# Potential Energy Surfaces, Newton Trajectories and Optimal Oriented External Electric Fields

Wolfgang Quapp, Josep Maria Bofill

(formerly) Mathematical Institute, University Leipzig, Germany
Universidad de Barcelona, Spain

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# Abstract

The talk begins with a discussion of the problems involved in defining a reaction pathway, in particular the steepest descent, the intrinsic reaction coordinate (IRC) and gradient extremals (GE). As an alternative, we propose Newton trajectories (NT).[1] An NT is a curve where the gradient of the PES points in the same direction at every point.
NTs connect stationary points of the PES, so they can be used to find saddle points.

Application: NTs describe the curves of the change of stationary points under a linear force.

A special application is the study of the smallest amplitude electric field that renders a barrierles chemical process with the smallest possible strength[2]. An example PES is explained.

[1] W.Quapp, M.Hirsch, O.Imig, D.Heidrich, J.Computat.Chem. 19 (1998) 1087; Theor.Chem.Acc. 100 (1998) 285.

[2] W.Quapp, J.M.Bofill, J.Phys.Chem.B 120 (2016) 2644. J.Chem.Theory Comput. 18 (2022) 935-952; Theoret.Chem.Acc. 142 (2023) 22; J.Chem.Phys. 159 (2023) 114112; Chem-Europ.J. 30 (2024) e202400173.

# Background: what is a Reaction Path?

The chemical bonds emerge by the overlapping of electrons in a molecule. Their description is the Schrödinger equation, together with the Born-Oppenheimer approximation, which separates kernels from the electrons. An N-dimensional molecule has 3N-6 internal degrees of freedom of the atoms. One can calculate to any constellation $(x_1, x_2, ..., x_{3N-6})$ the potential energy, as well as derivatives, for example, the second ones for comparison with spectroscopy. However, for medium or larger molecules one cannot calculate a net of raster-points in all dimensions, to get a 'full' potential energy surface (PES).

What one can do is the definition of a one-dimensional curve in the (3N-6)-dimensional configuration space of the molecule

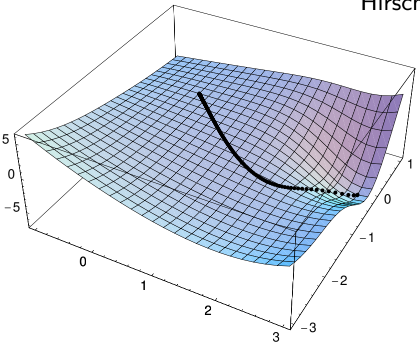
$$\mathbf{x}(s) = (x_1(s), x_2(s), ..., x_{3N-6}(s))$$

and calculation of the PES profile over this curve, in a (3N-6)+1 dimensional space. If this curve, or 'path' is more or less inside a valley of the PES then we name it $\boxed{\text{Reaction Coordinate}}$.

# 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, must 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

SD goes over a ridge !

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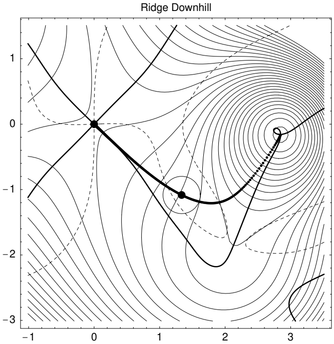

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# Definition of a Reaction Pathway

## Reaction path (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.

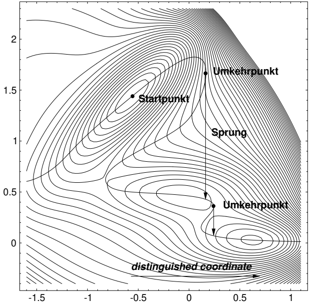
## Examples

- 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.

# 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 $\mathbf{r}$
- Build the Projector Matrix $\mathbf{P}_r=\mathbf{I}-\mathbf{r}\,\mathbf{r}^T$ . It is $\mathbf{P}_r\,\mathbf{r}=\mathbf{0}$.
- Search the Curve $\mathbf{P}_r\,\mathbf{g}=\mathbf{0}$. It is the Newton Trajectory.

# Predictor-Corrector Method

## 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 the top level quantum chemistry packet COLUMBUS.

# Branin is the desingularized, continuous Newton equation

- A Newton-Raphson 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. This happens on the path from minimum to SP. 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 named the Branin equation.

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

The name Newton trajectory is coming from this approach.

# Index Theorem

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

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

and the difference is one.

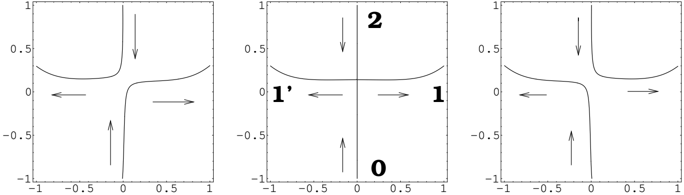


Figure by Michael Hirsch (2004)

# Forces and NTs – linear approach

If a linear force is applied to a molecule then the simplest approach for the potential energy is

$$V_f(\mathbf{x}) = V(\mathbf{x}) \; - F\,\mathbf{f}^T\,\mathbf{x}$$

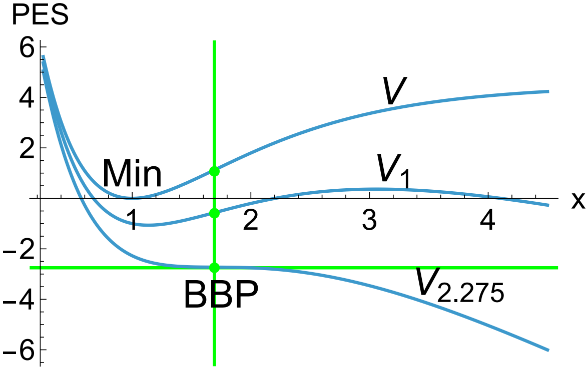
where **f** is the force direction and $F$ its amount. $\mathbf{f}^T\,\mathbf{x}$ is the scalar product of the force and the current coordinate point.
Stationary points of $V_f$ move along the conditions $\frac{\partial V_f}{\partial x_i} = 0$

$$\mathbf{g}(\mathbf{x}) \,||\, \mathbf{f}\ .$$

The curve which describes these force moved stationary points is a Newton trajectory. The search direction **r** of the NT is now the force **f**.

- W.Quapp,J.M.Bofill,J.Ribas-Arino: Int.J.Quant.Chem.118 (2018)e25775 "Towards a Theory of Mechanochemistry – Simple Models from the Early Beginnings"

Usually, an application of a force leads to a decreasing barrier of a reaction. This is the aim: gain of energy for a reaction, or change the direction of a reaction. Action of a force on a 1D Morse pot.



$$V_F = V - F\,x$$

W.Quapp, J.M.Bofill, TCA 135 (2016) 113

BBP means barrier breakdown point, or bond breaking point, where the former PES barrier disappears. It is the aim of many experiments to reach this point. Note: $V_{F\,xx} = 0$ there.

## Change of the Gradient along the Reaction Path

We search the turning point of the function $|g|$ along an NT: the directional derivative of $|g|$ along the NT has to be zero.

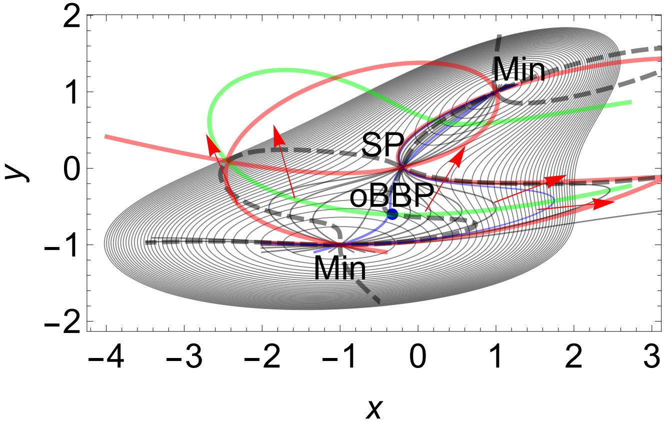
$$\frac{d}{ds}\sqrt{\mathbf{g}^T\mathbf{g}} = \frac{2}{\sqrt{\mathbf{g}^T\mathbf{g}}}\mathbf{g}^T\mathbf{H}\frac{d\mathbf{x}}{ds} =$$

$$\pm\frac{2}{\sqrt{\mathbf{g}^T\mathbf{g}}}\mathbf{g}^T\mathbf{HAg} = \pm 2\sqrt{\mathbf{g}^T\mathbf{g}}\ Det\,(\mathbf{H}) = 0$$

where first the concept of directional derivative is used and second the tangent vector, dx/ds, is replaced by the definition of Branin.

Thus $\boxed{Det(\mathbf{H}) = 0}$ is the condition of a BBP.

# Optimal BBP A family of NTs (thin) connects Min and SP.



Pulling into a defind direction makes a NT for the movement of minimum and SP. Red arrows point into gradient directions of corresponding NTs. There should be a lowest, optimal force $F$ over the green line. This lowest BBP is called the $\boxed{\text{optimal BBP}}$. It is the crossing of GE (dashed), blue NT, and green line.

The condition of the optimal BBP is quite simple

$$H(\mathbf{x})\ \mathbf{g}(\mathbf{x}) = \mathbf{0}$$

where $\mathbf{g}(\mathbf{x}) \neq \mathbf{0}$. The gradient is an eigenvector of the Hessian with null eigenvalue. The optimal BBP coincides with a point of the gradient extremal (GE) exactly at the intersection point with the $Det(H(\mathbf{x})) = 0$-line (green) and the ‘optimal’ NT. The location of optimal BBPs is extremely important in the context of electro- and mechano-chemistry. These points reveal which is the most efficient way to trigger a reaction by means of a force.

- W.Quapp, J.M.Bofill: Theoret. Chem. Acc. 135, iss. 4, (2016) 113-132,

  A Contribution to a Theory of Mechanochemical Pathways by means of Newton Trajectories
- J.M.Bofill, J.Ribas-Arino, S.P.Garcia, W.Quapp: J. Chem. Phys. 147, Iss.15 (2017) 152710,

  An algorithm to Locate Optimal Bond Breaking Points on a Potential Energy Surface for Applications in Mechanochemistry and Catalysis

# Calculation of BBPs

We use the norm of the Branin vector and search for its zero, the point where the Hessian has a zero eigenvalue. Locating this point is equivalent to finding the zero of the $\sigma$-function

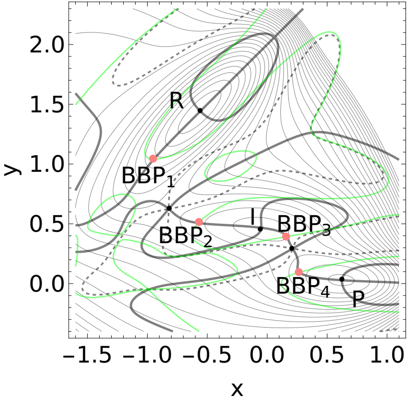
$$\sigma(x) = \frac{g^T(x)H^2(x)g(x)}{g^T(x)g(x)} = s^T(x)s(x)$$

where the vector s(x) is

$$s(x) = H(x)g(x)||g(x)||^{-1}.$$

The $\sigma$ function is a sum of squares, thus it is a non-negative function. We search $\sigma(xmin) = 0$.

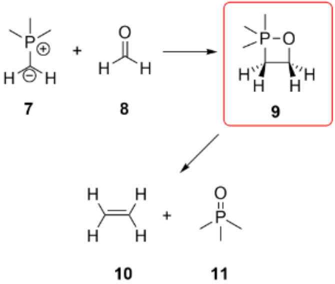
# BBPs of the MB potential



IB lines are green, BBPs are red, GEs are thick black.
(Dashed is the convexity border.)

- J.M.Bofill, J.Ribas-Arino, S.P.Garcia, W.Quapp: J.Chem.Phys. 147, Iss.15 (2017) 152710

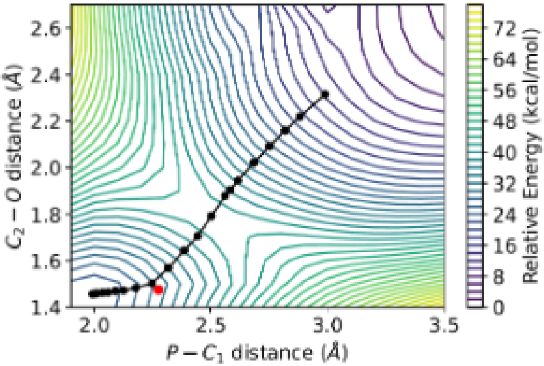
# Example: Wittig reaction



Simplified model of the Wittig reaction. The structure of the OP intermediate is crucial to control the stereochemistry of the resulting alkene. The ring opening is the limiting step of the Wittig reaction.

- J.M. Bofill, M. Severi, W. Quapp,J. Ribas-Ariño, I. de P. R. Moreira, G. Albareda: "Optimal oriented external electric fields to trigger a barrierless oxaphosphetane ring opening step of the Wittig reaction", Chem.-A Europ.J. 30 (2024), e202400173

# Example: Wittig reaction



PES in the subspace characterized by C-P and C-O bond distances. Black dots are points of the IRC. The red dot indicates the position of the optimal BBP (oBBP).

# 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 optimal BBPs by Hg=0 and a special Newton Trajectory:
  it is tractable.

## Acknowledgement

- I thank my collegues over many years
  Prof.Dr.D.Heidrich from Theoretical Chemistry, Leipzig
  Dr.M.Hirsch from Mathematics, Leipzig (now London)

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

# Appendix: Some References to Newton Trajectories

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# Appendix: 2D examples – Representation of NTs

In 2D toy examples, one can easyly represent NTs by graphic orders:
In two dimensions holds that the orthogonal direction to the search direction

$$\mathbf{r}=(r_1, r_2) \text{ is unique the direction } \mathbf{r}^{\perp} = (-r_2, r_1) \ .$$

Then the condition that $\mathbf{r} \,||\, \mathbf{grad}$ is the zero of the scalarproduct

$$\mathbf{grad}^T \ \mathbf{r}^{\perp} = \mathbf{0} \ .$$

In Mma one can use

```
ContourPlot[- g1[x,y] r2[x,y] + g2[x,y] r1[x,y], {x, 0,5}, {y,0,5},
ContourShading→False, PlotPoints→ 30, Contours→{0},
ContourStyle→{Thickness[ 0.008],Dashed}]
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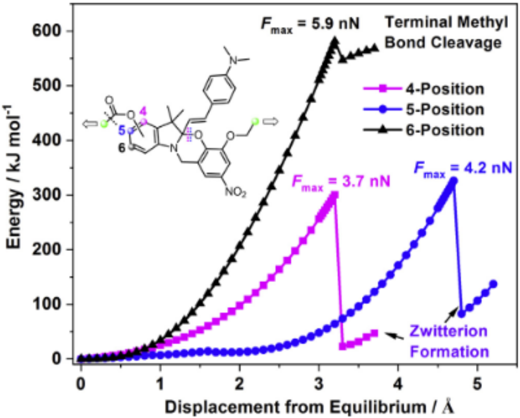
# Appendix: Example of a distiunguished coordinate

Example of a distiunguished coordinate

PES curves with jumps, in a paper in 2021



If You see such curves, You can assume that a very old and questionable method is used.

# Appendix: Eigenvectors and Eigenvalues of $A$

Relation of the matrix $H$ and its adjoint matrix $A$:
$\lambda_i, \mu_i$ 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 $\lambda_i$ belongs exactly one $\mu_i$.
- $\lambda_i \, \mu_i = Det(H) = \Pi_k \lambda_k$ .