Variational Nature, Integration and Properties of Newton Reaction Path.

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Abstract: The Distinguished Coordinate Path and the Reduced Gradient Following Path or its equivalent formulation, the Newton Trajectory, are analyzed and unified using the Theory of Calculus of Variations. It is shown that their minimum character is related to the fact that the curve is located in a valley floor. In this case we say that the Newton Trajectory is a reaction path with the category of minimum energy path. In addition to these findings a Runge-Kutta-Fehlberg algorithm to integrate these curves is also proposed.

Introduction.

One of the main problems in theoretical chemistry is to study the mechanisms associated with the chemical reactions. An important achievement in the development of models to understand the chemical reaction mechanisms was the introduction of the two following concepts, namely, Potential Energy Surface (PES) and Reaction Path (RP) as a way to describe the molecular system evolution from reactants to products in geometrical terms.[1,2] The impact of these concepts in chemistry during the last forty years can been justified by the intuitive and easy manner to visualize the evolution of any chemical reaction and its qualitative prediction power. This fact has been motivated by a continuous mathematical development on the grounds of the model and computational algorithms to compute RP as well.

The basic definition of RP is a curve line located in a PES that monotonically increases from a stationary point character minimum to a first order saddle point and from that point monotonically decreases to a new stationary point character minimum. The first order saddle point according to the previous definition is the highest energy point of the RP. The first and the second minima are labeled as reactants and products respectively, while the first order saddle point is the transition state (TS). The parameterization of a curve line, say t, satisfying the above RP requirements, is the reaction coordinate. More concisely, if $\mathbf{q}$ is a coordinate vector of dimension N, then RP is represented by $\mathbf{q}(t)$. Normally, the parameter arc-length of the curve, s, is taken as the reaction coordinate, however, the values of the PES can also be taken as reaction coordinate.[3]

There exist many curves on the PES that satisfy the RP conditions, this fact being the reason of the variety of RP curves. The curve most widely used as RP is the so-called Intrinsic Reaction Coordinate (IRC) this curve being a steepest descent curve in mass weighted coordinates. The IRC is a steepest descent curve joining two minima through a TS.[4] The other curve used as RP is the distinguished or driven coordinate method,[5,6,7] or a more recent version, the so-called reduced gradient following (RGF), [8,9] also labeled as Newton path or Newton trajectory (NT).[10] Additionally, we have the gradient extremals (GE),[11,12,13,14] however, their computational demand limited their applicability.

The RPs are static curves on the PES, which means that only geometry properties of the PES are taken into account, no dynamics information can be sought from these pathways. An effort to incorporate the dynamic information while, at the same time, keeping the philosophy of envisaging the reaction as a single path on the PES, was introduced with the formulation of the reaction-path Hamiltonian (RPH).[15] This views the reaction as a vibrating super-molecule, for which some geometry parameters undergo dramatic changes, those most properly describing the reaction and very often taken as reaction coordinate, whereas the remaining degrees of freedom experience some changes in the nature of the associated vibrational motion. Classical and quantum RPHs have been proposed recently.[16,17,18] Reaction theories like the famous Transitions State and Variational Transition State theory are also based at least implicitly or explicitly on the RP model.[19] Nevertheless, many times a well selected RP curve very close matches by to the average line of a set of molecular dynamics trajectories.[20] Maybe this observation gives physical grounds to the RP model, as well as to follow working on its development. Within the set of RP curves mentioned above the IRC is one that matches reasonably from both the theoretical and computational trajectories of classical and quantum models.[21]

Each type of a RP curve has different mathematical grounds despite many RPs as a common factor are geodesic curves on a surface. Due to this fact each RP has its own evolution in the PES to reach the first order TS from the minimum. The properties and features of some RP curves like its variational nature are briefly discussed below.

(I) The IRC curve possesses a variational nature, because it is a steepest descent curve and this type of curves extremalize a functional associated to a Fermat Variational Principle.[22,23,24] From this point of view, the conclusion is that the IRC propagates through the PES according to a speed law or continuous slowness model, related to inverse of the gradient norm of the PES. It travels through the surface varying the least potential energy. For this reason, the IRC minimizes the functional associated to this special type of Fermat principle.[24]

(II) The GE RP is defined as the curve that at each point cuts a member of isopotential hypersurfaces of the PES where the square of the gradient norm of this PES is stationary in respect of the variations of the positions within the isopotential hypersurface. From this definition it is clear that GE paths fall in the class of Variational problems with subsidiary conditions.[25,26] A study of its Variational nature was recently addressed by Quapp.[27]

(III) The RGF or NT RP is characterized by a curve in the PES such that at each point of this curve the gradient vector points at a constant direction.[8] This can be seen in another way, the RGF curve crosses the steepest descent curve at each point that at the same point the tangent has the same direction as the constant direction of the prescribed RGF direction. The possible variational nature of the RGF or NT RP was also discussed in references 27 and 28. The differences in both views are due to the integral functional used. The RGF possesses other important features largely studied by Hirsch and Quapp (see, e.g. ref. 29) in their studies on the convexity of the PES region where the RP is located.

Taking into account all the features of the RP and due to the increasing importance of the RGF or NT as RP in the present article, we present a unification of a variational point of view of the distinguished coordinate path (DC) and the RGF or NT path. The second variation is also derived and analyzed being related to the convexity property of the PES introduced by Hirsch and Quapp.[29] For these purposes the article is divided in the following way, first we derive the necessary and sufficient conditions such that the driven or DC path and the RGF or NT path should satisfy to be a variational minimum. Second, we present in detail the integration of the RGF equations being related to the NT. Based on these results an integration technique is proposed to obtain either RGF or NT paths. Finally, numerical results are given using a two dimensional PES.

The Driven Coordinate and Reduced Gradient Following Paths Derived from the Theory of Calculus of Variations.

A basic problem in the differential calculus is to find in the domain of an independent variable a point of this variable for which a given function takes its maximum or minimum value. The theory of Calculus of Variations is also a theory of maxima and minima but for variables and functions which are much more complicated than those which appear in the standard differential calculus. A general illustration of the problems that appear in this theory consists in finding a curve, $\mathbf{q}(t) = (q_1(t), \ldots, q_N(t))^T$, within a set of curves joining two points of on N-dimensional space such that a functional $I(\mathbf{q})$ depending on this N independent variables takes an extreme value, in principle maximum or minimum. Usually the functional $I(\mathbf{q})$ is an integral of the form,

$$I(\mathbf{q}) = \int_{t_0}^{t_f} F\left(t, \mathbf{q}(t), \mathbf{q}'(t)\right) dt \qquad (1)$$

where F is a given functional which is twice continuous differentiable with respect to its three arguments, t, $\mathbf{q}(t)$, $\mathbf{q}'(t) = d\mathbf{q}(t)/dt$. As noted above, the functions $\mathbf{q}(t)$ will be restricted to the class of admissible functions satisfying the conditions, $\mathbf{q}(t_0) = \mathbf{q}_o$, $\mathbf{q}(t_f) = \mathbf{q}_f$, $\mathbf{q}(t)$ continuous, and $\mathbf{q}'(t)$ piecewise continuous. The requirement that $I(\mathbf{q})$ be an extremum is that $I(\mathbf{q})$ is stationary with respect to the variation of the N functions $q_1(t)$, . . . , $q_N(t)$ considered independently. The necessary condition to be stationary is that the N Euler equations are satisfied,

$$\left\{F_{\mathbf{q}}\right\} = \nabla_{\mathbf{q}} F\left(t,\mathbf{q}(t),\mathbf{q}'(t)\right) - \frac{d}{dt}\nabla_{\mathbf{q}'} F\left(t,\mathbf{q}(t),\mathbf{q}'(t)\right) = \mathbf{0} \qquad (2)$$

where $\nabla_{\mathbf{q}}^T = (\partial/\partial q_1, \ldots, \partial/\partial q_N)$ and the superscript T means transposed. The notation $\{F_{\mathbf{q}}\}$ represents the Euler operator.[25]

Let us now construct a functional F such that the integration of the resulting Euler equations (2) result in the curve described by the driven coordinate method. As explained in the introduction, the driving coordinate or DC method consists in selecting a driving coordinate, say q_{rc}, along the valley of the minimum, then walking a step in the direction of this driving coordinate first and second performing an energy extremalization (stationarization) in the rest of coordinates, resulting in a curve on the PES, $V(\mathbf{q})$. In other words, this RP satisfies the next requirement at each point,

$$V\left(\mathbf{q}_{DC}\right) = \underset{q_1,\ldots,q_{i-1},q_{i+1},\ldots,q_N}{\text{extremalize}}\ V\left(q_1,\ldots,q_{i-1},q_{i=rc},q_{i+1},\ldots,q_N\right) = \underset{\bar{\mathbf{q}}}{\text{extremalize}}\ V\left(q_{rc},\bar{\mathbf{q}}\right) \qquad (3)$$

where $\bar{\mathbf{q}}^T = \left(q_1,\ldots,q_{i-1},q_{i+1},\ldots,q_N\right)$. Notice that in this context a point $\mathbf{q}$ can be represented as $\mathbf{q}^T = (q_{rc}, \bar{\mathbf{q}}^T)$. According to the equation (3) at each point of the driving coordinate curve, the gradient vector of the PES, $\mathbf{g} = \nabla_{\mathbf{q}} V(\mathbf{q})$, is equal zero for each coordinate except for the driving coordinate, q_{rc}. In other words, the gradient points into the direction of the driving coordinate. This direction is equal for all points of this path. In this manner the distinguished coordinate or driving coordinate path at each point satisfies the set of $N-1$ equations,

$$\nabla_{\bar{\mathbf{q}}} V\left(q_{rc},\bar{\mathbf{q}}\right) = \mathbf{0}_{N-1} \qquad (4)$$

where $\mathbf{0}_{N-1}$ is a zero vector of dimension $N-1$. It is clear that in the present case q_{rc} plays the rule of t, that is of reaction coordinate, and also that any functional F associated to this RP model, the corresponding set of Euler equations should be equal to equation (4). An integral functional satisfying all these requirements is,

$$I\left(\bar{\mathbf{q}}\right)=\int_{t_0}^{t_f}F\left(t,\bar{\mathbf{q}}\right)dt=\int_{q_{rc}^0}^{q_{rc}^f}V\left(q_{rc},\bar{\mathbf{q}}\right)dq_{rc} \quad (5)$$

Because of this variational problem the functional V does not involve the argument, $\bar{\mathbf{q}}'=d\bar{\mathbf{q}}/dq_{rc}$, the set of N-1 Euler equations reduces to the form given in equation (4). Notice that the dimension of the argument $\bar{\mathbf{q}}$ is N-1. In other words, the set of N-1 equations (4) is the set of the N-1 Euler equations associated to the variational problem (5). This set of equations (4) determines the function $\bar{\mathbf{q}}=\bar{\mathbf{q}}(q_{rc})$ implicitly. A point of this curve in the N dimensional space is represented as $\mathbf{q}^T(q_{rc})=(q_{rc},\ \bar{\mathbf{q}}^T(q_{rc}))$. We note that in this case the boundary values, $\mathbf{q}_0=\mathbf{q}(q^0_{rc})$ and $\mathbf{q}_f=\mathbf{q}(q^f_{rc})$, cannot be prescribed arbitrarily if the problem is to have a solution.[25] On the contrary, one has to look for a solution starting at $\mathbf{q}_0$ and take the value $\mathbf{q}_f$ from there.

From these results we conclude that the driving coordinate RP satisfies the extremal necessary conditions of the problem (5). Now two questions emerge, first, how to connect these results with the new reformulation of this type of RP, namely, the RGF method? Second, does the distinguished coordinate curve also satisfy the extremal sufficient conditions? In the next sections these questions are answered.

The Euler Equations.

The first question formulated above is addressed using the invariant character of the Euler equation (2) with respect to a change of coordinates.[30] We consider the transformation,

$$\mathbf{x}=\mathbf{D}\mathbf{q}=\mathbf{D}\begin{pmatrix} q_{rc} \\ \bar{\mathbf{q}} \end{pmatrix} \quad (6)$$

where $\mathbf{x}$ is the vector of dimension N of the new coordinates and $\mathbf{D}$ is an $N \times N$ matrix formed by N constant linear independent directions,

$$\mathbf{D}=\left[\mathbf{r}\,|\mathbf{s}_1|\,...\,|\mathbf{s}_{N-1}\right]=\left[\mathbf{r}\,|\mathbf{S}\right] \quad (7)$$

The notation $[\mathbf{r}\ /\ \mathbf{S}]$ means an $N \times N$ matrix, where the first column contains the normalized $\mathbf{r}$ vector, $\mathbf{r}^T\mathbf{r}=1$, and the rest of $N-1$ directions $\mathbf{s}_i$ are collected in the $N \times (N-1)$ $\mathbf{S}$ rectangular matrix. We select $\mathbf{S}$ such that $\mathbf{D}^T\mathbf{D}=\mathbf{I}$ implying that $\mathbf{S}^T\mathbf{r}=\mathbf{0}_{N-1}$ and $\mathbf{S}^T\mathbf{S}=\mathbf{I}_{N-1}$, being $\mathbf{I}_{N-1}$ the unit matrix of the N - 1 dimensional subspace. The transformation (6) is nonsingular because the determinant of their Jacobian is not null,

$det\ (\nabla_{\mathbf{q}}\ \mathbf{x}^T) = det\ (\mathbf{D}^T) \neq 0$, in other words the **D** matrix is formed by N linear independent vectors. This condition implies that this transformation is invertible, to every point **x** corresponds a unique point **q** satisfying equation (6). It is $\mathbf{q} = \mathbf{D}^T\mathbf{x}$ thus $q_{rc} = \mathbf{r}^T\mathbf{x}$ and $dq_{rc} = \mathbf{r}^T (d\mathbf{x} / dx_{rc})\ dx_{rc}$. We write again $d\mathbf{x} / dx_{rc} = \mathbf{x}'$. Now, taking equation (5), the transformation (6) also applied on the PES function, namely, $V(\mathbf{q}) = V(\mathbf{q}(\mathbf{x})) = U(\mathbf{x})$, and $dq_{rc} = \mathbf{r}^T\ \mathbf{x}'\ dx_{rc}$, we can write,

$$I(\bar{\mathbf{q}}) = \int_{q_{rc}^0}^{q_{rc}^f} F(q_{rc},\bar{\mathbf{q}})dq_{rc} = \int_{q_{rc}^0}^{q_{rc}^f} V(q_{rc},\bar{\mathbf{q}})dq_{rc} = \int_{x_{rc}^0}^{x_{rc}^f} V(q_{rc}(\mathbf{x}),\bar{\mathbf{q}}(\mathbf{x}))\mathbf{r}^T\mathbf{x}'dx_{rc} =$$
$$\int_{x_{rc}^0}^{x_{rc}^f} V(\mathbf{q}(\mathbf{x}))\mathbf{r}^T\mathbf{x}'dx_{rc} = \int_{x_{rc}^0}^{x_{rc}^f} U(x_{rc},\bar{\mathbf{x}})\left(r_{rc} + \bar{\mathbf{r}}^T\bar{\mathbf{x}}'\right)dx_{rc} = \qquad (8)$$
$$\int_{x_{rc}^0}^{x_{rc}^f} G(x_{rc},\bar{\mathbf{x}},\bar{\mathbf{x}}')dx_{rc} = I(\bar{\mathbf{x}})$$

where $\bar{\mathbf{x}}$ is the $\mathbf{x}$ vector without the x_{rc} element, $\mathbf{x}^T = \left(x_{rc},\bar{\mathbf{x}}^T\right)$ and $\bar{\mathbf{r}}$ is the $\mathbf{r}$ vector without the r_{rc} element, $\mathbf{r}^T = \left(r_{rc},\bar{\mathbf{r}}^T\right)$. Now, given the curve $\mathbf{q}^T(q_{rc}) = (q_{rc}, \bar{\mathbf{q}}^T(q_{rc}))$ in the **q** space of coordinates the transformation (6) defines the curve in the **x** space of coordinates by some function $\mathbf{x}^T(x_{rc}) = (x_{rc}, \bar{\mathbf{x}}^T(x_{rc}))$. The basic question on the invariant character of the Euler equation is the following: let $\bar{\mathbf{q}}(q_{rc})$ and $\bar{\mathbf{x}}(x_{rc})$ two curves related by the smooth and nonsingular transformation (6), then $\bar{\mathbf{x}}(x_{rc})$ is an extremal for $I(\bar{\mathbf{x}})$ if $\bar{\mathbf{q}}(q_{rc})$ is an extremal of $I(\bar{\mathbf{q}})$.[30] This is because the corresponding Euler equations are related by the transformation (6), and the equality, $\{G_{\bar{\mathbf{x}}}\} = \left[\nabla_{\bar{\mathbf{x}}}\bar{\mathbf{q}}^T\right]\{V_{\bar{\mathbf{q}}}\} = \mathbf{0}_{N-1}$, where $\{G_{\bar{\mathbf{x}}}\} = \mathbf{0}_{N-1}$ if $\{F_{\bar{\mathbf{q}}}\} = \mathbf{0}_{N-1}$ since $det\ (\mathbf{D}) \neq 0$. The vice versa is also true. In more detail the Euler equation (2) corresponding to the functional G of equation (8), $\{G_{\bar{\mathbf{x}}}\}$, is satisfied if equation (4), the Euler equation of the functional V of the variational problem (5), $\{V_{\bar{\mathbf{q}}}\}$, is also satisfied. Enunciated in another way and for the present case, given the PES function in the **q** system of coordinates, $V(\mathbf{q})$, and the selection of a coordinate as a reaction coordinate, q_{cr}, with these elements one constructs the functional V as given in equation (5), then using the inverse of the transformation (6) one obtains the functional G,

$$V\left(q_{rc}(\mathbf{x}),\bar{\mathbf{q}}(\mathbf{x})\right)\mathbf{r}^T\mathbf{x}' = V\left(\mathbf{q}\left(x_{rc},\bar{\mathbf{x}}\right)\right)\left(r_{rc} + \bar{\mathbf{r}}^T\bar{\mathbf{x}}'\right) = U\left(x_{rc},\bar{\mathbf{x}}\right)\left(r_{rc} + \bar{\mathbf{r}}^T\bar{\mathbf{x}}'\right) = G\left(x_{rc},\bar{\mathbf{x}},\bar{\mathbf{x}}'\right) \tag{9.a}$$

The Euler equation of this new functional G is related to equation (4), the Euler equation of the variational problem (5), by the equalities,

$$\mathbf{r}^T\mathbf{x}'\left[\nabla_{\bar{\mathbf{x}}}\mathbf{x}^T\right]\mathbf{S}\nabla_{\bar{\mathbf{q}}}V\left(\mathbf{q}\left(x_{rc},\bar{\mathbf{x}}\right)\right) - \left(\mathbf{x}'\right)^T\mathbf{S}\nabla_{\bar{\mathbf{q}}}V\left(\mathbf{q}\left(x_{rc},\bar{\mathbf{x}}\right)\right)\bar{\mathbf{r}} = \mathbf{0}_{N-1} \tag{9.b}$$

being satisfied if the equation (4) is also satisfied. Conversely, given the PES function in the **x** system of coordinates, $U(\mathbf{x})$, and a normalized vector, **r**, with these elements one constructs the functional G as given in equation (8), then using the expression (6) it is transformed to the functional V as exposed in the set of equalities,

$$G\left(x_{rc}(\mathbf{q}),\bar{\mathbf{x}}(\mathbf{q}),\left(d\bar{\mathbf{x}}/dq_{rc}\right)/\left(dx_{rc}/dq_{rc}\right)\right)\left(dx_{rc}/dq_{rc}\right) = U\left(x_{rc}(\mathbf{q}),\bar{\mathbf{x}}(\mathbf{q})\right) = U\left(\mathbf{x}\left(q_{rc},\bar{\mathbf{q}}\right)\right) = V\left(q_{rc},\bar{\mathbf{q}}\right) \tag{10.a}$$

and the Euler equation of the resulting functional V, which is equation (4), is related to the Euler equation of the functional G through the equalities,

$$\left(\nabla_{\bar{\mathbf{q}}}\mathbf{x}^T\right)\nabla_{\mathbf{x}}U\left(\mathbf{x}\left(q_{rc},\bar{\mathbf{q}}\right)\right) = \mathbf{S}^T\nabla_{\mathbf{x}}U\left(\mathbf{x}(\mathbf{q})\right) = \nabla_{\bar{\mathbf{q}}}V\left(q_{rc},\bar{\mathbf{q}}\right) = \mathbf{0}_{N-1} \tag{10.b}$$

being satisfied if the gradient of the PES function, $U(\mathbf{x})$, is null in its projection on the subspace spanned by the set of N-1 $\mathbf{s}_i$ vectors. An equivalent form to rewrite the second term of equation (10.b) is

$$\mathbf{r}\left(\nabla_{\mathbf{x}}^T U(\mathbf{x})\nabla_{\mathbf{x}}U(\mathbf{x})\right)^{1/2} = \nabla_{\mathbf{x}}U(\mathbf{x}) \tag{11}$$

since multiplying from the left by $\mathbf{S}^T$ one recovers the second term of (10.b). We recall that **r** is a given normalized vector. Equation (11) was introduced for the first time by Quapp et al. in their proposed RGF method.[8,10] The above equivalence between the variational problems characterized by the integrands V and G establishes the relation between both the RGF path and the distinguished reaction coordinate or DC path. If a column of the unit matrix **I** is selected as **r** vector, then the functional G of equation (8) is equal to the functional V of equation (5). In this case both the DC and the RGF methods coincide in the original system of coordinates. From this point of view the RGF is a generalization of the DC or driven coordinate method. However, the RGF method can always be transformed to the DC method by choosing the appropriate transformation of coordinates as that defined in the expression (6). We emphasize that each of the Euler equations, namely, (4), (10.b) or their equivalent (11), involve derivatives of the type, $d\bar{\mathbf{q}}/dq_{rc}$ or $d\bar{\mathbf{x}}/dx_{rc}$, respectively. This fact implies that the extremal curve, $\mathbf{q}(q_{cr})$ or $\mathbf{x}(x_{cr})$, should be obtained implicitly from the appropriated Euler equation.

The Extremal Sufficient Conditions.

The relation between the DC and the RGF methods from a variational point of view has been established, now we want to explore the extremal sufficient conditions of this type of RP curves. The Euler differential equation is a necessary condition for an extremum. However, a particular extremal curve satisfying the boundary conditions can furnish an actual extremal, say character minimum, only if it satisfies certain additional necessary conditions that take the form of inequalities, normally denoted as $\delta^2 I \geq 0$. The formulation of such inequalities, together with their refinement into sufficient conditions is an important part of the Theory of Calculus of Variations.[25,30] We address this problem from the functional G which is associated to the RGF method and is more general. This functional always can be transformed to the V functional thanks to the transformation (6) related to the DC method.

In the present case, the extremal curve $\mathbf{x}^T(x_{rc}) = \left(x_{rc}, \overline{\mathbf{x}}^T(x_{rc})\right)$ makes the integral $I\left(\overline{\mathbf{x}}\right)$ of equation (8) a minimum with respect to continuous comparison curves, $\mathbf{x}_c^T(x_{rc}) = \left(x_{rc}, \overline{\mathbf{x}}_c^T(x_{rc})\right)$, with piecewise continuous first derivatives if the condition,

$$\det\left(\mathbf{S}^T\left[\nabla_{\mathbf{x}}\nabla_{\mathbf{x}}^T U\left(\mathbf{x}(x_{rc})\right)\right]\mathbf{S}\right) \geq 0 \qquad (12)$$

is satisfied along the extremal curve $\mathbf{x}(x_{rc})$. To prove this assertion, first, we replace in the integral $I\left(\overline{\mathbf{x}}\right)$ of equation (8) the arguments $\overline{\mathbf{x}}$ and $d\overline{\mathbf{x}}/dx_{rc}$ by $\overline{\mathbf{x}}_c = \overline{\mathbf{x}} + \varepsilon\overline{\mathbf{y}}$ and $d\overline{\mathbf{x}}_c/dx_{rc} = d\overline{\mathbf{x}}/dx_{rc} + \varepsilon\, d\overline{\mathbf{y}}/dx_{rc}$, being ε a number, and $\mathbf{y}(x_{rc})$ an arbitrarily chosen function, $\mathbf{y}^T(x_{rc}) = (y_{rc}(x_{rc}), \overline{\mathbf{y}}^T(x_{rc}))$. Second, by the Taylor theorem we expand $I\left(\overline{\mathbf{x}}\right)$ until the second order in ε

$$H(\varepsilon) = I\left(\overline{\mathbf{x}} + \varepsilon\overline{\mathbf{y}}\right) = I\left(\overline{\mathbf{x}}\right) + \varepsilon\delta I\left(\overline{\mathbf{x}},\overline{\mathbf{y}}\right) + \frac{\varepsilon^2}{2}\delta^2 I\left(\overline{\mathbf{x}},\overline{\mathbf{y}}\right) + \mathrm{O}\left(\varepsilon^2\right) \qquad (13)$$

Since $I\left(\overline{\mathbf{x}}\right)$ is stationary for the $\mathbf{x}(x_{rc})$ curve then $dH(\varepsilon)/d\varepsilon\big|_{\varepsilon=0} = \delta I\left(\overline{\mathbf{x}},\overline{\mathbf{y}}\right)$ vanishes (from which follows the Euler equation $\left\{G_{\overline{\mathbf{x}}}\right\} = \mathbf{0}_{N-1}$) and a necessary condition for a minimum is $d^2H(\varepsilon)/d\varepsilon^2\big|_{\varepsilon=0} = \delta^2 I\left(\overline{\mathbf{x}},\overline{\mathbf{y}}\right) \geq 0$ for the arbitrarily chosen function $\overline{\mathbf{y}}(x_{rc})$. For the present variational problem we express the integrals $I\left(\bar{\mathbf{x}}+\varepsilon\bar{\mathbf{y}}\right)$ and $\delta^2 I\left(\bar{\mathbf{x}},\bar{\mathbf{y}}\right)$ of equation (13) as a function of the **q** coordinates through **x** using the transformation (6). The dependence of the **x** coordinates in respect to **q** coordinates for the present purposes is given by the following relation, $\mathbf{x}_c = \mathbf{x} + \varepsilon\mathbf{y} = \mathbf{D}\,\mathbf{q}_c = \mathbf{D}\,(\mathbf{q} + \varepsilon\mathbf{p})$ where $\mathbf{y}^T\,\mathbf{D} = \mathbf{p}^T = (p_{rc},\ \bar{\mathbf{p}}^T)$ and $p_{rc} = 0$ because $q^c_{rc} = q_{rc}$ implying that $\mathbf{y} = \mathbf{S}\,\bar{\mathbf{p}}$. With these considerations we have,

$$
\begin{aligned}
&I\left(\bar{\mathbf{x}}+\varepsilon\bar{\mathbf{y}}\right) = \int_{x_{rc}^0}^{x_{rc}^f} \left\{U\left(\mathbf{x}_c(\varepsilon)\right)\mathbf{r}^T\mathbf{x}_c'(\varepsilon)\right\}dx_{rc} = \\
&\int_{q_{rc}^0}^{q_{rc}^f} \left\{U\left(\mathbf{D}(\mathbf{q}+\varepsilon\mathbf{p})\right)\mathbf{r}^T\mathbf{D}(\mathbf{q}'+\varepsilon\mathbf{p}')\right\}dq_{rc} = \\
&\int_{q_{rc}^0}^{q_{rc}^f} V\left(q_{rc},\bar{\mathbf{q}}+\varepsilon\bar{\mathbf{p}}\right)dq_{rc} = I\left(\bar{\mathbf{q}}+\varepsilon\bar{\mathbf{p}}\right)
\end{aligned}
\tag{14}
$$

and

$$
\begin{aligned}
&\delta^2 I\left(\bar{\mathbf{x}},\bar{\mathbf{y}}\right) = \int_{x_{rc}^0}^{x_{rc}^f} \mathbf{y}^T\left[\nabla_{\mathbf{x}}\nabla_{\mathbf{x}}^T U\left(x_{rc},\bar{\mathbf{x}}(x_{rc})\right)\right]\mathbf{y}\,dx_{rc} = \\
&\int_{q_{rc}^0}^{q_{rc}^f} \bar{\mathbf{p}}^T\mathbf{S}^T\left[\nabla_{\mathbf{x}}\nabla_{\mathbf{x}}^T U\left(\mathbf{x}\left(q_{rc},\bar{\mathbf{q}}\right)\right)\right]\mathbf{S}\bar{\mathbf{p}}\,dq_{rc} = \delta^2 I\left(\bar{\mathbf{q}},\bar{\mathbf{p}}\right)
\end{aligned}
\tag{15}
$$

where $\mathbf{x}_c'(\varepsilon) = d\mathbf{x}_c(\varepsilon)/dx_{rc}$, $\mathbf{q}' = d\mathbf{q}/dq_{rc}$ and $\mathbf{p}' = d\mathbf{p}/dq_{rc}$. From equation (15) follows (12). The comparison curve $\mathbf{x}_c(x_{rc})$, and their derivative $\mathbf{x}_c$' tends to the extremal curve and their derivative, $\mathbf{x}(x_{rc})$ and **x**', as ε tends to zero. The variation, $\varepsilon\,\mathbf{y}(x_{rc})$, is called a weak variation because it satisfies these two conditions and geometrically means that the extremal curve $\mathbf{x}(x_{rc})$ is compared to curves that approximate to $\mathbf{x}(x_{rc})$ in the slope as well as position as ε tends to zero. Taking into account this definition we conclude that the DC curve or its generalization, the RGF or Newton path, satisfies the necessary weak relative minimum conditions if the inequality (12) is satisfied everywhere along the extremal path, $\mathbf{x}(x_{rc})$, joining the points $\mathbf{x}_0 = (x^0_{rc},\ \bar{\mathbf{x}}_0)$ and $\mathbf{x}_f = (x^f_{rc},\ \bar{\mathbf{x}}_f)$. If in the expression (12) the equality is dropped then the curve satisfies the sufficient weak relative minimum condition.

In contrast to these weak variations, we now consider a new type of strong variations whose smallness does not imply that of their derivatives. Since in the quadratic form of the integrand $\delta^2 I\left(\bar{\mathbf{x}},\bar{\mathbf{y}}\right)$ of equation (14) does not depend on the derivative and is positive if expression (12) is satisfied then the extremal curve, $\mathbf{x}(x_{rc})$, in the given region certainly furnishes a minimum. We conclude that the DC curve or its generalization, the RGF or Newton path, also satisfies the necessary strong minimum conditions. This extremal path joining two points of the PES function minimizes the integral functional given in the expression (8) if it evolves through a convex region of the PES. The sufficiency condition of the minimum character is achieved if the convexity is strict. In the next section we remark this conclusion from another point of view.

Transversality.

Now we analyze the concept of transversality which is important in the Theory of Calculus of Variations.[25,30] The transversality is a relation between the direction of the extremal curve, $\mathbf{x}^T(x_{rc}) = (x_{rc}, \bar{\mathbf{x}}^T(x_{rc}))$, and that of the given boundary curve, a member of the family of equipotential hypersurfaces of the PES, $U(\mathbf{x}) = v$. To get this relation we define an arbitrary curve, $\mathbf{x}_a^T(x_{rc}) = \left(x_{rc}, \bar{\mathbf{x}}_a^T(x_{rc})\right)$, which intersects the above family of equipotential hypersurfaces of the PES and touches them no where, thus if we set $v(x_{rc}) = U(\mathbf{x}_a(x_{rc}))$, then,

$$dv/dx_{rc} = \nabla_{\mathbf{x}}^T U(\mathbf{x})(d\mathbf{x}/dx_{rc})\Big|_{\mathbf{x}=\mathbf{x}_a(x_{rc})} \tag{16}$$

We express the value $I(\bar{\mathbf{x}})$ of equation (8) along the curve $\mathbf{x}_a(x_{rc})$ as a function of v obtaining,

$$I(\bar{\mathbf{x}}_a) = \int_{x_{rc}^0}^{x_{rc}^f} G\left(x_{rc}, \bar{\mathbf{x}}_a, \bar{\mathbf{x}}_a'\right) dx_{rc} = \int_{v_0}^{v_f} \frac{U(\mathbf{x}_a)\mathbf{r}^T\mathbf{x}_a'}{\nabla_{\mathbf{x}}^T U(\mathbf{x}_a)\mathbf{x}_a'} dv \tag{17}$$

where $\bar{\mathbf{x}}_a' = d\bar{\mathbf{x}}_a/dx_{rc}$ and $\mathbf{x}_a' = d\mathbf{x}_a / dx_{rc}$. We look for those tangent vectors, $\mathbf{x}_a'$, for which the integrand of the second integral of equation (17) is stationary in respect to these vectors. They satisfy the condition

$$\mathbf{r} = \frac{\mathbf{r}^T\mathbf{x}_a'}{\nabla_{\mathbf{x}}^T U(\mathbf{x}_a)\mathbf{x}_a'} \nabla_{\mathbf{x}} U(\mathbf{x}_a) \tag{18}$$

Since $\mathbf{r}$ is a normalized vector to the unity then $\mathbf{r}^T \mathbf{x}_a' / [\nabla^T_{\mathbf{x}} U(\mathbf{x}_a)\, \mathbf{x}_a'] = 1 / [\nabla^T_{\mathbf{x}} U(\mathbf{x}_a)\, \nabla_{\mathbf{x}} U(\mathbf{x}_a)]^{1/2}$. This condition is satisfied if the curve with tangent $\mathbf{x}_a'$ cuts the family of equipotential hypersurfaces of the PES, v, at the corresponding point where the gradient vector $\nabla_{\mathbf{x}} U(\mathbf{x}_a)$ points to the direction $\mathbf{r}$, $\nabla_{\mathbf{x}} U(\mathbf{x}_a) = \mathbf{r}\, [\nabla^T_{\mathbf{x}} U(\mathbf{x}_a)\, \nabla_{\mathbf{x}} U(\mathbf{x}_a)]^{1/2}$, which is nothing more than equation (11), the Euler equation of functional G of the variational problem (8). We conclude that the arbitrary curve $\mathbf{x}_a(x_{rc})$ satisfying the above condition is the RGF curve that extremalizes the functional (8), $\mathbf{x}_a(x_{rc}) = \mathbf{x}(x_{rc})$. Normally at each point of an equipotential hypersurface of the PES, the gradient vector points to different direction, on the other hand the functional G is parametrically dependent on the **r** vector. The **r** vector is not an argument of this functional and the resulting Euler equation is a function of this vector, from this fact we conclude that the variational problem (8) normally does not generate a field of RGF extremals with a given **r**. With the starting point or initial condition $\mathbf{x}_0 = \mathbf{x}(x^0_{rc})$ such that at this point the gradient of the PES points to the direction **r**, the equation (11) only generates a curve cutting the family of equipotential hypersurfaces of the PES at the points where the corresponding gradient vectors point to the same direction **r**. In other words, from these initial conditions only a curve is generated. The extremal curve is not imbedded in a field of extremal curves satisfying equation (11) and these initial conditions. Additionally, if we take into account the relation between the RGF and the DC method, we say that the functional V of equation (5) does not generate a field of extremals, since normally only a point of the equipotential hypersurface has a gradient that possesses the form given in equation (4).

Integration.

In the last section only the variational nature of both the DC and RGF methods have been analyzed. An important result is that the RGF method is a generalization of the DC method. Due to this fact, from now on we only deal with equation (11), the Euler equation associated to the RGF method. As noted above, this Euler equation is not a system of ordinary differential equations so that integration allows one to determine the curve. It is a system of N-first order partial differential equations, and the curve is obtained in this case through the corresponding treatment of this system. In this section we analyze the integration of this system of partial differential equations. We are facing a Cauchy or initial value problem.[25,31,32] Briefly it consists in the present case of constructing an $N-1$ dimensional surface, and through each point of this surface passes a curve which is not tangent to the surface and also varies sufficiently smoothly. The value of the surface, $U(\mathbf{x}) - v = 0$, their derivatives in the direction of the curve and the initial values are prescribed on the surface. Now the transformation (6) is used.

Because $det\ (\nabla_{\mathbf{q}}\ \mathbf{x}^T) \neq 0$ it is possible to replace the coordinates **x** by the new coordinates **q** of the surface. Now we multiply equation (11) from the left by $\mathbf{D}^T$ and from the resulting equation we apply the above change of coordinates,

$$\begin{pmatrix} \left(\nabla_{\mathbf{x}}^T U(\mathbf{x}) \nabla_{\mathbf{x}} U(\mathbf{x})\right)^{1/2} \\ \mathbf{0}_{N-1} \end{pmatrix} = \mathbf{D}^T \nabla_{\mathbf{x}} U(\mathbf{x}) = \left[\nabla_{\mathbf{q}} (\mathbf{D}\mathbf{q})^T\right] \nabla_{\mathbf{x}} U(\mathbf{x}) =$$
$$\left[\nabla_{\mathbf{q}} \mathbf{x}^T\right] \nabla_{\mathbf{x}} U(\mathbf{x}) = \nabla_{\mathbf{q}} U(\mathbf{D}\mathbf{q}) = \nabla_{\mathbf{q}} V\left(q_{rc}, \bar{\mathbf{q}}\right) = \begin{pmatrix} \partial V\left(q_{rc}, \bar{\mathbf{q}}\right) / \partial q_{rc} \\ \nabla_{\bar{\mathbf{q}}} V\left(q_{rc}, \bar{\mathbf{q}}\right) \end{pmatrix} \tag{19}$$

Using the resolution of identity $\mathbf{I} = \mathbf{D}\mathbf{D}^T$ and $\nabla_{\bar{\mathbf{q}}} V\left(q_{rc}, \bar{\mathbf{q}}\right) = \mathbf{0}_{N-1}$ which is equation (10.b) we have that

$$\left(\nabla_{\mathbf{x}}^T U(\mathbf{x}) \nabla_{\mathbf{x}} U(\mathbf{x})\right)^{1/2} = \left(\nabla_{\mathbf{x}}^T U(\mathbf{x}) \mathbf{D}\mathbf{D}^T \nabla_{\mathbf{x}} U(\mathbf{x})\right)^{1/2} =$$
$$\left(\left(\mathbf{D}^T \nabla_{\mathbf{x}} U(\mathbf{x})\right)^T \left(\mathbf{D}^T \nabla_{\mathbf{x}} U(\mathbf{x})\right)\right)^{1/2} = \left(\nabla_{\mathbf{q}}^T V\left(q_{rc}, \bar{\mathbf{q}}\right) \nabla_{\mathbf{q}} V\left(q_{rc}, \bar{\mathbf{q}}\right)\right)^{1/2} = \tag{20}$$
$$\partial V\left(q_{rc}, \bar{\mathbf{q}}\right) / \partial q_{rc}$$

In this way the equation (11) in the new coordinates **q** takes the form,

$$\nabla_{\mathbf{q}} V\left(q_{rc}, \bar{\mathbf{q}}\right) = \begin{pmatrix} \partial V\left(q_{rc}, \bar{\mathbf{q}}\right) / \partial q_{rc} \\ \nabla_{\bar{\mathbf{q}}} V\left(q_{rc}, \bar{\mathbf{q}}\right) \end{pmatrix} = \begin{pmatrix} \partial V\left(q_{rc}, \bar{\mathbf{q}}\right) / \partial q_{rc} \\ \mathbf{0}_{N-1} \end{pmatrix} \tag{21}$$

with the initial condition

$$\nabla_{\mathbf{q}} V\left(q_{rc}, \bar{\mathbf{q}}\right)\Big|_{\substack{q_{rc} = q_{rc}^0 \\ \mathbf{q} = \mathbf{q}_0}} = \begin{pmatrix} \partial V\left(q_{rc}, \bar{\mathbf{q}}\right) / \partial q_{rc} \\ \mathbf{0}_{N-1} \end{pmatrix}\Bigg|_{\substack{q_{rc} = q_{rc}^0 \\ \mathbf{q} = \mathbf{q}_0}} \tag{22}$$

In the **q** system of coordinates we say that the curve going through a point of the surface depends on *N-1* parameters for which we can take the coordinates $\bar{\mathbf{q}}$ of the point of the surface. The q_{rc} denotes the coordinate that varies along the curve. In other words, q_{rc} is the parameter of a point on the curve and $\bar{\mathbf{q}}$ are the *N-1* parameters of the curve itself. Through each point of the surface one and only one curve goes implying that the numbers **q** may be taken as new coordinates of the point **x**. The normal to the plane tangent to the surface is the vector $\nabla_{\mathbf{q}} V(q_{rc}, \bar{\mathbf{q}})$ of equation (21). Because this vector possesses a nonzero component in the **r** direction and null components in the set of the *N-1* directions collected in the **S** matrix, the plane tangent at the initial point $\mathbf{q}_0$ is given by $0 = q_{rc} - q^0_{rc}$. In the **x** coordinates this plane is $0 = q_{rc} - q^0_{rc} = (q_{rc} - q^0_{rc}) + \mathbf{0}^T_{N-1} (\bar{\mathbf{q}} - \bar{\mathbf{q}}_0) = \mathbf{r}^T \mathbf{D} (\mathbf{q} - \mathbf{q}_0) = \mathbf{r}^T (\mathbf{x} - \mathbf{x}_0)$ being the **r** vector the normal to the plane in the **x** coordinates. The curve that passes through the plane $0 = q_{rc} - q^0_{rc}$ at the point $\mathbf{q}_0 = (q^0_{rc},$

$\bar{\mathbf{q}}_0$) is obtained by applying the Implicit Function Theorem [33] to the set of *N-1* functions, $\nabla_{\bar{\mathbf{q}}} V\left(q_{rc}, \bar{\mathbf{q}}\right) = \mathbf{0}_{N-1}$, being this curve the solution to the system of first order partial differential equations (21) with the initial conditions (22). If at the point $\mathbf{q}_0 = (q^0_{rc}, \bar{\mathbf{q}}_0^T)$ the above *N-1* equations are satisfied and $\det\left(\nabla_{\bar{\mathbf{q}}} \nabla^T_{\bar{\mathbf{q}}} V\left(q_{rc}, \bar{\mathbf{q}}\right)\Big|_{\substack{q_{rc}=q^0_{rc} \\ \bar{\mathbf{q}}=\bar{\mathbf{q}}_0}} \right) \neq 0$ then according to the Implicit Function Theorem there exist in a certain neighborhood of the point q^0_{rc} one and only one system of continuous functions $\bar{\mathbf{q}} = \bar{\mathbf{q}}(q_{rc})$ satisfying the two conditions, $\bar{\mathbf{q}}_0 = \bar{\mathbf{q}}\left(q^0_{rc}\right)$ and $\nabla_{\bar{\mathbf{q}}} V\left(q_{rc}, \bar{\mathbf{q}}(q_{rc})\right) = \mathbf{0}_{N-1}$. In addition the first derivative $d\bar{\mathbf{q}}/dq_{rc}$ exists in the same region, it is a continuous function of q_{rc} and it is obtained through the equation

$$\left[\nabla_{\bar{\mathbf{q}}} \nabla^T_{\bar{\mathbf{q}}} V\left(q_{rc}, \bar{\mathbf{q}}\right)\right] \frac{d\bar{\mathbf{q}}}{dq_{rc}} + \frac{\partial}{\partial q_{rc}}\left(\nabla_{\bar{\mathbf{q}}} V\left(q_{rc}, \bar{\mathbf{q}}\right)\right) = \mathbf{0}_{N-1} \tag{23}$$

The functions $\bar{\mathbf{q}} = \bar{\mathbf{q}}(q_{rc})$ describe the curve and $d\bar{\mathbf{q}}/dq_{rc}$ their tangent. Now we transform equation (23) from **q** coordinates to **x** coordinates using (6),

$$\begin{aligned} \mathbf{0}_{N-1} &= \mathbf{S}^T\left[\nabla_{\mathbf{x}} \nabla^T_{\mathbf{x}} U(\mathbf{x})\right]\mathbf{S}\left(\frac{d\bar{\mathbf{q}}}{dq_{rc}}\right) + \mathbf{S}^T\left[\nabla_{\mathbf{x}} \nabla^T_{\mathbf{x}} U(\mathbf{x})\right]\mathbf{r} = \\ \mathbf{S}^T\left[\nabla_{\mathbf{x}} \nabla^T_{\mathbf{x}} U(\mathbf{x})\right]\mathbf{D}\left(\frac{d\mathbf{q}}{dq_{rc}}\right) &= \mathbf{S}^T\left[\nabla_{\mathbf{x}} \nabla^T_{\mathbf{x}} U(\mathbf{x})\right]\left(\frac{d\mathbf{x}}{dx_{rc}}\right)\frac{dx_{rc}}{dq_{rc}} \end{aligned} \tag{24}$$

Since $dx_{rc} / dq_{rc} \neq 0$ and the matrix $\mathbf{SS}^T$ is a representation of the projector $(\mathbf{I} - \mathbf{rr}^T)$ we rewrite equation (24) after multiplying it from the left by **S** as

$$\left(\mathbf{I} - \mathbf{rr}^T\right)\left[\mathbf{H}(\mathbf{x})\right]\frac{d\mathbf{x}}{dx_{rc}} = \mathbf{0} \tag{25}$$

where $\mathbf{H}(\mathbf{x})$ is the Hessian matrix, $\mathbf{H}(\mathbf{x}) = \nabla_{\mathbf{x}}\nabla_{\mathbf{x}}^T U(\mathbf{x})$. The equation (25) has been reported many times as the basic equation to integrate the RGF method.[10,34] This equation tells us that the *N-1* components, $\mathbf{s}_i^T[\mathbf{H}(\mathbf{x})]\mathbf{x}' = 0$, but we are free for the $\mathbf{r}^T[\mathbf{H}(\mathbf{x})]\mathbf{x}'$ component. Due to this fact and for convenience we take $\mathbf{r}^T[\mathbf{H}(\mathbf{x})]\mathbf{x}' = (\mathbf{g}^T(\mathbf{x})\mathbf{g}(\mathbf{x}))^{1/2} \det(\mathbf{H}(\mathbf{x}))$. With these considerations, to obtain the tangent vector, $d\mathbf{x} / dx_{rc}$, we write $[\mathbf{H}(\mathbf{x})]\mathbf{x}'$ vector as follows

$$\left[\mathbf{H}(\mathbf{x})\right]\frac{d\mathbf{x}}{dx_{rc}} = \mathbf{r}\left(\mathbf{g}^T(\mathbf{x})\mathbf{g}(\mathbf{x})\right)^{1/2}\det\left(\mathbf{H}(\mathbf{x})\right) \tag{26}$$

which satisfies the above requirements. Now, multiplying equation (26) from the left by $\mathbf{A}(\mathbf{x})$, the adjoint matrix of the Hessian, and finally using equation (11), we get the equation,

$$\frac{d\mathbf{x}}{dx_{rc}} = [\mathbf{A}(\mathbf{x})]\mathbf{r}(\mathbf{g}^T(\mathbf{x})\mathbf{g}(\mathbf{x}))^{1/2} = [\mathbf{A}(\mathbf{x})]\mathbf{g}(\mathbf{x}) \qquad (27)$$

where the identity has been employed,

$$[\mathbf{A}(\mathbf{x})][\mathbf{H}(\mathbf{x})] = [\mathbf{H}(\mathbf{x})][\mathbf{A}(\mathbf{x})] = \mathbf{I}\det(\mathbf{H}(\mathbf{x})) \qquad (28)$$

The equation (27) is the Branin equation.[35,36] The basic equation (25) of the RGF method is related to the Branin equation (27) if the $\mathbf{r}^T[\mathbf{H}(\mathbf{x})]\mathbf{x}'$ component is that given above. The vector $\nabla_{\mathbf{x}}U(\mathbf{x}) = \mathbf{g}(\mathbf{x})$ varies through the direction of the curve (27) according to the equation,

$$\frac{d\mathbf{g}(\mathbf{x})}{dx_{rc}} = \frac{d\nabla_{\mathbf{x}}U(\mathbf{x})}{dx_{rc}} = [\nabla_{\mathbf{x}}\nabla_{\mathbf{x}}^T U(\mathbf{x})]\left(\frac{d\mathbf{x}}{dx_{rc}}\right) = [\mathbf{H}(\mathbf{x})]\left(\frac{d\mathbf{x}}{dx_{rc}}\right) = \mathbf{r}(\mathbf{g}^T(\mathbf{x})\mathbf{g}(\mathbf{x}))^{1/2}\det(\mathbf{H}(\mathbf{x})) = \mathbf{g}(\mathbf{x})\det(\mathbf{H}(\mathbf{x})) \qquad (29)$$

where equations (27) and (28) have been used. Integrating equation (29) we conclude that $\nabla_{\mathbf{x}}U(\mathbf{x})$ only varies in the $\mathbf{r}$ direction, $\nabla_{\mathbf{x}}U(\mathbf{x}) = \mathbf{g}(\mathbf{x}) = \mathbf{r}\,(\mathbf{g}^T(\mathbf{x})\mathbf{g}(\mathbf{x}))^{1/2}$, and null in the $N-1$ $\mathbf{s}_i$ directions as is expected looking at the system of partial differential equations (11). Finally the variation of $U(\mathbf{x})$ through this curve is given by the expression,

$$\frac{dU(\mathbf{x})}{dx_{rc}} = \left(\frac{d\mathbf{x}}{dx_{rc}}\right)^T \nabla_{\mathbf{x}}U(\mathbf{x}) = \mathbf{r}^T[\mathbf{A}(\mathbf{x})]\mathbf{r}(\mathbf{g}^T(\mathbf{x})\mathbf{g}(\mathbf{x})) = \mathbf{g}^T(\mathbf{x})[\mathbf{A}(\mathbf{x})]\mathbf{g}(\mathbf{x}) \qquad (30)$$

where again equations (11) and (27) have been used. The system (27), (29) and (30) is called the characteristic system of differential equations belonging to the equation (11). At each point of the curve given by the set of ordinary differential equations (27) and (29), the coordinates $\mathbf{x}$ and the vector $\nabla_{\mathbf{x}}U(\mathbf{x})$, satisfy the system of partial differential equations (11). The system of ordinary differential equations (27), (29) and (30) is not autonomous because it involves arguments that do not appear in the partial differential equation (11). The direction, $d\mathbf{x} / dx_{rc}$, given by the expression (27) is called characteristic direction and in the point $\mathbf{x}$ where $\det(\mathbf{S}^T[\nabla_{\mathbf{x}}\nabla_{\mathbf{x}}^T V(\mathbf{x})]\mathbf{S}) \neq 0$ we say that the hypersurface $U(\mathbf{x}) - v = 0$ is noncharacteristic, the curve transverses it at this point.

The Case of Turning Points.[37]

The solution of the initial value problem or Cauchy problem fails in the case where $\det(\nabla_{\bar{\mathbf{q}}}\nabla_{\bar{\mathbf{q}}}^T V(q_{rc},\bar{\mathbf{q}})) = \det(\mathbf{S}^T[\nabla_{\mathbf{x}}\nabla_{\mathbf{x}}^T U(\mathbf{x})]\mathbf{S}) = 0$. In this point the Implicit Function Theorem cannot be applied and the immediate consequence is that it is not possible to write $\bar{\mathbf{q}}$ as a function of q_{rc}. In this situation we take t as the parameter that characterizes the curve, $\mathbf{q}(t) = (q_{rc}(t), \bar{\mathbf{q}}(t))$. Now we look for the solution of the initial value problem for this case. First we differentiate $\nabla_{\bar{\mathbf{q}}} V(q_{rc}, \bar{\mathbf{q}}) = \mathbf{0}_{N-1}$ in respect to t,

$$\begin{aligned} &\frac{dq_{rc}}{dt}\frac{\partial}{\partial q_{rc}}\nabla_{\bar{\mathbf{q}}} V(q_{rc}, \bar{\mathbf{q}}) + \left[\nabla_{\bar{\mathbf{q}}}\nabla_{\bar{\mathbf{q}}}^T V(q_{rc}, \bar{\mathbf{q}})\right]\frac{d\bar{\mathbf{q}}}{dt} = \\ &\mathbf{S}^T\left[\mathbf{H}(\mathbf{x})\right]\mathbf{r}\frac{dq_{rc}}{dt} + \mathbf{S}^T\left[\mathbf{H}(\mathbf{x})\right]\mathbf{S}\frac{d\bar{\mathbf{q}}}{dt} = \mathbf{0}_{N-1} \end{aligned} \tag{31}$$

where we applied that $\mathbf{H}(\mathbf{x}) = \nabla_{\mathbf{x}}\nabla_{\mathbf{x}}^T U(\mathbf{x})$. If $\det\left(\nabla_{\bar{\mathbf{q}}}\nabla_{\bar{\mathbf{q}}}^T V(q_{rc}, \bar{\mathbf{q}})\right) = \det\left(\mathbf{S}^T\left[\mathbf{H}(\mathbf{x})\right]\mathbf{S}\right) = 0$ implies that at least one eigenvalue of $\mathbf{S}^T[\mathbf{H}(\mathbf{x})]\mathbf{S}$ matrix is zero. To analyze this case we transform the equation (31) to the system of coordinates, $(q_{rc}, \bar{\mathbf{z}}^T)$, that diagonalize the $\mathbf{S}^T[\mathbf{H}(\mathbf{x})]\mathbf{S}$ matrix,

$$\begin{aligned} &\mathbf{W}^T\mathbf{S}^T\left[\mathbf{H}(\mathbf{x})\right]\mathbf{r}\frac{dq_{rc}}{dt} + \mathbf{h}\mathbf{W}^T\frac{d\bar{\mathbf{q}}}{dt} = \\ &\mathbf{b}\frac{dq_{rc}}{dt} + \mathbf{h}\frac{d\bar{\mathbf{z}}}{dt} = \mathbf{0}_{N-1} \end{aligned} \tag{32}$$

where $\mathbf{W}$ is the unitary matrix of eigenvectors and $\mathbf{h}$ the diagonal matrix of the eigenvalues of the $\mathbf{S}^T[\mathbf{H}(\mathbf{x})]\mathbf{S}$ matrix, in other words, $\mathbf{S}^T[\mathbf{H}(\mathbf{x})]\mathbf{S} = \mathbf{W}\ \{\mathbf{h}_{ij}\delta_{ij}\}\ \mathbf{W}^T$. Let us assume that the eigenvalue $\mathbf{h}_{jj} = h_j = 0$ and the corresponding j element of the $\mathbf{b}$ vector is non-zero, $b_j \neq 0$, then the solution of equation (32) is $dq_{rc} / dt = 0$ and $\left(d\bar{\mathbf{z}}/dt\right)^T = \left(0_1,\ldots,0_{j-1},1_j,0_{j+1},\ldots,0_{N-1}\right)$ and from this $d\bar{\mathbf{q}}/dt = \mathbf{W}\,d\bar{\mathbf{z}}/dt = \mathbf{w}_j$ being $\mathbf{w}_j$ the j column vector of $\mathbf{W}$ matrix.[34] The tangent vector in this case lies in the plane $0 = q_{rc} - q^0_{rc}$ which is tangent to the constant energy contour curve, $V(q_{rc}, \bar{\mathbf{q}}) - v = 0$, and orthogonal to the gradient vector, $\nabla_{\mathbf{q}}^T V(q_{rc}, \bar{\mathbf{q}}) = \left(\partial V(q_{rc}, \bar{\mathbf{q}})/\partial q_{rc},\ \ \mathbf{0}_{N-1}^T\right)$, since the $\mathbf{r}$ component is zero, $dq_{rc} / dt = 0$. The curve at this point does not satisfy the transversality condition. Such a point will normally mark a switch from going uphill in potential energy to going downhill or vice versa, but may in principle also be a tangential touching of the constant energy contour curve, $V(q_{rc}, \bar{\mathbf{q}}) - v = 0$. Such cases are denoted as ‘‘turning points’’ TP.[10] In this case the curve solution is characteristic at this point.

If the diagonal $\mathbf{h}$ matrix has more than one eigenpairs with null eigenvalues, and their corresponding elements of the $\mathbf{b}$ vector are different from zero then there exist infinitely many characteristic curves, all lying in the plane $0 = q_{rc} - q^{0}_{rc}$ tangent to the constant energy contour curve, $V\left(q_{rc},\bar{\mathbf{q}}\right) - v = 0$.

The Case of Valley-Ridge Inflection Points: their Consequences in the Extremal Sufficient Conditions.

In the case that the eigenvalue $\mathbf{h}_{jj} = h_j = 0$ and the corresponding *j* element of the **b** vector is zero, $b_j = 0$, there are only $N - 2$ independent equations in the system of equations (32) (or $N - 1$ if one includes the normalization condition), which does not allow a unique determination of the tangent curve at this point. Rather the whole subspace spanned by the vectors $\left(dq_{rc}/dt, d\bar{\mathbf{q}}^T/dt\right) = \left(dq_{rc}/dt, d\bar{\mathbf{z}}^T/dt\,\mathbf{W}^T\right)$ where $dq_{rc}/dt \neq 0$ and $\left(d\bar{\mathbf{z}}/dt\right)^T = \left(b_1/h_1,\ldots,b_{j-1}/h_{j-1},0_j,b_{j+1}/h_{j+1},\ldots,b_{N-1}/h_{N-1}\right)$ and $\left(dq_{rc}/dt, d\bar{\mathbf{q}}^T/dt\right) = \left(0, d\bar{\mathbf{z}}^T/dt\,\mathbf{W}^T\right)$ where $\left(d\bar{\mathbf{z}}/dt\right)^T = \left(0_1,\ldots,0_{j-1},1_j,0_{j+1},\ldots,0_{N-1}\right)$ is a solution to the matrix equation (32). The former vector is noncharacteristic and transverses the constant energy contour curve while the latest is characteristic lying in the contour energy curve. Thus the condition of a bifurcation point of RGF curves of the same **r** vector is $b_j = h_j = 0$, named also valley-ridge inflection point (VRI).

In these points the set of characteristic differential equations (27), (29) and (30) are still valid. To proof this assertion first we transform equation (27) from **x** coordinates to **q** coordinates using the transformation (6) and the resolution of identity, and second we multiply from the left the resulting equation by the unitary matrix,

$$\begin{pmatrix} 1 & \mathbf{0}^T_{N-1} \\ \mathbf{0}_{N-1} & \mathbf{W}^T \end{pmatrix} \tag{33}$$

obtaining,

$$\begin{pmatrix} \dfrac{dq_{rc}}{dt} \\ \dfrac{d\bar{\mathbf{z}}}{dt} \end{pmatrix} = \begin{bmatrix} \mathbf{r}^T\left[\mathbf{A}(\mathbf{x})\right]\mathbf{r} & \mathbf{r}^T\left[\mathbf{A}(\mathbf{x})\right]\mathbf{SW} \\ \mathbf{W}^T\mathbf{S}^T\left[\mathbf{A}(\mathbf{x})\right]\mathbf{r} & \mathbf{W}^T\mathbf{S}^T\left[\mathbf{A}(\mathbf{x})\right]\mathbf{SW} \end{bmatrix} \begin{pmatrix} \dfrac{\partial V\left(q_{rc},\bar{\mathbf{q}}\right)}{\partial q_{rc}} \\ \mathbf{0}_{N-1} \end{pmatrix} \tag{34}$$

Using the definition of adjoint matrix we have the element $\mathbf{r}^T\left[\mathbf{A}(\mathbf{x})\right]\mathbf{r} = \det\left(\nabla_{\bar{\mathbf{q}}}\nabla^T_{\bar{\mathbf{q}}}V\left(q_{rc},\bar{\mathbf{q}}\right)\right) = \det(\mathbf{h}) = 0$ because $h_j = 0$. In the case that $b_j \neq 0$ the element $(\mathbf{W}^T\mathbf{S}^T[\mathbf{A}(\mathbf{x})]\mathbf{r})_j \neq 0$ and the rest of elements is equal zero. From these results one follows that the tangent vector takes the same structure as given above for this situation. However, when $b_j = 0$ the vector $\mathbf{W}^T\mathbf{S}^T[\mathbf{A}(\mathbf{x})]\mathbf{r} = \mathbf{0}_{N-1}$ and due to this fact $\left(dq_{rc}/dt, d\bar{\mathbf{z}}^T/dt\right) = \mathbf{0}^T$.

With the above results one concludes that both the stationary points and VRI points of a PES are singular points for RGF or NT curves. These curves stop in these points because $\mathbf{g}(\mathbf{x}) = \mathbf{0}$, stationary point, or $[\mathbf{A}(\mathbf{x})]\mathbf{g}(\mathbf{x}) = \mathbf{0}$, VRI point, and from this the tangent of the curve in these points is $\mathbf{x}' = \mathbf{0}$. The existence of VRI points has an important consequence on the extremal conditions of RGF or NT curves. If an NT curve starts in a stationary point of the PES with character minimum and stops at a stationary point character of first order, then the value of the integral $\delta^2 I$ of equation (15) is positive definite and we say that this NT is a minimizing extremal curve. To prove this assertion we say that because the NT path at each point transverses the family of equipotential hypersurfaces and due to the continuity and the non-existence of VRI points we have $\det\left(\mathbf{S}^T\left[\mathbf{H}(\mathbf{x})\right]\mathbf{S}\right) > 0$ at each point of the curve and from this one concludes that $\delta^2 I > 0$. On the other hand, if the NT curve has a VRI point and transverses the equipotential hypersurface that contains this point it stops to a stationary point but no statement can be made on the character of this NT curve. To prove the latest assertion we say that the NT path transverses the family of equipotential hypersurfaces, $\det\left(\mathbf{S}^T\left[\mathbf{H}(\mathbf{x})\right]\mathbf{S}\right) > 0$ holds from the minimum to the VRI point. From the VRI point to the stationary point holds $\det\left(\mathbf{S}^T\left[\mathbf{H}(\mathbf{x})\right]\mathbf{S}\right) < 0$ since the curve enters a ridge and due to this fact the sign of the integral $\delta^2 I$ cannot be determined until its explicit evaluation.

Runge-Kutta-Fehlberg Technique.

Taking into account the overall analysis, we conclude that the set of ordinary differential equations (27), (29) and (30) can be used to integrate the system of partial differential equations (11), but any algorithm based on this set of equations stops at both stationary points and VRI points. We propose to integrate this set of ordinary differential equations using the Runge-Kutta-Fehlberg technique with τ-stage and p-algebraic order (RKF-τp).[38] We note that the RKF technique has been used before as a part of other proposed algorithms to locate RPs of the type IRC.[39,40,41,42] The RKF- τp algorithm is used for the evaluation of a general vectorial function, say $\mathbf{y}_{n+1} = \mathbf{y}(x_{n+1})$, when $\mathbf{y}_n = \mathbf{y}(x_n)$ is known. The vectorial function $\mathbf{y}_{n+1}$ is computed by the equations,

$$\mathbf{y}_{n+1} = \mathbf{y}_n + \sum_{i=1}^{\tau} b_i \mathbf{k}_i \tag{35.a}$$

$$\mathbf{k}_i = \mathbf{f}\left(x_n + c_i h, \mathbf{y}_n + h \sum_{j=1}^{i-1} a_{ij} \mathbf{k}_j \right) \qquad i = 1,...,\tau \tag{35.b}$$

where $\mathbf{f}(x, \mathbf{y}(x))$ is the vectorial function of the problem under consideration. The coefficients, $\{a_{ij}\}^{\tau,\tau-1}_{i=1,j=1}$, $\{b_i\}^{\tau}_{i=1}$, $\{c_i\}^{\tau}_{i=1}$, that appear in equations (35) satisfy some relations that are given through the so-called Butcher formula-table.[38] The set of coefficients, $\{c_i\}^{\tau}_{i=1}$, are computed through the equation,

$$c_i = \sum_{j=1}^{i-1} a_{ij} \qquad i = 2,...,\tau \tag{36}$$

To solve the set of first order ordinary differential equations (27) and (29) using equations (35) we take $\mathbf{y}^T = (\mathbf{x}^T, \mathbf{g}^T)$ and the $\mathbf{f}$ vector is constructed using the right-hand side part of the equations (27) and (29), the former for the $\mathbf{x}$ vector and the latter for the $\mathbf{g}$ vector. In the present study we take $\tau = 4$ and $p = 8$, in other words the algorithm used is labeled as RKF(4,8).

Example, analysis and discussion.

In this section, using a two dimensional example we show the properties of the NT curves as RP using as integration algorithm the above explained RKF(4,8). As a two dimensional case we take the PES initially proposed by Wolfe et al.[43] and later modified by Quapp.[44] The so-called Wolfe- Quapp PES is characterized by the following expression,

$$U(x,y) = x^4 + y^4 - 2x^2 - 4y^2 + xy + 0.3x + 0.1y \tag{37}$$

This equation describes a "three and a half"-well PES. In this PES there are three minima M1, M2, and M3 which are located in (-1.174, 1.477), (-0.822, -1.367), and (1.124, -1.485) with energies -6.762, -4.137, and -6.369, respectively, three saddle points labeled as TS1, TS2, and TS3 which are located in (-1.022, -0.116), (-0.303, -1.401), and (0.941, 0.131) with energies –1.251, -3.980, and –0.637 respectively, a stationary point character maximum labeled as MAX located at the point (0.081, 0.023) with energy 0.013. The coordinates and energies are given in arbitrary units.

In Figure 1 an NT curve that emerges from the minimum MIN1 with direction (0.707, -0.707) transverses the family of equipotential curves to achieve the first order stationary point TS3. During this evolution the totality of the curve remains in the bowl of MIN1, never crosses the valley-ridged border line, $det\ (\mathbf{S}^{T}[\mathbf{H}(\mathbf{x})]\mathbf{S}) = \mathbf{r}^{T}[\mathbf{A}(\mathbf{x})]\mathbf{r} = \mathbf{g}(\mathbf{x})^{T}[\mathbf{A}(\mathbf{x})]\mathbf{g}(\mathbf{x}) / (\mathbf{g}^{T}(\mathbf{x})\mathbf{g}(\mathbf{x})) = 0$,[45] is located in a valley region as a consequence at each point of the curve $det\ (\mathbf{S}^{T}[\mathbf{H}(\mathbf{x})]\mathbf{S}) > 0$, due to this fact the NT is a minimizing extremal curve. Note that $\mathbf{x} = (x, y)$ is set. This NT is an RP of the category of MEP at least until TS3.

In Figure 2 the NT curve also emerges from MIN1 but with direction (0.643, -0.766). The curve achieves the TS3 stationary point, however, at the point (-0.493, 0.814) crosses the valley-ridged border line, it leaves a valley or bowl of MIN1 and enters a ridge, but at the point (0.040, 1.210) the curve enters again the bowl of MIN1. The former point is of the type mixed-VRI[46] while the latter point is a turning point, in this case the NT curve touches the equipotential curve at this point, resulting that $dU(\mathbf{x}) / dt = 0$. For the sub-arc within the VRI and the TP holds that at each point $det\ (\mathbf{S}^{T}[\mathbf{H}(\mathbf{x})]\mathbf{S}) < 0$ because it is located on a ridge. The rest of the curve is located in a valley region. The present NT curve does not achieve even the category of RP because does not increase monotonically from the minimum MIN1 to the first saddle point TS3. The subarc between the points (-0.493, 0.814) and (0.040, 1.210) the potential energy decreases, $dU(\mathbf{x}) / dt < 0$. In this case the sign of the integral $\delta^2 I$ cannot be determined until its explicit evaluation. The cases exposed in Figures 1 and 2 are examples of the conclusions discussed in the last paragraph of the subsection *The Case of Valley-Ridge Inflection Points*.

In Figure 3 we show the RGF curves that start in the three first order saddle points, TS1, TS2 and TS3 with the directions (1.0, 0.0) (0.0, 1.0) (-1.0, 0.0) respectively. The selected tangent in the Branin equation is negative, $d\mathbf{x} / dt = -[\mathbf{A}(\mathbf{x})]\,\mathbf{g}(\mathbf{x})$. The three curves end at the MAX point, showing the property that RGF curves join stationary points. These curves are labeled as ‘cTS1MAX’, ‘cTS2MAX’ and ‘cTS3MAX’. The other curves start at the same stationary point but different directions. The two curves labeled as ‘cTS1MIN1’ and ‘cTS1MIN2’ start at TS1 with the directions (0.0, 1.0) and (0.0, -1.0) and end at MIN1 and MIN2 respectively, while the curves ‘cTS2MIN2’ and ‘cTS2MIN3’ start at TS2 with the directions (-1.0, 0.0) and (1.0, 0.0) end at MIN2 and MIN3 respectively. Finally, the two curves labeled as ‘cTS3MIN3’ and ‘cTS3MIN1’ start at TS3 with directions (0.0, -1.0) and (0.77, 0.64) and end at MIN3 and MIN1 respectively. The curve ‘cTS3MIN1’ is the curve labeled as ‘NT_MEP’ of Figure 1. These nine RGF curves show the important fact that with the negative option in the RGF tangent the integrated curve ends at the stationary points such that their corresponding Hessian matrix has an even number of negative eigenvalues. Starting at any minima, MIN1, MIN2, MIN3 and taking the positive option in the tangent, the corresponding curves end at the stationary points such that their Hessian matrices have an odd number of negative eigenvalues. The three NT or RGF curves, namely, ‘cTS1MAX’, ‘cTS2MAX’ and ‘cTS3MAX’ show a negative value for the integral $\delta^2 I$, of equation (15), which means that these three curves present a maximum character. They are maximizing extremal curves. On the other hand, the integral $\delta^2 I$ takes a positive value for the other curves, which means that these curves show a minimum character. It is important to see that the curves with a minimum character are located in a valley region while the curves with a maximum character are located on a ridge region of the PES.

In Figure 4 a curve that starts in TS3 with direction (0.407, 0.914) ends at the MAX point. In the point (0.573, 1.339) of this curve the tangent is orthogonal to the gradient vector, in other words, $- (d\mathbf{x} / dt)^T \mathbf{g}(\mathbf{x}) = - \mathbf{g}^T(\mathbf{x}) [\mathbf{A}(\mathbf{x})] \mathbf{g}(\mathbf{x}) = - dU(\mathbf{x}) / dt = 0$, and due to this fact this point is another example of a TP. Notice that the curve takes a descent direction from TS3 to this TP and an ascent direction from the TP to the MAX point. The other curve that also starts at the same point TS3 but with a direction slightly different, (0.423, 0.906), ends at the MIN1 point. It shows a first TP near the above TP and a second TP located in (-0.515, 0.838). This curve shows a behavior very close to the latter curve, however, thanks to the second TP it starts to a decreasing direction until reaching, the MIN1 point. The integral associated to the second variation, $\delta^2 I$, is positive and the curve is located in a valley region. Again we find a relation between the minimum character and that the RGF curve is fully located in a valley. The former curve shows a negative value for $\delta^2 I$ in the last straight line step. This sub-arc that is a straight line is located on a ridge.

The curve from MIN1 to the VRI point is a curve in the bowl of the minimum, thus it is a valley curve. Its bifurcation, however, is not the bifurcation of the two valleys, neither from MIN1 to TS1, nor to TS3. That bifurcation already happens at the minimum. The VRI indicates the transition from the bowl of MIN1 to the summit of MAX, thus it indicates a valley-ridge inflection, as the name implies.

Conclusion.

We have proved the variational nature of the Distinguished Coordinate Path, the Reduced Gradient Following Path or its equivalent formulation, the Newton Trajectory. All these paths are extremal curves of a variational problem that can be formulated in different forms, which are given in expression (8). If the curve starts in a minimum of the PES and ends at a first order stationary point the extremal curve achieves its condition of minimum. However, if this curve has a VRI point and transverses the equipotential hypersurfaces at this point, its extremal condition can only be determined by an explicit evaluation of equation (15). Finally, the RKF technique has been proposed as a tool to integrate NT curves, showing a robust behavior as an integration tool.

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Figure Captions.

Figure 1. The blue curve is the NT or RGF curve joining the stationary points MIN1 and TS3 of the Wolfe-Quapp PES. The green curve is the valley-ridge border line, where $det\ (\mathbf{S}^T[\mathbf{H}(\mathbf{x})]\mathbf{S}) = 0$. The red lines are the equipotential curves of the PES. In this case the NT or RGF curve is an RP with the category of MEP and is a minimizing extremal curve.

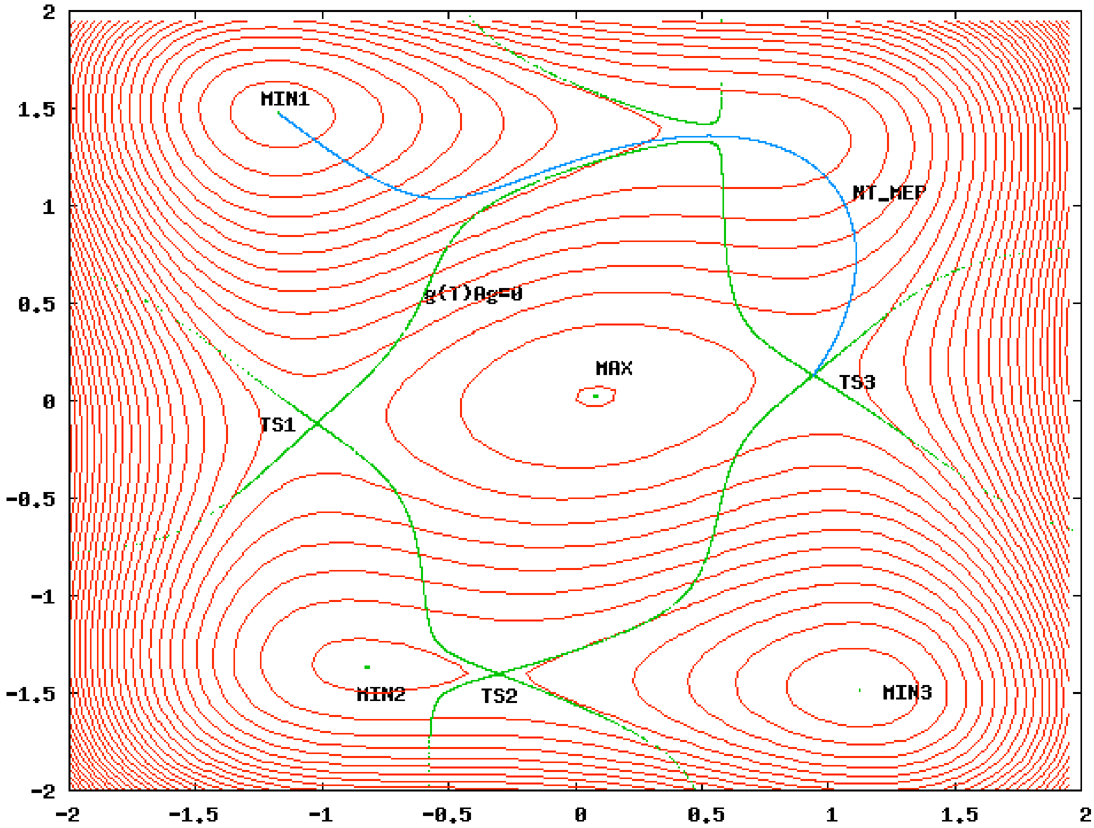
Figure 2. The blue curve is the NT or RGF curve joining the stationary points MIN1 and TS3 of the Wolfe-Quapp PES. The green curve is the valley-ridge border line, where $det\ (\mathbf{S}^T[\mathbf{H}(\mathbf{x})]\mathbf{S}) = 0$. The red lines are the equipotential curves of the PES.

In this case the NT or RGF curve is not RP because does not increase always monotonically from MIN1 to TS3.

Figure 3. A set of RGF or NT curves joining all stationary points of the Wolfe-Quapp PES. The curves, cTS1MIN1, cTS1MIN2, cTS2MIN2, cTS2MIN3, cTS3MIN3, and cTS3MIN1 are minimizing extremal curves while the curves cTS1MAX, cTS2MAX, and cTS3MAX are maximizing extremal curves.

Figure 4. Two curves, cTS3MIN1TP, and cTS3MAXTP both start at the first order saddle point TS3 but end at different stationary points. The initial direction between both is slightly different. The different evolution is due to the existence of a mixed type VRI point.

Figure 1.



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1
0.5
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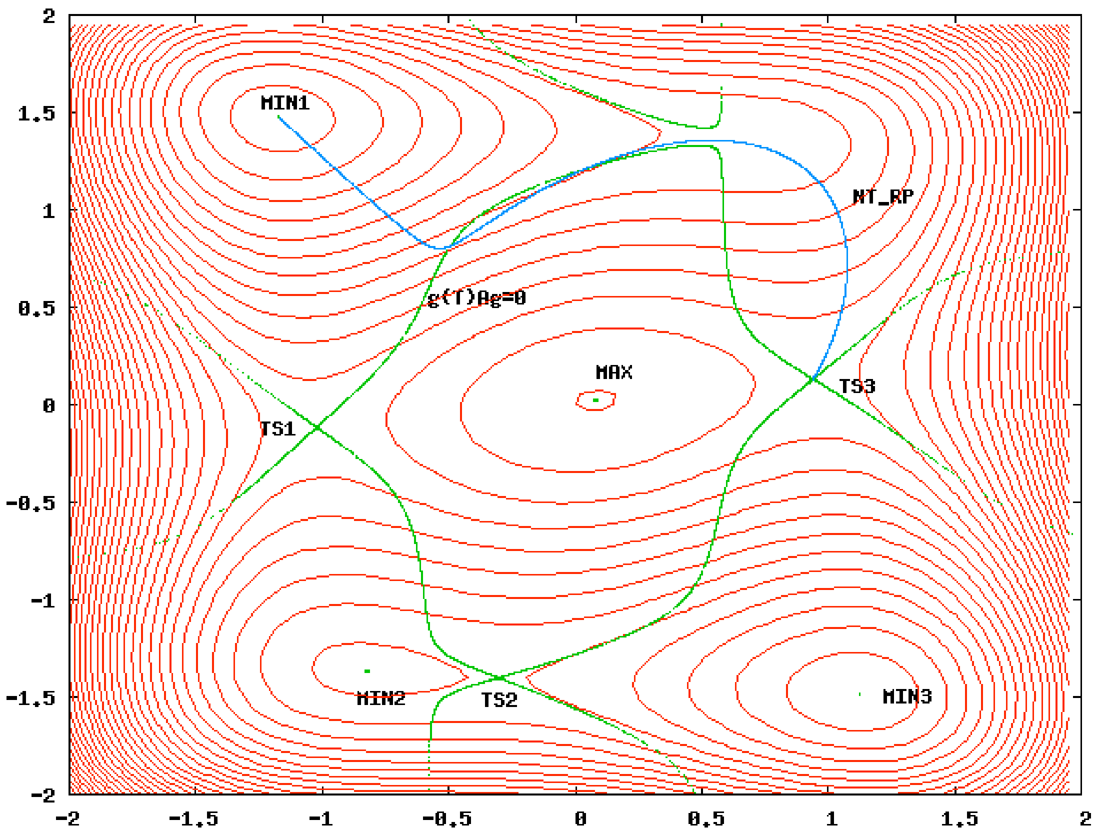
-1
-1.5
-2
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
MIN1
NT_MEP
g(T)Ag=0
MAX
TS1
TS3
MIN2
TS2
MIN3

Figure 2.



MIN1
NT_RP
g(T)Ag=0
MAX
TS1
TS3
MIN2
TS2
MIN3
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1.5
1
0.5
0
-0.5
-1
-1.5
-2
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-1.5
-1
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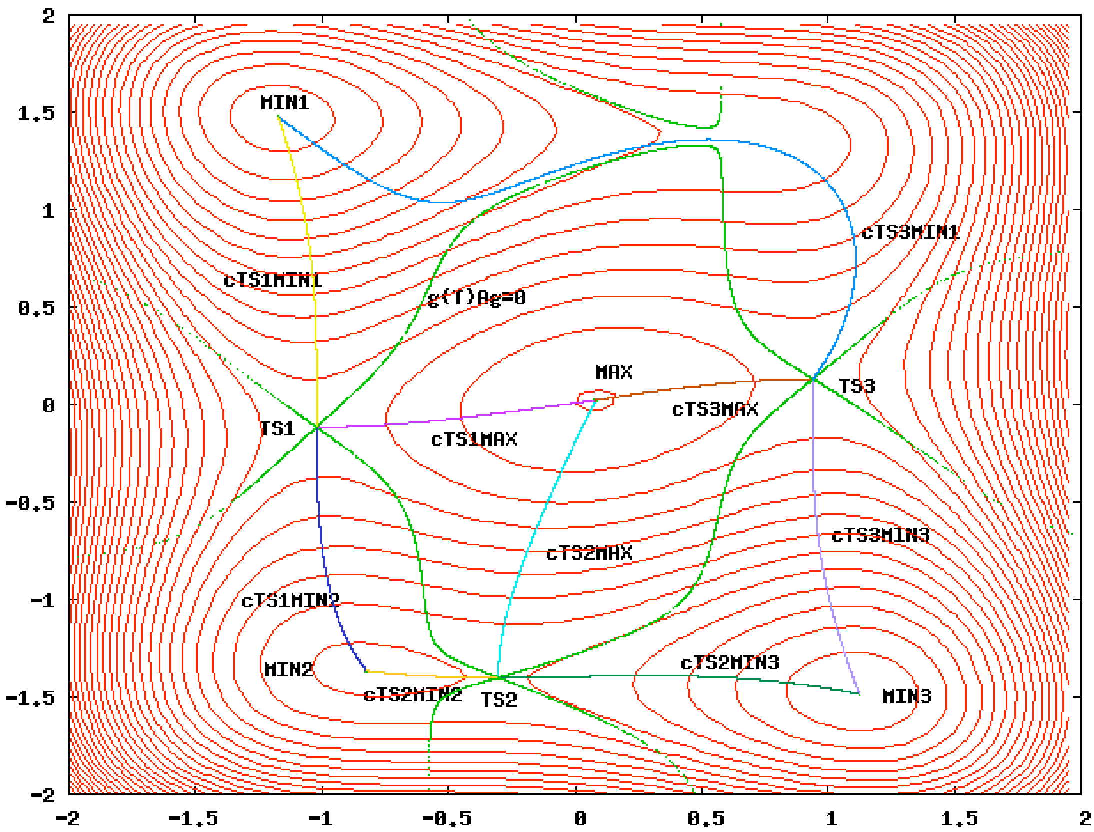
0
0.5
1
1.5
2

Figure 3.



MIN1
cTS3MIN1
cTS1MIN1
g(T)Ag=0
MAX
TS3
cTS3MAX
TS1
cTS1MAX
cTS3MIN3
cTS2MAX
cTS1MIN2
cTS2MIN3
MIN2
cTS2MIN2
TS2
MIN3
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2
-1.5
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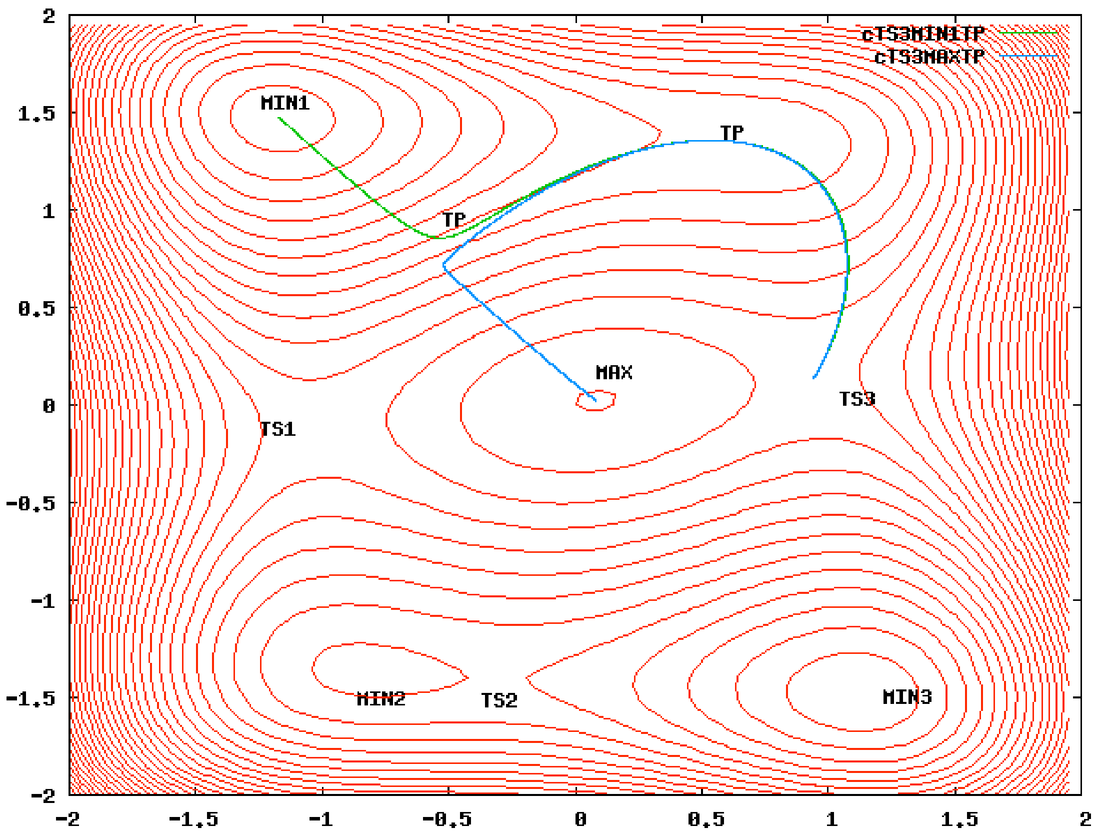
-0.5
0
0.5
1
1.5
2

Figure 4.


cTS3MIN1TP
cTS3MAXTP
MIN1
TP
TP
MAX
TS1
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MIN2
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MIN3
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-1
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-2
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0.5
1
1.5
2

References.

1 P. G. Mezey, *Potential Energy Hypersurfaces*, (Elsevier, Amsterdam, 1987).

2 D. Heidrich, *The Reaction Path in Chemistry: Current Approaches and Perspectives*, (Kluwer, Dordrecht, 1995).

3 W. Quapp, Chem. Phys. Lett. **253**, 286 (1996).

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

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

6 P. Scharfenberg, Chem. Phys. Lett. **79**, 115 (1981).

7 I. H. Williams, and G. M. Maggiora, J. Mol. Struct. (Theochem) **89**, 365 (1982).

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

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

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

11 D. K. Hoffman, R. S. Nord, and K. Ruedenberg, Theor. Chim. Acta **69**, 265 (1986).

12 W. Quapp, Theor. Chim. Acta **75**, 447 (1989).

13 M. V. Basilevsky, Chem. Phys. **67**, 337 (1982).

14 J.-Q. Sun, and K. Ruedenberg, J. Chem. Phys. **98**, 9707 (1993).

15 W. H. Miller, N. C. Handy, and J. E. Adams, J. Chem. Phys. **72**, 99 (1980).

16 J. González, X. Giménez, and J. M. Bofill, J. Phys. Chem. A **105**, 5022 (2001).

17 J. González, X. Giménez, and J. M. Bofill, J. Comput. Chem. **28**, 2111 (2007).

18 J. González, X. Giménez, and J. M. Bofill, J. Chem. Phys. **131**, 054108 (2009).

19 D. G. Truhlar, and B. C. Garret, Annu. Rev. Phys. Chem. **35**, 159 (1984).

20 J. González, X. Giménez, and J. M. Bofill, Phys. Chem. Chem. Phys. **4**, 2921 (2002).

21 A. S. Sanz, X. Giménez, J. M. Bofill, and S. Miret-Artés, Chem. Phys. Lett. **478**, 89 (2009); **488**, 235(E) (2010).

22 K. Fukui, Int. J. Quantum Chem., Quantum Chem. Symp. **15**, 633 (1981).

23 R. Olender, and R. Elber, J. Mol. Struct. (Theochem) **398**, 63 (1997).

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

25 R. Courant, and D. Hilbert, *Methods of Mathematical Physics*, (Wiley, New York, 1953), vol. 1.

26 J. M. Bofill, Submitted for publication.

27 W. Quapp, Theor. Chem. Acc. **121**, 227 (2008).

28 J. M. Bofill, J. Chem. Phys. **130**, 176102 (2009).

29 M. Hirsch, and W. Quapp, J. Math. Chem. **36**, 307 (2004).

30 I. M. Gelfand, and S. V. Fomin, *Calculus of Variations*, (Dover Publications, New York, 2000).

31 I. G. Petrovsky, *Lectures on partial differential equations*, (Dover Publications, New York, 1991).

32 F. John, *Partial differential equations*, (Springer, Heidelberg, 1974).

33 G. A. Bliss, *Lectures on the Calculus of Variations*, (The University Chicago Press, Chicago, 1946).

34 R. Crehuet, J. M. Bofill, and J. M. Anglada, Theor. Chem. Acc. **107**, 130 (2002).

35 D. F. Davidenko, Dokl. Akad. Nauk. SSSR **88**, 601 (1953).

36 F. H. Branin, IBM J. Res. Develop. 504 (1972).

37 K. Müller, and L. D. Brown, Theor. Chim. Acta **53**, 75 (1979).

38 G. Engeln-Müllges, and F. Uhlig, *Numerical Algorithms with Fortran*, (Springer-Verlag, Berlin, 1996).

39 E. Ren, W. E, and E. Vanden-Eijnden, J. Chem. Phys. **126**, 164103 (2007).

40 V. S. Melissas, D. G. Truhlar, and B. C. Garret, J. Chem. Phys. **96**, 5758 (1992).

41 A. Aguilar-Mogas, X. Giménez, and J. M. Bofill, Chem. Phys. Lett. **432**, 375 (2006).

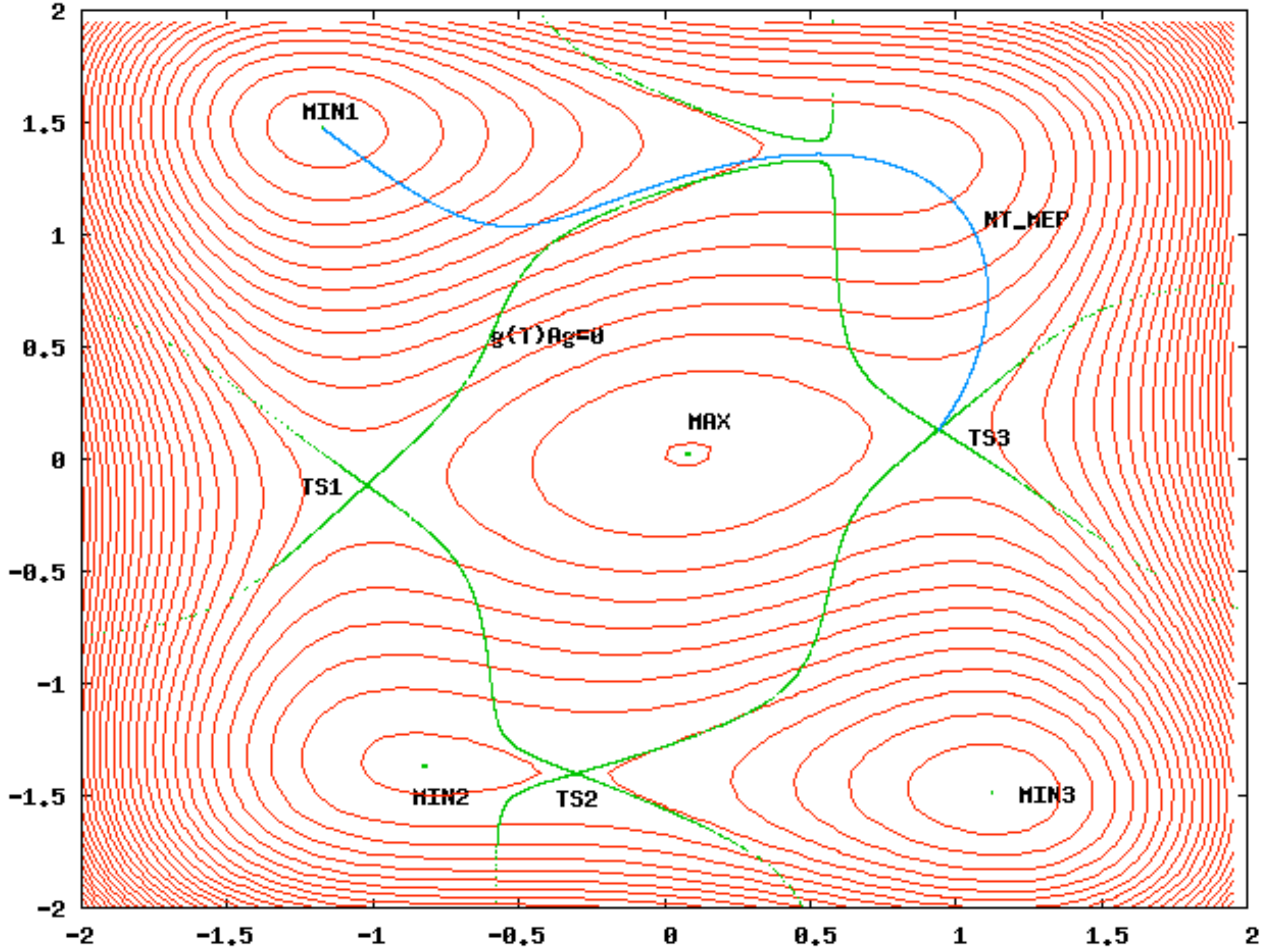
42 A. Aguilar-Mogas, X. Giménez, and J. M. Bofill, J. Comput. Chem. **31**, 2510 (2010).

43 S. Wolfe, H. B. Schlegel, I. G. Csizmadia, and F. Bernardi, J. Am. Chem. Soc. **97**, 2020 (1975).

44 W. Quapp, J. Chem. Phys. **122**, 174106 (2005).

45 W. Quapp, M. Hirsch, and D. Heidrich, Theor. Chem. Acc. **112**, 40 (2004).

46 W. Quapp, J. Mol. Struct. (Theochem) **695-696**, 95 (2004).



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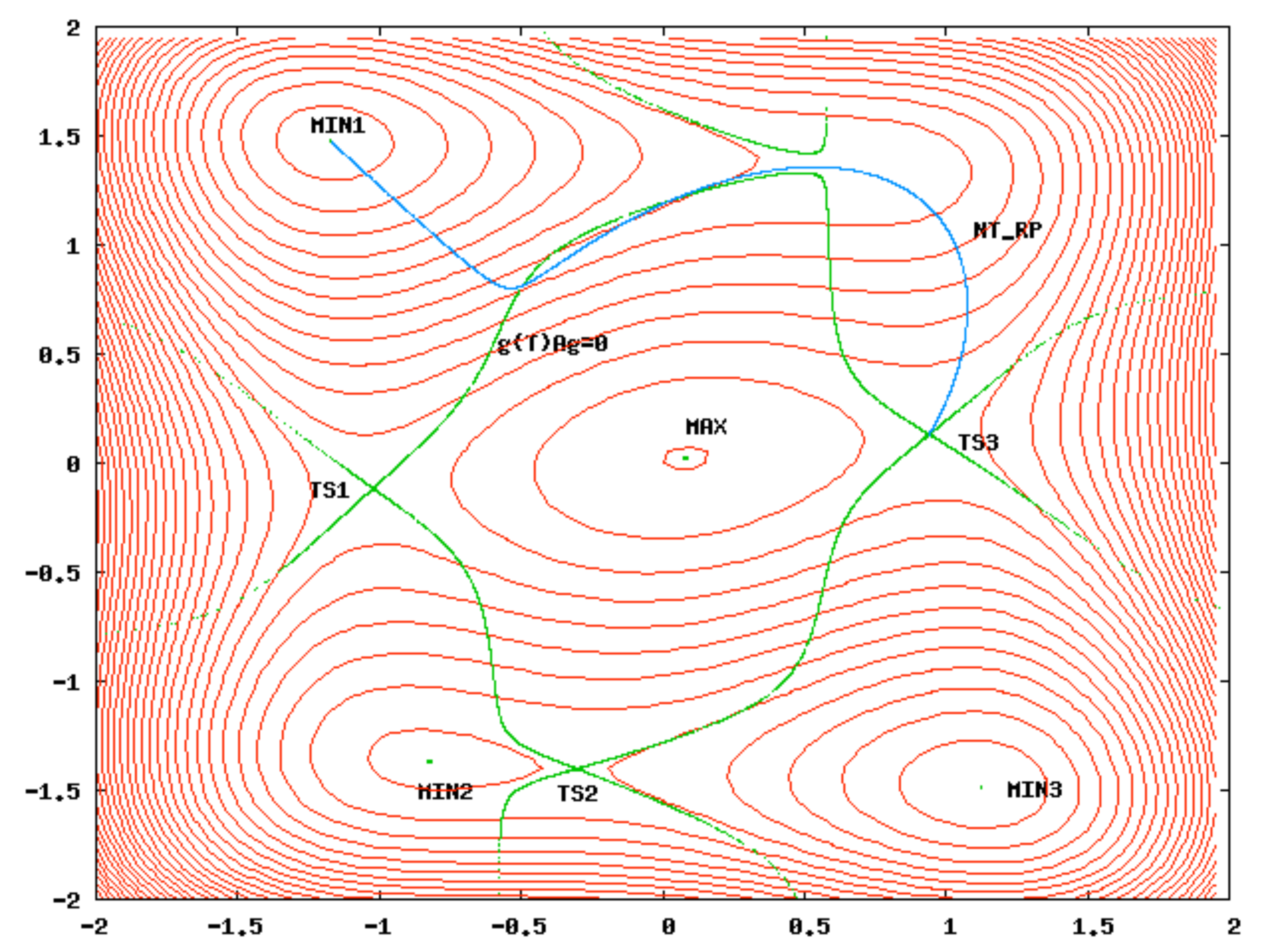

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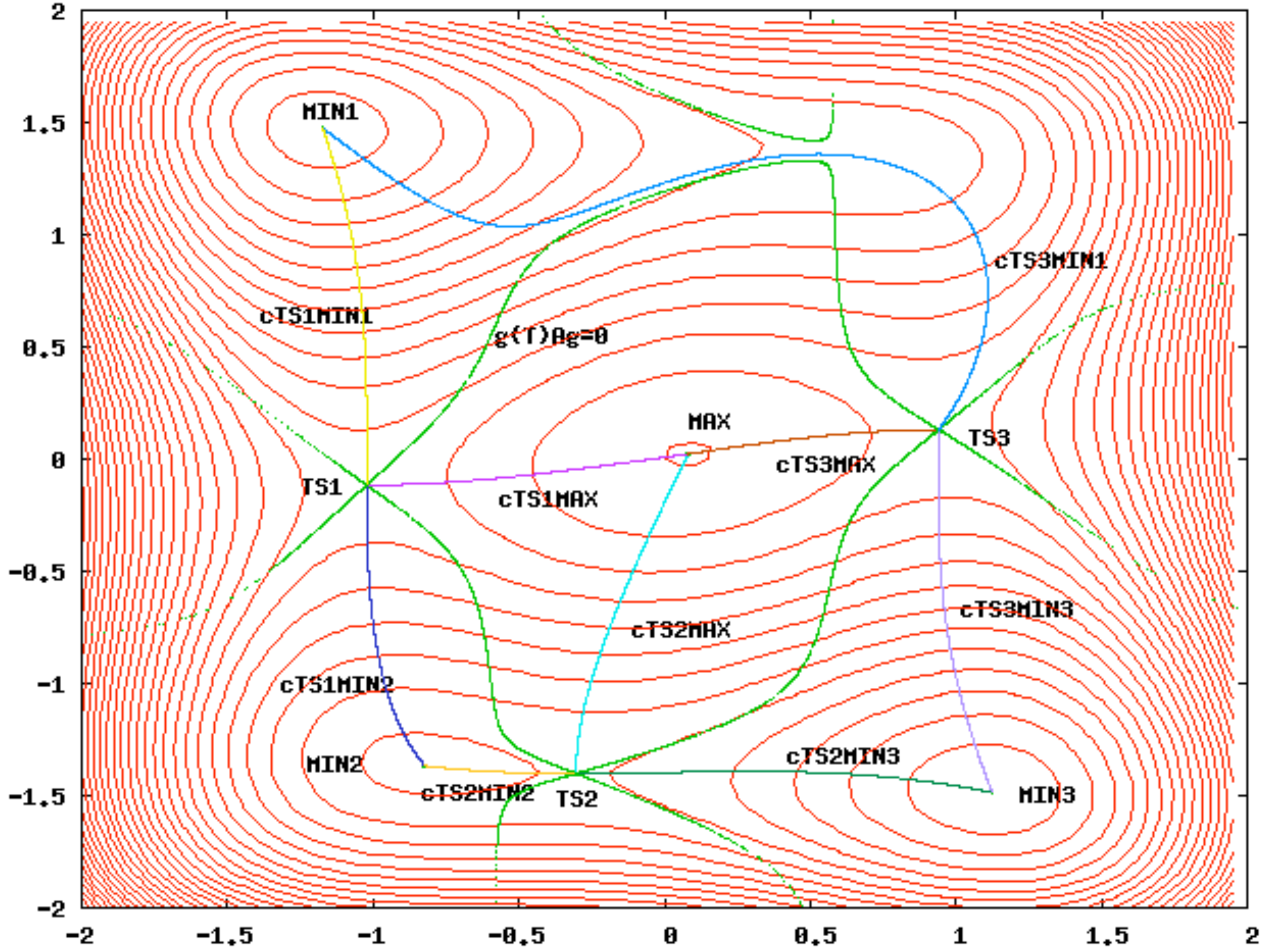

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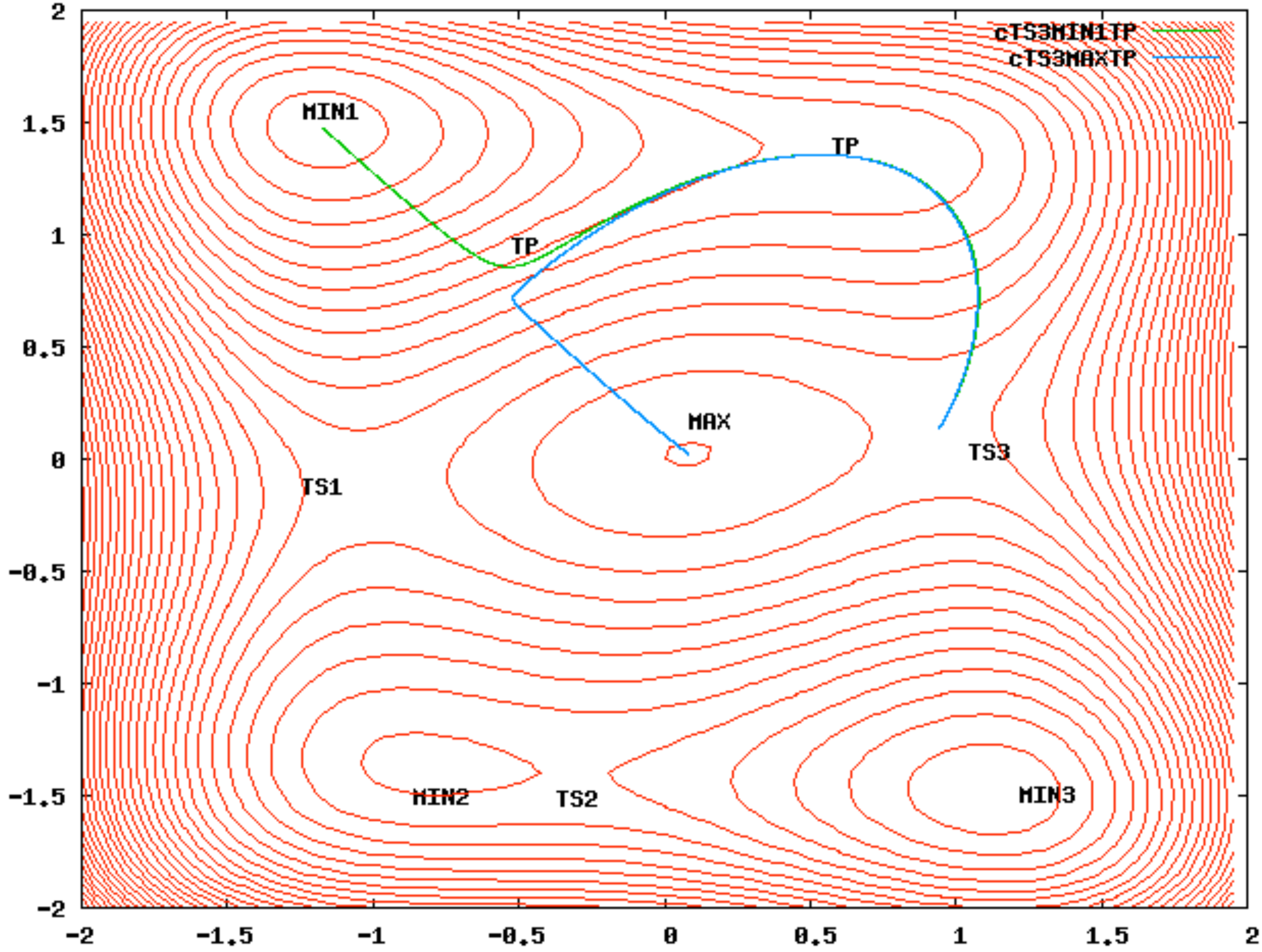

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