Bases and Features of the Potential Energy Surface and Reaction Path Models, their Extensions, and Beyond.

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and

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Abstract

The Potential Energy Surface (PES) is a mathematical object represented by a continuous function of N variables. It represents the changes of the energy which occurs if a molecular system is deformed. The minimums are related to stable molecular structures. It is impossible a completly display the PES if the molecule has more than 2 atoms.

The concept of a Reaction Path (RP) reduces the problem since it represents a-one-dimensional curve on the PES. Then the knowledge of the whole PES is not necessary. The RP is a monotonically increasing curve from a minimum to a first order saddle-point (TS) and a monotonically decreasing curve from the TS to the next minimum. There exist different RP models: Intrinsic Reaction Coordinate (IRC), Newton Trajectories (NT), Gradient Extremals (GE), ... and many others. From a physical point of view any 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 gives support to the dynamical theories: TST, and RP-Hamiltonian. The mathematical basis of different RP model is discussed. In this aspect the theory of Calculus of Variations plays an important role. Some features of the PES like valley-ridged inflection points (VRI) and Conical Intersections (CI) are also revisited. Finally, a new view of PES model is also given and briefly discussed.

Index.

1.- The Reaction Path Concept.

The Reaction Path Concept.

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

Potential Energy Profile

Reaction Path

Type of Reaction Path: Intrinsic Reaction Coordinate

Potential Energy Surface
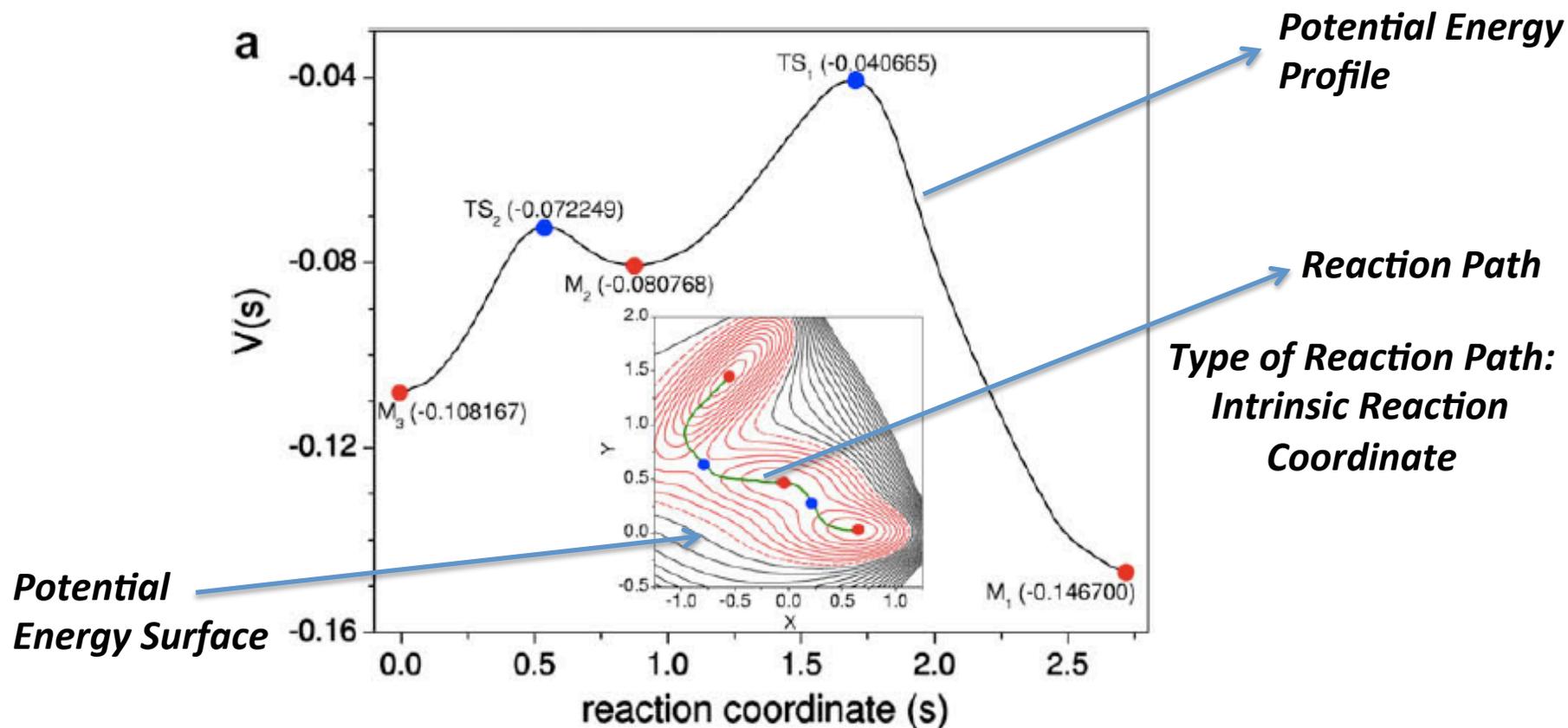
Reaction Path: A continuous curve monotonicaly increasing in energy from a minimum of the Potential Energy Surface to a First Order Saddle Point and monotonicaly decreasing from this point to a new minimum of this Potential Energy Surface.
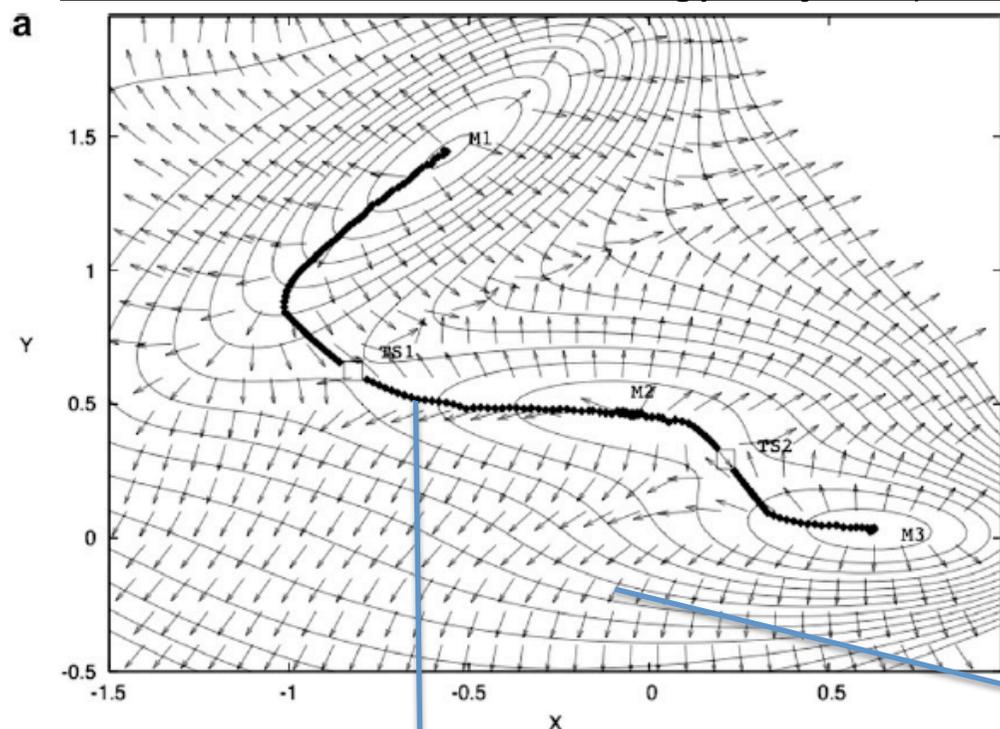
2.- *a*) Variational Nature of the Intrinsic Reaction Coordinate (Steepest Descent Path).

Variational Nature of Intrinsic Reaction Coordinate Path.

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

Gradient curve 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: $\text{tangent curve} = \mathbf{t}(\mathbf{x}) = d\mathbf{x}/dt = \nabla_{\mathbf{x}} V(\mathbf{x})$

Müller-Brown Potential Energy Surface (PES) On a PES there exists a field of gradients.

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

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

Gradient field

Intrinsic Reaction Coordinate Path

Variational Nature of 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).

Theory of Calculus of Variations.

$$I_{M \to q}(\mathbf{q}) = \int_0^t f(\mathbf{q}) \sqrt{(d\mathbf{q}/dt')^T (d\mathbf{q}/dt')} \, dt' = \int_0^t \sqrt{G(\mathbf{q})} \sqrt{(d\mathbf{q}/dt')^T (d\mathbf{q}/dt')} \, dt'$$

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

Gradient norm: $G(q)=(g^T(q)g(q))$, Speed Law.

Euler-Lagrange equation: the tangent of the path $\mathbf{q}(t)$ that extremalizes the variational integral, $I(\mathbf{q})$, is $d\mathbf{q}/dt = \mathbf{g}(\mathbf{q})$. **The extremal curve is a Steepest Ascent.** Hamilton-Jacobi equation.

Evaluated through the Steepest Ascent curve, $I_{M\to q}(\mathbf{q}) = V(\mathbf{q}_q) - V(\mathbf{q}_M)$.

At the point ($\mathbf{q}_q$, t' = t):
$\delta I_{M\to q}(\mathbf{q}) = dV = \mathbf{g}^T(\mathbf{q})d\mathbf{q}$, a total differential form.

Variational Nature of 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, $I_{M \to q}(\mathbf{q}) = V(\mathbf{q}_q) - V(\mathbf{q}_M)$. *(Fermat Variational Principle).*

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

$$\frac{\left(\nabla_{\mathbf{q}} V\right)^T \left(\nabla_{\mathbf{q}} V\right)}{G(\mathbf{q})} = 1 \qquad \text{where} \qquad \nabla_{\mathbf{q}} = \begin{pmatrix} \partial/\partial q_1 \\ \vdots \\ \partial/\partial q_N \end{pmatrix}$$

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

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

Variational Nature of Intrinsic Reaction Coordinate Path.
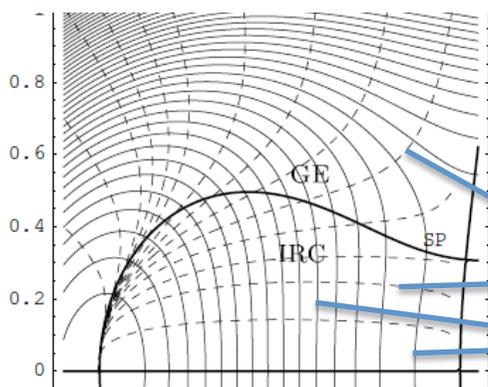
Dashed curves are SA curves emerging from the minimum located at (0,0). Thin curves, equipotential energy curves, (*V(**q**)* = v = *constant*) solution of Eikonal equation.

SA curves (extremal curve).

Family of equipotential energy curves, *V(**q**)* = v.

Canonical equations of SA curves:
$$\begin{cases} \dfrac{d\mathbf{q}}{dt} = \nabla_{\mathbf{q}} V(\mathbf{q}) = \mathbf{g} \\[4mm] \dfrac{d\mathbf{g}}{dt} = \nabla_{\mathbf{q}} G(\mathbf{q}) \end{cases}$$

"The like Hamilton canonical equations for the SA extremal curves."

These equations are the basis of many algorithms to compute the SA (SD) reaction path, see e.g. the review: H. B. Schlegel, J. Comput. Chem. **24**, 1514 (2003).

Variational Nature of Intrinsic Reaction Coordinate Path.

<u>Second order variations</u>. We compare the value of the basic integral 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).
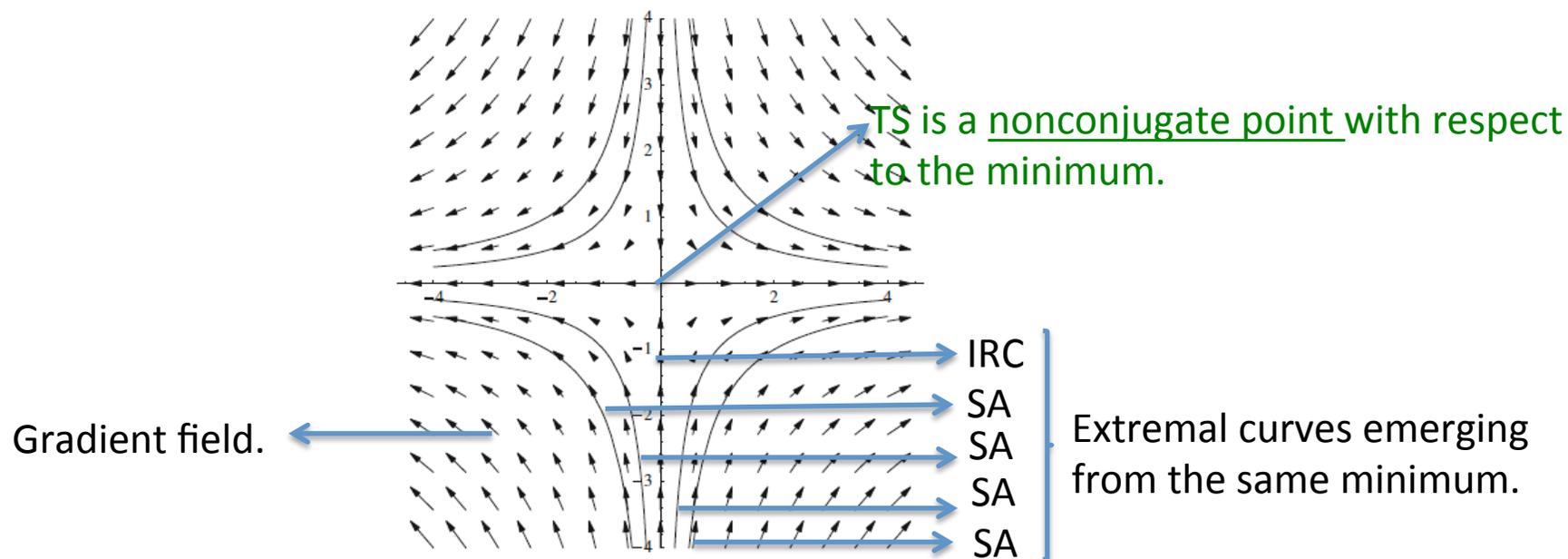
$$I_{M \to q}(\mathbf{q}_{AC}) - I_{M \to q}(\mathbf{q}_{SA}) =$$

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

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**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 $I_{M \text{->} q}$(**q**). **The sufficient condition is satisfied if and only if the Steepest Ascent (Descent) curve joining two consecutive minimae 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 Coordiante Path is the unique Steepest Descent curve of character minimum.***

Variational Nature of 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).

TS is a nonconjugate point with respect to the minimum.

IRC
SA
SA
SA
SA

Extremal curves emerging from the same minimum.

Gradient field.

Variational Nature of Intrinsic Reaction Coordinate Path.

Applications: Location of an Intrinsic Reaction Coordinate curve between two minima using the minimization of the Weierstrass E-function.
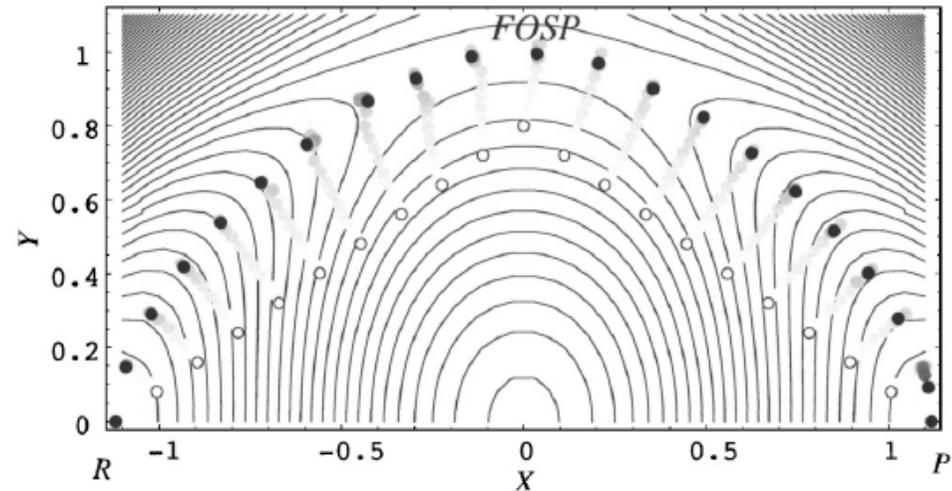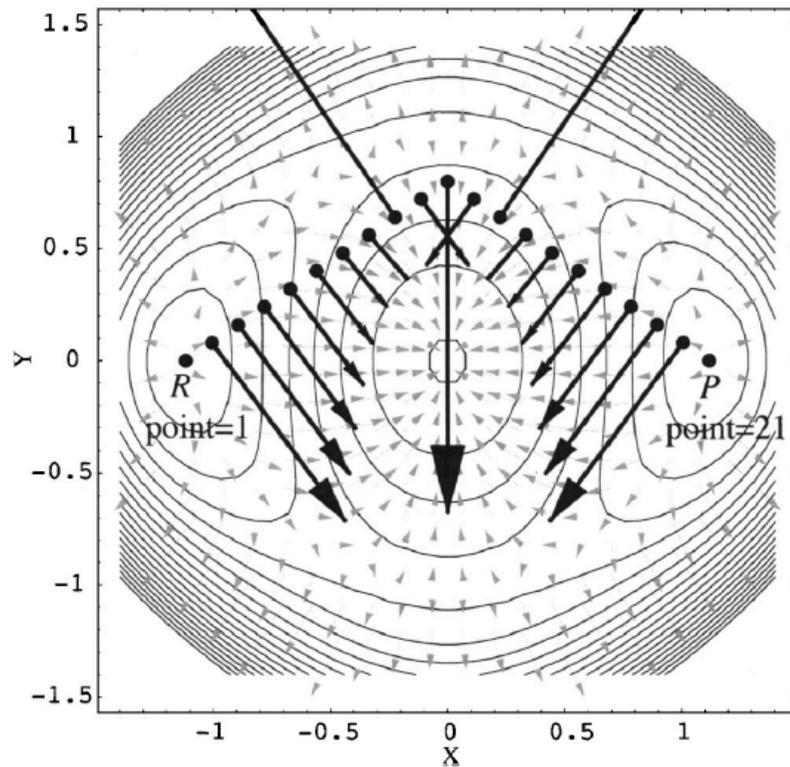
The **white open dots** are the set of 21 points of the initial guess curve. The **dark dots** indicate the final converged position of the 21 points. In this final position, all points are located in the Intrinsic Reaction Coordinate curve.

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.

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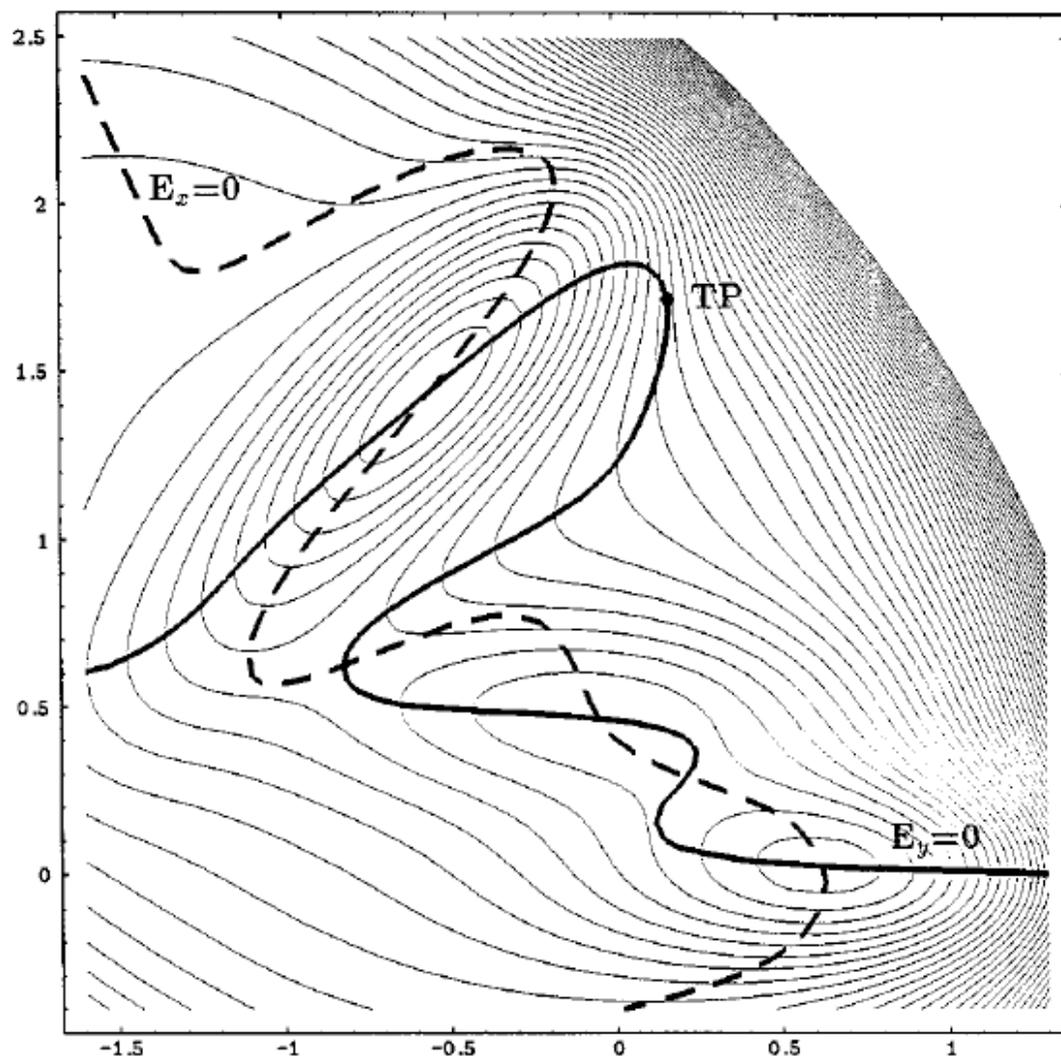
The Müller-Brown potential energy surface, *E(x,y)*. **Reduced Gradient Following** or **Newton Trajectory** solutions $(E_x = 0 , E_y)$ (dashed curve) and $(E_x , E_y = 0)$ (bold curve). They connect the three minima with the two saddle points. TP marks one of the turning points of the **Reduced Gradient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

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

where **r** is the selected unit vector of the search direction.

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

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:

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

Where **A***(x)* is the adjoint matrix of the Hessian matrix **H***(x)* and **g***(x)* is the gradient vector all computed at the position **x**.

The ``+'' option is used for searching stationary points with odd index (stationary points with an odd number of negative eigenvalues of the Hessian), whereas 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 (**g***(x)* = **0**) and points where **g***(x)* ≠ **0** but **A***(x)* **g***(x)* = **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 <u>extremal curves of the integral functional</u>

$$I\left(\overline{\mathbf{x}}\right) = \int_{x_{rc}^0}^{x_{rc}} V\left(x_{rc}', \overline{\mathbf{x}}\right) dx_{rc}' \quad \text{where} \quad \overline{\mathbf{x}}^T = \left(x_1, \cdots, x_{rc-1}, x_{rc+1}, \cdots, x_N\right)$$

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

<u>The Euler-Lagrange equation is</u>

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

This set of Euler-Lagrange equations determines the **<u>reaction path function x = x(x_{rc}) implicitly</u>**. **<u>We note that in this case the boundary values</u>**, $\mathbf{x}_0 = \mathbf{x}(x_{rc}^0)$ **<u>and</u>** $\mathbf{x}_f = \mathbf{x}(x_{rc}^f)$, **<u>cannot be prescribed arbitrarily if the problem should have a solution</u>**.

<u>The tangent of this curve is</u>: *dx/dx_{rc} = A(x)g(x) = A(x)D_xV(x).*
Where the **A(x)** matrix is the adjoint of the Hessian matrix.

The Variational Nature of the Newton Trajectory Reaction Path.

The extremal curve **x** = **x**(x_{rc}) makes the integral $I\left(\overline{\mathbf{x}}\right) = \int_{x_{rc}^0}^{x_{rc}} V\left(x_{rc}^{'}, \overline{\mathbf{x}}\right) dx_{rc}^{'}$
a minimum: **If the determinant of the Hessian matrix,** $\nabla_{\mathbf{x}} \nabla_{\mathbf{x}}^{T} V\left(\mathbf{x}\right)$
projected in the subspace orthogonal to r (normalized gradient vector) is positive definited at each point of the curve.

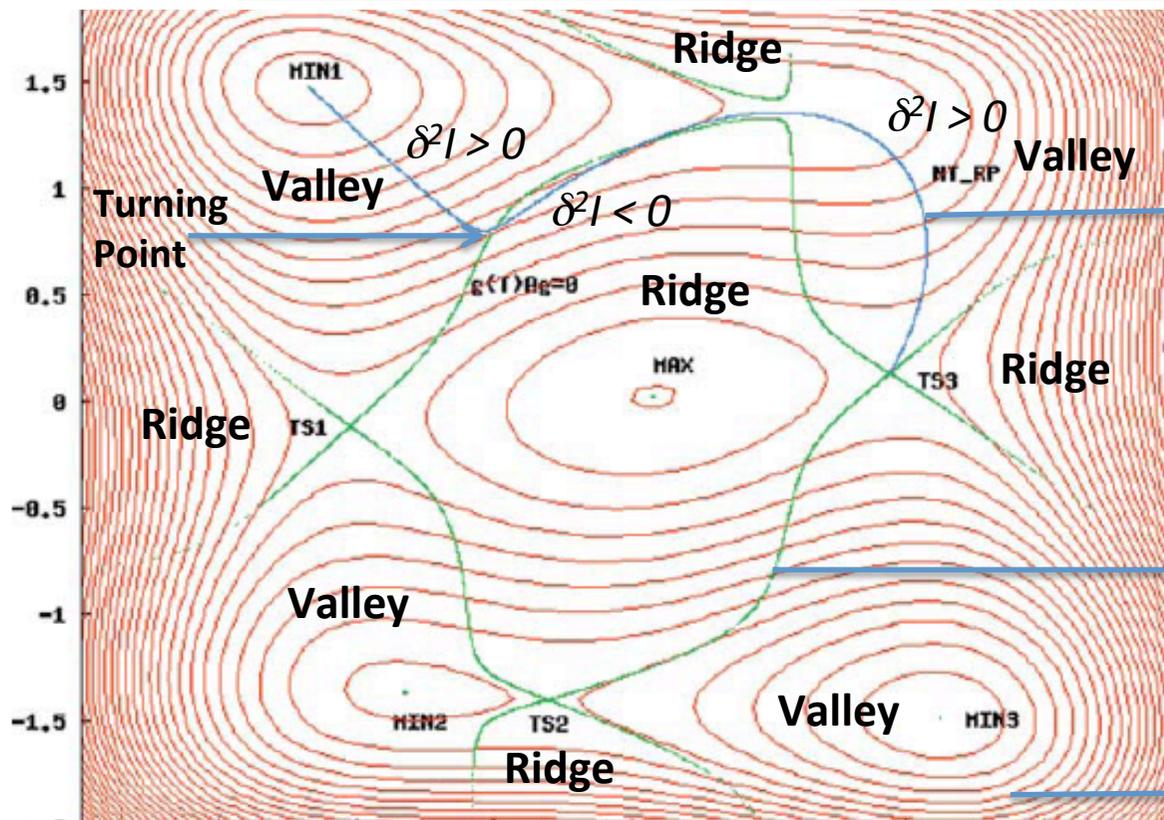*V(x,y)*: The Wolfe-Quapp Potential Energy Surface .
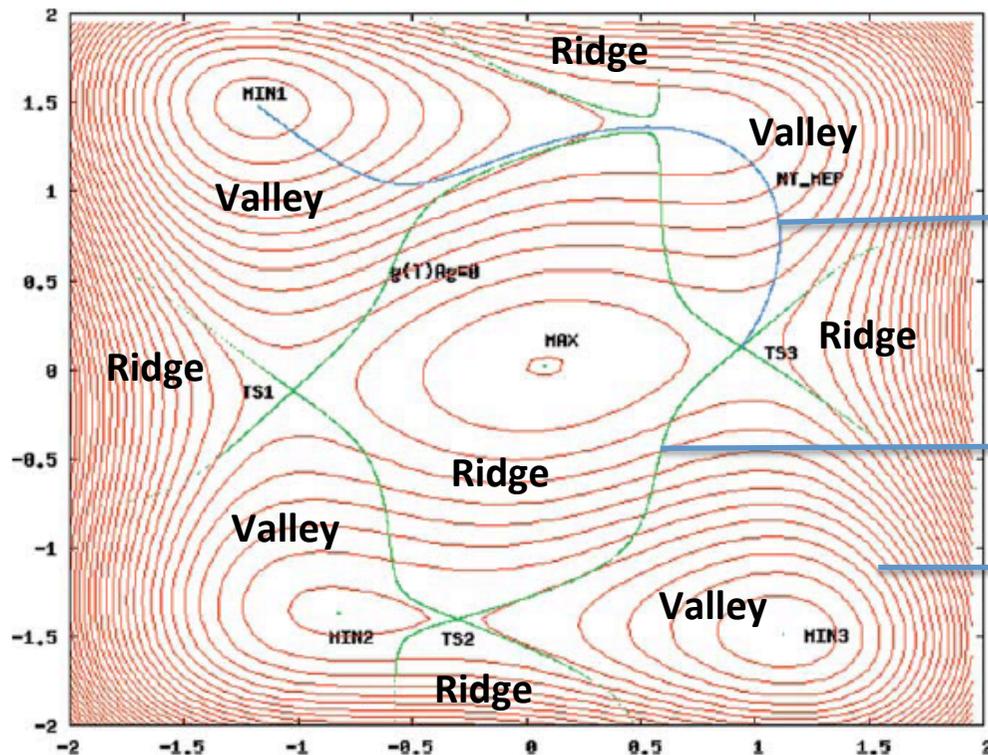
Newton Trajectory reaction path.
Because $\delta^2 I \geq 0$ then this rection path is a MEP (minimum energy path).

Valley-ridged border line.

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 <u>not monotonically increasing curve</u> 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 **S** collects the set of linear independent vectors orthogonal to **g(x)**.

The Variational Nature of the Newton Trajectory Reaction Path.
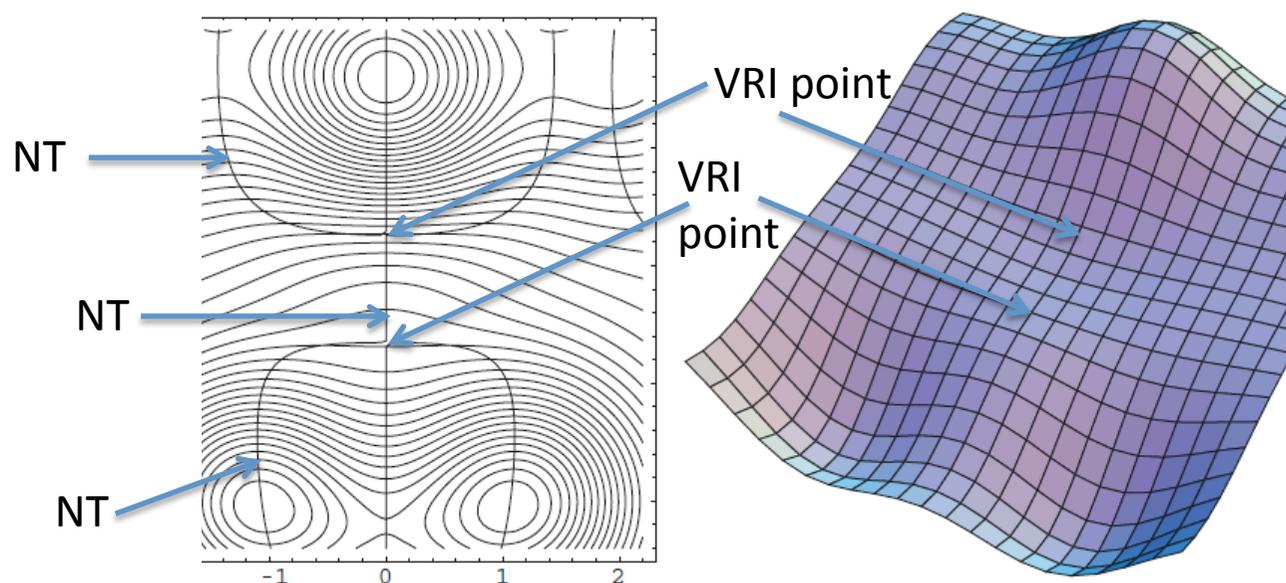
A **Newton Trajectory** <u>curve starting in a minimum minimizes the variational integral $I(\mathbf{x})$ if the curve does not have a Valley Ridged Inflection point otherwise no statement can be made</u>. In the former situation the Newton Trajectory locates a Transition State and the whole curve is located in a walley. 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 ($d\mathbf{x}/dt = \mathbf{A(x)g(x)}$) locate both stationary points, $\mathbf{g(x)} = \mathbf{0}$ and Valley-Ridged-Inflection points $\mathbf{A(x)g(x)} = \mathbf{0}$. <u>It can be used to locate Conical Intersections</u>. (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 Eenergy Surface. To get this we need to test a somehow greater number of **Newton Trajectory** curves.

See e.g. applications in 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)).

Other applications to chemical reactivity:

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

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 $V(q) = v$. At this point the norm $g^T(q)g(q)$ is stationary with respect to any displacement whitin the equipotential curve .


$g^T(q)g(q)$ stationary
with respect to q in the curve $V(q) - v = 0$
GE(bold curve): Gradient Extremals curves.
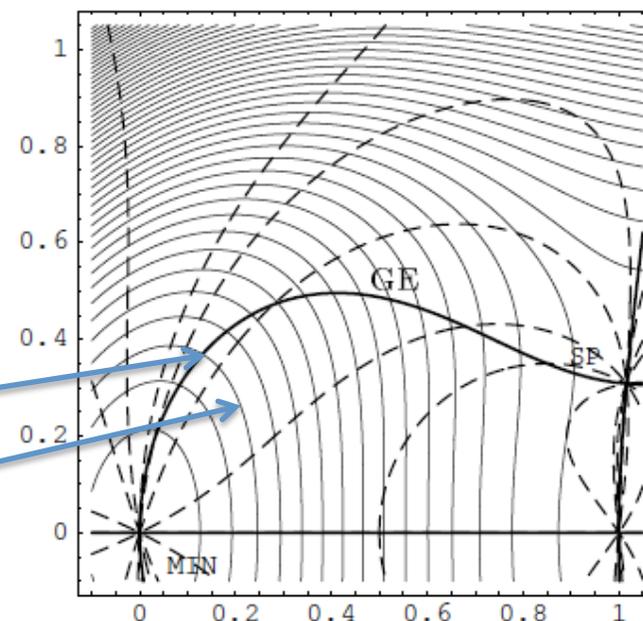
Pancir, J. Collect. Czech. Chem. Commun. **40**, 1112 (1975); Basilevsky, M. V.; Shamov, A. G. Chem. Phys. **60**, 347 (1981); Basilevsky, M. V. Chem. Phys. **67**, 337 (1982); Hoffman, D. K.; Nord, R. S.; Ruedenberg, K. Theor. Chim. Acta **69**, 265 (1986); Jørgensen, P.; Jensen, H. J. Aa.; Helgaker, T. Theor. Chim. Acta **73**, 55 (1988); Quapp, W. Theor. Chim. Acta **75**, 447 (1989); Schlegel, H. B. Theor. Chim. Acta **83**, 15 (1991); Sun, J.-Q.; Ruedenberg, K. J. Chem. Phys. **98**, 9707 (1993); Bondensgård,K.; Jensen,F. J.Chem.Phys. **104**, 8025 (1996).

This curve is not widely used due to their computation cost. Nevertheless, still are very appropriated as reaction paths.
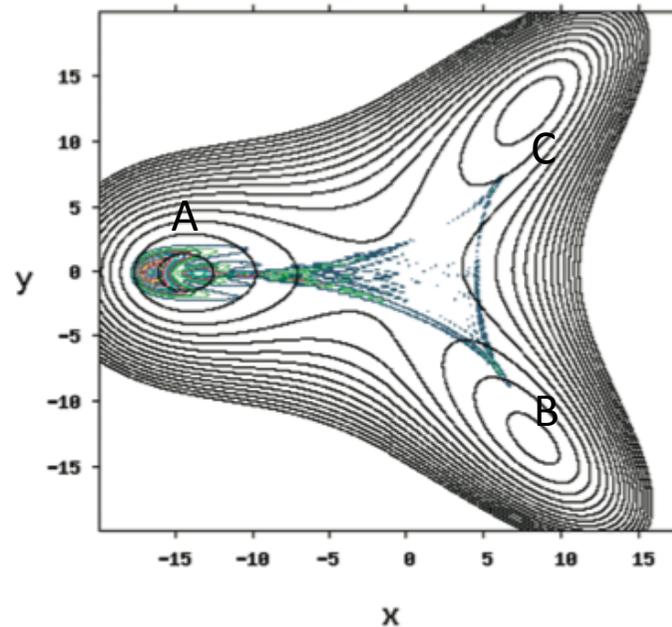
The Variational Nature of Gradient Extremals Path.
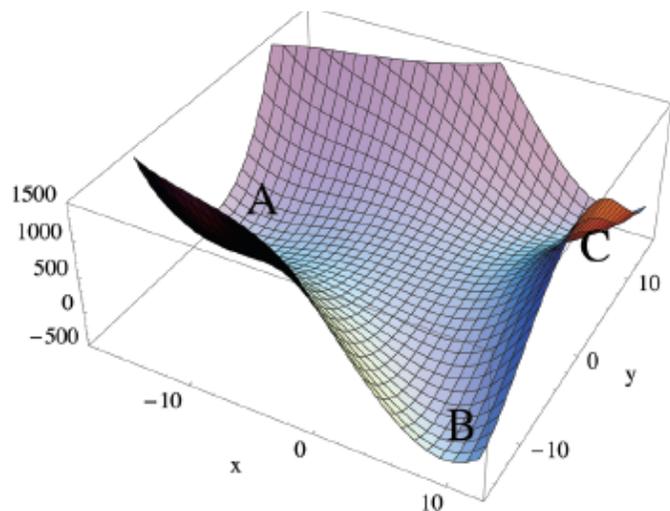
There does not exist an Intrinsic Reaction Coordinate Path connecting the minimum A with the minimum C.
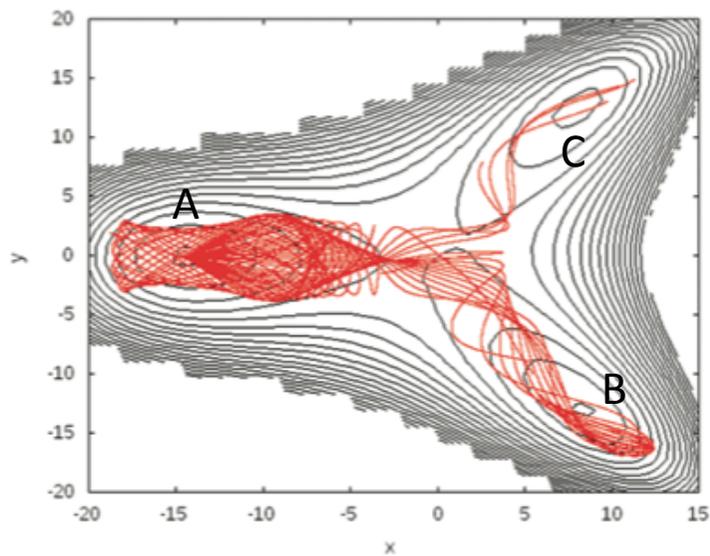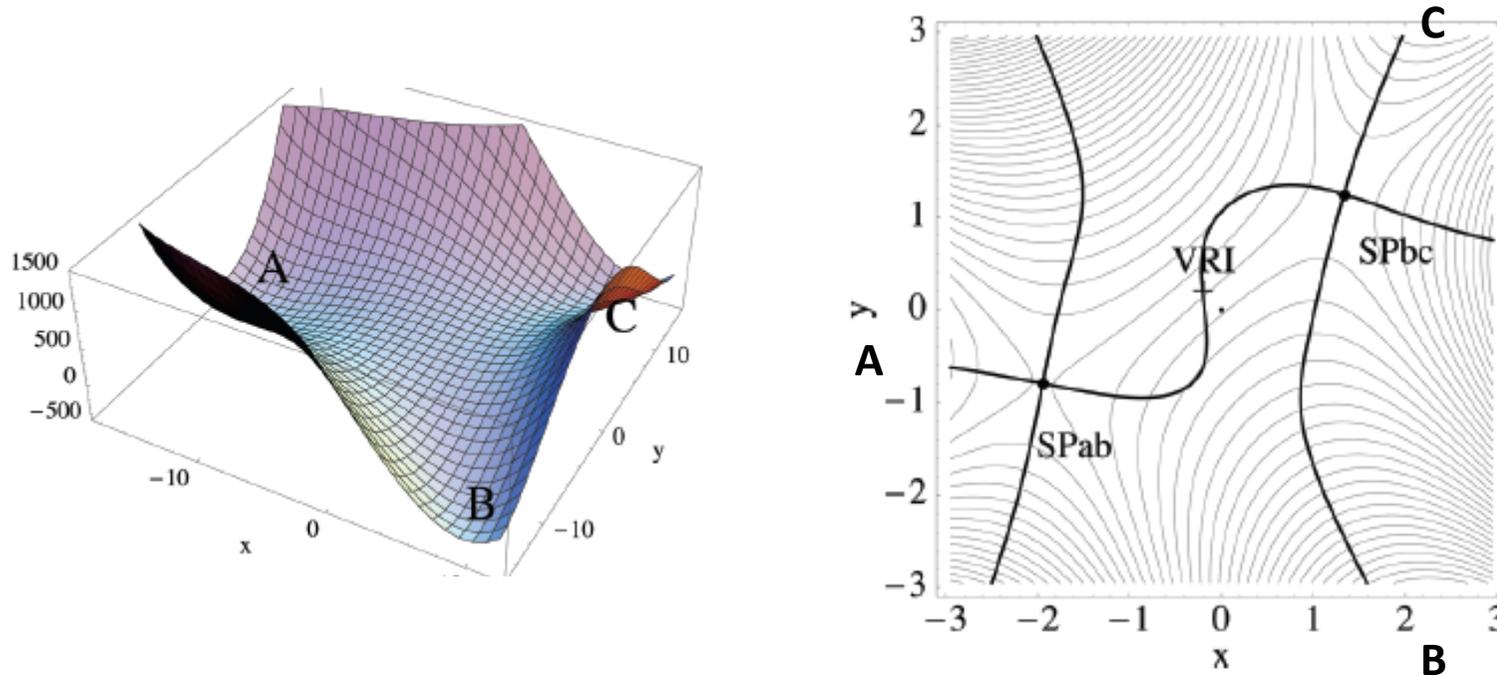

Classical dynamics.

Quantum dynamics.

The Variational Nature of Gradient Extremals Path.

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

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

The resulting Euler-Lagrange equation: $\mathbf{Hg} = \lambda\mathbf{g}$ where **H** is the Hessian matrix.

The Variational Nature of Gradient Extremals Path.

The Euler-Lagrange equation, **H(q)g(q) = λ(q)g(q)** , **determines the Gradient Extremals curve**, **q** = **q**(t), **implicitly**. We note that in this case **the boundary values**, **q$_0$** = **q**(t$_0$) and **q$_f$** = **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 with respect to position.

Using the perturbation theory due to McWeeny (R. McWeeny, Phys. Rev. **126**, 1028 (1961)) can be derived this tangent curve equation (J. M. Bofill, W. Quapp, and M. Caballero, J. Chem. Theory Comput. **8**, 927 (2012)).

The Variational Nature of Gradient Extremals Path.

Special points of the Gradient Extremals (GE) curve.

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

The points where the matrix in the brakets is not invertible are **_Turning Points_** or **_Bifurcation Points_** of the Gradient Extremals curve.
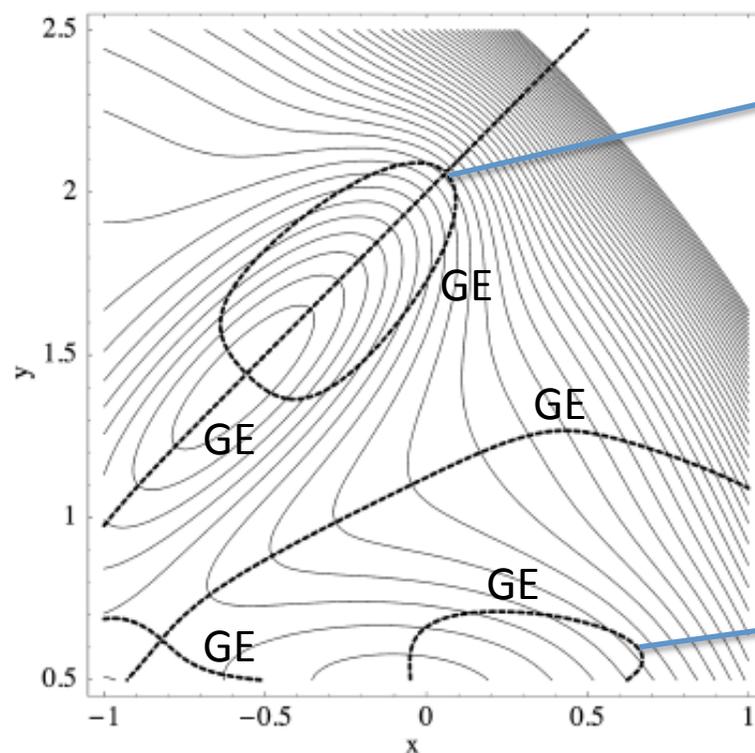
Bifurcation Point

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. Conjugate Points of GE Curves.

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

Sufficient condition, the second variation: $\delta^2 I(\mathbf{q}) > 0$ minimum ($\delta^2 I(\mathbf{q}) < 0$ maximum).
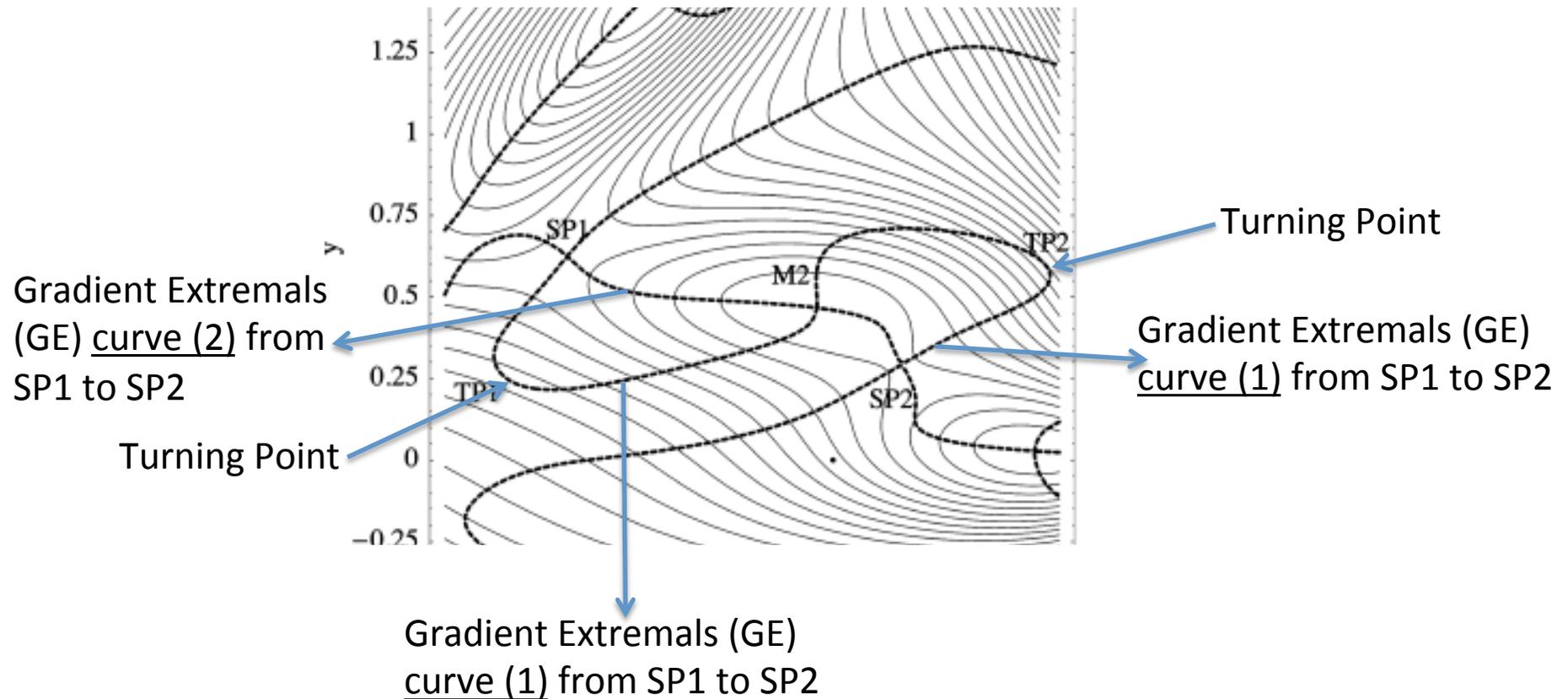
$$\delta^2 I(\mathbf{q}, \mathbf{p}) = \int_{t_0}^{t'} \mathbf{p}^T \left[\langle \mathbf{Fg} \rangle + \mathbf{H}^2 - \lambda\mathbf{H} \right] \mathbf{p}\, dt = \int_{t_0}^{t'} \mathbf{p}^T \mathbf{Cp}\, dt$$

If *det (C) > 0* along the interval $t_0 \leq t \leq t'$ then the Gradient Extremals curve minimizes the variational integral, *I(q)*, otherwise maximizes *I(q)*.

If the Gradient Extremals curve from t_0 to t_1 the *det (C) > 0*, but at t_1 the *det (C) = 0* and from this point until *t'* the *det (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(q)* lower with respect to the value of the same integral computed using the Gradient Extremals curve.

The points where the Gradient Extremals curve has *det (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.

Turning Point

Gradient Extremals (GE) curve (2) from SP1 to SP2

Turning Point

Gradient Extremals (GE) curve (1) from SP1 to SP2

Gradient Extremals (GE) curve (1) from SP1 to SP2

Basic Gradient Extremals Variational Integral:

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

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

3.- Extensions of the Reaction Path Model: the Reaction Path Hamiltonian.

Extensions of the Reaction Path Model: The Reaction Path Hamiltonian.

Reaction Path model is linked to the path described on a multidimensional, configuration space potential-energy surface, when the transformation from reactants to products is considered. <u>To use configuration space instead of phase space</u> obviously means neglecting the contribution of the kinetic energy of the nuclei.

An effort to incorporate the dynamic information while, at the same time, keeping the simplicity of envisaging the reaction as a single path on the potential energy surface, was introduced with the formulation of the reaction-path Hamiltonian (RPH) [W.H. Miller, N.C. Handy, J.E. Adams, *J Chem Phys* **72**, 99 (1980); W.H. Miller, *J Phys Chem* **87**, 3811 (1983).]

Variety of formulations, e.g., G. D. Billing, *Mol Phys* **89**, 355 (1996); J. González, X. Giménez, J.M. Bofill, *J Phys Chem A* **105**, 5022 (2001); J. González, X. Giménez, J.M. Bofill, *J Chem Phys* **116**, 8713 (2002); J. González, X. Giménez, J.M. Bofill, *Theor Chem Acc* **112**, 75 (2004). **<u>The list is very far to be complete.</u>**

Extensions of the Reaction Path Model: The Reaction Path Hamiltonian.

B. A. Ruf and W. H. Miller, J. Chem. Soc., Faraday Trans. 2 **84**, 1523 (1988); D. P. Tew, N. C. Handy, S. Carter, S. Irle, and J. M. Bowman, Mol. Phys. **101**, 3513 (2003); K. A. Nguyen, C. F. Jackels, and D. G. Truhlar, J. Chem. Phys. **104**, 6491 (1996); G. A. Natanson, B. C. Garret, T. N. Truong, T. Joseph, and D. G. Truhlar, J. Chem. Phys. **94**, 7875 (1991); Y. Okuno, J. Chem. Phys. **113**, 3130 (2000); Y. Okuno, S. Yokohama, and S. Mashiko, ibid. **113**, 3136 (2000); S. J. Klippenstein, J. Chem. Phys. **96**, 367 (1992); V. B. Pavlov-Verevkin and J. C. Lorquet, J. Chem. Phys. **123**, 074324 (2005); V. Szalay, A. G. Csaszar, J. Santos, and J. Ortigoso, J. Chem. Phys. **118**, 6801 (2003); T. Carrington, Jr. and W. H. Miller, J. Chem. Phys. **81**, 3942 (1984); **84**, 4364 (1986); T. Taketsugu and M. S. Gordon, J. Chem. Phys. **104**, 2834 (1996); C. Coletti and G. D. Billing, Phys. Chem. Chem. Phys. **1**, 4141 (1999); T. Taketsugu and T. Hirano, J. Chem. Phys. **99**, 9806 (1993); J. Mol. Struct.: THEOCHEM **116**, 169 (1994); C. Minichino and V. Barone, J. Chem. Phys. **100**, 3717 (1994); A. Palma, E. Semprini, F. Stefani, and A. Talamo, J. Chem. Phys. **105**, 5091 (1996); T. Yanai, T. Taketsugu, and K. Hirao, J. Chem. Phys. **107**, 1137 (1997); B. Lasorne, G. Dive, D. Lauvergnat, and M. Desouter-Lecomte, J. Chem. Phys. **118**, 5831 (2003); W. H. Miller, J. Chem. Phys. **76**, 4904 (1982); **87**, 3811 (1983); N. R. Walet, A. Klein, and G. D. Dang, J. Chem. Phys. **91**, 2848 (1989); W. H. Miller, J. Am. Chem. Soc. **105**, 216 (1983); S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaeffer III, J. Chem. Phys. **73**, 2733 (1980); J. Am. Chem. Soc. **103**, 1900 (1981); G. D. Billing, Chem. Phys. **89**, 199 (1984); W. H. Miller, B. A. Ruf, and Y. T. Chang, J. Chem. Phys. **89**, 6298 (1988); G. D. Billing, Chem. Phys. **277**, 325 (2002); W. H. Miller and S. Shi, J. Chem. Phys. **75**, 2258 (1981); W. H. Miller and S. D. Schwartz, J. Chem. Phys. **77**, 2378 (1982); S. Lee and J. T. Hynes, J. Chem. Phys. **88**, 6853 (1988); S. Jang and S. A. Rice, J. Chem. Phys. **99**, 9585 (1993); J.-Y. Fang and S. Hammes-Schiffer, J. Chem. Phys. **108**, 7085 (1998); **109**, 7051 (1998); B. Fehrensen, D. Luckhaus, M. Quack, M. Villehe, and T. Rizzo, J. Chem. Phys. **119**, 5534 (2003); S. P. Shah and S. A. Rice, Faraday Discuss. Chem. Soc. **113**, 319 (1999); T. Taketsugu and M. S. Gordon, J. Chem. Phys. **103**, 10042 (1995); J. González, X. Giménez, and J. M. Bofill, J. Chem. Phys. **116**, 8713 (2002);…

The list is far to be complete.

# Extensions of the Reaction Path Model: The Reaction Path Hamiltonian.

How good is the dynamics on a Reaction Path?

Müller-Brown PES
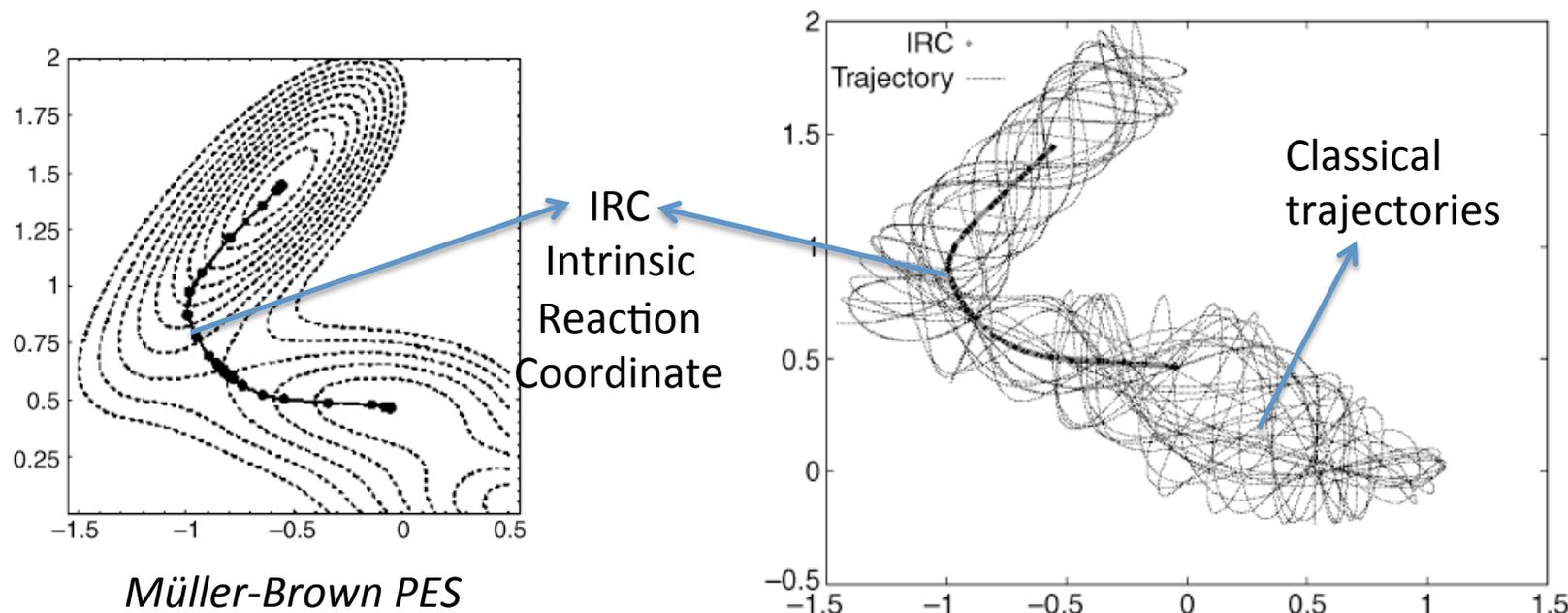
A comparison between the path described by the Intrinsic Reaction Coordinate and a representative, long exact classical trajectories. **From a physical point of view any Reaction Path (RP) can be seen as if one envisions a large cloud of classical trajectories evolving on the PES. Very often the average trajectory is going to be close to the curve selected for the RP. This gives support to the dynamical theories: Transition State Theory (TST), and RP-Hamiltonian.**

Extensions of the Reaction Path Model: The Reaction Path Hamiltonian.

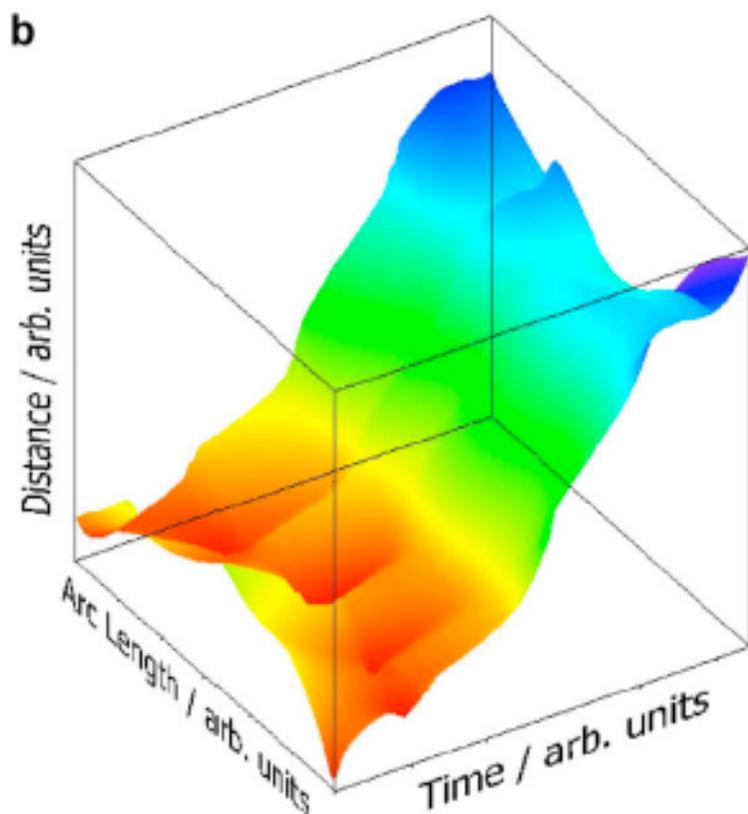Comparison between Reaction Path and Quantum Trajectories.
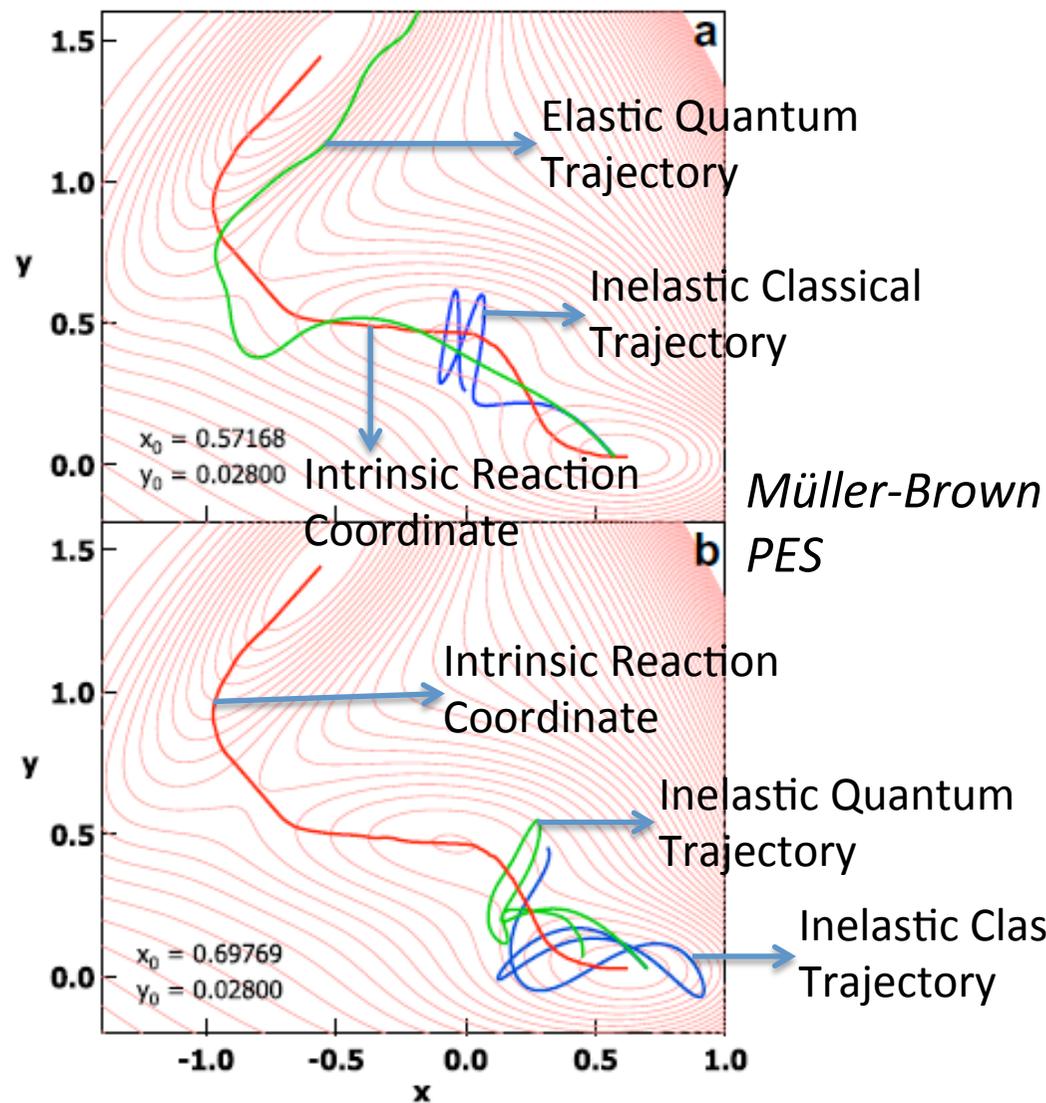
The Elastic Quantum Trajectory follows the Reaction Path (Intrinsic Reaction Coordinate), it is a reactive trajectory and contributes to the Tunneling Effect.

The Inelastic Quantum Trajectory does not follow the Reaction Path (Intrinsic Reaction Coordinate), it is a non-reactive trajectory.

Extensions of the Reaction Path Model: The Reaction Path Hamiltonian.

For a big set of quantum trajectories the comparison is done using the <u>Caratheodory matrix</u>. Each element of this matrix is a distance between two curves: $C_{ij} = |\mathbf{x}_{QT}(t_i) - \mathbf{x}_{RP}(s_j)|$. Quantum Trajectory (QT) Time $t_0 \leq t_i \leq t_f$, Reaction Path (RP) Arc-Lenght $s_0 \leq s_j \leq s_f$.

b

Distance / arb. units

Arc Length / arb. units

Time / arb. units

Carathéodory plot associated with the Quantum Trajectories computed on Müller-Brown Potential Energy Surface. The transition from red to blue indicates an increasing distance between the Reaction Path and the respective Quantum Trajectory.

A big subset of Quantum Trajectories follows the Reaction Path (Intrinsic Reaction Coordinate).

A.S. Sanz, X. Giménez, J.M. Bofill, S. Miret-Artés, Chem. Phys. Lett. **478**, 89 (2009).

Extensions of the Reaction Path Model: The Reaction Path Hamiltonian.

The above results suggest a Quantum Reaction Path Hamiltonian (QRPH).

In their formulation is assumed that highest value of $|\Psi(\mathbf{x},t)|^2$ is mainly located in the reaction path region of the Potential Energy Surface.

$$H_{QRPH} = -\frac{\hbar^2}{2}\left[\frac{1}{m(s)}\right]^{1/4}\frac{\partial}{\partial s}\left[\frac{1}{m(s)}\right]^{1/2}\frac{\partial}{\partial s}\left[\frac{1}{m(s)}\right]^{1/4} + V\left(\mathbf{x}(s)\right)$$
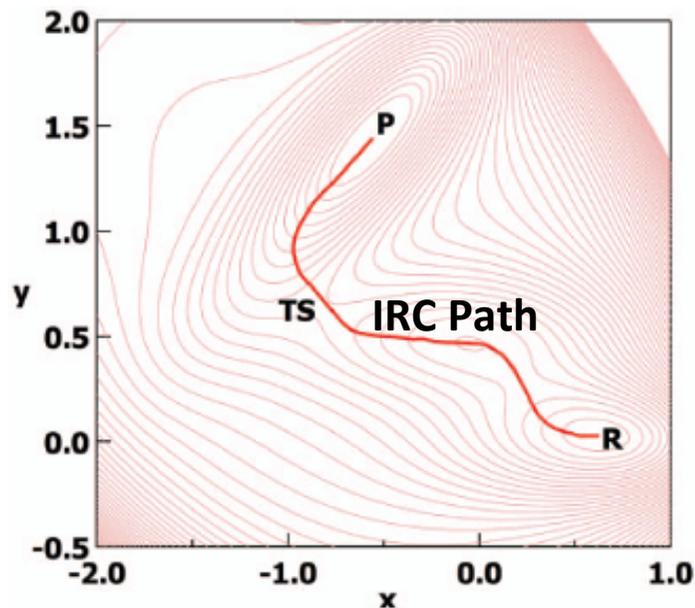
m(s) is a function of the tangent and curvature of the reaction path.
It is a Schrödinger equation where the mass is a function of the position, *s* (the arc-lenght of the reaction path).
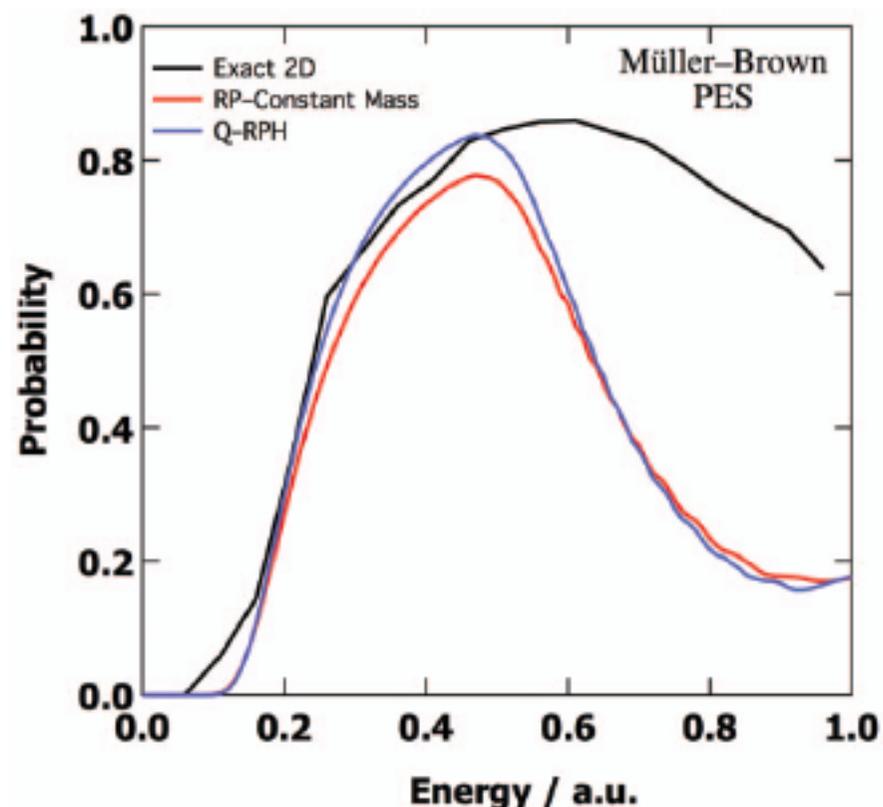
$$H_{QRPH}\Psi\left(s,t\right) = i\hbar\frac{\partial\Psi\left(s,t\right)}{\partial t}$$

Solved using the sincDVR functions as a basis of wave function expansion.

Extensions of the Reaction Path Model: The Reaction Path Hamiltonian.

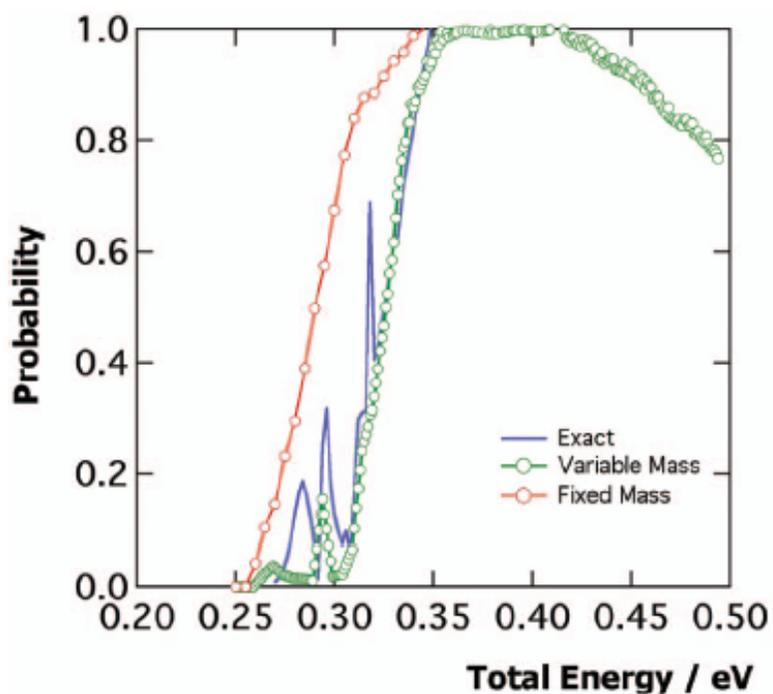Müller-Brown Potential Energy Surface

The transmission coefficient as a function of total energy for a wave packet evolving on a Müller–Brown Potential Energy Surface for three different cases: A 1-Dimensional motion along the Intrinsic Reaction Coordinate with a constant mass term, a 1-Dimensional motion with a variable mass term as obtained from the present Quantum Reaction Path Hamiltonian theory, and the exact 2-Dimensional term for a system having a perpendicular energy corresponding to the ground vibrational energy. (J. González, X. Giménez, J. M. Bofill, J. Chem. Phys. **131**, 054108 (2009)).

Extensions of the Reaction Path Model: The Reaction Path Hamiltonian.

<u>*A more realistic example:*</u> *F + H$_2$* ➜ *FH + H*

The 3-Dimensional with total angular momentum set to zero of the F + H$_2$ reaction dynamics is considered on the well-known <u>Stark–Werner </u>(SW) PES.

This reaction has also been used as a compelling system to test the approximate quantum methods.


The transmission coefficient as a function of total energy for a system corresponding to the 3-Dimensional J=0 F + H$_2$ reaction on the Stark-Werner PES. The present Quantum Reaction Path Hamiltonian results with (green trace) and without (red trace) the variable mass term are compared against exact 3-Dimensional quantum scattering calculations (blue trace).

4.- A New View of Potential Energy Surface:
The Huyghens Construction.

A New View of Potential Energy Surfaces: The Huyghens Construction.

The figure of a set (field) of Steepest Ascent (Descent) curves (extremal curves of a Variational Principle) transversing a family of energetically equidistant equipotential surfaces **is completly analogous to the Fermat-Huyghens contruction of the propagation of light rays in an non-isotropic medium studied in optics.**

Field of Steepest Ascent curves

Family equidistant equipotential surfaces.
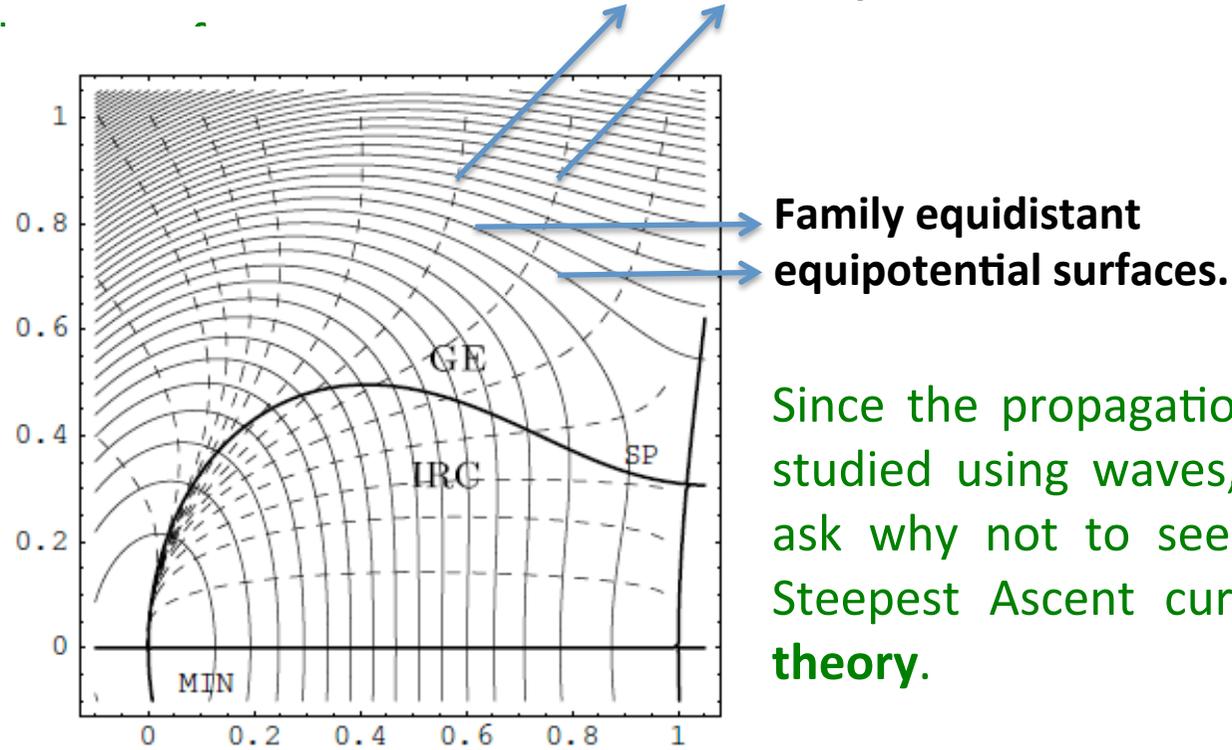
Since the propagation of light rays can be studied using waves, then it is obvious to ask why not to see the propagation of Steepest Ascent curves using the **wave's theory**.

A New View of Potential Energy Surfaces: The Huyghens Construction.

Question: Which the equation is that governs the propagation?

The only possibility is a second order partial differential equation type hyperbolic related in some way (through the Characteristic Theory) with the Potential Energy Surface.

$$\frac{\nabla_{\mathbf{x}}^T V \nabla_{\mathbf{x}} V}{G(\mathbf{x})} = 1 \qquad \xrightarrow{\text{Solution: Characteristic Surface}} \qquad \underbrace{v = V(\mathbf{x})}$$

$\underbrace{\phantom{\frac{\nabla_{\mathbf{x}}^T V \nabla_{\mathbf{x}} V}{G(\mathbf{x})}}}$
Characteristic Equation:
Eikonal Equation

Characteristic Surface:
Family of Equipotential Surface

The solutions of the hyperbolic partial differential equation are "wave-like".

The solution of the proposed hyperbolic differential equation will result in a wave function of position, **x**, and energy surface, v, $\Psi(\mathbf{x}, v)$, being $v = V(\mathbf{x})$.

A New View of Potential Energy Surfaces: The Huyghens Construction.

The hyperbolic differential equation satisfying the above requirements is:

$$\nabla^2_{\mathbf{x}}\Psi(\mathbf{x},v) - G(\mathbf{x})\frac{\partial^2\Psi(\mathbf{x},v)}{\partial v^2} + Trace\big[\mathbf{H}(\mathbf{x})\big]\frac{\partial\Psi(\mathbf{x},v)}{\partial v} = 0$$

where, $\nabla^2_{\mathbf{x}} = \partial^2/\partial x_1^2 + \ldots + \partial^2/\partial x_N^2$,

$G(\mathbf{x})$ is the square of the gradient norm,
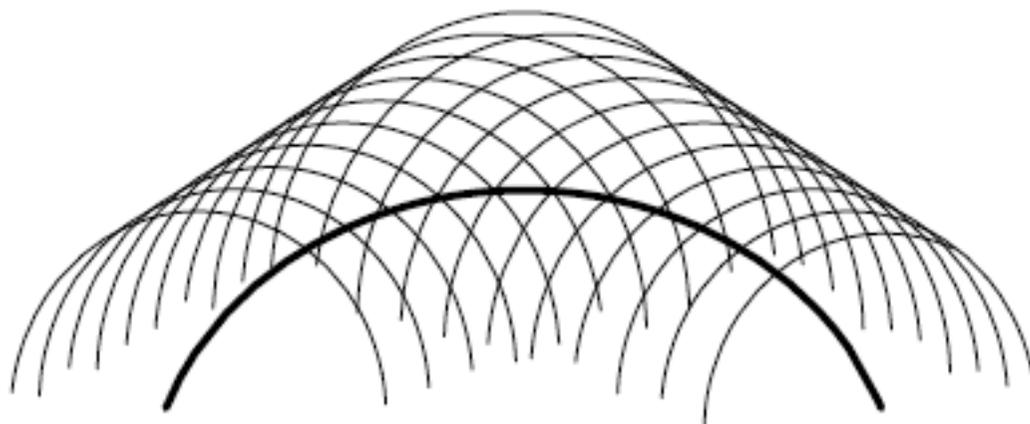
$\mathbf{H}(\mathbf{x})$ is the Hessian matrix and

v is the equipotential energy surface, $v = V(\mathbf{x})$.

A solution:

$$\Psi(\mathbf{x},v) = \exp\big(i\big(v - V(\mathbf{x})\big)\big) - 1$$

A New View of Potential Energy Surfaces: The Huyghens Construction.

A graphical view.

Model for the action of Huygens Construction. Wavelets of different "speed", $1/G(x)^{1/2}$, start from a lower level line, an equipotential energy surface (the bold curve). They build an envelope. It is the new wave front, or the new level line or equipotential energy surface , respectively. (J.M. Bofill, W. Quapp, M. Caballero (to be publish).

The Huyghens Construction may be open a new view of the Potential Energy Surface and Reaction Path Models.

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