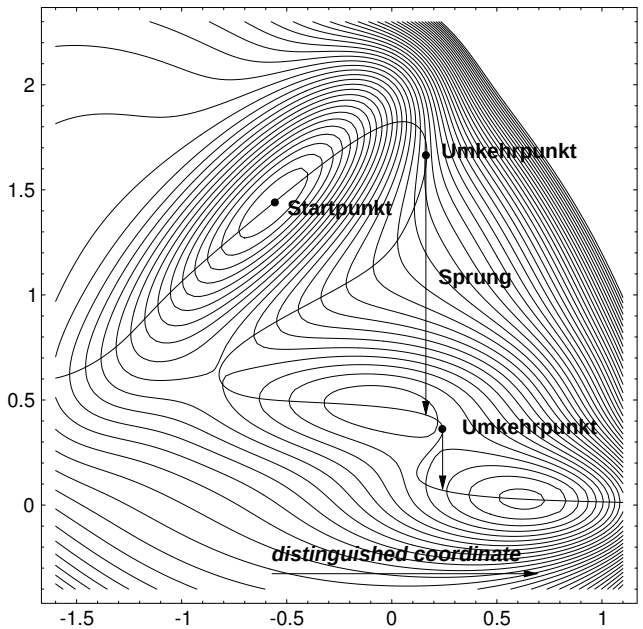

Alternative

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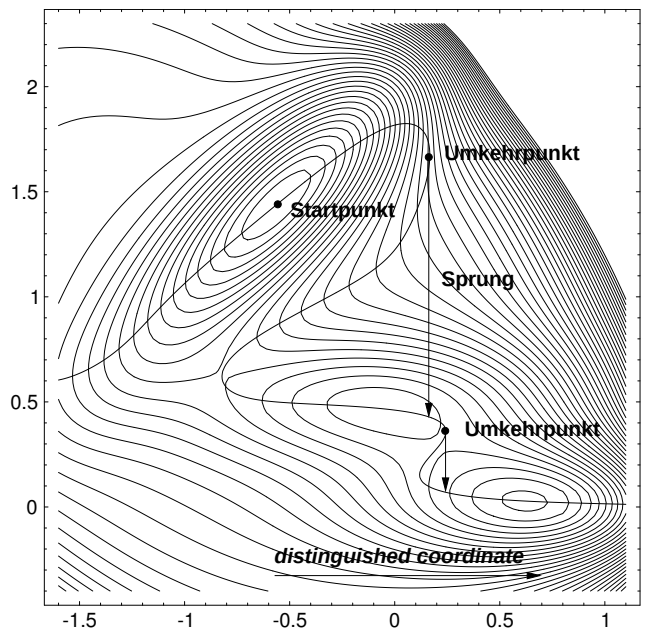
Definition of Newton Trajectory

- 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 $\mathbf{P}_r = \mathbf{I} - \mathbf{r}\,\mathbf{r}^T$
- 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).

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

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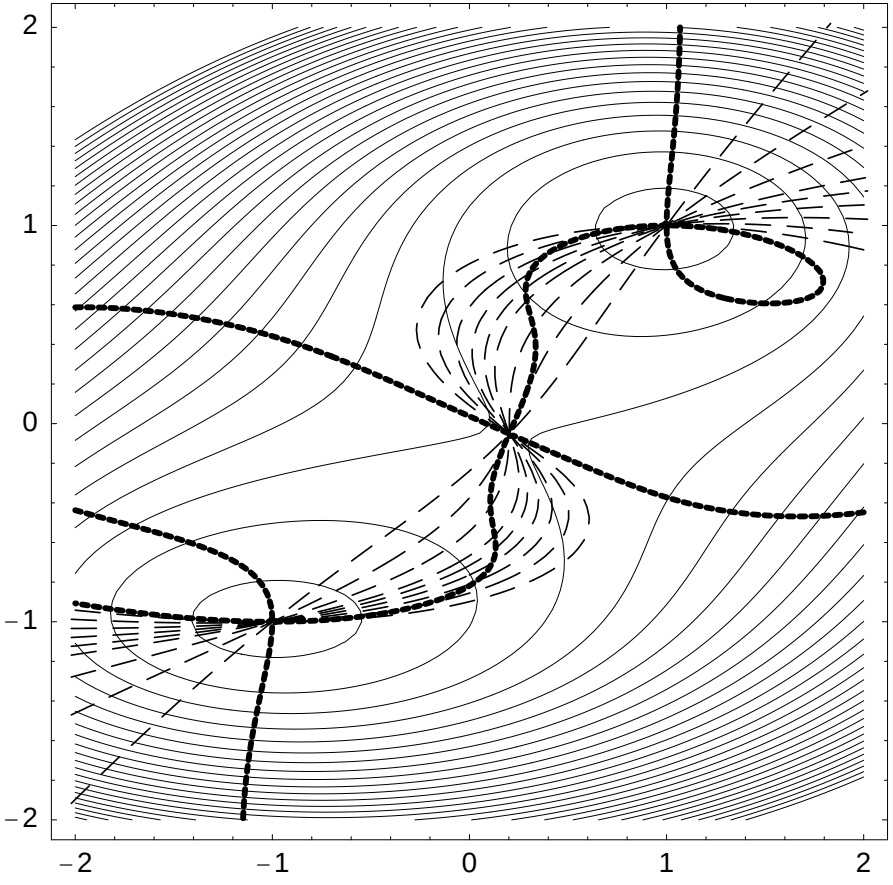
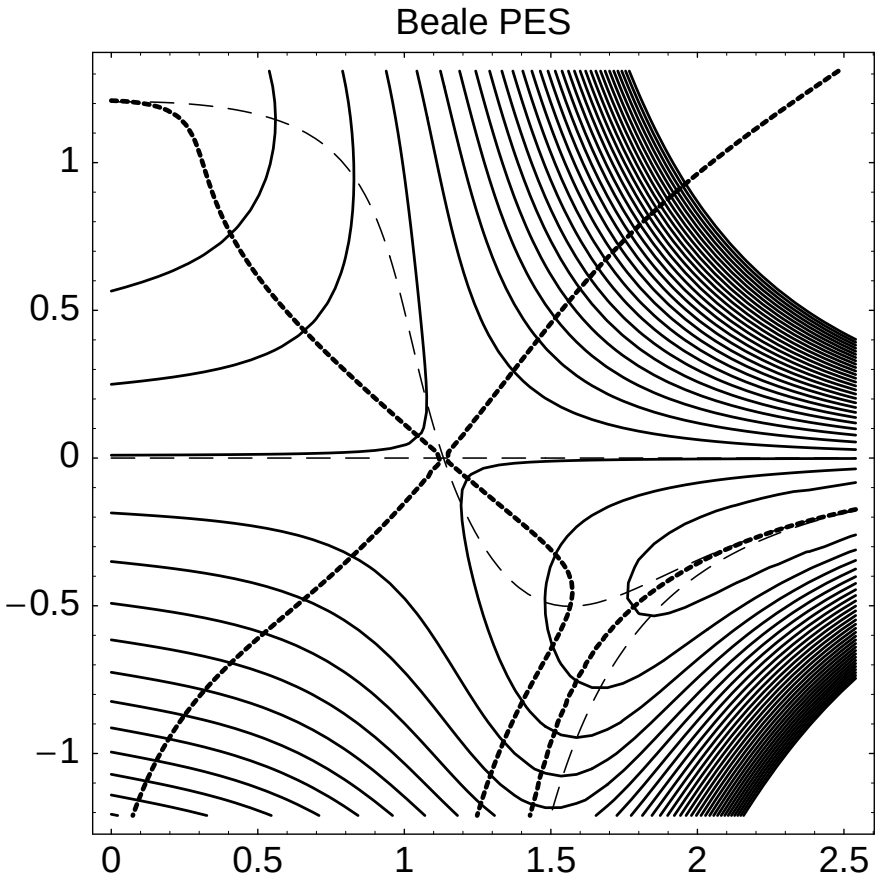


The fat curves are the GEs,
the thin dashes are NTs.

Gradient Extremal

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,
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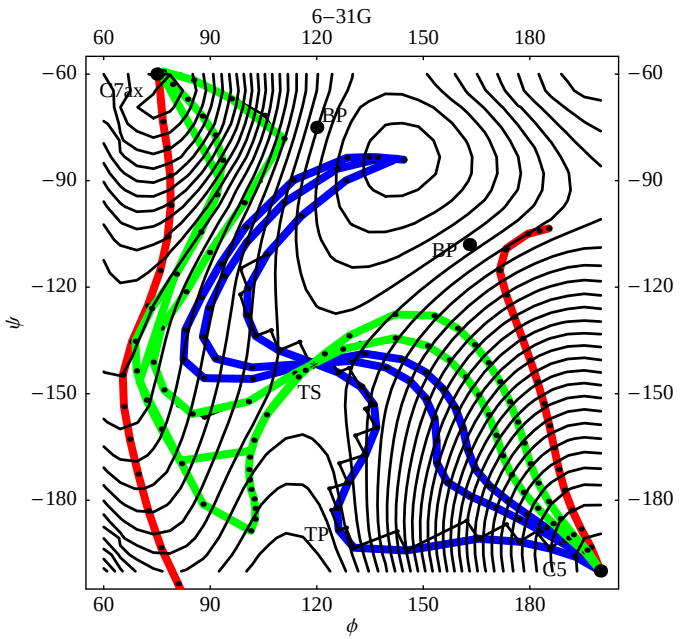
Applications of NTs: Reaction Pathways, TSs (Examples only)

- H.Valdes, J.A.Sordo et al.: CPL 309 (1999) 265, 333 (2001) 130, 392 (2004) 236 and JCC 24 (2003) 2044: Cl + nitrobenzene, Cl + propene
- K.Schiele, R.Hemmecke: ZAMM 81 (2001) 291: driven multiple pendula
- M.Dallos et al.: JCC 23 (2002) 576, JCP 118 (2003)1702, CPC 5 (2004) 1365, PP Columbus: formaldehyle, acetylene
- M.Hirsch, W.Quapp: JCC 23 (2002) 887 "Improved RGF Method to Find Saddle Points" HCP, H_2CO, C_4H_{10}, ring opening of sym-tetrazine
- O.Castano et al.: JCC 23 (2002) 732: cyclooctatetraene
- B.Lasorne et al.: JCP 118 (2003) 5831, and 122 (2005) 184304, Chem.Phys.326 (2006) 500: H_3CO, dimerization of cyclopentadiene

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: $CH_3CO\text{-}NHCHCH_3CO\text{-}NHCH_3$

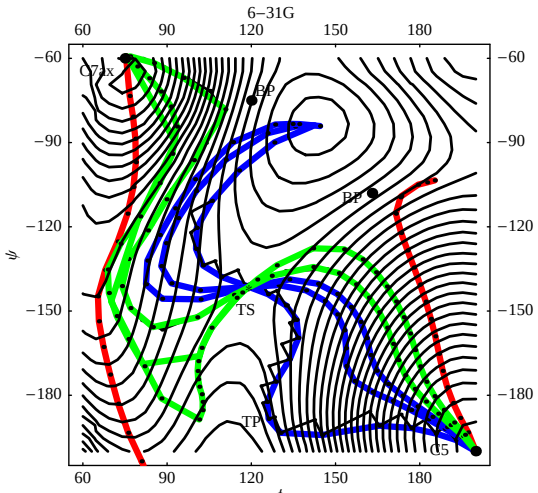
The dimension is (3N-6)=60, N=22 atoms

One of the blue NTs shows Predictor- and Corrector steps

String Method

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.

Higher-dimensional NTs

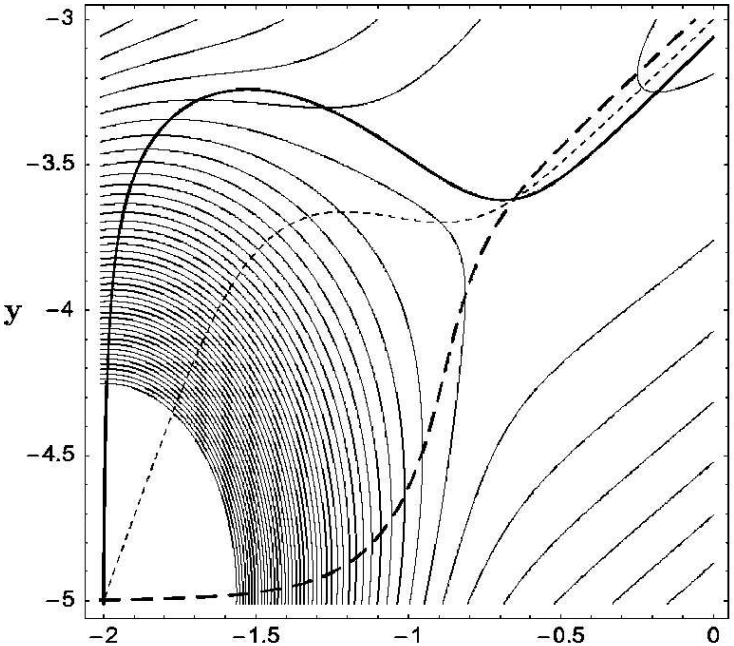
- Use a path following method in a reduced PES
- Predictor: IRC- or eigenvector-following technique
- Corrector: Newton-Raphson method

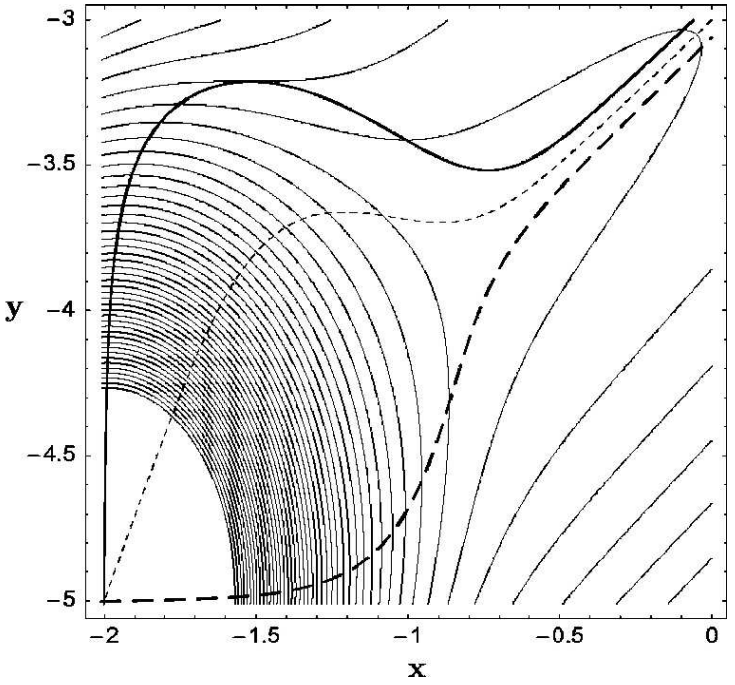
The reduced PES is defined by a set of molecular geometry parameters, (bond distances, bond angles, or dihedrals) that undergo the largest change for the reaction.
The remainder of the coordinates are forced to have a zero gradient.

- Thus again use $\mathbf{P}_r\ \mathbf{g}=0$ in a reduced space.
- Anglada, Besalu, Bofill, Crehuet: JCC 22 (2001) 387.
- Bofill, Anglada: TCA 105 (2001) 463.
- Hirsch, Quapp: TCA 113 (2005) 58,
  Examples of so called Newton Leaves
- I.Berente, G.Naray-Szabo: JPC A 110 (2006) 772. "Multicoordinate Driven Method for Approximating Enzymatic Reaction Paths: ..."

Application

- Search the way out of a barrierless PES by NTs





- Quapp, Kraka, Cremer: JPC A 111 (2007) 11287
- Joo, Kraka, Quapp, Cremer: Mol.Phys.105 (2007) 2697

Further Applications of NTs (Examples only)

- W.Quapp, D.Heidrich: JMSt, THEOCHEM 585 (2002) 105
  "Exploring the PES of ethyl cation ..."
- D.H.Ess et al.: JOC 73 (2008) 7472, and 7586, Angew.Chem.In.Ed.47 (2008) 7592: dimerization of 1,3-cyclohexadiene, isomerization of methoxy radical to hydroxymethylene radical, semibullvalene, aldaldehyde radical anion additions to alkyl halides, Cyclopropylidene to allene, deazetization of heterocyclic nitrosimines, 1,2,6-heptatriene to 3-methylene-1,5-hexadiene, endo cyclopentadiene dimerization,...
- G.Rossmueller, ..., Ch.Haettig: JPC C 113 (2009) 1418.
  "... methanol synthesis .. on the .. ZnO(0001j) Surface"

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

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

- what is noting else then the Branin equation.

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

Eigenvectors and Eigenvalues of A

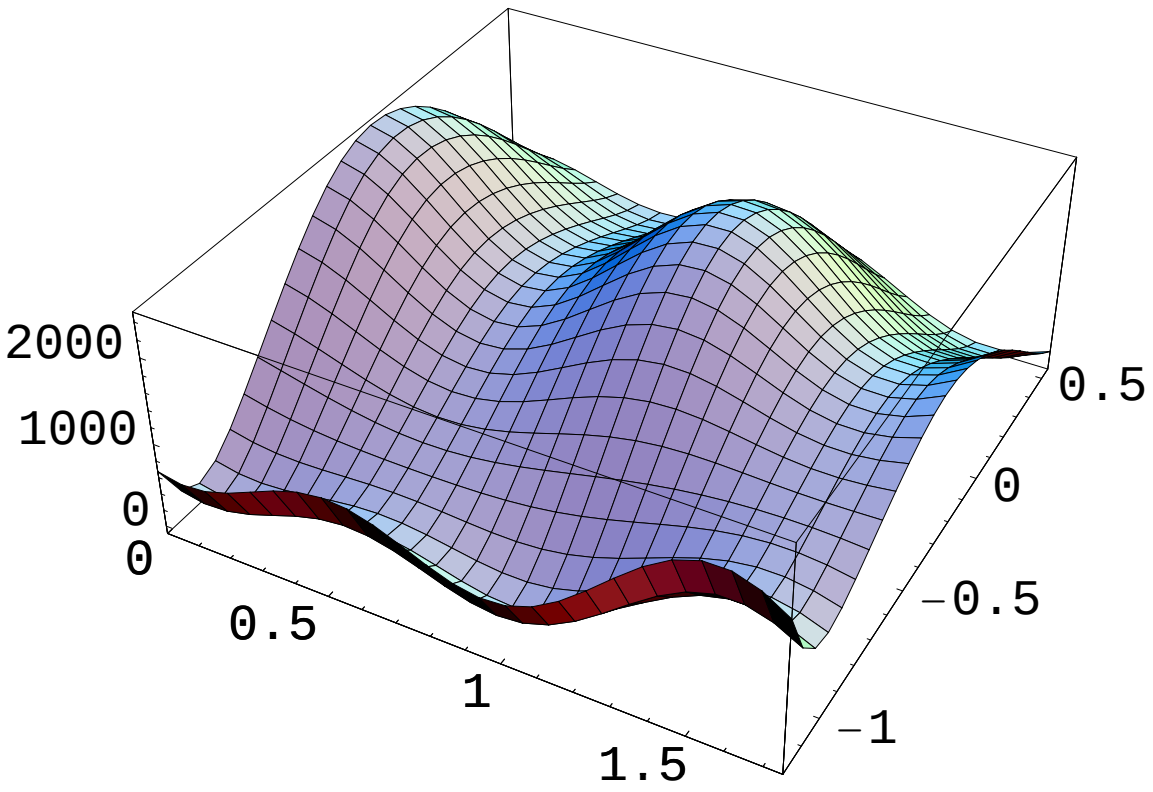
λ_i, μ_i are the eigenvalues of H and A.

- H is regular then and only then if A is regular.
- H and A have the same eigenvectors. Thus, to any λ_i belongs exactly one μ_i.
- $\lambda_i \mu_i = DetH = \Pi_k \lambda_k$.

Bifurcations

Bifurcation points of NTs are valley-ridge inflection points (VRI)

$\mathbf{A}(\mathbf{x})\,\mathbf{g}(\mathbf{x}) = 0$ and $\mathbf{g}(\mathbf{x}) \neq 0$



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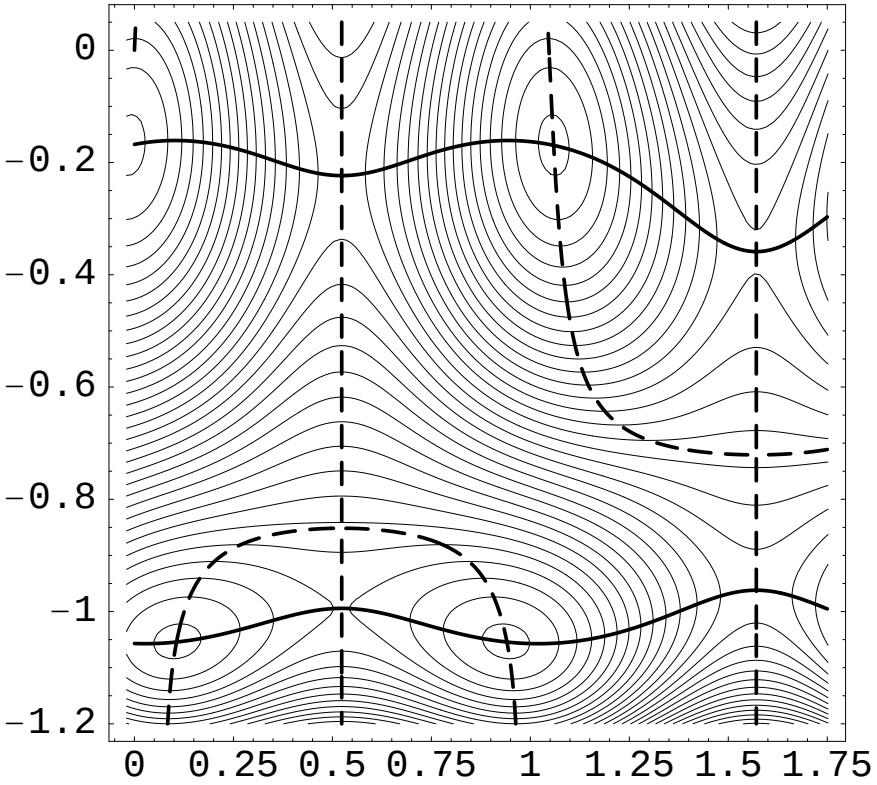

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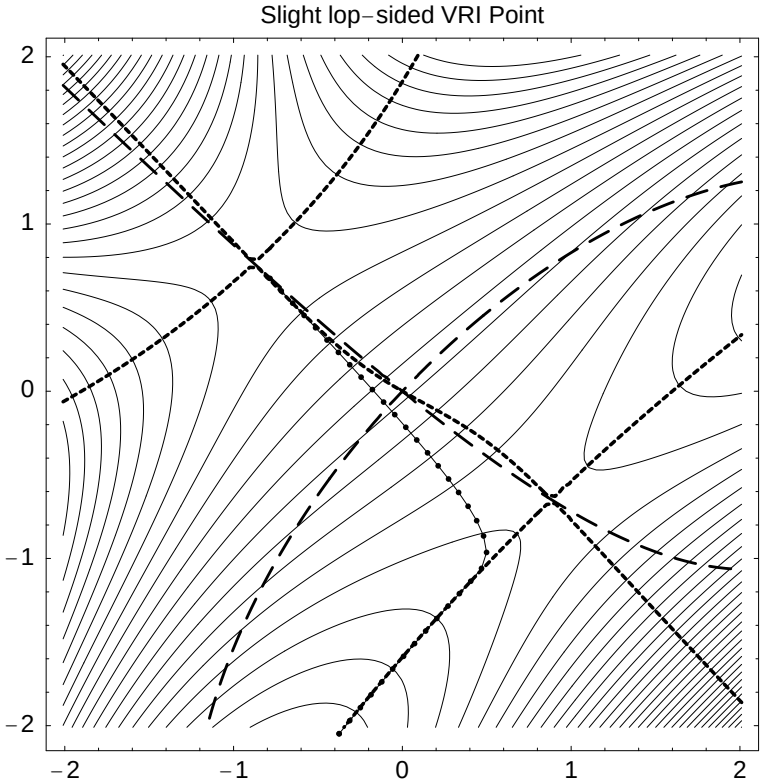

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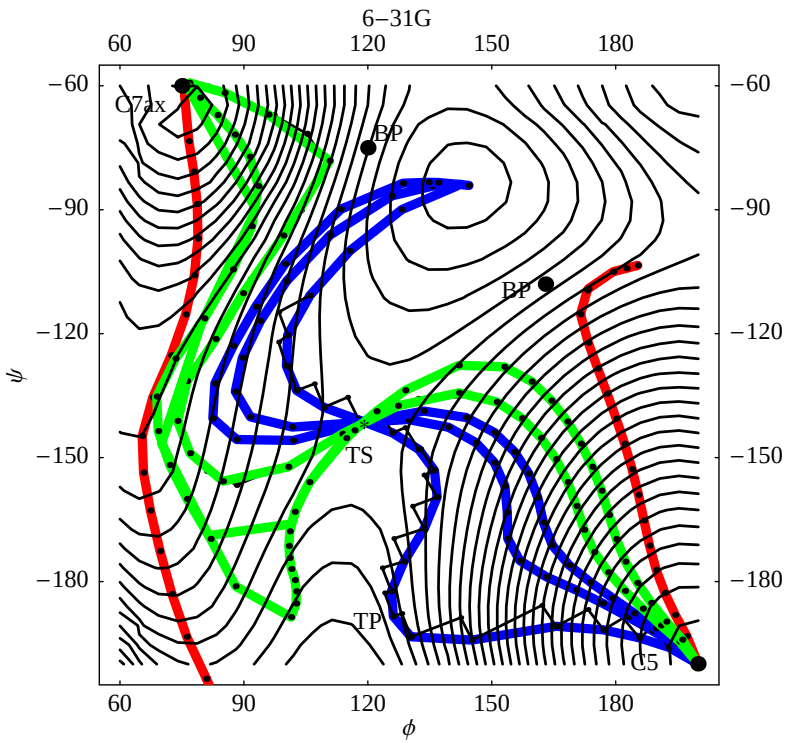
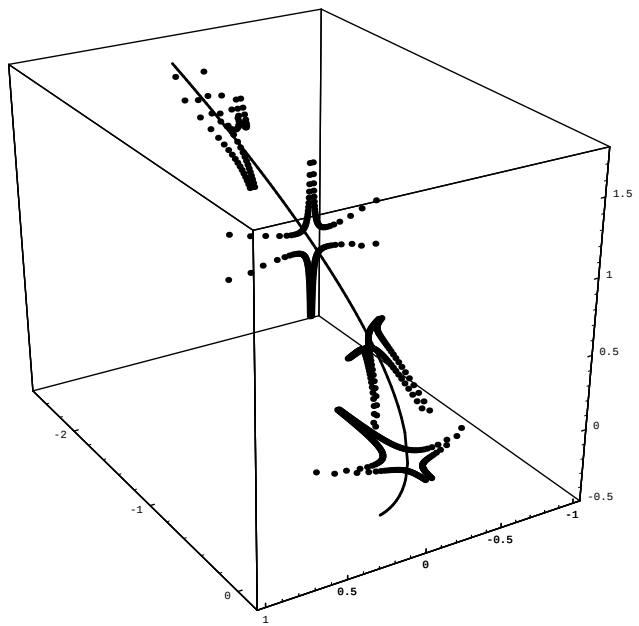


Dimension of ”Bifurcation Points”

- Note: in higher dimensional configuration space, the definition of VRIs can result in a higher dimensional VRI-manifold. It may be at least (N-2)-dim.



- Quapp, Hirsch, Heidrich,
  TCA 100 (1998) 285
  3D example of a test PES
  (derived from malone aldehyde PES)
- Hirsch, Quapp, Heidrich, PCCP 1 (1999) 5291
  3D example: PES of water
- Quapp, Melnikov, PCCP 3 (2001) 2735
  6D example: PES of formaldehyde

Channels and Index Theorem

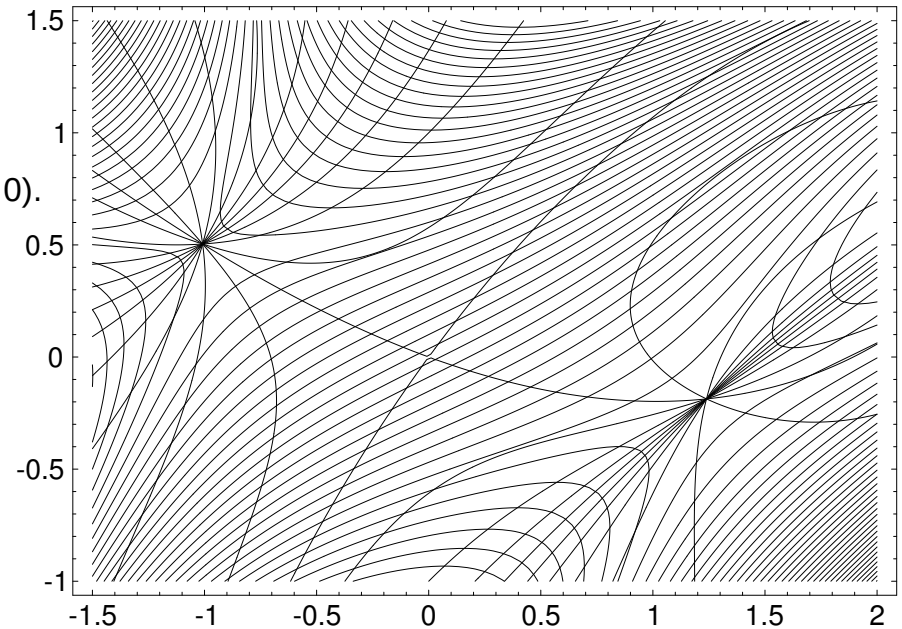
Index Theorem Let **a** and **b** be stationary points connected by a regular Newton trajectory. Then it holds

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

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



All NTs which connect a minimum and a SP are a Reaction Channel

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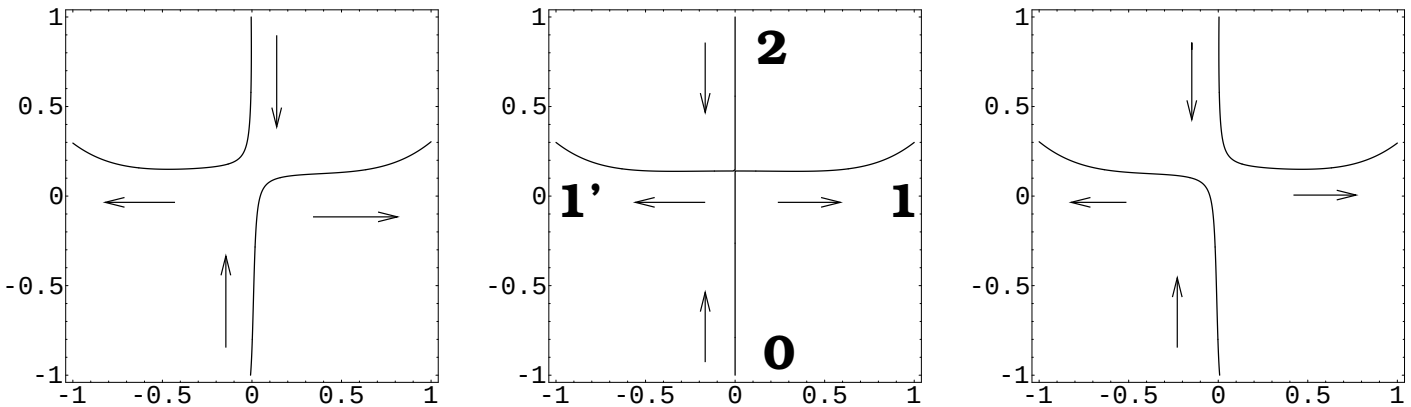

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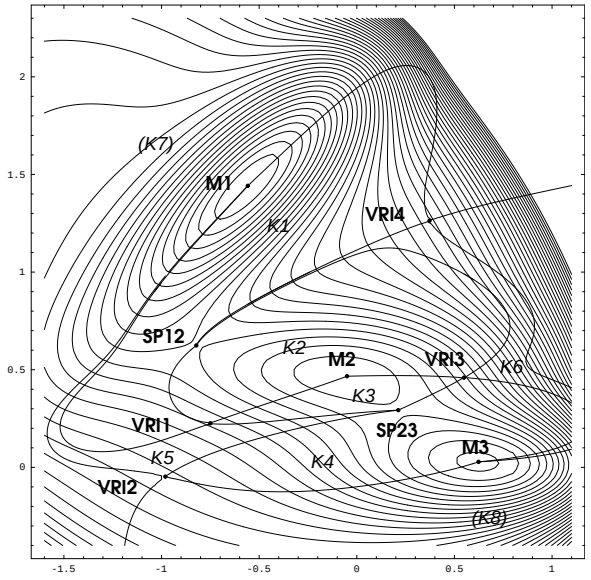
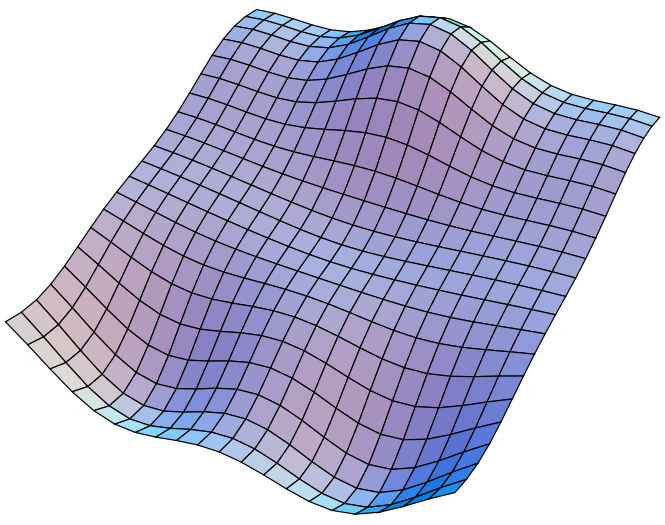


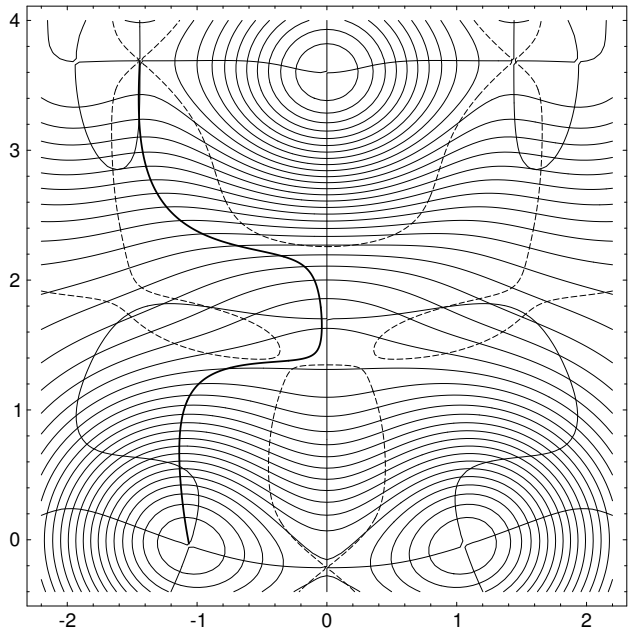
All NTs which connect a minimum and a SP are a Reaction Channel

Convexity

Convexity Theorem

A regular NT may connect minimum and SP.
If the PES along the NT is monotone increasing, then the NT goes through a valley.





Monotone increasing means for NTs, there is no Turning point.

Hirsch, Quapp: J Math Chem 36 (2004) 307

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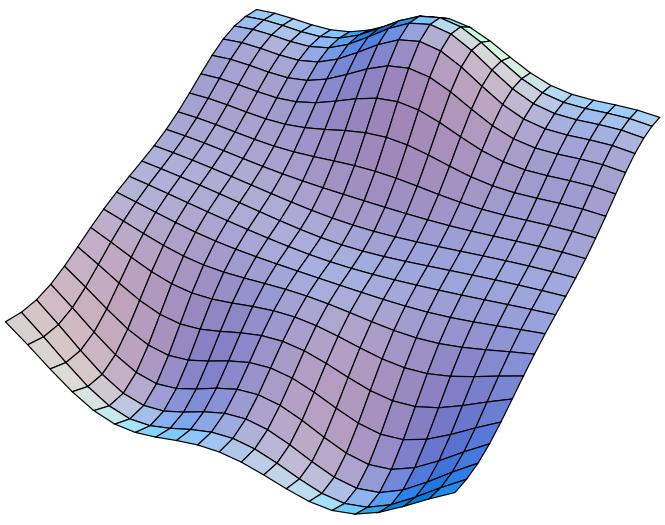
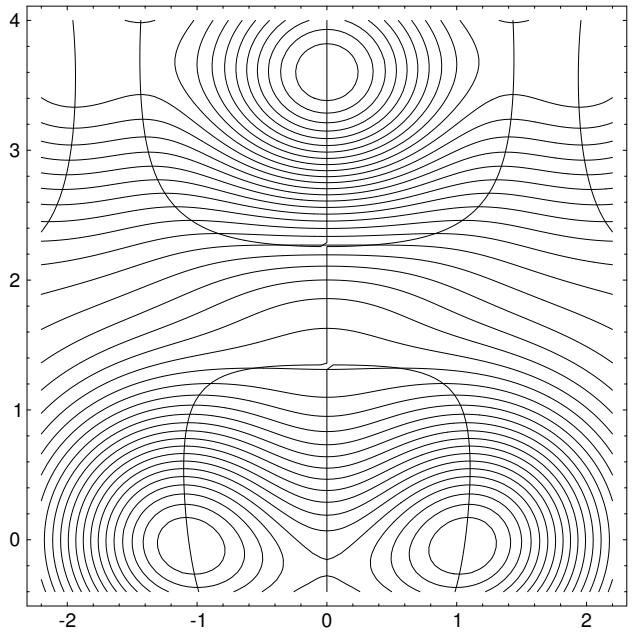
A regular NT may connect minimum and SP.
If the PES along the NT is monotone increasing, then the NT goes through a valley.



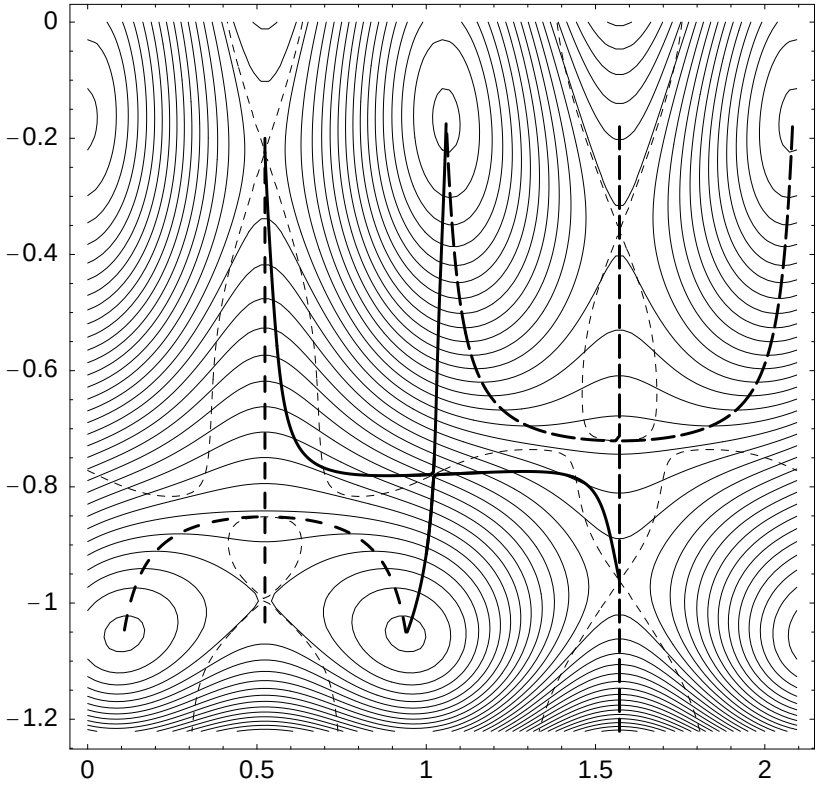


Monotone increasing means for NTs, there is no Turning point.

Hirsch, Quapp: J Math Chem 36 (2004) 307

Unsymmetric VRIs

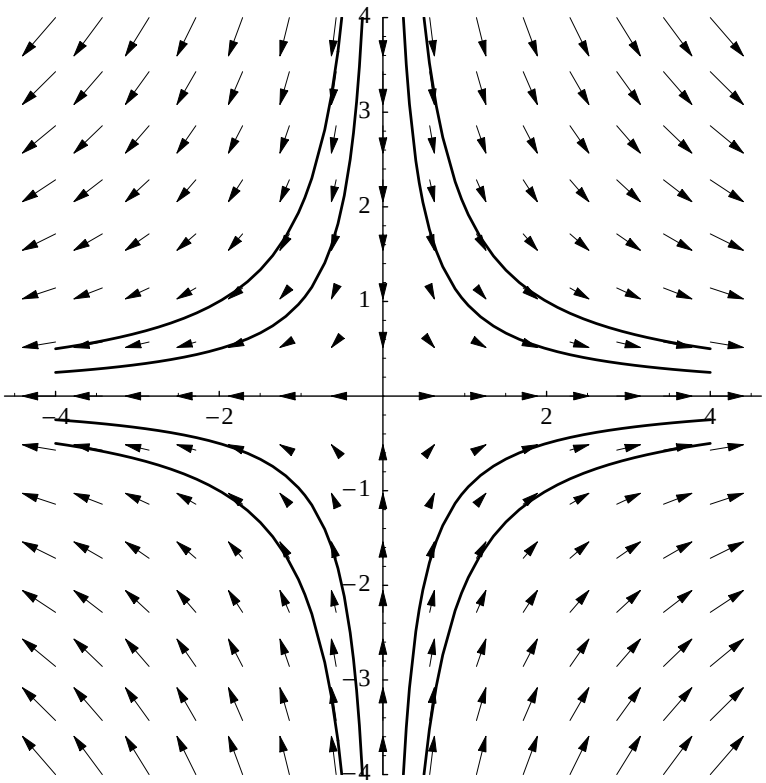
Object of the search are unsymmetric VRIs:



Included is the border between ridge and valley regions

$$\mathbf{g}(\mathbf{x})^T \mathbf{A}(\mathbf{x})\, \mathbf{g}(\mathbf{x}) = 0$$

Idea



The pattern of the flow of steepest descent lines around a SP is exactly the same like the flow of NTs around a VRI point.

Calculus of Variations is already used for the IRC.
(Crehuet and Bofill, JCP 122, 234105 (2005).)

We plan to transform the method to NTs.

Variational NTs

- It is possible to formulate a variational ansatz for NTs

$$I(a,b) = \int_a^b F(x_1(t),...,x_n(t),x_1'(t),...,x_n'(t))\,dt \rightarrow Min!$$

with a variational functional

$$F(\mathbf{x},\mathbf{x}') = \left(\mathbf{x}' \mp A(\mathbf{x})\,\mathbf{g}(\mathbf{x})\right)^T \left(\mathbf{x}' \mp A(\mathbf{x})\,\mathbf{g}(\mathbf{x})\right)$$

Of course, it uses the differential equation of Branin.
(Quapp, TCA 121 (2008) 227)

Variational NTs II

Bofill proposes another variational functional in a recent note (JCP **130** (2009) 176102)

$$F(t, \mathbf{x}(t), \mathbf{x}'(t)) = t \left(\mathbf{g}^T \mathbf{g}\right)^{1/2} \left(\mathbf{r}^T \mathbf{x}'\right) + E(\mathbf{x}(t))$$

where E is the PES, $\mathbf{g}$ is the gradient, and $\mathbf{r}$ is the search direction for a special NT.

Summary: How to find a RP, If You Must

Properties of NTs

- Describe the RP by (some) Newton Trajectories: it is tractable – in many practical cases.
- Find TS by Newton Trajectories: it is tractable.
- Find Bifurcations by special Newton Trajectories: it is tractable.

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  Prof.Dr.D.Heidrich from Theoretical Chemistry
  Dr.M.Hirsch from Mathematics.

  A row of results (which are presented here)
  are born in discussions with them.

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