Variational nature, integration, and properties of Newton reaction path

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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 region. 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. © *2011 American Institute of Physics*. [doi:10.1063/1.3554214]

I. 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 following two 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 40 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, s, of the curve is taken as the reaction coordinate; however, the values of the PES can also be taken as reaction coordinates.[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 the steepest descent curve in mass weighted coordinates. The IRC is the steepest descent curve joining two minima through a TS.[4] The other curve used as RP is the distinguished or driven coordinate method,[5–7] 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 (GEs);[11–14] however, their computational demand limits their applicability.

The RPs are static curves on the PES, which means that only geometric properties of the PES are taken into account and no dynamic 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 geometric parameters undergo dramatic changes; these parameters most properly describe the reaction and are very often taken as reaction coordinates, 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.[16–18] Reaction theories like the famous transition state and variational transition state are also based at least implicitly or explicitly on the RP model.[19] Nevertheless, many times a well selected RP curve very closely matches the average line of a set of molecular dynamic trajectories.[20] Maybe this observation gives physical grounds to the RP model. Within the set of RP curves mentioned above, the IRC is one that matches both the theoretical and the computational trajectories of classical and quantum models reasonably.[21]

Despite many RPs commonly being geodesic curves on a surface, each type of the RP curve has different mathematical grounds. 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, such as its variational nature, are briefly discussed below:

(i) The IRC curve possesses a variational nature because it is the steepest descent curve, and this type of curve extremalizes a function associated to a Fermat variational principle.[22–24] From this point of view, we

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conclude that the IRC propagates through the PES according to a speed law or continuous slowness model related to the 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 function associated to this special type of Fermat principle.[24]

(ii) The GE RP is defined as the curve which 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 to 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 so 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 Refs. 27 and 28. The differences in both the views are due to the integral function 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 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 (DC) path and the RGF or NT path. The second variation is also derived and analyzed being related to the convex 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 path. Finally, numerical results are given using a two-dimensional PES.

II. 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 not only a theory of maxima and minima but also a theory of 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 on N-dimensional space such that a function $I(\mathbf{q})$, depending on these N independent variables, takes an extreme value, in principle, maximum or minimum. Usually, the function $I(\mathbf{q})$ is an integral of the form

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

where F is a given function which is twice continuous differentiable with respect to its three arguments, t, $\mathbf{q}(t)$, and $\mathbf{q}'(t) = d\mathbf{q}(t)/dt$. As noted above, the functions $\mathbf{q}(t)$ will be restricted to the class of admissible functions satisfying the conditions, $\mathbf{q}(t_0) = \mathbf{q}_0$, $\mathbf{q}(t_f) = \mathbf{q}_f$, $\mathbf{q}(t)$ 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 $q_1(t), \ldots, q_N(t)$ considered independently. The necessary condition to be stationary is that the N Euler equations are satisfied,

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

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

Let us now construct a function F such that the integration of the resulting Euler Eq. (2) results in the curve described by the driven coordinate method. As explained in the Introduction section, the driving coordinate or DC method consists in selecting a driving coordinate, say $q_{\rm rc}$, 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 the coordinates, resulting in a curve on the PES, $V(\mathbf{q})$. In other words, this RP satisfies the next requirement at each point

$$\begin{aligned} V(\mathbf{q}_{\rm DC}) &= \underset{q_1,\ldots,q_{i-1},q_{i+1},\ldots,q_N}{\text{extremalize}} V(q_1,\ldots,q_{i-1},q_{i=rc},q_{i+1},\ldots,q_N) \\ &= \underset{\overline{\mathbf{q}}}{\text{extremalize}}\, V(q_{\rm rc}, \overline{\mathbf{q}}), \end{aligned} \tag{3}$$

where $\overline{\mathbf{q}}^T = (q_1,\ldots,q_{i-1},q_{i+1},\ldots,q_N)$. Notice that in this context a point $\mathbf{q}$ can be represented as $\mathbf{q}^T = (q_{rc}, \bar{\mathbf{q}}^T)$. According to Eq. (3) at each point of the driving coordinate curve, the gradient vector of the PES, $\mathbf{g} = \boldsymbol{\nabla}_{\mathbf{q}} V(\mathbf{q})$, is equal to zero for each coordinate except for the driving coordinate, $q_{\rm rc}$. 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

$$\nabla_{\overline{\mathbf{q}}} V(q_{\rm rc}, \overline{\mathbf{q}}) = \mathbf{0}_{N-1}, \tag{4}$$

where $\mathbf{0}_{N-1}$ is a zero vector of dimension $N-1$. It is clear that in the present case, $q_{\rm rc}$ plays the role of t, that it is reaction coordinate, and also that for any function F associated to this

RP model, the corresponding set of Euler equations should be equal to Eq. (4). An integral function satisfying all these requirements is

$$I(\overline{\mathbf{q}}) = \int_{t_0}^{t_f} F(t, \overline{\mathbf{q}})\, dt = \int_{q_{\rm rc}^0}^{q_{\rm rc}^f} V(q_{\rm rc}, \overline{\mathbf{q}})\, dq_{\rm rc}. \tag{5}$$

Because of this variational problem, the function V does not involve the argument, $\overline{\mathbf{q}'} = d\overline{\mathbf{q}}/dq_{\rm rc}$, the set of $N-1$ Euler equations reduces to the form given in Eq. (4). Notice that the dimension of the argument $\overline{\mathbf{q}}$ is $N-1$. In other words, the set of $N-1$ equations [Eq. (4)] is the set of the $N-1$ Euler equations associated to the variational problem (5). This set of equations [Eq. (4)] determines the function $\overline{\mathbf{q}} = \overline{\mathbf{q}}(q_{\rm rc})$ implicitly. A point of this curve in the N-dimensional space is represented as $\mathbf{q}^T(q_{rc}) = (q_{\rm rc}, \overline{\mathbf{q}}^T(q_{\rm rc}))$. We note that in this case the boundary values, $\mathbf{q}_0 = \mathbf{q}(q_{\rm rc}^0)$ and $\mathbf{q}_f = \mathbf{q}(q_{\rm rc}^f)$, 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 subsections, II A, II B, and II C, these questions are answered.

A. The Euler equations

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

$$\mathbf{x} = \mathbf{D}\mathbf{q} = \mathbf{D}\begin{pmatrix} q_{\rm rc} \\ \overline{\mathbf{q}} \end{pmatrix}, \tag{6}$$

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

$$\mathbf{D} = [\mathbf{r}|\, \mathbf{s}_1|\ \cdots |\, \mathbf{s}_{N-1}] = [\mathbf{r}|\, \mathbf{S}]. \tag{7}$$

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

$$\begin{aligned} I(\overline{\mathbf{q}}) &= \int_{q_{\rm rc}^0}^{q_{\rm rc}^f} F(q_{\rm rc}, \overline{\mathbf{q}})\, dq_{\rm rc} = \int_{q_{\rm rc}^0}^{q_{\rm rc}^f} V(q_{\rm rc}, \overline{\mathbf{q}})\, dq_{\rm rc} \\ &= \int_{x_{\rm rc}^0}^{x_{\rm rc}^f} V(q_{\rm rc}(\mathbf{x}), \overline{\mathbf{q}}(\mathbf{x}))\, \mathbf{r}^T\mathbf{x}' dx_{\rm rc} \\ &= \int_{x_{\rm rc}^0}^{x_{\rm rc}^f} V(\mathbf{q}(\mathbf{x}))\, \mathbf{r}^T\mathbf{x}' dx_{\rm rc} \\ &= \int_{x_{\rm rc}^0}^{x_{\rm rc}^f} U(x_{\rm rc}, \overline{\mathbf{x}})\left(r_{\rm rc} + \overline{\mathbf{r}}^T\overline{\mathbf{x}}'\right) dx_{\rm rc} \\ &= \int_{x_{\rm rc}^0}^{x_{\rm rc}^f} G\left(x_{\rm rc}, \overline{\mathbf{x}}, \overline{\mathbf{x}}'\right) dx_{\rm rc} = I(\overline{\mathbf{x}}), \end{aligned} \tag{8}$$

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

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

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

$$\begin{aligned} &\mathbf{r}^T\mathbf{x}'[\nabla_{\overline{\mathbf{x}}}\mathbf{x}^T]\mathbf{S}\nabla_{\overline{\mathbf{q}}}V(\mathbf{q}(x_{\rm rc}, \overline{\mathbf{x}})) - (\mathbf{x}')^T\mathbf{S}\nabla_{\overline{\mathbf{q}}}V(\mathbf{q}(x_{\rm rc}, \overline{\mathbf{x}}))\overline{\mathbf{r}} \\ &= \mathbf{0}_{N-1} \end{aligned} \tag{9.b}$$

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

$$\begin{aligned} &G(x_{rc}(\mathbf{q}), \overline{\mathbf{x}}(\mathbf{q}), (d\overline{\mathbf{x}}/dq_{rc})/(dx_{rc}/dq_{rc}))(dx_{rc}/dq_{rc}) \\ &\quad = U(x_{rc}(\mathbf{q}), \overline{\mathbf{x}}(\mathbf{q})) \\ &\quad = U(\mathbf{x}(q_{rc}, \overline{\mathbf{q}})) \\ &\quad = V(q_{rc}, \overline{\mathbf{q}}) \end{aligned} \qquad (10.a)$$

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

$$\begin{aligned} (\nabla_{\overline{\mathbf{q}}}\mathbf{x}^T)\nabla_{\mathbf{x}}U(\mathbf{x}(q_{rc}, \overline{\mathbf{q}})) &= \mathbf{S}^T\nabla_{\mathbf{x}}U(\mathbf{x}(\mathbf{q})) \\ &= \nabla_{\overline{\mathbf{q}}}V(q_{rc}, \overline{\mathbf{q}}) = \mathbf{0}_{N-1} \end{aligned} \qquad (10.b)$$

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 Eq. (10.b) is

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

since multiplying from the left by $\mathbf{S}^T$ one recovers the second term of Eq. (10.b). We recall that $\mathbf{r}$ 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 $\mathbf{I}$ is selected as $\mathbf{r}$ vector, then the function G of Eq. (8) is equal to the function V of Eq. (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 that are defined in the expression (6). We emphasize that each of the Euler equations, namely, Eqs. (4) and (10.b) or their equivalent equation [Eq. (11)], does not involve derivatives of the type, $d\overline{\mathbf{q}}/dq_{rc}$ or $d\overline{\mathbf{x}}/dx_{rc}$, respectively. This fact implies that the extremal curve, $\mathbf{q}(q_{rc})$ or $\mathbf{x}(x_{rc})$, should be obtained implicitly from the appropriated Euler equation.

B. The extremal sufficient conditions

Since the relation between the DC and the RGF methods from a variational point of view has been established, we now 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 function G which is associated to the RGF method and is more general. This function can always be transformed into the V function, thanks to the transformation (6) related to the DC method.

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

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

is satisfied along the extremal curve $\mathbf{x}(x_{rc})$. To prove this assertion, first, we replace in the integral $I(\overline{\mathbf{x}})$ of Eq. (8) the arguments $\overline{\mathbf{x}}$ and $d\overline{\mathbf{x}}/dx_{rc}$ with $\overline{\mathbf{x}}_c = \overline{\mathbf{x}} + \varepsilon\overline{\mathbf{y}}$ 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 $I(\overline{\mathbf{x}})$ until the second order in ε

$$\begin{aligned} H(\varepsilon) &= I(\overline{\mathbf{x}} + \varepsilon\overline{\mathbf{y}}) \\ &= I(\overline{\mathbf{x}}) + \varepsilon\delta I(\overline{\mathbf{x}}, \overline{\mathbf{y}}) + \frac{\varepsilon^2}{2}\delta^2 I(\overline{\mathbf{x}}, \overline{\mathbf{y}}) + \mathrm{O}(\varepsilon^2). \end{aligned} \qquad (13)$$

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

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

and

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

where $\mathbf{x}'_c(\varepsilon) = d\mathbf{x}_c(\varepsilon)/dx_{\mathrm{rc}}$, $\mathbf{q}' = d\mathbf{q}/dq_{\mathrm{rc}}$, and $\mathbf{p}' = d\mathbf{p}/dq_{\mathrm{rc}}$. From Eq. (15) follows Eq. (12). The comparison curve, $\mathbf{x}_c(x_{\mathrm{rc}})$, and its derivative, $\mathbf{x}'_c$, tends to the extremal curve and its derivative, $\mathbf{x}(x_{\mathrm{rc}})$ and $\mathbf{x}'$, as ε tends to zero. The variation, $\varepsilon\ \mathbf{y}(x_{\mathrm{rc}})$, is called a weak variation because it satisfies these two conditions and geometrically means that the extremal curve $\mathbf{x}(x_{\mathrm{rc}})$ is compared to the curves that approximate to $\mathbf{x}(x_{\mathrm{rc}})$ 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, $\mathbf{x}(x_{\mathrm{rc}})$, joining the points $\mathbf{x}_0 = (x^0_{\mathrm{rc}}, \bar{\mathbf{x}}_0)$ and $\mathbf{x}_f = (x^f_{\mathrm{rc}}, \bar{\mathbf{x}}_f)$. 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 the smallness of which does not apply to that of its derivatives. Since the quadratic form of the integrand $\delta^2 I\,(\bar{\mathbf{x}}, \bar{\mathbf{y}})$ of Eq. (14) does not depend on the derivative and is positive if expression (12) is satisfied then the extremal curve, $\mathbf{x}(x_{\mathrm{rc}})$, 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 Sec. II C, we remark this conclusion from another point of view.

C. 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, $\mathbf{x}^T(x_{rc}) = (x_{\mathrm{rc}}, \bar{\mathbf{x}}^T(x_{\mathrm{rc}}))$ 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, $\mathbf{x}_a^T(x_{\mathrm{rc}}) = (x_{\mathrm{rc}}, \bar{\mathbf{x}}_a^T(x_{\mathrm{rc}}))$, which intersects the above family of equipotential hypersurfaces of the PES and touches them nowhere; thus if we set $v(x_{\mathrm{rc}}) = U(\mathbf{x}_a(x_{\mathrm{rc}}))$, then

$$dv/dx_{\mathrm{rc}} = \nabla_{\mathbf{x}}^T U(\mathbf{x}) \left(\frac{d\mathbf{x}}{dx_{\mathrm{rc}}}\right)\bigg|_{\mathbf{x}=\mathbf{x}_a(x_{\mathrm{rc}})}. \tag{16}$$

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

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

where $\bar{\mathbf{x}}'_a = d\bar{\mathbf{x}}_a/dx_{\mathrm{rc}}$ and $\mathbf{x}'_a = d\mathbf{x}_a/dx_{\mathrm{rc}}$. We look for those tangent vectors, $\mathbf{x}'_a$, for which the integrand of the second integral of Eq. (17) is stationary with 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, $\mathbf{r}^T\mathbf{x}'_a/[\nabla_x^T U(\mathbf{x}_a)\mathbf{x}'_a] = 1/[\nabla_x^T U(\mathbf{x}_a)\nabla_x U(\mathbf{x}a)]^{1/2}$. 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 Eq. (11), the Euler equation of function G of the variational problem (8). We conclude that the arbitrary curve $\mathbf{x}_a(x_{\mathrm{rc}})$ satisfying the above condition is the RGF curve that extremalizes the functional (8) is the extremal $\mathbf{x}_a(x_{\mathrm{rc}}) = \mathbf{x}(x_{\mathrm{rc}})$. Normally, at each point of an equipotential hypersurface of the PES, the gradient vector points to different directions, on the other hand the function G is parametrically dependent on the $\mathbf{r}$ vector. The $\mathbf{r}$ vector is not an argument of this function, 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 $\mathbf{r}$. With the starting point or initial condition $\mathbf{x}_0 = \mathbf{x}(\mathbf{x}^0_{\mathrm{rc}})$ so that at this point the gradient of the PES points to the direction $\mathbf{r}$, Eq. (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 $\mathbf{r}$. In other words, only from these initial conditions a curve is generated. The extremal curve is not imbedded in a field of extremal curves satisfying Eq. (11) and these initial conditions. Additionally, if we take into account the relation between the RGF and the DC methods, we say that the function V of Eq. (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 Eq. (4).

III. INTEGRATION

In Sec. II C, only the variational nature of both the DC and the RGF methods has 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 Eq. (11), the Euler equation associated to the RGF method. As noted above, this Euler equation is not a system of ordinary differential equations; therefore, straight forward integration is not possible to determine the curve. It is a system of N-first order partial differential equations, and in this case, the curve is obtained 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, in the present case, it consists 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 quite smoothly. The value of the surface, $U(\mathbf{x}) - v = 0$, its derivatives in the direction of the curve, and the initial values are prescribed on the surface. Now the transformation (6) is used because det $(\nabla_{\mathbf{q}}\,{}_{\mathbf{x}}{}^T) \neq 0$, and it is possible to replace the coordinates $\mathbf{x}$ by the new coordinates $\mathbf{q}$ of the surface. Now we multiply Eq. (11) from the left by $\mathbf{D}^T$ and for the resulting equation, we apply the above change of coordinates

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

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

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

In this way, Eq. (11) in the new coordinates $\mathbf{q}$ takes the form

$$\nabla_{\mathbf{q}} V(q_{\mathrm{rc}}, \overline{\mathbf{q}}) = \begin{pmatrix} \partial V(q_{\mathrm{rc}}, \overline{\mathbf{q}})/\partial q_{\mathrm{rc}} \\ \nabla_{\overline{\mathbf{q}}} V(q_{\mathrm{rc}}, \overline{\mathbf{q}}) \end{pmatrix}$$
$$= \begin{pmatrix} \partial V(q_{\mathrm{rc}}, \overline{\mathbf{q}})/\partial q_{\mathrm{rc}} \\ \mathbf{0}_{N-1} \end{pmatrix} \quad (21)$$

with the initial condition

$$\nabla_{\mathbf{q}} V(q_{\mathrm{rc}}, \overline{\mathbf{q}})\Big|_{\substack{q_{\mathrm{rc}}=q_{\mathrm{rc}}^0 \\ \overline{\mathbf{q}}=\overline{\mathbf{q}}_0}} = \begin{pmatrix} \partial V(q_{\mathrm{rc}}, \overline{\mathbf{q}})/\partial q_{\mathrm{rc}} \\ \mathbf{0}_{N-1} \end{pmatrix}\Bigg|_{\substack{q_{\mathrm{rc}}=q_{\mathrm{rc}}^0 \\ \overline{\mathbf{q}}=\overline{\mathbf{q}}_0}}. \quad (22)$$

In the $\mathbf{q}$ 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 $\overline{\mathbf{q}}$ 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 $\overline{\mathbf{q}}$ 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 $\mathbf{q}$ may be taken as new coordinates of the point $\mathbf{x}$. The normal to the plane tangent to the surface is the vector $\nabla_{\mathbf{q}} V(q_{\mathrm{rc}}, \overline{\mathbf{q}})$ of Eq. (21). Since this vector possesses a nonzero component in the $\mathbf{r}$ direction and null components in the set of the $N-1$ directions collected in the $\mathbf{S}$ matrix, the plane tangent at the initial point $\mathbf{q}_0$ is given by $0 = q_{\mathrm{rc}} - q_{\mathrm{rc}}^0$. In the $\mathbf{x}$ coordinates this plane is $0 = q_{\mathrm{rc}} - q_{\mathrm{rc}}^0 = (q_{\mathrm{rc}} - q_{\mathrm{rc}}^0) + \mathbf{0}_{N-1}^T(\overline{\mathbf{q}} - \overline{\mathbf{q}}_0) = \mathbf{r}^T \mathbf{D}(\mathbf{q} - \mathbf{q}_0) = \mathbf{r}^T(\mathbf{x} - \mathbf{x}_0)$ being the $\mathbf{r}$ vector the normal to the plane in the $\mathbf{x}$ coordinates. The curve that passes through the plane $0 = q_{\mathrm{rc}} - q_{\mathrm{rc}}^0$ at the point $\mathbf{q}_0 = (q_{\mathrm{rc}}^0, \ \overline{\mathbf{q}}_0)$ is obtained by applying the implicit function theorem[33] to the set of $N-1$ functions, $\nabla_{\overline{\mathbf{q}}} V(q_{\mathrm{rc}}, \ \overline{\mathbf{q}}) = \mathbf{0}_{N-1}$, this curve being the solution to the system of first order partial differential equation (21) with the initial condition (22). If at the point $\mathbf{q}_0 = \left(q_{\mathrm{rc}}^0, \ \overline{\mathbf{q}}_0^T\right)$ the above $N-1$ equations are satisfied and $\det(\nabla_{\overline{\mathbf{q}}} \nabla_{\overline{\mathbf{q}}}^T V(q_{\mathrm{rc}}, \overline{\mathbf{q}})|_{\substack{q_{\mathrm{rc}}=q_{\mathrm{rc}}^0 \\ \overline{\mathbf{q}}=\overline{\mathbf{q}}_0}}) \neq 0$ then according to the implicit function theorem there exists in a certain neighborhood of the point q_{rc}^0 one and only one system of continuous functions $\overline{\mathbf{q}} = \overline{\mathbf{q}}(q_{\mathrm{rc}})$ satisfying the two conditions, $\overline{\mathbf{q}}_0 = \overline{\mathbf{q}}(q_{\mathrm{rc}}^0)$ and $\nabla_{\overline{\mathbf{q}}} V(q_{\mathrm{rc}}, \overline{\mathbf{q}}(q_{\mathrm{rc}})) = \mathbf{0}_{N-1}$. In addition, the first derivative $d\overline{\mathbf{q}}/dq_{\mathrm{rc}}$ exists in the same region and it is a continuous function of q_{rc} and is obtained through the equation

$$\left[\nabla_{\overline{\mathbf{q}}} \nabla_{\overline{\mathbf{q}}}^T V(q_{\mathrm{rc}}, \overline{\mathbf{q}})\right] \frac{d\overline{\mathbf{q}}}{dq_{\mathrm{rc}}} + \frac{\partial}{\partial q_{\mathrm{rc}}} (\nabla_{\overline{\mathbf{q}}} V(q_{\mathrm{rc}}, \overline{\mathbf{q}})) = \mathbf{0}_{N-1}. \quad (23)$$

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

$$\mathbf{0}_{N-1} = \mathbf{S}^T \left[\nabla_{\mathbf{x}} \nabla_{\mathbf{x}}^T U(\mathbf{x})\right] \mathbf{S} \left(\frac{d\overline{\mathbf{q}}}{dq_{\mathrm{rc}}}\right) + \mathbf{S}^T \left[\nabla_{\mathbf{x}} \nabla_{\mathbf{x}}^T U(\mathbf{x})\right] \mathbf{r}$$
$$= \mathbf{S}^T \left[\nabla_{\mathbf{x}} \nabla_{\mathbf{x}}^T U(\mathbf{x})\right] \mathbf{D} \left(\frac{d\mathbf{q}}{dq_{\mathrm{rc}}}\right)$$
$$= \mathbf{S}^T \left[\nabla_{\mathbf{x}} \nabla_{\mathbf{x}}^T U(\mathbf{x})\right] \left(\frac{d\mathbf{x}}{dx_{\mathrm{rc}}}\right) \frac{dx_{\mathrm{rc}}}{dq_{\mathrm{rc}}}. \quad (24)$$

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

$$(\mathbf{I} - \mathbf{r}\mathbf{r}^T)[\mathbf{H}(\mathbf{x})] \frac{d\mathbf{x}}{dx_{\mathrm{rc}}} = \mathbf{0}, \quad (25)$$

where $\mathbf{H}(\mathbf{x})$ is the Hessian matrix, $\mathbf{H}(\mathbf{x}) = \nabla_{\mathbf{x}} \nabla_{\mathbf{x}}{}^T U(\mathbf{x})$. 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, $\mathbf{s}_i{}^{\mathrm{T}}[\mathbf{H}(\mathbf{x})]\mathbf{x}' = 0$, 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, $d\mathbf{x}/dx_{\mathrm{rc}}$, we write $[\mathbf{H}(\mathbf{x})]\mathbf{x}'$ vector as follows:

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

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

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

where the next identity has been employed

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

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 the one 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

$$\begin{aligned}\frac{d\mathbf{g}(\mathbf{x})}{dx_{\mathrm{rc}}} &= \frac{d\nabla_{\mathbf{x}} U(\mathbf{x})}{dx_{\mathrm{rc}}} = \left[\nabla_{\mathbf{x}}\nabla_{\mathbf{x}}^T U(\mathbf{x})\right]\left(\frac{d\mathbf{x}}{dx_{\mathrm{rc}}}\right)\\ &= [\mathbf{H}(\mathbf{x})]\left(\frac{d\mathbf{x}}{dx_{\mathrm{rc}}}\right)\\ &= \mathbf{r}\left(\mathbf{g}^T(\mathbf{x})\,\mathbf{g}(\mathbf{x})\right)^{1/2}\det(\mathbf{H}(\mathbf{x}))\\ &= \mathbf{g}(\mathbf{x})\det(\mathbf{H}(\mathbf{x})),\end{aligned} \tag{29}$$

where Eqs. (27) and (28) have been used. Integrating Eq. (29), we conclude that $\nabla_{\mathbf{x}} U(\mathbf{x})$ varies only 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 equation (11). Finally the variation of $U(\mathbf{x})$ through this curve is given by the expression

$$\begin{aligned}\frac{dU(\mathbf{x})}{dx_{\mathrm{rc}}} &= \left(\frac{d\mathbf{x}}{dx_{\mathrm{rc}}}\right)^T \nabla_{\mathbf{x}} U(\mathbf{x}) = \mathbf{r}^T[\mathbf{A}(\mathbf{x})]\,\mathbf{r}(\mathbf{g}^T(\mathbf{x})\,\mathbf{g}(\mathbf{x}))\\ &= \mathbf{g}^T(\mathbf{x})[\mathbf{A}(\mathbf{x})]\,\mathbf{g}(\mathbf{x}),\end{aligned} \tag{30}$$

where again Eqs. (11) and (27) have been used. The system [Eqs. (27), (29), and (30)] is called the characteristic system of differential equations belonging to Eq. (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, $d\mathbf{x}/dx_{\mathrm{rc}}$, 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.

A. The case of turning points

The solution of the initial value problem or Cauchy problem fails in the case where $\det(\nabla_{\bar{\mathbf{q}}}\nabla_{\bar{\mathbf{q}}}^T V(q_{\mathrm{rc}}, \bar{\mathbf{q}})) = \det(\mathbf{S}^T[\nabla_{\mathbf{x}}\nabla_{\mathbf{x}}^T U(\mathbf{x})]\mathbf{S}) = 0$. At 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, $\mathbf{q}(t) = (q_{\mathrm{rc}}(t),\ \bar{\mathbf{q}}(t))$. Now we look for the solution of the initial value problem for this case. First we differentiate $\nabla_{\bar{\mathbf{q}}} V(q_{\mathrm{rc}}, \bar{\mathbf{q}}) = \mathbf{0}_{N-1}$ with respect to t

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

where we applied that $\mathbf{H}(\mathbf{x}) = \nabla_{\mathbf{x}}\nabla_{\mathbf{x}}{}^T U(\mathbf{x})$. If $\det(\nabla_{\bar{\mathbf{q}}}\nabla_{\bar{\mathbf{q}}}^T V(q_{\mathrm{rc}}, \bar{\mathbf{q}})) = \det(\mathbf{S}^T[\mathbf{H}(\mathbf{x})]\,\mathbf{S}) = 0$ 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 Eq. (31) into the system of coordinates, $(q_{\mathrm{rc}},\ \bar{\mathbf{z}}^T)$, that diagonalize the $\mathbf{S}^T[\mathbf{H}(\mathbf{x})]\mathbf{S}$ matrix

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

where $\mathbf{W}$ is the unitary matrix of eigenvectors and $\mathbf{h}$ is 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 nonzero, $b_j \neq 0$, then the solution of Eq. (32) is $dq_{\mathrm{rc}}/dt = 0$ and $(d\bar{\mathbf{z}}/dt)^T = (0_1, \ldots, 0_{j-1}, 1_j, 0_{j+1}, \ldots, 0_{N-1})$, 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 $0 = q_{\mathrm{rc}} - q_{\mathrm{rc}}^0$ which is tangent to the constant energy contour curve, $V(q_{\mathrm{rc}}, \bar{\mathbf{q}}) - v = 0$, and orthogonal to the gradient vector, $\nabla_{\mathbf{q}}^T V(q_{\mathrm{rc}}, \bar{\mathbf{q}}) = (\partial V(q_{\mathrm{rc}}, \bar{\mathbf{q}})/\partial q_{\mathrm{rc}}, \mathbf{0}_{N-1}^T)$, since the $\mathbf{r}$ component is zero, $dq_{\mathrm{rc}}/dt = 0$. 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, $V(q_{\mathrm{rc}}, \bar{\mathbf{q}}) - v = 0$. Such cases are denoted as ''turning points'' TP.[10,37] 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 $0 = q_{\mathrm{rc}} - q_{\mathrm{rc}}^0$ tangent to the constant energy contour curve, $V(q_{\mathrm{rc}}, \bar{\mathbf{q}}) - v = 0$.

B. 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 $\mathbf{b}$ vector is zero, $b_j = 0$, there are only $N-2$ independent equations in the system of equations [Eq. (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 $(dq_{\mathrm{rc}}/dt, d\bar{\mathbf{q}}^T/dt) = (dq_{\mathrm{rc}}/dt, d\bar{\mathbf{z}}^T/dt\mathbf{W}^T)$, where $dq_{\mathrm{rc}}/dt \neq 0$ and $(d\bar{\mathbf{z}}/dt)^T = (b_1/h_1, \ldots, b_{j-1}/h_{j-1}, 0_j, b_{j+1}/h_{j+1}, \ldots, b_{N-1}/h_{N-1})$ and $(dq_{\mathrm{rc}}/dt, d\bar{\mathbf{q}}^T/dt) = (0, d\bar{\mathbf{z}}^T/dt\mathbf{W}^T)$, where $(d\bar{\mathbf{z}}/dt)^T = \left(0_1, \ldots, 0_{j-1}, 1_j, 0_{j+1}, \ldots, 0_{N-1}\right)$ 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 $\mathbf{r}$ 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 prove this assertion, first, we transform equation (27) from $\mathbf{x}$ coordinates to $\mathbf{q}$ coordinates using the transformation (6) and the resolution of identity; and second, we multiply from the left the resulting equation by the unitary matrix

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

obtaining

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

Using the definition of adjoint matrix, we have the element $\mathbf{r}^T[\mathbf{A}(\mathbf{x})]\mathbf{r} = \det(\nabla_{\overline{\mathbf{q}}}\nabla_{\overline{\mathbf{q}}}^T V(q_{\rm rc},\overline{\mathbf{q}})) = \det(\mathbf{h}) = 0$ 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 to 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 $\left(dq_{\rm rc}/dt,\, d\overline{\mathbf{z}}^T/dt\right) = \mathbf{0}^T$.With the above results one concludes that both the stationary points and the 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 Eq. (15) is positive definite, and we say that this NT is a minimizing extremal curve. To prove this assertion, we say that since the NT path at each point transverses the family of equipotential hypersurfaces and because of the continuity and the nonexistence of VRI points, we have $\det\left(\mathbf{S}^T\,[\mathbf{H}\,(\mathbf{x})]\,\mathbf{S}\right) > 0$ at each point of the curve. 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, $\det\left(\mathbf{S}^T\,[\mathbf{H}\,(\mathbf{x})]\,\mathbf{S}\right) > 0$ holds from the minimum to the VRI point. From the VRI point to the stationary point holds $\det\left(\mathbf{S}^T\,[\mathbf{H}\,(\mathbf{x})]\,\mathbf{S}\right) < 0$ since the curve enters a ridge and because of this fact the sign of the integral $\delta^2 I$ cannot be determined until its explicit evaluation.

C. 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 equation (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.[39–42] 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

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

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

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

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

To solve the set of first order ordinary differential equations (27) and (29) using Eq. (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).

IV. EXAMPLE, ANALYSIS AND DISCUSSION

In this section, using a two-dimensional example we show the properties of the NT curves as RP and 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 Fig. 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

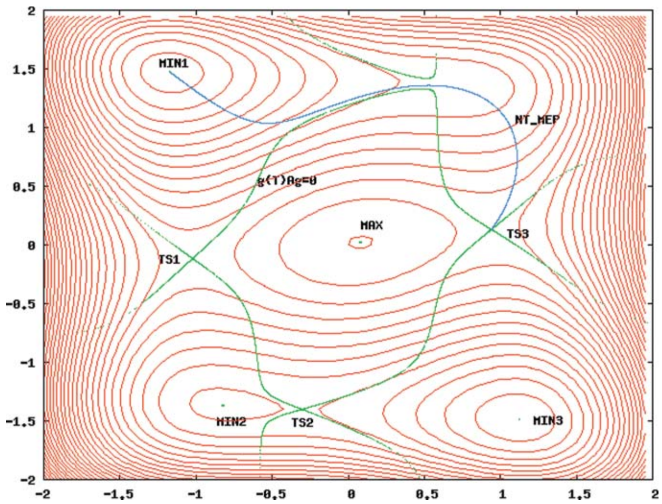

FIG. 1. The blue curve is the NT or RGF curve joining the stationary points MIN1 and TS3 of the Wolfe–Quapp PES. The green curve is the valley-ridge border line, where det $(\mathbf{S}^T[\mathbf{H}(\mathbf{x})]\mathbf{S}) = 0$. The red lines are the equipotential curves of the PES. In this case the NT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

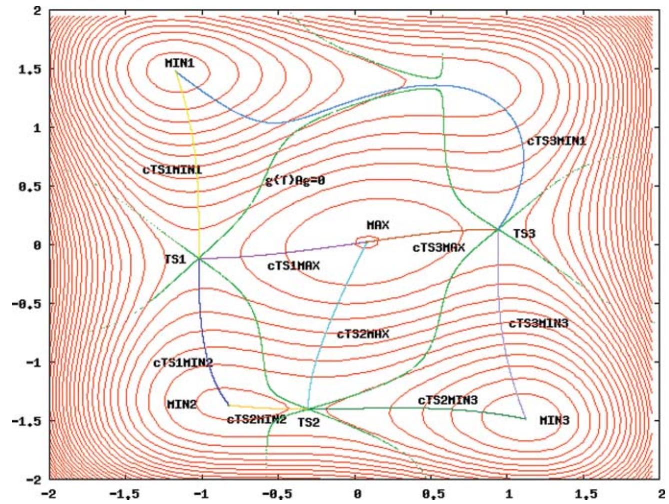

FIG. 3. A set of RGF or NT curves joining all stationary points of the Wolfe–Quapp PES. The curves, cTS1MIN1, cTS1MIN2, cTS2MIN2, cTS2MIN3, cTS3MIN3, and cTS3MIN1 are minimizing extremal curves while the curves cTS1MAX, cTS2MAX, and cTS3MAX are maximizing extremal curves.

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 $(\mathbf{S}^T[\mathbf{H}(\mathbf{x})]\mathbf{S}) > 0$. As a result of this, 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 Fig. 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 the bowl of MIN1 again. The former point is of the mixed-type VRI[46] while the latter point is a turning point; in this case, the NT curve touches the equipotential curve at

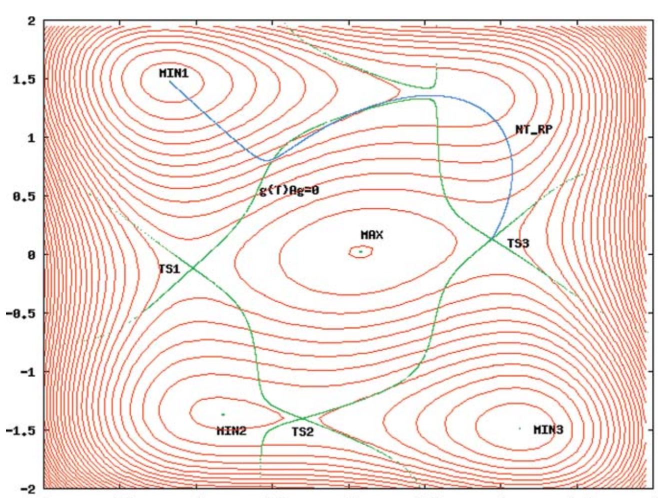

FIG. 2. The blue curve is the NT or RGF curve joining the stationary points MIN1 and TS3 of the Wolfe–Quapp PES. The green curve is the valley-ridge border line, where det $(\mathbf{S}^T[\mathbf{H}(\mathbf{x})]\mathbf{S}) = 0$. The red lines are the equipotential curves of the PES. In this case the NT or RGF curve is not RP because does not increase always monotonically from MIN1 to TS3.

this point, resulting in $dU(\mathbf{x})/dt = 0$. For the subarc 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 it does not increase monotonically from the minimum MIN1 to the first saddle point TS3. At 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 Figs. 1 and 2 are examples of the conclusions discussed in the last paragraph of Sec. III B.

In Fig. 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), and (−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 in 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) and 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 Fig. 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, and MIN3 and taking the positive option in the tangent, the corresponding curves end at the stationary points so that their Hessian matrices have an odd number of negative eigen-

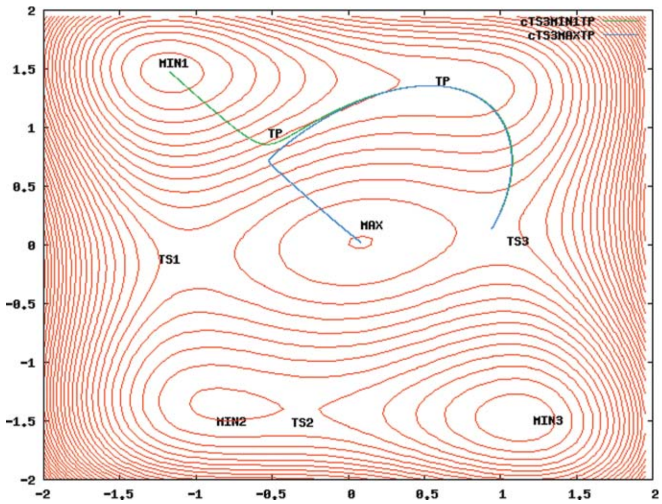

FIG. 4. Two curves, cTS3MIN1TP, and cTS3MAXTP both start at the first order saddle point TS3 but end at different stationary points. The initial direction between both is slightly different. The different evolution is due to the existence of a mixed-type VRI point.

values. The three NT or RGF curves, namely, cTS1MAX, cTS2MAX, and cTS3MAX show a negative value for the integral $\delta^2 I$, of Eq. (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 Fig. 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) and 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 subarc 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 from MIN1 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.

V. CONCLUSION

We have proved the variational nature of the distinguished coordinate path and 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 Eq. (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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