

The Variational Nature of some Reaction Path Models.

Josep Maria Bofill & Wolfgang Quapp

*Bridging-Time Scale Techniques
and their Applications in Atomistic
Computational Science*

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Abstract

The reaction path is a central subject in theoretical chemistry. It is a pathway imagined on the potential energy surface (PES). It provides a one-dimensional description of a chemical reaction in an N-dimensional configuration space. There are a variety of reaction path models. Each type of reaction path has advantages and inconvenients in the description of the process. We present the variational nature of the most widely used models, namely, Intrinsic Reaction Coordinate, Newton Trajectory, Gradient Extremal, and Gentles Ascent Dymanic Path. Extensions of the Reaction Path model is also discussed.

Index.

1.- The Reaction Path Model.

2.- Variational Nature of Some Reaction Path Models:

a) Intrinsic Reaction Coordinate (Steepest Descent Path).

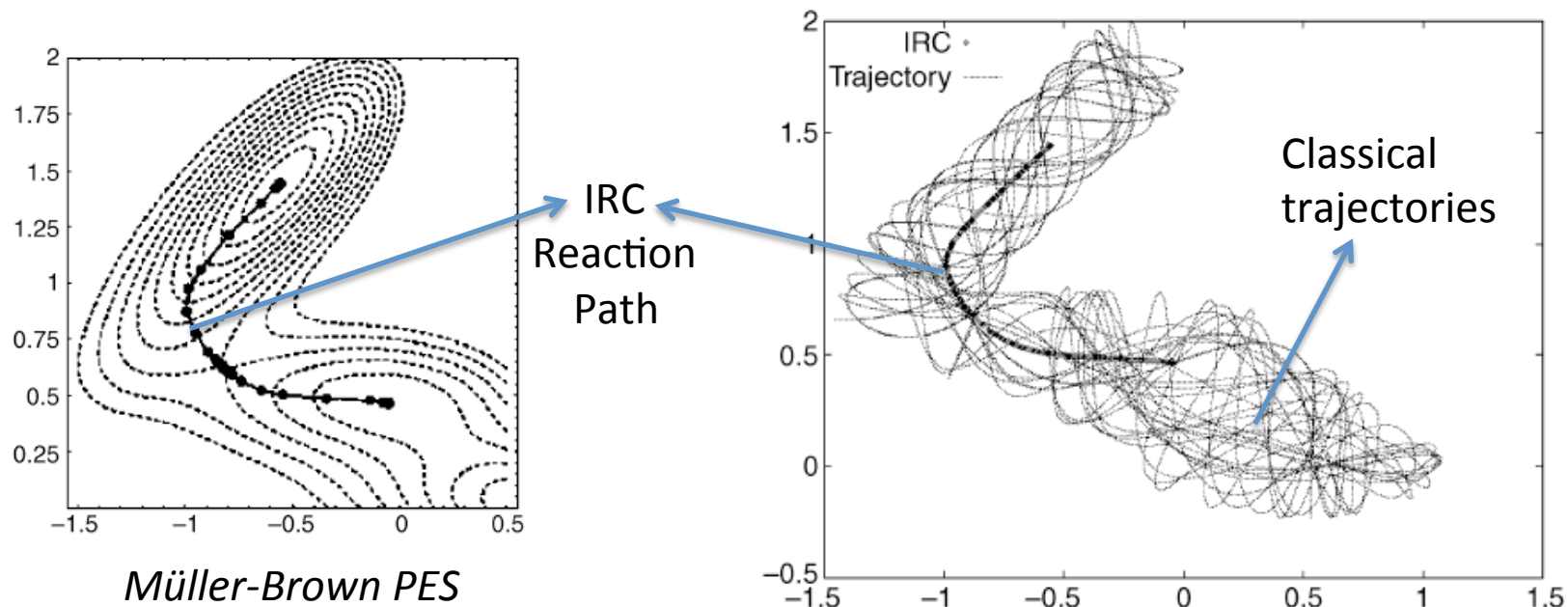
b) Newton Trajectory (Distinguished Coordinate Path).

c) Gradient Extremals Path.

d) Gentlest Ascent Dynamics Path.

1.- The Reaction Path Model.

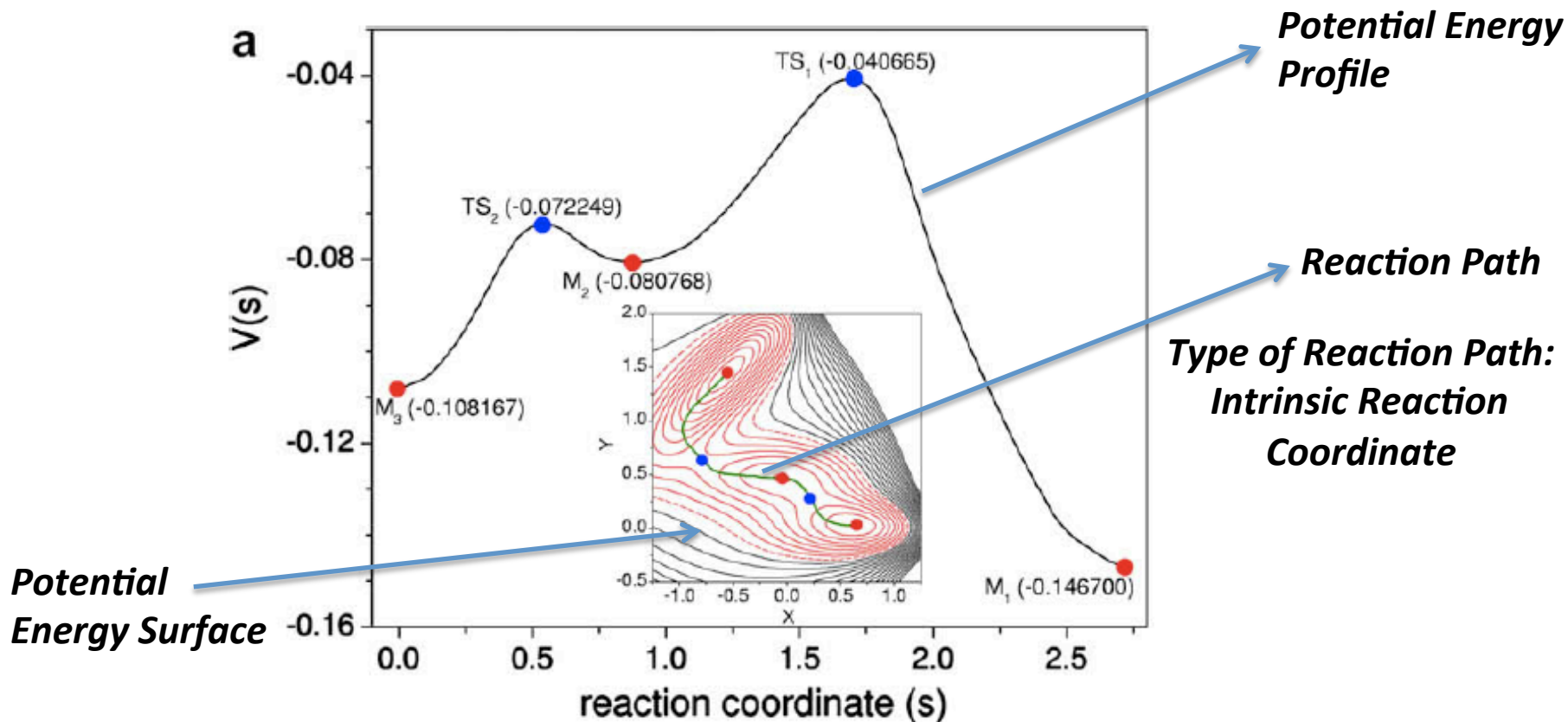
The Reaction Path Model.



A comparison between the Reaction Path described by the Intrinsic Reaction Coordinate and a representative, long exact classical trajectories. **From a physical point of view any Reaction Path (RP) can be seen as if one envisions a large cloud of classical trajectories evolving on the PES. Very often the average trajectory is going to be close to the curve selected for the RP. This is the physical meaning of the Reaction Path Model. (J. González, X. Giménez, J. M. Bofill, *Phys. Chem. Chem. Phys.* 4, 2921 (2002))**

The Reaction Path Model.

The model of Reaction Path: R.A. Marcus, *J. Chem. Phys.* **49**, 2610, 2617 (1968) and K. Fukui, *J. Phys. Chem.* **74**, 4161 (1970).



Reaction Path: A continuous curve monotonically increasing in energy from a minimum of the Potential Energy Surface to a First Order Saddle Point and monotonically decreasing from this point to a new minimum of this Potential Energy Surface.

There is different type of curves satisfying the definition of Reaction Path.

Brief and incomplete chronology of the most widely used curves:

The Steepest Descent Curve (Intrinsic Reaction Coordinate)

K. Fukui, *J. Phys. Chem.* **74**, 4161 (1970)

Gradient Extremal

J. Pancir, *Collect. Czech. Chem. Commun.* **40**, 1112 (1975)

M. V. Basilevsky, A. G. Shamov, *Chem. Phys.* **60**, 347 (1981)

Newton Trajectory (Distinguished Reaction Coordinate)

M. J. Rothman, L. L. Lohr, *Chem. Phys. Lett.* **70**, 405 (1980);

W. Quapp, M. Hirsch, O. Imig, D. Heidrich, *J. Comput. Chem.* **19**, 1087 (1998);

J. M. Anglada, E. Besalú, J. M. Bofill, R. Crehuet, *J. Comput. Chem.* **22**, 387 (2001)

Gentlest Ascent Dynamics

W. E, X. Zhou, *Nonlinearity* **24**, 1831 (2011); J. M. Bofill, W. Quapp, M. Caballero, *Chem. Phys. Lett.* **583**, 203 (2013)

**2.- *a*) Variational Nature of the Intrinsic Reaction Coordinate
(Steepest Descent Path).**

Variational Nature of Steepest Descent (Intrinsic Reaction Coordinate) Path.

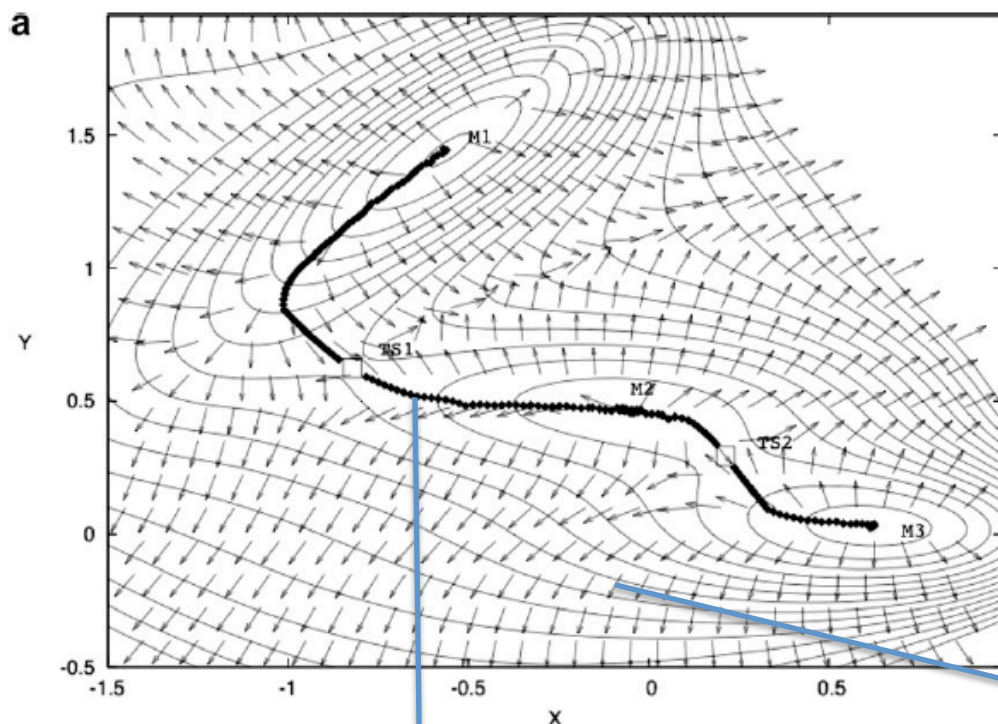
The Intrinsic Reaction Coordinate is the path that follows a gradient curve.

It is also known as Steepest Descent (SD) or Ascent curve (SA).

Introduced by: K. Fukui, *J. Phys. Chem.* **74**, 4161 (1970).

Mathematically is characterized by: tangent curve = $\mathbf{t}(\mathbf{x}) = d\mathbf{x}/dt = \nabla_{\mathbf{x}} V(\mathbf{x})$

Müller-Brown Potential Energy Surface (PES)



- On a PES there exists a field of gradients.

- Except for stationary points, at each point of the PES only a Steepest Descent or Steepest Ascent passes through this point.

- The Intrinsic Reaction Coordinate is the only Steepest Descent or Steepest Ascent connecting two minima through a first order saddle point (Transition State).

Intrinsic Reaction Coordinate Path

The set of vectors indicates the Gradient field

Variational Nature of Steepest Descent (Intrinsic Reaction Coordinate) Path.

A. Tachibana and K. Fukui, *Theor. Chim. Acta* **57**, 81 (1980); K. Fukui, *Int. J. Quantum Chem., Quantum Chem. Symp.* **15**, 633 (1981).

R. Crehuet, J.M. Bofill, *J. Chem. Phys.* **122**, 234105 (2005).

Using the Theory of Calculus of Variations.

$$I_{M \rightarrow q}(\mathbf{q}) = \int_0^t \sqrt{G(\mathbf{q})} \sqrt{\left(\frac{d\mathbf{q}}{dt'}\right)^T \left(\frac{d\mathbf{q}}{dt'}\right)} dt'$$

Arc length: ds

We take $(\mathbf{q}_M, t' = 0)$ as fixed initial point and $(\mathbf{q}_q, t' = t)$ as variable end point.

Gradient norm: $G(\mathbf{q}) = (\mathbf{g}^T(\mathbf{q})\mathbf{g}(\mathbf{q}))$.

Speed Law. Where, $\mathbf{g}(\mathbf{q})$, is the gradient vector of the Potential Energy Surface.

The tangent of the path $\mathbf{q}(t)$ that extremalizes the above variational integral, $I_{M \rightarrow q}(\mathbf{q})$, is: $d\mathbf{q}/dt = \mathbf{g}(\mathbf{q})$.

Conclusion: the extremal curve is a Steepest Descent/ Ascent.

Evaluating the integral, $I_{M \rightarrow q}(\mathbf{q})$ through the Steepest Ascent curve, we obtain,

$$I_{M \rightarrow q}(\mathbf{q}) = V(\mathbf{q}_q) - V(\mathbf{q}_M).$$

At the point $(\mathbf{q}_q, t' = t)$:

$dI_{M \rightarrow q}(\mathbf{q})/dt = dV/dt = \mathbf{g}^T(\mathbf{q})d\mathbf{q}/dt = \mathbf{g}^T(\mathbf{q})\mathbf{g}(\mathbf{q})$, a total differential form.

Variational Nature of Steepest Descent (Intrinsic Reaction Coordinate) Path.

Impact: a Steepest Ascent or Steepest Descent curve, starts at the point \mathbf{q}_M , propagates through the PES according to the speed law or continuous slowness model, $(G(\mathbf{q}))^{1/2}$, arrives at the point \mathbf{q}_q , traveling with the extremal (least) potential energy variation, $I_{M \rightarrow q}(\mathbf{q}) = V(\mathbf{q}_q) - V(\mathbf{q}_M)$. (Fermat Variational Principle).

Hamilton-Jacobi equation. At the variable end point $(\mathbf{q}_q, t' = t)$ we have $dI_{M \rightarrow q}(\mathbf{q}) = dV$ and from this we derive the **Eikonal equation**

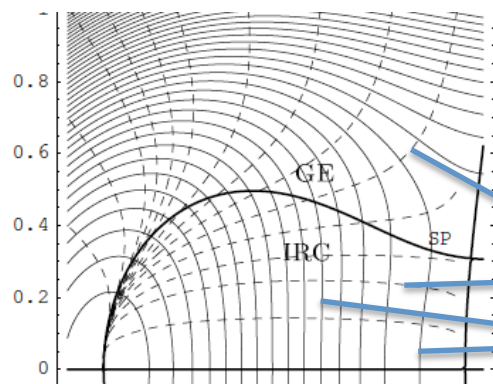
$$\begin{array}{l} \text{Speed law} \\ \text{(Gradient Norm)} \end{array} \longrightarrow \frac{(\nabla_{\mathbf{q}} V)^T (\nabla_{\mathbf{q}} V)}{G(\mathbf{q})} = 1 \quad \text{where} \quad \nabla_{\mathbf{q}} = \begin{pmatrix} \partial/\partial q_1 \\ \vdots \\ \partial/\partial q_N \end{pmatrix}$$

Let $V(\mathbf{q})$ a solution of the above equation, then the Steepest Ascent/Descent curves (extremal curves) transverse the family of equipotential energy surfaces $V(\mathbf{q}) = v = \text{constant}$.

The construction of solutions of the eiconal equation as a set of equipotential energy surfaces is similar to the **Fermat-Huyghens principle** for the construction of wave fronts.

J.M. Bofill, W. Quapp, M. Caballero, *J. Chem. Theory Comput.* **8**, 4856 (2012)

Variational Nature of Steepest Descent (Intrinsic Reaction Coordinate) Path.



Dashed curves are Steepest Ascent/Descent curves emerging from the minimum located at (0,0). Thin curves, equipotential energy curves, ($V(\mathbf{q}) = \nu = \text{constant}$) solution of Eikonal equation.

Steepest Ascent/Descent curves (extremal curve).

Family of equipotential energy curves, $V(\mathbf{q}) = \nu$.

Canonical equations of SA curves:

$$\begin{cases} \frac{d\mathbf{q}}{dt} = \mathbf{g} \\ \frac{d\mathbf{g}}{dt} = \nabla_{\mathbf{q}} G(\mathbf{q}) \end{cases}$$

“The like Hamilton canonical equations for the SA extremal curves.”

These equations are the basis of many algorithms to compute the Steepest Ascent/Descent (Intrinsic Reaction Coordinate) reaction path, see e.g. the review: H. B. Schlegel, *J. Comput. Chem.* **24**, 1514 (2003). One of the most widely used algorithm to integrate these curves: G. Henkelman, B. P. Uberuaga, and H. Jónsson, *J. Chem. Phys.* **113**, 9901 (2000).

Variational Nature of Steepest Descent (Intrinsic Reaction Coordinate) Path.

Second order variations. We compare the value of the basic integral, $I_{M \rightarrow q}(\mathbf{q})$, evaluated through an arbitrary curve (AC) and that evaluated through the Steepest Ascent curve both joining the same initial and final points, namely, $(\mathbf{q}_M, t' = 0)$ and $(\mathbf{q}_q, t' = t)$.

$$I_{M \rightarrow q}(\mathbf{q}_{AC}) - I_{M \rightarrow q}(\mathbf{q}_{SA}) =$$

$$\underbrace{\int_0^t \sqrt{G(\mathbf{q}_{AC})} \sqrt{(d\mathbf{q}_{AC}/dt')^T (d\mathbf{q}_{AC}/dt')} dt'}_{\text{Computed through the Arbitrary Curve (AC) that joints the points M and q.}} - \underbrace{\int_0^t \sqrt{G(\mathbf{q}_{SA})} \sqrt{(d\mathbf{q}_{SA}/dt')^T (d\mathbf{q}_{SA}/dt')} dt'}_{\text{Computed through the Steepest Ascent Curve (SA) that joints the points M and q.}}$$

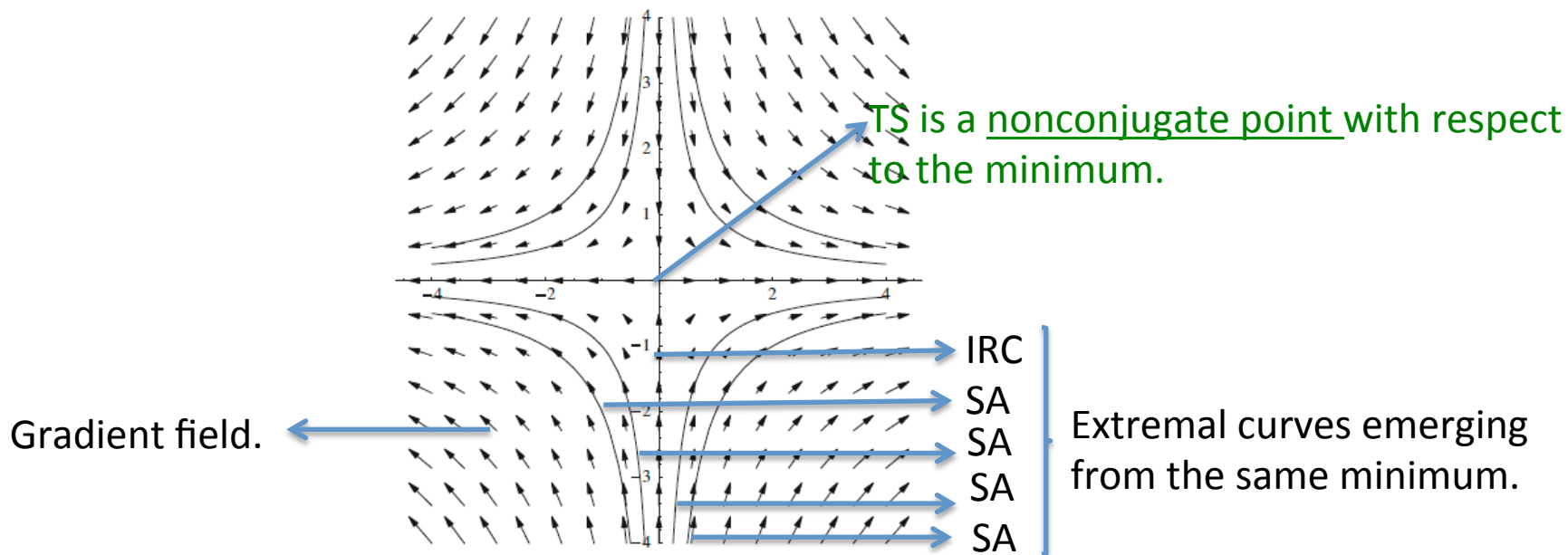
Computed through the Arbitrary Curve (AC) that joints the points M and q.

Computed through the Steepest Ascent Curve (SA) that joints the points M and q.

This difference between integrals is the **Weierstrass E-function** or **Error Function**, that in the present case is ***always positive***. The Weierstrass E-function is related with the second or higher order variation of the tangent argument, $d\mathbf{q}/dt$. ***The Steepest Ascent (Descent) curves make positive the Error Function.*** Nevertheless, this is a necessary condition but not sufficient to ensure that any Steepest Ascent (Descent) curve minimizes the functional integral $I_{M \rightarrow q}(\mathbf{q})$. **The sufficient condition is satisfied if and only if the Steepest Ascent (Descent) curve joining two consecutive minima does not contain a point that is second of higher order saddle point.** These points are conjugate points of the starting minima. **The Intrinsic Reaction Coordinate Path is the unique Steepest Descent curve of character minimum.**

Variational Nature of Steepest Descent (Intrinsic Reaction Coordinate) Path.

The second order variation: R. Crehuet, J.M. Bofill, *J. Chem. Phys.* **122**, 234105 (2005); A. Aguilar-Mogas, R. Crehuet, X. Giménez, J. M. Bofill, *Mol. Phys.* **105**, 2475 (2007); W. Quapp, *Theor. Chem. Acc.* **121**, 227 (2008).



Conjugate Point: If an extremal curve starting at any point and a second “neighboring” extremal curve, also starts at the same point, intersects to the first curve in a next point, then this intersection point is a conjugate point.

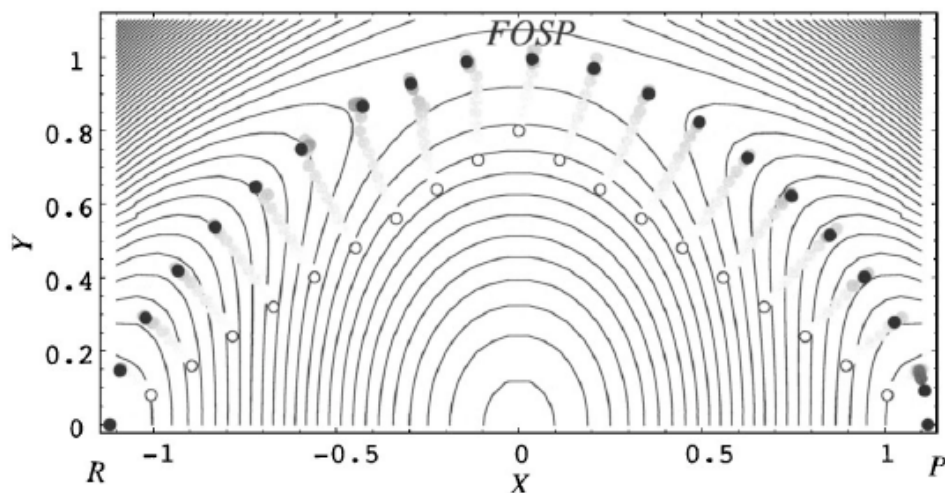
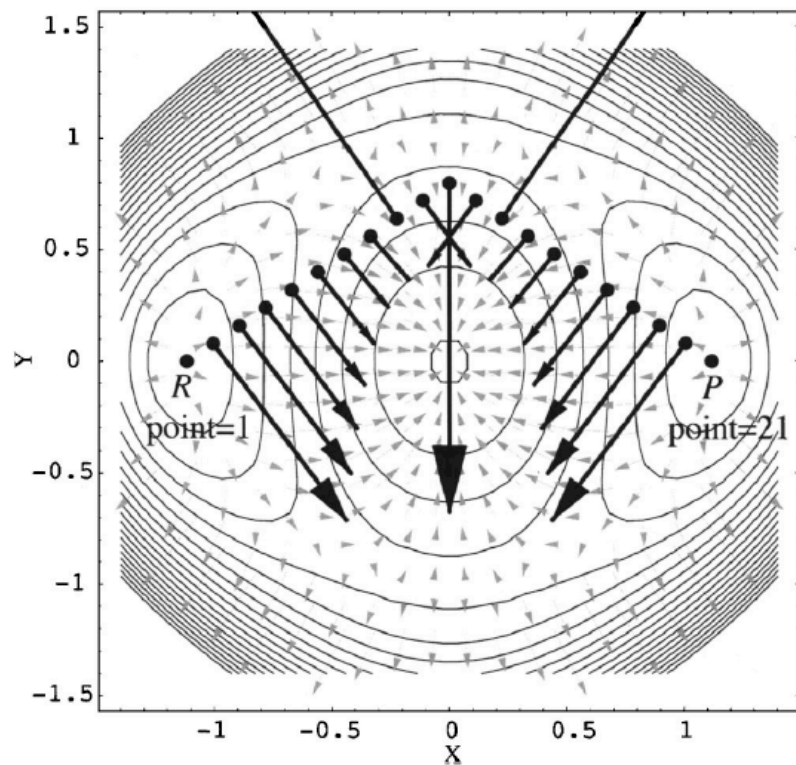
Variational Nature of Steepest Descent (Intrinsic Reaction Coordinate) Path.

Applications: Location of an Intrinsic Reaction Coordinate curve between two minima using the minimization of the Weierstrass E-function:

$$I_{M \rightarrow q}(\mathbf{q}_{AC}) - I_{M \rightarrow q}(\mathbf{q}_{SA}) = \int_0^t \sqrt{G(\mathbf{q}_{AC})} \sqrt{(d\mathbf{q}_{AC}/dt')^T (d\mathbf{q}_{AC}/dt')} dt' - \int_0^t \sqrt{G(\mathbf{q}_{SA})} \sqrt{(d\mathbf{q}_{SA}/dt')^T (d\mathbf{q}_{SA}/dt')} dt'$$

Computed through the Arbitrary Curve (AC) that joins the points M and q. Computed through the Steepest Ascent Curve (SA) that joins the points M and q.

Algorithm details: R. Crehuet, J.M. Bofill, *J. Chem. Phys.* **122**, 234105 (2005).



The **white open dots** are the set of 21 points of the initial guess curve. The **dark dots** indicate the final converged position of the 21 points. In this final position, all points are located in the Intrinsic Reaction Coordinate curve.

The **dark dots** are the set of 21 points of the guess curve. The point R is labeled as 1 and the point P as 21. The bold faced arrows are the gradient vectors of the **Weierstrass E-function** computed at each point of the guess curve. See also A.B. Birkholz, H.B. Schlegel, *J. Chem. Phys.* **143**, 244101 (2015).

2.- b) Variational Nature of Newton Trajectory (Distinguished Coordinate Path).

The Variational Nature of the Newton Trajectory Reaction Path.

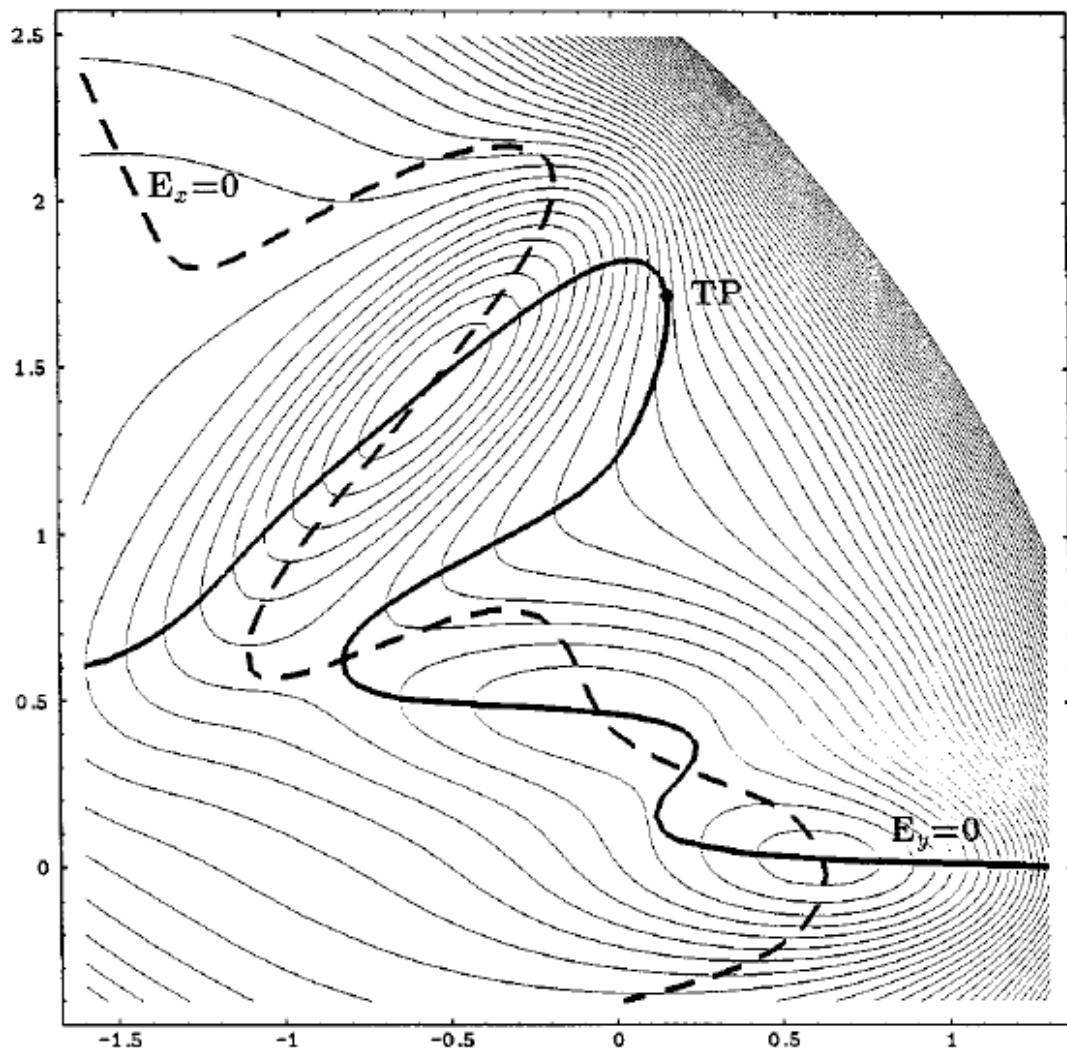
*The other curve used as Reaction Path is the **Distinguished or Driven Coordinate Path (DC)**, (M. J. Rothman and L. L. Lohr, Jr., *Chem. Phys. Lett.* **70**, 405 (1980)) or a more recent version, the so-called **Reduced Gradient Following (RGF)**, (W. Quapp, M. Hirsch, O. Imig, D. Heidrich, *J. Comput. Chem.* **19**, 1087 (1998), J. M. Anglada, E. Besalú, J. M. Bofill, R. Crehuet, *J. Comput. Chem.* **22**, 387 (2001)) *also labeled as **Newton Path or Newton Trajectory (NT)*** (W. Quapp, M. Hirsch, D. Heidrich, *Theor. Chem. Acc.* **100**, 285 (1998)).*

The Reduced Gradient Following or Newton Trajectory Reaction Path is characterized by a curve in the PES such that at each point of this curve, the gradient vector points at a constant direction.

This can be seen in another way, the **Reduced Gradient Following** curve crosses the steepest descent curve at each point so that at the same point the tangent has the same direction as the constant direction of the prescribed **Reduced Gradient Following** direction.

The **Reduced Gradient Following or Newton Trajectory Reaction Path** possesses other important features largely studied by Hirsch and Quapp (M. Hirsch, W. Quapp, *J. Math. Chem.* **36**, 307 (2004)) in their studies on the convexity of the PES region where the reaction path is located.

The Variational Nature of the Newton Trajectory Reaction Path.



The Müller-Brown potential energy surface, $E(x,y)$. **Reduced Gradient Following** or **Newton Trajectory** solutions ($E_x = 0$, E_y) (dashed curve) and (E_x , $E_y = 0$) (bold curve). They connect the three minima with the two saddle points. TP marks one of the turning points of the **Reduced Gradient Following** or **Newton Trajectory** curve (E_x , $E_y = 0$).

The concept may be generalized by the challenge that any selected gradient direction is fixed

$$\nabla_{\mathbf{x}} E(\mathbf{x}) / \|\nabla_{\mathbf{x}} E(\mathbf{x})\| = \mathbf{r}$$

where \mathbf{r} is the selected unit vector of the search direction.

The Variational Nature of the Newton Trajectory Reaction Path.

The **Reduced Gradient Following** approach or **Driven Coordinate** method shows an important analogy to the mathematical theory of Branin, the **global Newton method**, that is given by the equation:

$$\frac{d\mathbf{x}}{dt} = \pm \mathbf{A}(\mathbf{x}) \mathbf{g}(\mathbf{x}) \quad \text{equivalent behavior to} \quad \frac{\mathbf{g}(\mathbf{x})}{|\mathbf{g}(\mathbf{x})|} = \mathbf{r}.$$

Where $\mathbf{A}(\mathbf{x})$ is the adjoint matrix of the Hessian matrix $\mathbf{H}(\mathbf{x})$ and $\mathbf{g}(\mathbf{x})$ is the gradient vector all computed at the position \mathbf{x} , \mathbf{r} is the predefined unit vector.

The "+" option is used for searching stationary points with odd index (stationary points with an odd number of negative eigenvalues of the Hessian), where the "-" option searches for stationary points with even index (minima, or stationary points with an even number of negative eigenvalues of the Hessian). (W.Quapp, M.Hirsch, D.Heidrich, *Theor. Chem. Acc.* **100**, 285 (1998)).

Limit points: stationary points ($\mathbf{g}(\mathbf{x}) = \mathbf{0}$) and points where $\mathbf{g}(\mathbf{x}) \neq \mathbf{0}$ but $\mathbf{A}(\mathbf{x}) \mathbf{g}(\mathbf{x}) = \mathbf{0}$. In these points the **Newton Trajectory** or **Reduced Gradient Following** curve bifurcates.

The Variational Nature of the Newton Trajectory Reaction Path.

The **Reduced Gradient Following** curves or that is the same the **Newton Trajectory** curves are extremal curves of the integral functional (J. M. Bofill, W. Quapp, *J. Chem. Phys.* **134**, 074101 (2011))

$$I(\bar{\mathbf{x}}) = \int_{x_{rc}^0}^{x_{rc}} V(x'_{rc}, \bar{\mathbf{x}}) dx'_{rc} \quad \text{where} \quad \bar{\mathbf{x}}^T = (x_1, \dots, x_{rc-1}, x_{rc+1}, \dots, x_N)$$

and $V(\mathbf{x})$ is the potential energy surface, $\mathbf{x}^T = (x_{rc}, \bar{\mathbf{x}}^T)$.

The Euler-Lagrange equation is

$$\nabla_{\bar{\mathbf{x}}} V(x_{rc}, \bar{\mathbf{x}}) = \mathbf{0}_{N-1} \quad \text{because } \partial V / \partial x_{rc} \neq 0 \text{ then } \nabla_{\mathbf{x}} V(x_{rc}, \bar{\mathbf{x}}) / \|\nabla_{\mathbf{x}} V(x_{rc}, \bar{\mathbf{x}})\| = \mathbf{r} = \begin{pmatrix} 0_1 \\ \vdots \\ 0_{rc-1} \\ 1_{rc} \\ 0_{rc+1} \\ \vdots \\ 0_N \end{pmatrix}$$

This set of equations determines the reaction path function $\mathbf{x} = \mathbf{x}(x_{rc})$ implicitly.

The tangent of this curve is: $d\mathbf{x} / dx_{rc} = \mathbf{A}(\mathbf{x})\mathbf{g}(\mathbf{x}) = \mathbf{A}(\mathbf{x})\nabla_{\mathbf{x}} V(\mathbf{x})$.

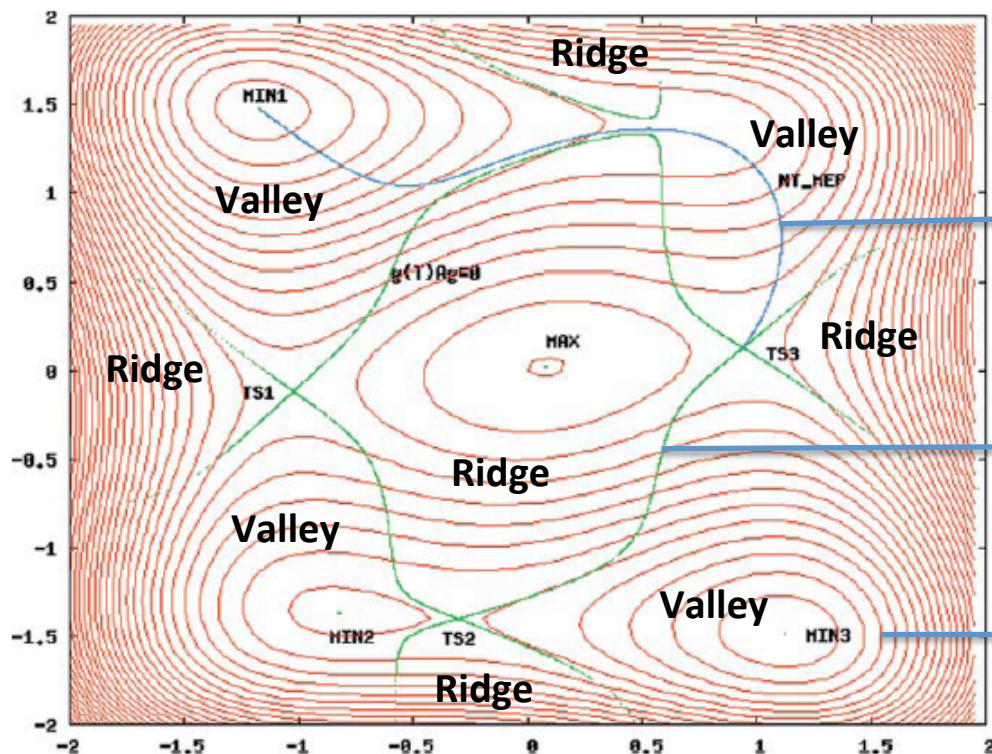
Where the $\mathbf{A}(\mathbf{x})$ matrix is the adjoint of the Hessian matrix.

The Variational Nature of the Newton Trajectory Reaction Path.

The extremal curve $\mathbf{x} = \mathbf{x}(x_{rc})$ makes the integral $I(\bar{\mathbf{x}}) = \int_{x_{rc}^0}^{x_{rc}} V(x_{rc}', \bar{\mathbf{x}}) dx_{rc}'$ a minimum: If the determinant of the Hessian matrix, $\nabla_{\mathbf{x}} \nabla_{\mathbf{x}}^T V(\mathbf{x})$

projected in the subspace orthogonal to \mathbf{r} is positive definited at each point of the curve, $\det[S^T (\nabla_{\mathbf{x}} \nabla_{\mathbf{x}}^T V(\mathbf{x})) S]_{\mathbf{x}=\mathbf{x}(x_{rc})} > 0$; $S = [s_1 \cdots s_{N-1}]$; $S^T \mathbf{r} = \mathbf{0}_{N-1}$.

$V(x,y)$: The Wolfe-Quapp Potential Energy Surface .



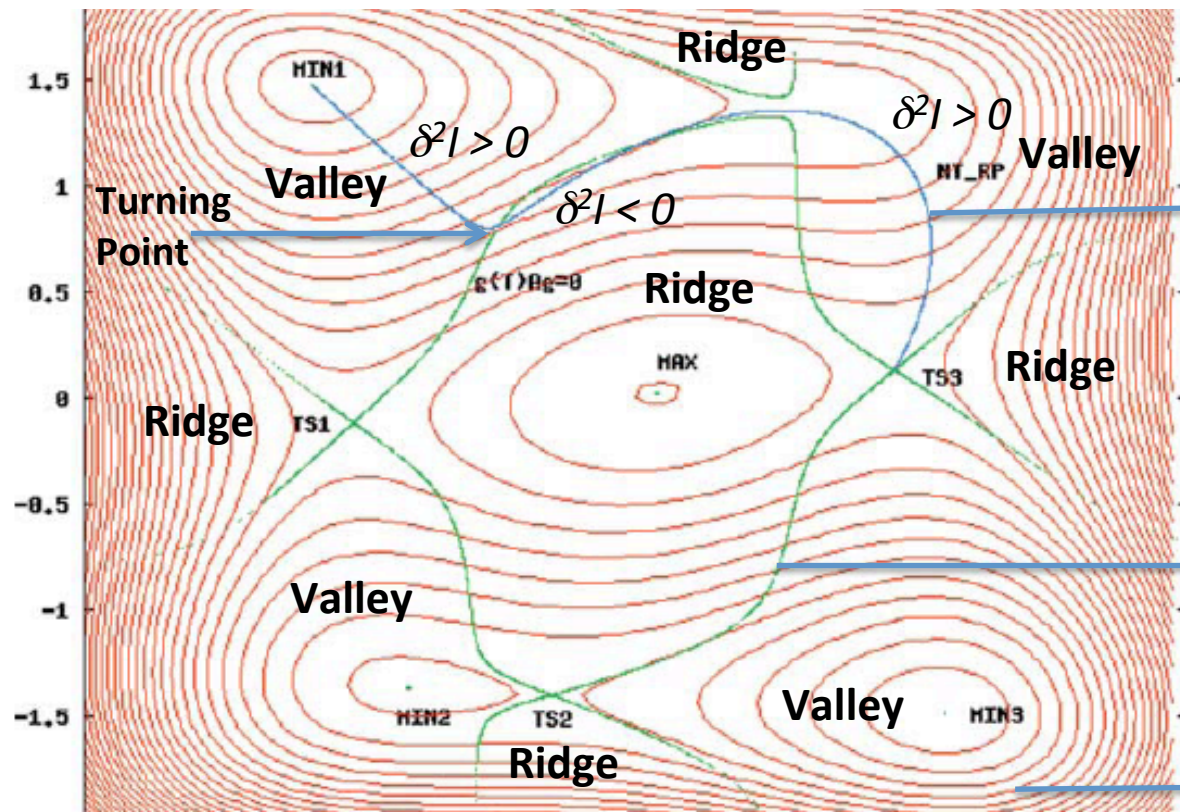
Newton Trajectory reaction path. Because $\delta^2 I \geq 0$ then this reaction path is a MEP (minimum energy path).

Valley-ridge border line where, $\det[S^T (\nabla_{\mathbf{x}} \nabla_{\mathbf{x}}^T V(\mathbf{x})) S] = 0$; $S = [s_1 \cdots s_{N-1}]$; $S^T \mathbf{g}(\mathbf{x}) = \mathbf{0}_{N-1}$.

Equipotential curves of the PES.

The Variational Nature of the Newton Trajectory Reaction Path.

$V(x,y)$: The Wolfe-Quapp Potential Energy Surface .



Newton Trajectory curve is not a reaction path because is not monotonically increasing curve from minimum to TS.

Valley-ridge border line:

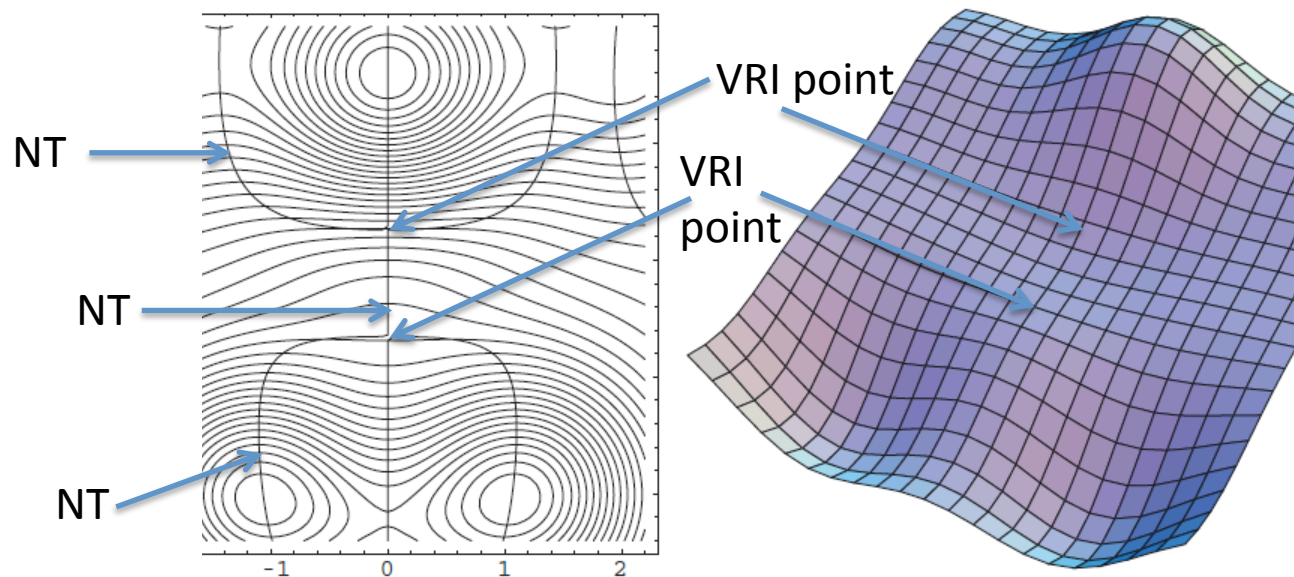
$$\det\left(\mathbf{S}^T \left[\nabla_{\mathbf{x}} \nabla_{\mathbf{x}}^T V(\mathbf{x}) \right] \mathbf{S}\right) = 0$$

Equipotential curves of the PES (red curves).

In the turning point the **Newton Trajectory** curve has $dV/dx_{rc} = 0$

At each point of the valley-ridge border line the determinant of the Hessian matrix projected in the subspace orthogonal to the gradient is zero. The matrix \mathbf{S} collects the set of linear independent vectors orthogonal to $\mathbf{g}(\mathbf{x})$.

The Variational Nature of the Newton Trajectory Reaction Path.



A **Newton Trajectory** curve starting in a minimum minimizes the variational integral $I(\mathbf{x})$ if the curve does not have a Valley Ridged Inflection point otherwise no statement can be made. In the former situation the Newton Trajectory locates a Transition State and the whole curve is located in a valley. The Newton Trajectory is a Reaction Path with character Minimum Energy Path. (J. M. Bofill, W. Quapp, *J. Chem. Phys.* **134**, 074101 (2011)).

Newton Trajectories ($d\mathbf{x}/dt = \mathbf{A}(\mathbf{x})\mathbf{g}(\mathbf{x})$) locate both stationary points, $\mathbf{g}(\mathbf{x}) = \mathbf{0}$ and Valley-Ridged-Inflection points $\mathbf{A}(\mathbf{x})\mathbf{g}(\mathbf{x}) = \mathbf{0}$. It can be used to locate Conical Intersections. (W. Quapp, J. M. Bofill, M. Caballero, *Chem. Phys. Lett.* **541**, 122 (2012)).

The Variational Nature of the Newton Trajectory Reaction Path.

The **Reduced Gradient Following** or **Newton Trajectory** curves open a cornucopia of insights into the structure/topography of the Potential Energy Surface. To get this we need to test a somehow greater number of **Newton Trajectory** curves.

- **For applications see e.g.**, the topography of cyclopropyl radical (W. Quapp, J.M. Bofill, J. Aguilar-Mogas, *Theor. Chem. Acc.* **129**, 803 (2011); W. Quapp, J.M. Bofill, *J. Math. Chem.* **50**, 2061 (2012)); ring opening cyclobutene (W. Quapp, J.M. Bofill, *Int. J. Quantum Chem.* **115**, 1635 (2015)).

- **Other applications to chemical reactivity:**

M. Hirsch, W. Quapp, *J. Mol. Struct. THEOCHEM* **683**, 1 (2004).

- **Newton Trajectories as basis of a Theory for Mechanochemistry and Catalysis:**

W. Quapp, J.M. Bofill, *J. Phys. Chem. B* **120**, 2644 (2016); W. Quapp, J.M. Bofill, *Theor. Chem. Acc.* **135**, 113 (2016); W. Quapp, J.M. Bofill, *J. Comput. Chem.* DOI: 10.1002/jcc.24470, (2016); W. Quapp, J.M. Bofill, J. Ribas-Ariño, *Phys. Chem. Chem. Phys.* (submitted). Also the lecture of Dr. W. Quapp in this meeting.

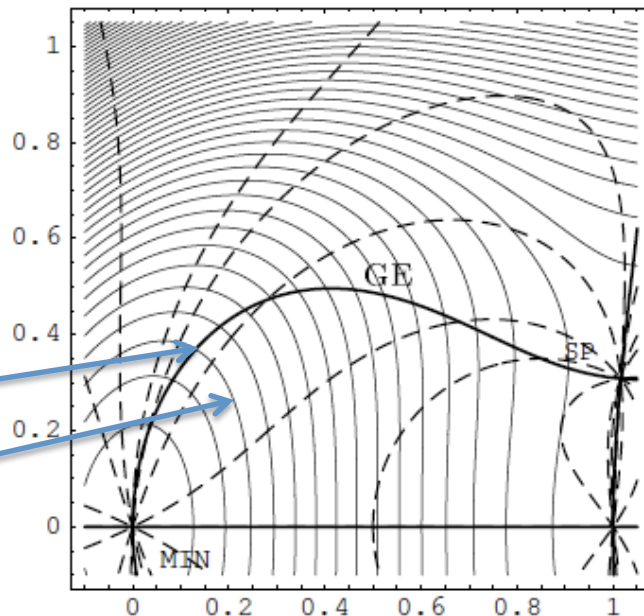
2.- c) Variational Nature of Gradient Extremals Path.

The Variational Nature of Gradient Extremals Path.

The curve where at each point the gradient norm is stationary in the equipotential surface is called Gradient Extremals.

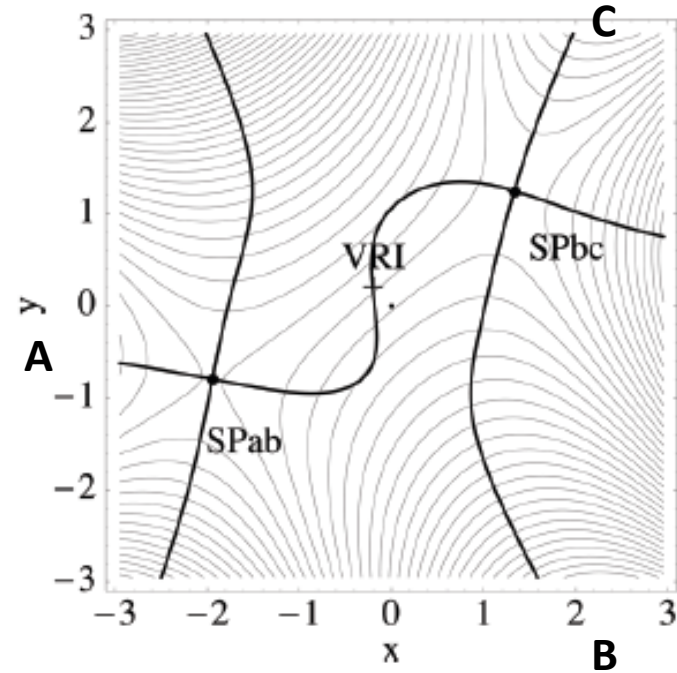
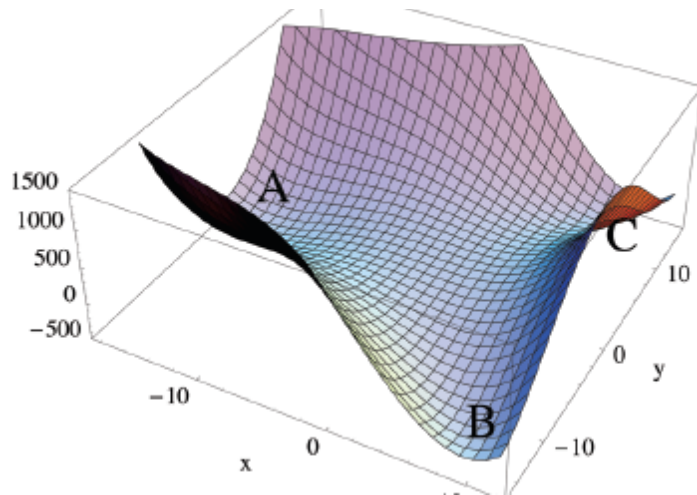
The curve at each point transverses the equipotential curve $V(\mathbf{q}) = v$. At this point the norm $\mathbf{g}^T(\mathbf{q})\mathbf{g}(\mathbf{q})$ is stationary with respect to any displacement within the equipotential curve.

$\mathbf{g}^T(\mathbf{q})\mathbf{g}(\mathbf{q})$ stationary
with respect to \mathbf{q} in the curve $V(\mathbf{q}) - v = 0$



J. Pancir, *Collect. Czech. Chem. Commun.* **40**, 1112 (1975); M.V. Basilevsky, A.G. Shamov, *Chem. Phys.* **60**, 347 (1981); M.V. Basilevsky, *Chem. Phys.* **67**, 337 (1982); D. K. Hoffman, R.S. Nord, K. Ruedenberg, *Theor. Chim. Acta* **69**, 265 (1986); P. Jørgensen, H.J.Aa. Jensen, T. Helgaker, *Theor. Chim. Acta* **73**, 55 (1988); W. Quapp, *Theor. Chim. Acta* **75**, 447 (1989); H.B. Schlegel, *Theor. Chim. Acta* **83**, 15 (1991); J.-Q. Sun, K. Ruedenberg, *J. Chem. Phys.* **98**, 9707 (1993); K. Bondensgård, F. Jensen, *J.Chem.Phys.* **104**, 8025 (1996); J.M. Bofill, W. Quapp, M. Caballero, *J. Chem. Theory Comput.* **8**, 927 (2012). This curve is not widely used due to their computation cost. **Nevertheless, still is very appropriated as Reaction Path and in the Theory of the Mechanochemistry** (W. Quapp, J. M. Bofill, *Theor. Chem. Acc.* **135**, 113 (2016) Dr. W. Quapp in this meeting).

The Variational Nature of Gradient Extremals Path.



Mathematical Basis: An example of Lagrange-Bolza Variational Problem.

$$I(\mathbf{q}) = \int_{t_0}^{t'} \left\{ \frac{1}{2} \mathbf{g}^T(\mathbf{q}) \mathbf{g}(\mathbf{q}) - \lambda(\mathbf{q}) (V(\mathbf{q}) - \nu) \right\} dt$$

The resulting Euler-Lagrange equation: $\mathbf{H}\mathbf{g} = \lambda\mathbf{g}$ where \mathbf{H} is the Hessian matrix and \mathbf{g} is the gradient vector at the point \mathbf{q} . At each point of a Gradient Extremal curve this eigenvalue equation is satisfied.

The Variational Nature of Gradient Extremals Path.

The eigenvalue equation, $\mathbf{H}(\mathbf{q})\mathbf{g}(\mathbf{q}) = \lambda(\mathbf{q})\mathbf{g}(\mathbf{q})$, determines the Gradient Extremal (GE) curve, $\mathbf{q} = \mathbf{q}(t)$, implicitly. We note that in this case the boundary values, $\mathbf{q}_0 = \mathbf{q}(t_0)$ and $\mathbf{q}_f = \mathbf{q}(t_f)$, cannot be prescribed arbitrarily if the problem should have a solution. The tangent curve was first derived by J.-Q. Sun, K. Ruedenberg, *J. Chem. Phys.* **98**, 9707 (1993):

$$\left(\mathbf{I} - \frac{\mathbf{g}\mathbf{g}^T}{\mathbf{g}^T\mathbf{g}} \right) \left[\langle \mathbf{F}\mathbf{g} \rangle + \mathbf{H}^2 - \frac{\mathbf{g}^T\mathbf{H}\mathbf{g}}{\mathbf{g}^T\mathbf{g}} \mathbf{H} \right] \frac{d\mathbf{q}}{dt} = \mathbf{0}$$

Third derivative tensor
of the energy.

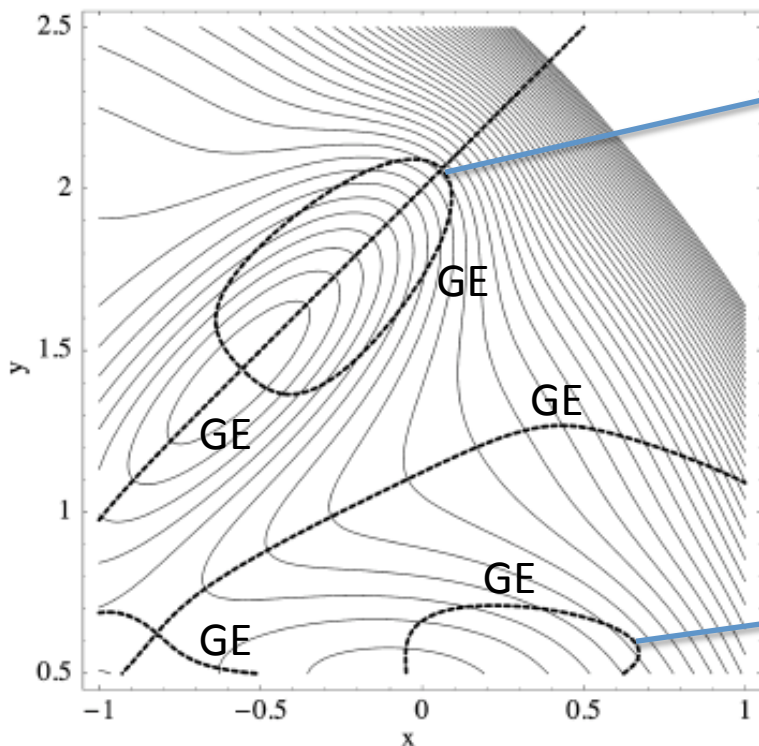
Using the perturbation theory applied to the eigenvalue equation, $\mathbf{H}\mathbf{g} = \lambda\mathbf{g}$, as formulated by McWeeny (R. McWeeny, *Phys. Rev.* **126**, 1028 (1961)) can be derived this tangent curve equation (J. M. Bofill, W. Quapp, M. Caballero, *J. Chem. Theory Comput.* **8**, 927 (2012)).

The Variational Nature of Gradient Extremals Path.

Special points of the Gradient Extremals (GE) curve.

$$\left(\mathbf{I} - \frac{\mathbf{g}\mathbf{g}^T}{\mathbf{g}^T\mathbf{g}} \right) \left[\langle \mathbf{F}\mathbf{g} \rangle + \mathbf{H}^2 - \frac{\mathbf{g}^T\mathbf{H}\mathbf{g}}{\mathbf{g}^T\mathbf{g}} \mathbf{H} \right] \frac{d\mathbf{q}}{dt} = \mathbf{0}$$

The points where the matrix in the brackets is not invertible are Turning Points or Bifurcation Points of the Gradient Extremals curve.



Bifurcation Point

K. Bondensgård, F. Jensen, *J. Chem. Phys.* **104**, 8025 (1996); J. M. Bofill, W. Quapp, and M. Caballero, *J. Chem. Theory Comput.* **8**, 927 (2012)

Turning Point

GE: Gradient Extremals curve

The Variational Nature of Gradient Extremals Path.

The Extremal Sufficient Conditions. Conditioned by the existence of Conjugate Points in the Gradient Extremal Curves.

Necessary condition, the stationary condition: $\mathbf{H}\mathbf{g} = \lambda\mathbf{g}$.

Sufficient condition, the second variation: $\delta^2 I(\mathbf{q}) > 0$ minimum ($\delta^2 I(\mathbf{q}) < 0$ maximum).

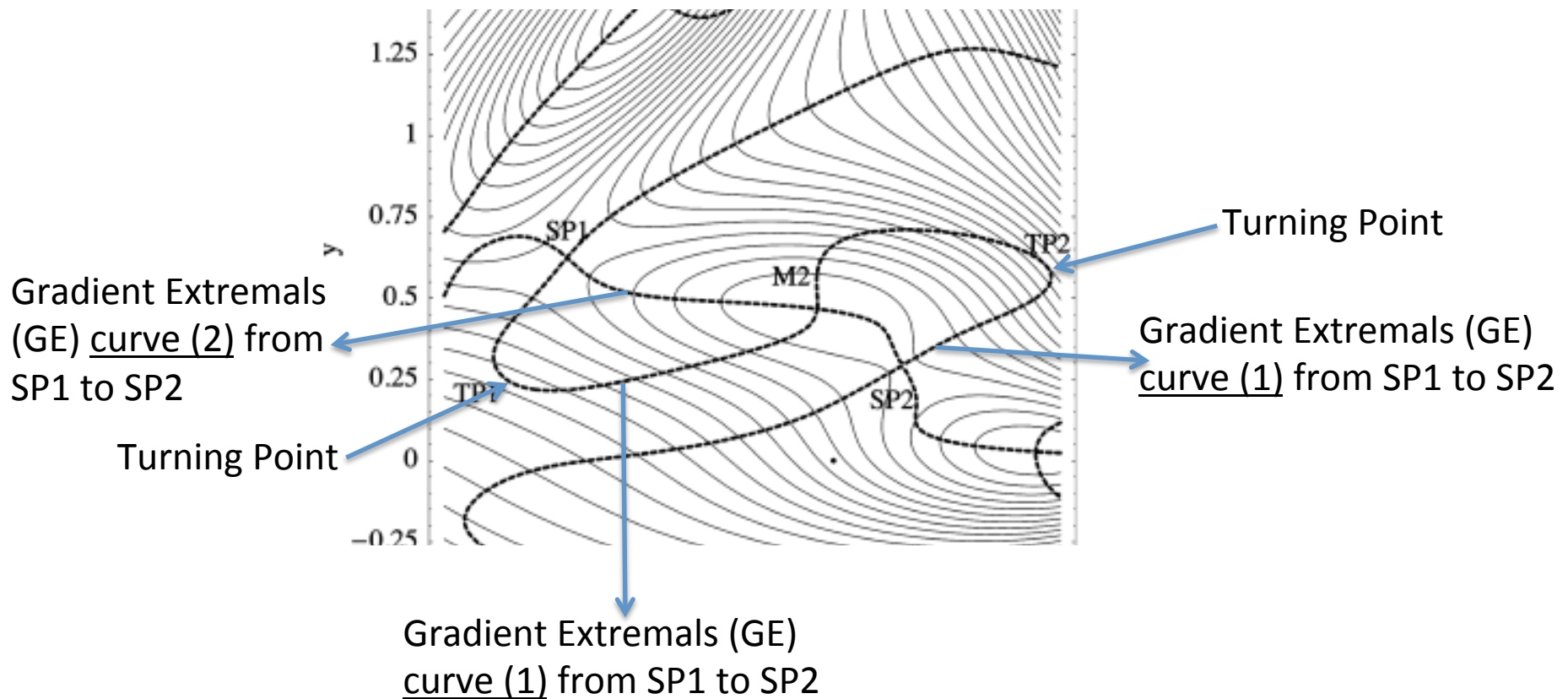
$$\delta^2 I(\mathbf{q}, \mathbf{p}) = \int_{t_0}^{t'} \mathbf{p}^T \left[\langle \mathbf{F}\mathbf{g} \rangle + \mathbf{H}^2 - \lambda\mathbf{H} \right] \mathbf{p} dt = \int_{t_0}^{t'} \mathbf{p}^T \mathbf{C}\mathbf{p} dt$$

Where $\mathbf{p}^T \mathbf{g} = 0$ and $\mathbf{p}(t_0) = \mathbf{0}$. If $\det(\mathbf{C}) > 0$ along the interval $t_0 \leq t \leq t'$ then the **Gradient Extremals** curve minimizes the variational integral, $I(\mathbf{q})$, otherwise maximizes $I(\mathbf{q})$.

If the **Gradient Extremals** curve from t_0 to t_1 the $\det(\mathbf{C}) > 0$, but at t_1 the $\det(\mathbf{C}) = 0$ and from this point until t' the $\det(\mathbf{C}) < 0$ then the **Gradient Extremals** curve loses the minimum character. There exists an arbitrary curve joining the the same points $\mathbf{q}(t_0)$ and $\mathbf{q}(t')$ that makes the value of the integral $I(\mathbf{q})$ lower with respect to the value of the same integral computed using the **Gradient Extremals** curve.

The points where the **Gradient Extremals** curve have $\det(\mathbf{C}) = 0$ are Turning Points or Bifurcation Points. The **Turning Points** and **Bifurcation Points** can be seen as the **Conjugate Points of Gradient Extremals curves**.

The Variational Nature of Gradient Extremals Path.



Basic Gradient Extremals
Variational Integral:

$$I(\mathbf{q}) = \int_{t_0}^{t'} \left\{ \frac{1}{2} \mathbf{g}^T(\mathbf{q}) \mathbf{g}(\mathbf{q}) - \lambda(\mathbf{q})(V(\mathbf{q}) - v) \right\} dt$$

$I(\mathbf{q})$ evaluated on GE curve (1) > $I(\mathbf{q})$ evaluated on GE curve (2)

2.- d) Variational Nature of Gentlest Ascent Dynamics Path.

The Variational Nature of Gentlest Ascent Dynamics Path.

We assume that the system under consideration is defined by a PES, $V(\mathbf{x})$, N is the number of degrees of freedom. The PES is assumed to be smooth. The $\mathbf{g}(\mathbf{x})$ is the gradient vector and $\mathbf{H}(\mathbf{x})$ the Hessian matrix at the point \mathbf{x} of $V(\mathbf{x})$. The equations that govern the gentlest ascent dynamics path (GAD) are as follows:

$$d\mathbf{x} / dt = -[\mathbf{I} - 2\mathbf{w}\mathbf{w}^T] \mathbf{g}(\mathbf{x}) = -[\mathbf{I} - \mathbf{w}\mathbf{w}^T] \mathbf{g}(\mathbf{x}) + \mathbf{w}\mathbf{w}^T \mathbf{g}(\mathbf{x}),$$

$$d\mathbf{w} / dt = -[\mathbf{I} - \mathbf{w}\mathbf{w}^T] \mathbf{H}(\mathbf{x}) \mathbf{w} = -\mathbf{H}(\mathbf{x}) \mathbf{w} + \mathbf{w}\mathbf{w}^T \mathbf{H}(\mathbf{x}) \mathbf{w}, \quad \mathbf{w}^T \mathbf{w} = 1.$$

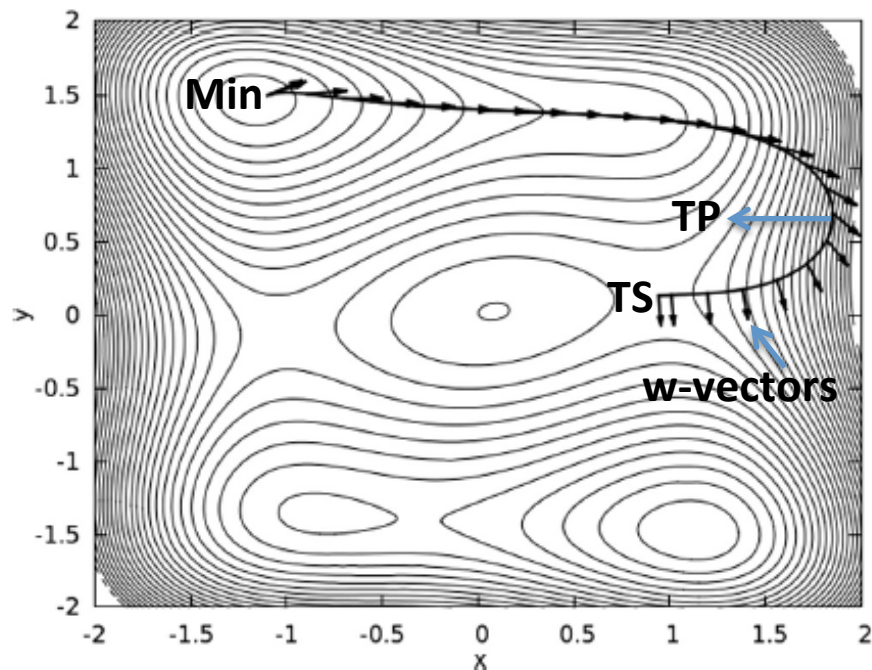
Where \mathbf{I} is the unit matrix.

The first equation means that we reverse the components of the gradient vector in the subspace orthogonal to $\mathbf{w}(t)$ and is preserved in the direction of $\mathbf{w}(t)$. Thus it walks towards a saddle point of index-one. The $[\mathbf{I} - 2\mathbf{w}\mathbf{w}^T]$ matrix is an orthogonal transformation, $[\mathbf{I} - 2\mathbf{w}\mathbf{w}^T][\mathbf{I} - 2\mathbf{w}\mathbf{w}^T] = \mathbf{I}$ since $\mathbf{w}^T \mathbf{w} = 1$.

The second equation defines the dynamics of the descent direction $\mathbf{w}(t)$. The first term on the right hand side ensures that $\mathbf{w}(t)$ converges to an eigenvector associated with the smallest eigenvalue of $\mathbf{H}(\mathbf{x})$ matrix. The second term ensures that the length of \mathbf{w} is fixed at 1. Note that $\mathbf{w}^T(t_0)\mathbf{w}(t_0) = 1$.

GAD curve model was proposed by E and Zhou (W. E, X. Zhou, *Nonlinearity* **24**, 1831 (2011).)

The Variational Nature of Gentlest Ascent Dynamics Path.



Behaviour of the GAD curve on the Wolfe-Quapp PES. The GAD curve starts at the point near the minimum **Min**. The curve evolution ends at the **TS** point. The curve achieves the highest energy at the point **TP** (turning point). The curve leaves the valley where the starting minimum is located. The set of **w**-vectors generated during the search are indicated by the set of bold arrows.

The turning point (TP) occurs at the point of the GAD curve where the gradient vector, $\mathbf{g}(\mathbf{x})$, and the \mathbf{w} -vector forms an angle equal to $\pi/4$ radians. (J.M. Bofill, W. Quapp, M. Caballero, *Chem. Phys. Lett.* **583**, 203 (2013))

The Variational Nature of Gentlest Ascent Dynamics Path.

The GAD curve is the counterpart of well-known classical navigation problem posed and solved by Zermelo an optimal control problem (E. Zermelo, *Z. Angew. Math. Mech.* **11**, 114 (1931); C. Carathéodory, *Variationsrechnung und partielle Differentialgleichungen erster Ordnung*. B. G. Teubner, Berlin (1935)):

Classical navigation problem: *it is given the present location of a ship in the sea, with a given current distribution characterized by a location dependent vector field. One desires to find the optimal control of the ship so as to reach the destination in the shortest possible time.*

Back to GAD curve: *the gradient vector field of the PES function can be thought of as representing the current of the sea, which we cannot change, whereas the normalized vector \mathbf{w} determines the control. The destination is the next Stationary Point of the PES.*

In a more precise way, *the GAD model consists of the determination of the minimum of the t -parameter, $J[\mathbf{x}_{TS}(\mathbf{w}(t_f))] = t_f - t_0$, in which a controlled point can be evolved from a given minimum point of the PES, $\mathbf{x}_{Min} = \mathbf{x}(t_0)$, to a final transition state of this PES, $\mathbf{x}_{TS} = \mathbf{x}(t_f)$, boundary conditions, $\mathbf{g}(\mathbf{x}(t_0)) = \mathbf{g}(\mathbf{x}(t_f)) = \mathbf{0}$. The evolution of the test point is described by the system of ordinary differential equations: $d\mathbf{x}/dt = - [\mathbf{I} - 2\mathbf{w}\mathbf{w}^T]\mathbf{g}(\mathbf{x})$, where $\mathbf{w}(t)$ is a normalized N -dimensional vector of the control parameters.*

The Variational Nature of Gentlest Ascent Dynamics Path.

*Since t_0 is fixed, the required minimum t_f is merely the minimization of the functional $J[\mathbf{x}_{TS}(\mathbf{w}(t_f))]$ that depends on the chosen $\mathbf{w}(t)$ -control normalized vector. Thus the GAD curve model is a t-parameter-optimal control problem and can be considered as a particular instance of the **Mayer problem of the Theory of Calculus of Variations**. Also the GAD, as a case of an optimal control problem, must satisfy the **Pontryagin Maximum Principle**. (J.M. Bofill, W. Quapp, *Theor. Chem. Acc.* **135**, 11 (2016); J.M. Bofill, W. Quapp, *An Application of the Maximum Principle in Chemistry: A Method to Locate Transition States*, Apple Academic Press, New Jersey (2016)).*

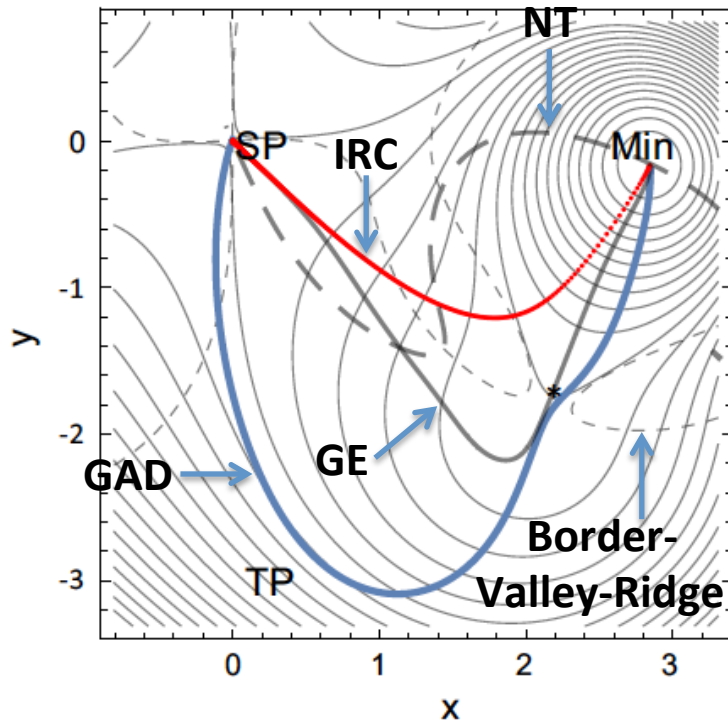
Applying a device due to Zermelo (see also Carathéodory), the GAD Hamiltonian of this type Mayer variational problem is:

$$2H(\mathbf{x}, \mathbf{y}) = (2\mathbf{w}^T \mathbf{g}(\mathbf{x}))^2 (\mathbf{y}^T \mathbf{y}) - (1 + \mathbf{y}^T \mathbf{g}(\mathbf{x}))^2 = 0 \quad \text{where } \mathbf{y} \text{ is the conjugate variable}$$

of \mathbf{x} related with \mathbf{w} through the relation $\mathbf{w}(1 + \mathbf{y}^T \mathbf{g}(\mathbf{x})) = (2\mathbf{w}^T \mathbf{g}(\mathbf{x}))\mathbf{y}$.

*The two canonical equations associated to this Hamiltonian are the GAD system of ordinary differential equations, namely, $d\mathbf{x}/dt = -[\mathbf{I} - 2\mathbf{w}\mathbf{w}^T]\mathbf{g}(\mathbf{x})$ and $d\mathbf{w}/dt = -[\mathbf{I} - \mathbf{w}\mathbf{w}^T]\mathbf{H}(\mathbf{x})\mathbf{w}$, where $\mathbf{w}^T\mathbf{w}=1$, ($d\mathbf{w}/dt$ related with $d\mathbf{y}/dt$) . The minimum or maximum character of GAD extremal curve is analyzed through the positivity or negativity value of the Weierstrass error function, $E(\mathbf{x}, d\mathbf{x}/dt, d\mathbf{x}'/dt) = 2[1 - (\mathbf{w}^T\mathbf{w}')(\mathbf{g}^T(\mathbf{x})\mathbf{w}')/(\mathbf{g}^T(\mathbf{x})\mathbf{w})]$. This is an indirect proof of Pontryagin Maximum Principle. (J.M. Bofill, W. Quapp, *Theor. Chem. Acc.* **135**, 11 (2016)).*

The Variational Nature of Gentlest Ascent Dynamics Path.



The *turning point (TP)* occurs at the point of the **GAD** curve where the gradient vector, $\mathbf{g}(\mathbf{x})$, and the $\mathbf{w}(t)$ -control vector forms an angle equal to $\pi/4$ radians.

A **GAD** curve (blue) by Eq. $\frac{dx}{dt} = -[\mathbf{I} - 2\mathbf{w}\mathbf{w}^T]\mathbf{g}$ on a two-dimensional toy potential. The control vector, $\mathbf{w}(t)$, is throughout the first eigenvector, calculated by Eq. $\frac{d\mathbf{w}}{dt} = -[\mathbf{I} - \mathbf{w}\mathbf{w}^T]\mathbf{H}\mathbf{w}$. The surface is a modified Neria-Fischer-Karplus case [M. Hirsch, W. Quapp, *Chem. Phys. Lett.* **395**, 150 (2004)]. The asterisk (*) marks a *quasi-shoulder*, and the thin dashes mark the *borderline between valleys and ridges*. **TP** is the *turning point* of the **GAD** curve. For comparisons are given: the valley *Gradient Extremal (GE)* by a bold faced black curve, the *Intrinsic Reaction Coordinate (IRC)* by a red curve, and a *Newton Trajectory (NT)* by a dashed black curve. Note that the **IRC** starts near the **SP of index one**, but the **GAD** starts near the **Min**.

In this case **GAD** does not satisfy the Reaction Path requirements. It goes over the borderline between valley and ridge.

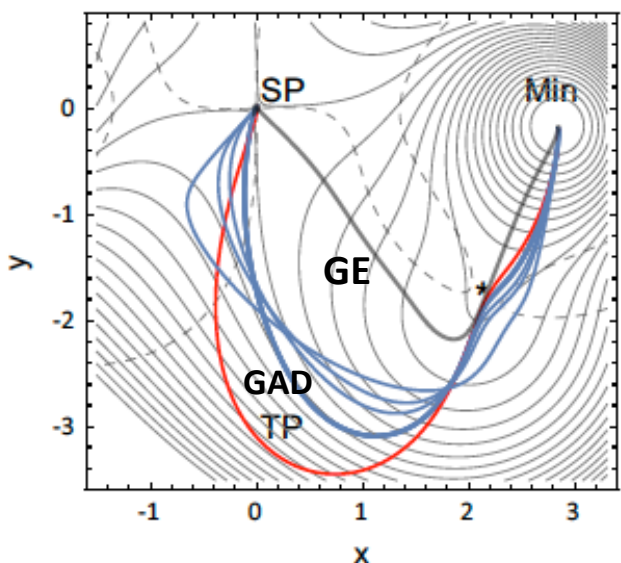
The Variational Nature of Gentlest Ascent Dynamics Path.

Proposed Reaction Path curves based on the model of Zermelo's problem. It is proposed a generic type curve where its general tangent is given by the expression:

$$d\mathbf{x} / dt = -\mathbf{g}(\mathbf{x}) + f(\phi, \mathbf{x}, \mathbf{w}) \mathbf{w}, \quad \mathbf{w}^T \mathbf{w} = 1.$$

Where \mathbf{w} is the control vector. The function $f(\phi, \mathbf{x}, \mathbf{w})$ is a continuous and differentiable function with respect to \mathbf{x} and ϕ is a constant. Taking $f(\phi, \mathbf{x}, \mathbf{w}) = \phi \mathbf{w}^T \mathbf{g}(\mathbf{x})$ with ϕ larger than one. The $d\mathbf{w}/dt$ is given by the expression:

$$d\mathbf{w} / dt = -[\mathbf{I} - \mathbf{w}\mathbf{w}^T] (\nabla_{\mathbf{x}} f(\phi, \mathbf{x}, \mathbf{w}) - \mathbf{H}(\mathbf{x}) \mathbf{w}) = -(\phi - 1) [\mathbf{I} - \mathbf{w}\mathbf{w}^T] \mathbf{H}(\mathbf{x}) \mathbf{w}.$$



Curves (blue with $\phi \geq 2$, red with $\phi = (2)^{1/2}$) of the Eq. $d\mathbf{x}/dt$ with $f(\phi, \mathbf{x}, \mathbf{w}) = \phi \mathbf{w}^T \mathbf{g}(\mathbf{x})$. Start is at minimum. The **bold blue** curve is the GAD curve with $\phi = 2$, the other blue curves are to $\phi = 3, 4$, and 10 . The control vector is calculated by Eq. $d\mathbf{w}/dt$. The asterisk (*) marks a quasi-shoulder, and the thin dashes mark the borderline between valleys and ridges. For comparison, the GE is given (thick black curve) which is here the valley floor pathway between **SP** and **Min**. (J.M.Bofill, W.Quapp, *Theor. Chem. Acc.* **135**, 11 (2016)).

The Variational Nature of Gentlest Ascent Dynamics Path.

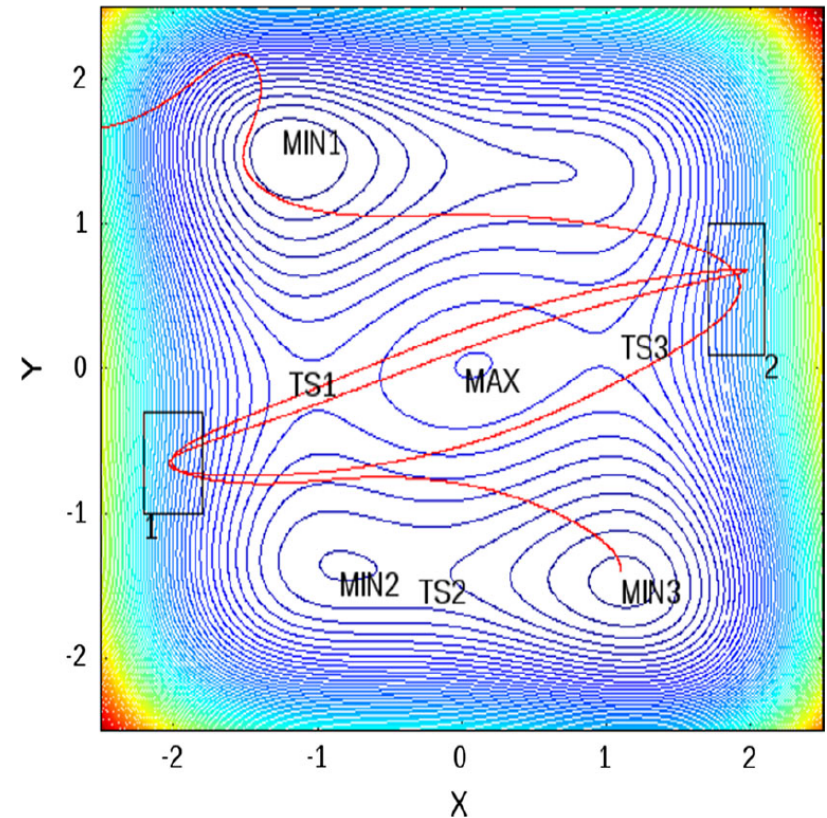
The extension of GAD to a kind of molecular dynamics. It was proposed by Samanta and E (A. Samanta, W. E, *J. Chem. Phys.* **136**, 124104 (2012); J. M. Bofill, W. Quapp, E. Bernuz, *J. Math. Chem.* **53**, 41 (2015)). The dynamical equations are:

$$d\mathbf{x} / dt = \mathbf{p},$$

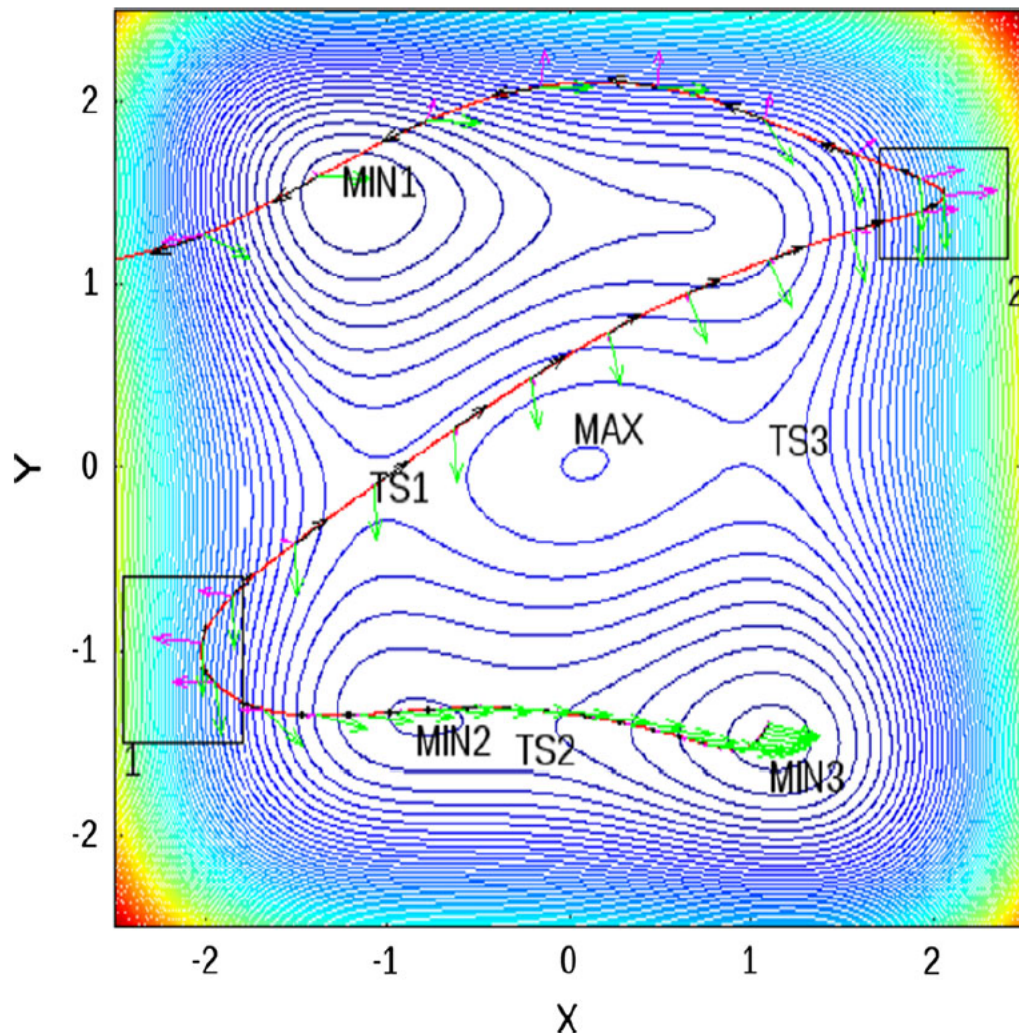
$$d\mathbf{p} / dt = -[\mathbf{I} - 2\mathbf{w}\mathbf{w}^T] \mathbf{g}(\mathbf{x}),$$

$$d\mathbf{w} / dt = -[\mathbf{I} - \mathbf{w}\mathbf{w}^T] \mathbf{H}(\mathbf{x})\mathbf{w}, \quad \mathbf{w}^T \mathbf{w} = 1.$$

MD-GAD trajectory, depicted in red color, but starting at the point $(x, y, p_x, p_y, w_x, w_y) = (1.1, -1.4, 0, 0, 0, 1)$. The initial \mathbf{w} vector is the second column of the unit matrix. The regions marked by a black square contain a Turning Point of the trajectory. The trajectory also shows 'some chaotic' behavior in the region where **TS1**, **TS3** and **MAX** stationary points are located.



The Variational Nature of Gentlest Ascent Dynamics Path.



An MD-GAD trajectory in red color, starting at the point $(x, y, p_x, p_y, w_x, w_y) = (1.1, -1.4, 0, 0, 0.982, -0.189)$. The initial control vector, \mathbf{w} , is the eigenvector of the second eigenvalue of the Hessian matrix evaluated at the starting point. The **black arrows** are the momentum or tangent vectors of the trajectory, $d\mathbf{x}/dt = \mathbf{p}$, the **green arrows** are the control \mathbf{w} -vectors while the **arrows in magenta** are the gradient vectors of the PES, $\mathbf{g}(\mathbf{x})$. The regions marked by a black square are where a Turning Point of the trajectory occurs. This trajectory here does not show any 'chaotic' behavior.

Josep Maria Bofill Villà

Departament de Química Inorgànica i Orgànica, Secció de Química Orgànica and Institut de Química Teòrica i Computacional, Universitat de Barcelona, Martí i Franquès, 1, 08028 Barcelona, Catalunya, Spain.

Wolfgang Quapp

Mathematisches Institut, Universität Leipzig, PF 100920, D-04009 Leipzig, Germany.

Students: *Marc Caballero Puig and Efrem Bernuz Fitó*

Departament de Ciència de Materials i Química Física, Secció de Química Física and Institut de Química Teòrica i Computacional, Universitat de Barcelona, Martí i Franquès, 1, 08028 Barcelona, Catalunya, Spain.

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