The reaction path intrinsic reaction coordinate method and the Hamilton–Jacobi theory

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The definition and location of an intrinsic reaction coordinate path is of crucial importance in many areas of theoretical chemistry. Differential equations used to define the path hitherto are complemented in this study with a variational principle of Fermat type, as Fukui [Int. J. Quantum Chem., Quantum Chem. Symp. **15**, 633 (1981)] reported in a more general form some time ago. This definition is more suitable for problems where initial and final points are given. The variational definition can naturally be recast into a Hamilton–Jacobi equation. The character of the variational solution is studied via the Weierstrass necessary and sufficient conditions. The characterization of the local minima character of the intrinsic reaction coordinate is proved. Such result leads to a numerical algorithm to find intrinsic reaction coordinate paths based on the successive minimizations of the Weierstrass *E*-function evaluated on a guess curve connecting the initial and final points of the desired path. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1927521]

I. INTRODUCTION

An interesting problem in theoretical chemistry is to find the lowest energy path of an adiabatic potential energy surface (PES) associated to a molecular rearrangement from a stable configuration state to another, normally associated to reactants and products. This lowest energy path or minimum energy path (MEP) is often referred as reaction path (RP). From a mathematical point of view, the RP is defined as a curved line in the coordinate space, connecting two minima through a first-order saddle point (FOSP), also known as the transition state of a PES. The RPs are the grounds of many dynamical theories. The saddle point gives us the energy barrier, which is the most important quantity to evaluate the transition rates of the rearrangements within the harmonic transition state theory.[1] The reformulation of the famous reaction path Hamiltonian (RPH) shows the importance to evaluate first a RP and second to run molecular dynamics constrained to this path. In this way, the RPH methodology and in turn the RP offers the possibility to study dynamics. Using this type of restricted nuclear movement one recovers many important molecular dynamic effects.[2]

Different definitions of RP produce different curve lines in the PES and the parametrization of these lines, *s*, is called the reaction coordinate. The reaction coordinate is in fact an arc-length of the RP. In theoretical chemistry, one of the most used RP is the corresponding steepest descent (SD) curve from the FOSP to reactant or product. This SD reaction path in mass weighted coordinates is normally called intrinsic reaction coordinate (IRC).[3] However, in some cases the IRC is not the most appropriated MEP.[1] The tangent vector of the SD lines and specifically the IRC curve line is characterized by an autonomous system of first-order differential equations. The tangent vector at each point of the line, $\mathbf{t}[\mathbf{q}(s)]$, is equated to the normalized gradient vector, $\mathbf{g}(\mathbf{q})=\nabla_{\mathbf{q}}V(\mathbf{q})$, of this point of the PES, $V(\mathbf{q})$,

$$\mathbf{t}[\mathbf{q}(s)]=\left.\frac{d\mathbf{q}(s')}{ds'}\right|_{s'=s}=\frac{\mathbf{g}[\mathbf{q}(s)]}{|\mathbf{g}[\mathbf{q}(s)]|}, \tag{1}$$

where $\mathbf{q}(s)$ represents a point of the curve and $|\mathbf{g}[\mathbf{q}(s)]|$ the norm of the vector $\mathbf{g}(\mathbf{q})$ evaluated at the point $\mathbf{q}(s)$ of the curve. The dimension of $\mathbf{q}(s)$ position vector and the gradient vector $\mathbf{g}(\mathbf{q})$ is *N*, *N* being the number of independent variables. There are a variety of numerical methods to solve the differential equation (1). We propose an analysis of the SD curves and specifically of IRC curve through the calculus of variations and Hamilton–Jacobi theory.[4,5] The Hamilton–Jacobi theory has been used in other fields to deal with the integration of ordinary differential equations. This theory formulates the calculus of variations through a nonlinear first-order partial differential equation, called Hamilton–Jacobi equation.[6]

The integration of the partial differential equations is in general much more difficult than the integration of the ordinary differential equations. The Hamilton–Jacobi theory achieves, in a beautiful manner, to reverse this relationship in some situations. Very often, many applied mathematical problems lead to a system of ordinary differential equations as in the calculus of variations. These equations may be difficult to integrate by elementary methods, but the corre-

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sponding partial differential equation can be transformed easily into a complete integral by the separation of variables. If the complete integral is obtained, then one solves the corresponding system of characteristic differential equations by a process based on differentiation and elimination.[6] Because the proposed IRC reaction path is described mathematically by the total differential equation (1), it should be interesting to investigate the possibility to derive the corresponding Hamilton–Jacobi equation for this type of RP. In addition the resulting Hamilton–Jacobi equation may open other ways to evaluate the IRC curve line. Tachibana and Fukui were the first authors to investigate the IRC path nature from the calculus of variations.[7–11] These authors obtained the variational results by using different ways, namely, the Synge's geodesic principle, the Hamilton principle through an extended Lagrangian, and finally geodesic lines in a Riemannian space.[11] The results obtained by these authors have been developed to propose new methods to evaluate the IRC path. The first attempt to find an IRC based on variational methods, as far as we know, is due to Stachó and Bán.[12] In fact the algorithm proposed by these authors consists in the variation of a guess curve and the successive correction of this curve based on Mezey's theory of catchment regions of the gradient field of the PES.[13] Other methods to obtain the IRC path based on variations or shifts of an initial guess curve have been proposed and are now widely used.[14–24]

The IRC path defined by Eq. (1) is in fact an orthogonal trajectory to the contour surface, $V(\mathbf{q})=\text{const}$. In the determination of this type of paths the relation between the gradient fields and the associated maps of these orthogonal trajectories is relevant.[25] Due to this relation, there exists thus both theoretical and practical reasons for expecting to gain insight into the structural characteristics of the gradient fields of potential energy surfaces and the IRC paths. On the other hand, the basic and complete picture of the problems in the calculus of variations from the Hamilton–Jacobi theory consists in a relation between contours of a surface and curves. These curves are never tangent to these contour surfaces. In addition the difference between two contour lines of these surfaces is related to a functional depending on some arguments that characterize these curves.[26] The parallelism between the IRC curve model and the Hamilton–Jacobi theory of the calculus of variations opens the question in both the reformulation of the IRC path from this point of view and new possibilities for determining this type of paths. These two points are the aim of this paper.

The SD curves emerging from a stationary point character minimum in the PES can be seen as traveling in an orthogonal manner through the contour lines of this PES. In addition, it should be noted that the construction of contour potential energy surfaces, $V(\mathbf{q})=\text{const}$, such that all points satisfying this equation possess the same equipotential difference with respect to another contour line and specifically with the value of the PES in the minimum, is similar to the construction of the Fermat–Huyghens of propagation of the cone rays. This similarity gives the possibility to study the SD curves from Hamilton–Jacobi theory and the calculus of variations point of view. It is important to remember that the Hamilton–Jacobi theory was formulated for the first time to describe, from a rigorous mathematical point of view, the Fermat–Huyghens construction of propagation of light.[27] As pointed out before, Tachibana and Fukui studied and analyzed the IRC curve using the calculus of variations and Synge's principle,[10,11] however, we revisit this study starting from a functional like the one that appears in the description of Fermat-type variational principles.

We emphasize that the main aim of this work is to formulate, in a consistent and mathematically precise way, the variational character of the IRC curves in terms of the Hamilton–Jacobi theory. Thus we give a sound basis to many of the ideas proposed and used in previous works,[24] as well as suggest a new algorithm, which we will describe later.

The present work is organized as follows: first, in Sec. II we present a derivation of the SD curves based on the Fermat variational principle. The goal of this section is also to provide the necessary background on the Hamilton–Jacobi theory for a sufficient understanding of this paper. The formulation is written using the symbolism normally employed in the Hamilton–Jacobi theory. We derive the corresponding Hamilton–Jacobi equation, the characteristic equations for the SD curve lines. The concept of the field of extremals applied to SD curves is introduced, too. Two different derivations of Hamilton–Jacobi equation are reported. The second-order necessary and sufficient variational conditions are also studied to analyze the character of the extremal curves, the SD curves. This result is done through the so-called Weierstrass necessary and sufficient conditions and the Jacobi equation.[26] In particular, the solution of the Jacobi equation for the SD curve situated in a region sufficiently close to a first-order saddle point is reported and analyzed. In Sec. III a new method to evaluate the IRC path is formulated. In order to obtain a variational method, which actually specifies how to correct the set of parameters that characterize a trial curve, one must expand the corresponding functional beyond first order in the set of variational parameters. However, to obtain sufficient conditions one must allow each parameter to vary in the correct direction. As a consequence, the proposed method is based on the nature of the second-order necessary and sufficient variational conditions associated with the IRC curve line. Finally an example is given and some conclusions are drawn.

II. THE FERMAT VARIATIONAL PRINCIPLE AS A THEORETICAL BASIS OF IRC MODEL

A. The first-order necessary condition

We consider the SD as a path that propagates in a media, the PES, employing the minimum travel potential energy. The travel potential energy of this steepest descent is from a fixed point $\mathbf{q}_R$ to a variable end point $\mathbf{q}$ in the PES. For future purpose, the fixed point $\mathbf{q}_R$ is taken as a stationary point character minimum of the PES. Using the calculus of variations, the above problem with these conditions can be formulated as follows: we are choosing the curve from the set of all smooth curves $\mathbf{q}(s)$ all starting from the point $\mathbf{q}_R=\mathbf{q}(0)$ and passing through the point $\mathbf{q}=\mathbf{q}(s)$, with tangent $d\mathbf{q}/ds$ that minimizes the integral,

$$\Delta V_{R\to q} = \int_0^s \frac{ds'}{v(s')}, \tag{2}$$

where s is the arc-length of the path joining the points $\mathbf{q}_R$ and $\mathbf{q}$, and $v(s')$ is a "velocity" or the continuous slowness model. The magnitude $v(s')$ is taken non-negative, $v(s') \geqslant 0$. In order to connect this variational principle with the SD curve lines and specifically with the IRC, we take using Eq. (1), $v(s') = |\mathbf{g}[\mathbf{q}(s')]|^{-1}$, the inverse of the gradient norm. On the other hand, we consider the arc-length s' to be a function of a new parameter t' defined as

$$ds' = \sqrt{\left(\frac{d\mathbf{q}}{dt'}\right)^T\left(\frac{d\mathbf{q}}{dt'}\right)}dt', \tag{3}$$

where the superscript T means transposed. With these two definitions, the above variational problem given in Eq. (2) can be reformulated in the form

$$\Delta V_{R\to q}(\mathbf{q}) = \int_0^t \sqrt{[\mathbf{g}(\mathbf{q})]^T[\mathbf{g}(\mathbf{q})]}\sqrt{(d\mathbf{q}/dt')^T(d\mathbf{q}/dt')}dt' = \int_0^t F(\mathbf{q}, d\mathbf{q}/dt')dt'. \tag{4}$$

This integral functional (4) is positive homogeneous of degree one with respect to the tangent vector $d\mathbf{q}/dt'$ and does not depend explicitly on the choice of the parameter t' that characterizes the curve.[6,26] This type of functional was also proposed some time ago by Fukui *et al.*[10,11] and Elber *et al.*[16] In this formulation of the variational problem, the solution consists in finding the curve $\mathbf{q}(t')$ connecting both points of the PES, $\mathbf{q}_R = \mathbf{q}(0)$ and $\mathbf{q} = \mathbf{q}(t)$, which minimize the integral functional (4). The integral functional $\Delta V_{R\to q}(\mathbf{q})$ given either in Eq. (2) or Eq. (4) is of the same type as that appearing in Fermat variational principles.[6] From the calculus of variations, we apply the basic formula for the general variation of the functional to the problem (4), $\Delta V_{R\to q}(\mathbf{q})$, regarding the point $\mathbf{q}_R$ as a fixed point and the point $\mathbf{q}$ as a variable. In the region of the PES, $\Delta V_{R\to q}(\mathbf{q})$ is a single-valued function of the coordinates of the point $\mathbf{q}$. The basic formula which gives the first-order variation of the functional $\Delta V_{R\to q}(\mathbf{q})$ with respect to $\mathbf{q}$ and t is

$$\delta\Delta V_{R\to q} = \int_0^t \left[\nabla_{\mathbf{q}} F - \frac{d}{dt'}(\nabla_{d\mathbf{q}/dt'}F)\right]^T \mathbf{z}(t')dt' + \left\{(\nabla_{d\mathbf{q}/dt'}F)^T\Delta\mathbf{q} + \left[F - (\nabla_{d\mathbf{q}/dt'}F)^T d\mathbf{q}/dt'\right]\Delta t\right\}_t, \tag{5}$$

where $\nabla_{\mathbf{x}}^T = (\partial/\partial\mathbf{x}_1, \ldots, \partial/\partial\mathbf{x}_N)$, $\mathbf{z}(t') = \mathbf{q}^*(t') - \mathbf{q}(t')$, $\mathbf{q}^*(t')$ and $\mathbf{q}(t')$ being two neighboring curves in this region of the PES, both starting at the point $\mathbf{q}_R$. The curve $\mathbf{q}^*(t')$ connects the points $\mathbf{q}_R, t' = 0$ and $\mathbf{q} + \Delta\mathbf{q}, t' = t + \Delta t$ and the curve $\mathbf{q}(t')$ connects the points $\mathbf{q}_R, t' = 0$ and $\mathbf{q}, t' = t$. The tangent $d\mathbf{q}/dt'$ is evaluated at the point $\mathbf{q}(t)$. Then, the condition $\delta\Delta V_{R\to q}(\mathbf{q}) = 0$ implies that the curve $\mathbf{q}(t')$ must be an extremal, i.e., a solution of Euler–Lagrange equation (also known as Euler equation or Lagrange equation),

$$\nabla_{\mathbf{q}} F - \frac{d}{dt'}(\nabla_{d\mathbf{q}/dt'}F) = \mathbf{0}. \tag{6}$$

If the curve $\mathbf{q}(t')$ is an extremal, the integral in Eq. (5) vanishes, then the condition $\delta\Delta V_{R\to q}(\mathbf{q}) = 0$ takes the form

$$\left\{(\nabla_{d\mathbf{q}/dt'}F)^T\Delta\mathbf{q} + \left[F - (\nabla_{d\mathbf{q}/dt'}F)^T d\mathbf{q}/dt'\right]\Delta t\right\}\Big|_t = 0. \tag{7}$$

Applying these general results to the present problem, the Euler–Lagrange equation (6) takes the form

$$\left(\mathbf{I} - \frac{\left(\frac{d\mathbf{q}}{dt'}\right)\left(\frac{d\mathbf{q}}{dt'}\right)^T}{\left(\frac{d\mathbf{q}}{dt'}\right)^T\left(\frac{d\mathbf{q}}{dt'}\right)}\right) \times \left(\frac{\mathbf{H}\mathbf{g}}{\sqrt{\mathbf{g}^T\mathbf{g}}} - \frac{\frac{d^2\mathbf{q}}{dt'^2}}{\sqrt{\left(\frac{d\mathbf{q}}{dt'}\right)^T\left(\frac{d\mathbf{q}}{dt'}\right)}}\frac{\sqrt{\mathbf{g}^T\mathbf{g}}}{\sqrt{\left(\frac{d\mathbf{q}}{dt'}\right)^T\left(\frac{d\mathbf{q}}{dt'}\right)}}\right) = \mathbf{0}, \tag{8}$$

where $\mathbf{H}$ is the Hessian matrix, $\mathbf{H} = \nabla_{\mathbf{q}}\mathbf{g}^T$, and $\mathbf{I}$ is the identity matrix. The $d\mathbf{q}/dt'$ vector is the tangent vector of the $\mathbf{q}(t')$ curve. The solution of Eq. (8) is the autonomous differential equation

$$\frac{d\mathbf{q}}{dt'} = \mathbf{g}[\mathbf{q}(t')], \tag{9}$$

where $\mathbf{g}[\mathbf{q}(t')]$ is the gradient vector evaluated at the point $\mathbf{q}(t')$ of the curve. The normalization of Eq. (9) leads to Eq. (1). We conclude that expression (1) is the normalized tangent vector of the path that extremalizes the functional $\Delta V_{R\to q}(\mathbf{q})$ defined in Eq. (4). In other words, the SD curve connecting the points $\mathbf{q}_R$ and $\mathbf{q}$ is an extremal curve of the variational problem defined in expression (4), $\Delta V_{R\to q}(\mathbf{q})$. This point may be envisaged in the following way: a path $\mathcal{P}$, starting at the point $\mathbf{q}_R = \mathbf{q}(0)$, propagates through the PES according to the speed law or continuous slowness model, $v(s) = |\mathbf{g}[\mathbf{q}(s)]|^{-1}$, arrives at the point $\mathbf{q} = \mathbf{q}(s)$, traveling with the least potential energy variation $\Delta V_{R\to q}(\mathbf{q})$, as defined in Eq. (4), then this path is characterized by the normalized tangent given in Eq. (1). We note that the condition of least potential energy variation, $\Delta V_{R\to q}(\mathbf{q})$, as defined in Eq. (4), will be proved below.

B. Derivation of the Hamilton–Jacobi equation and the corresponding characteristic system of equations

The functional $F(\mathbf{q}, d\mathbf{q}/dt')$, given in Eq. (4), is defined on the curves lying in some region of the PES. We take the unique extremal curve that goes through the point $\mathbf{q}_R$ to the arbitrary point $\mathbf{q}$. The integral (4) evaluated along this extremal curve, namely, the SD curve, joining these two points takes the value $J(\mathbf{q}) = \Delta V_{R\to q}(\mathbf{q})$. Using the language of Hamilton–Jacobi theory, this function $J(\mathbf{q})$ is called the geodetic distance between the points $\mathbf{q}_R$ and $\mathbf{q}$. As explained in the Introduction, to see the IRC method through the Hamilton–Jacobi theory, we use the symbols and the defini-

tions normally employed in this mathematical theory. Applying Eq. (5) to the extremal curve, SD, at the point $\mathbf{q}(t)$, and taking the first-order variation in both $\Delta\mathbf{q}$ and Δt, i.e., $\Delta\mathbf{q} \rightarrow d\mathbf{q}, \Delta t \rightarrow dt$, and the value of the tangent vector of the extremal curve at this point, $d\mathbf{q}/dt'|_{t'=t} = d\mathbf{q}/dt$, $\delta\Delta V_{R\rightarrow q}(\mathbf{q})$ is transformed into a total differential equation, $\delta\Delta V_{R\rightarrow q}(\mathbf{q}) = dJ(\mathbf{q})$, namely,

$$\delta\Delta V_{R\rightarrow q}(\mathbf{q}) = dJ(\mathbf{q}) = (\boldsymbol{\nabla}_{d\mathbf{q}/dt}F)^T d\mathbf{q} + \left[F - (\boldsymbol{\nabla}_{d\mathbf{q}/dt}F)^T d\mathbf{q}/dt\right]dt \tag{10}$$

evaluated at the point $\mathbf{q}, t$. From this total differential equation, we introduce the definition of the $\mathbf{p}$ vector, namely,

$$\boldsymbol{\nabla}_{d\mathbf{q}/dt}F = \frac{d\mathbf{q}}{dt}\frac{\sqrt{\mathbf{g}^T\mathbf{g}}}{\sqrt{\left(\frac{d\mathbf{q}}{dt}\right)^T\left(\frac{d\mathbf{q}}{dt}\right)}} = \boldsymbol{\nabla}_{\mathbf{q}}J = \mathbf{p} \tag{11}$$

and

$$F - (\boldsymbol{\nabla}_{d\mathbf{q}/dt}F)^T d\mathbf{q}/dt = \frac{\partial J}{\partial t} = 0. \tag{12}$$

In the evaluation of both Eqs. (11) and (12), the functional form of F given in the expression (4) has been used. The result of Eq. (12) is the reason why the geodetic distance function J and its total differential form, given in Eq. (10), depend only on $\mathbf{q}$. Proceeding as in the normal calculus of variations, from the expression (10) and using the Legendre transformation, one derives the Hamilton–Jacobi equation.[6,26] However in this case the Legendre transformation cannot be applied since the function F is homogeneous of degree one with respect to $d\mathbf{q}/dt$ argument. This is the reason why both Eq. (12) and the determinant of the matrix

$$\boldsymbol{\nabla}_{d\mathbf{q}/dt}\boldsymbol{\nabla}^T_{d\mathbf{q}/dt}F = \frac{\sqrt{\mathbf{g}^T\mathbf{g}}}{\sqrt{\left(\frac{d\mathbf{q}}{dt}\right)^T\left(\frac{d\mathbf{q}}{dt}\right)}}\left(\mathbf{I} - \frac{\left(\frac{d\mathbf{q}}{dt}\right)\left(\frac{d\mathbf{q}}{dt}\right)^T}{\left(\frac{d\mathbf{q}}{dt}\right)^T\left(\frac{d\mathbf{q}}{dt}\right)}\right) \tag{13}$$

vanish. In the present case we proceed in the following way, from Eq. (11) we obtain the $d\mathbf{q}/dt$ argument

$$\frac{d\mathbf{q}}{dt} = \boldsymbol{\nabla}_{\mathbf{q}}J\frac{\sqrt{\left(\frac{d\mathbf{q}}{dt}\right)^T\left(\frac{d\mathbf{q}}{dt}\right)}}{\sqrt{\mathbf{g}^T\mathbf{g}}}. \tag{14}$$

From the homogeneity relation of F, we have

$$F = \left(\frac{d\mathbf{q}}{dt}\right)^T\boldsymbol{\nabla}_{d\mathbf{q}/dt}F = \left(\frac{d\mathbf{q}}{dt}\right)^T\boldsymbol{\nabla}_{\mathbf{q}}J = \sqrt{\mathbf{g}^T\mathbf{g}}\sqrt{\left(\frac{d\mathbf{q}}{dt}\right)^T\left(\frac{d\mathbf{q}}{dt}\right)}. \tag{15}$$

Multiplying Eq. (14) from the left by $(\boldsymbol{\nabla}_{\mathbf{q}}J)^T$ and using Eq. (15) we obtain

$$\frac{(\boldsymbol{\nabla}_{\mathbf{q}}J)^T(\boldsymbol{\nabla}_{\mathbf{q}}J)}{\mathbf{g}^T\mathbf{g}} = 1. \tag{16}$$

Equation (16) is a partial differential equation in the $\boldsymbol{\nabla}_{\mathbf{q}}J$ taking the place of the Hamilton–Jacobi equation or eiconal equation in the present variational problem. The connection between expression (16) and the Hamilton–Jacobi equation is explained in detail in Appendix A, where another derivation of Eq. (16) is also given. As far as we know, this is the first time the Hamilton–Jacobi equation is formulated for the SD path, however, as indicated in the Introduction close results were obtained by Tachibana and Fukui.[7–11]

Equation (16) tells us that as the parameter t evolves, the coordinates $\mathbf{q}(t)$ evolve and the contour line with constant potential energy J changes, through the coordinates $\mathbf{q}$, and a point of this contour line is linked to a point of the neighborhood contour line. This set of points defines a curve which extremalizes the functional (4). This curve is in the present case the SD line that goes from the $\mathbf{q}_R$ point to the $\mathbf{q}$ point in the PES. Now we can establish some analogies between the propagation of light through a medium having a variable index of refraction and the present problem. The light rays are given as extremal paths of least time, now the SD curves are extremal paths of the PES. The construction of solutions of the eiconal equation (16) as a contour line with constant potential energy is similar to the Fermat–Huyghens principle for the construction of wave fronts.

For future purposes, at this point, we deal briefly with the concept of field of extremal curves which satisfy the trivial Hamilton–Jacobi equation (16). The geodetic distance introduced above is defined from a fixed point $\mathbf{q}_R$ of the extremal curve to a point of a fixed surface $\Pi(\mathbf{q}, t) = \text{const}$. This concept of geodetic distance arises by considering the initial point $\mathbf{q}_R$ of an extremal curve as fixed and seeking a final point $\mathbf{q}$ on the given surface $\Pi(\mathbf{q}, t) = \text{const}$ in such a way that the geodetic distance J remains stationary under variations of the point $\mathbf{q}$. Thus in formula (10) we have introduced the value zero for the variation of $d\mathbf{q}$ and dt of the end point $\mathbf{q}$ since $dJ(\mathbf{q}) = 0$ and the initial point $\mathbf{q}_R$ is fixed. This condition is always satisfied if the point $\mathbf{q}$ is varied on the surface $\Pi(\mathbf{q}, t) = \text{const}$, which means that the vanishing of Eq. (10) is a consequence of the fact that the differentiated form of the surface, $\Pi(\mathbf{q}, t) = \text{const}$, vanishes,

$$d\Pi = (\boldsymbol{\nabla}_{\mathbf{q}}\Pi)^T d\mathbf{q} + \frac{\partial\Pi}{\partial t}dt = 0. \tag{17}$$

Comparing both Eqs. (10) and (17) and using Eqs. (11) and (12) we see that $\mathbf{p} = \boldsymbol{\nabla}_{\mathbf{q}}J = \boldsymbol{\nabla}_{\mathbf{q}}\Pi = \boldsymbol{\nabla}_{d\mathbf{q}/dt}F$, and $\partial J/\partial t = \partial\Pi/\partial t = F - (\boldsymbol{\nabla}_{d\mathbf{q}/dt}F)^T d\mathbf{q}/dt = 0$. Notice that in the present case the surface depends only on the coordinates $\mathbf{q}, \Pi(\mathbf{q}) = \text{const}$, and from this we infer that $\Pi(\mathbf{q})$ corresponds to $J(\mathbf{q})$. The last result is the so-called transversality condition[6,26] which in the present problem is a relation between the coordinates $\mathbf{q}$ of a point of the surface $\Pi(\mathbf{q}) = \text{const}$, the $\mathbf{p}$ vector, and the tangent $d\mathbf{q}/dt$ of the extremal curve, a SD line. Finally in the present problem, the field of extremal curves is centered in the point $\mathbf{q}_R$, where all the extremal curves, the SD lines, emerge.

Expression (10) gives us the derivatives of J, and its total differential form enables the evaluation of the geodetic distance of an extremal curve as a line integral of this total differential form and also the computation of this geodetic distance independent of the curve used. Let us assume an arbitrary piecewise smooth curve $\mathcal{C}$ defined in the region of

the PES connecting the fixed point $\mathbf{q}_R$ and the variable end point $\mathbf{q}$. This arbitrary curve, not necessarily an extremal curve (SD curve), is defined at each point of this region by the function $\mathbf{q}_C(t)$ and its tangent by $d\mathbf{q}_C/dt$. According to the previous discussion, in the present field of extremals, the characterization of the extremal curves at each point of the considered region, $\mathbf{q}(t)$, embedded in this field, is given by the corresponding tangent vector $d\mathbf{q}/dt$ and the $\mathbf{p}$ vector defined in Eq. (11). The function $J(\mathbf{q})$, as the line integral of the total differential form defined in Eq. (10) is

$$J(\mathbf{q}) = \int_{\mathbf{q}_{R,0}}^{\mathbf{q},t} \left[(\boldsymbol{\nabla}_{\mathbf{q}} J)^T d\mathbf{q}_C + \frac{\partial J}{\partial t'} dt' \right] = \int_0^t \left[(\boldsymbol{\nabla}_{\mathbf{q}} J)^T \frac{d\mathbf{q}_C}{dt'} + \frac{\partial J}{\partial t'} \right] dt'. \tag{18}$$

Equation (18) is the Hilbert's invariant integral.[6,26] Using Eqs. (9), (11), and (12), Eq. (18) takes the simple form

$$J(\mathbf{q}) = \int_0^t \left(\mathbf{p}^T \frac{d\mathbf{q}_C}{dt'} \right) dt' = \int_0^t \left(\mathbf{g}_C^T \frac{d\mathbf{q}_C}{dt'} \right) dt' = \int_0^t \left[\frac{\mathbf{g}_C^T (d\mathbf{q}_C/dt')}{\sqrt{\mathbf{g}_C^T \mathbf{g}_C} \sqrt{(d\mathbf{q}_C/dt')^T (d\mathbf{q}_C/dt')}} F(\mathbf{q}_C, d\mathbf{q}_C/dt') \right] dt' \tag{19}$$

with $\mathbf{p}$ being the vector field at the point $\mathbf{q}_C(t')$ and $\mathbf{g}_C = \mathbf{g}[\mathbf{q}_C(t')]$. According to the definition of geodetic distance $J(\mathbf{q})$ given at the beginning of this section and the expression (19), we have the next equality

$$J(\mathbf{q}) = \int_0^t \sqrt{\mathbf{g}^T \mathbf{g}} \sqrt{\left(\frac{d\mathbf{q}}{dt'} \right)^T \left(\frac{d\mathbf{q}}{dt'} \right)^T} dt' = \int_0^t \left(\mathbf{g}_C^T \frac{d\mathbf{q}_C}{dt'} \right) dt' = \int_0^t F(\mathbf{q}, d\mathbf{q}/dt') dt' = \int_0^t \left[\frac{\mathbf{g}_C^T (d\mathbf{q}_C/dt')}{\sqrt{\mathbf{g}_C^T \mathbf{g}_C} \sqrt{(d\mathbf{q}_C/dt')^T (d\mathbf{q}_C/dt')}} F(\mathbf{q}_C, d\mathbf{q}_C/dt') \right] dt', \tag{20}$$

where $\mathbf{g}$ is evaluated at the point $\mathbf{q}(t')$ of the extremal curve. We emphsize that $d\mathbf{q}/dt'$ is the tangent vector of the extremal curve, namely, the SD curve joining the points $\mathbf{q}_R$ and $\mathbf{q}$, and the vector $d\mathbf{q}_C/dt'$ is the tangent vector of an arbitrary curve joining the same points. Both curves are embedded in the field of the vectors $\mathbf{p}$. In the present variational problem, this field of $\mathbf{p}$ vectors are the gradient vectors, $\mathbf{p} = \mathbf{g}(\mathbf{q})$. The two field vectors, namely, the tangent vector of the extremal curves $d\mathbf{q}/dt'$ and the $\mathbf{p}$ vector, are regarded as a given function of the coordinates $\mathbf{q}$. Equation (20) will be used in the following section.

Now, the two vectors, $d\mathbf{q}/dt'$ and $\mathbf{p}$, evolve in the field of extremal curves through $\mathbf{q}(t')$ according to the following equations. From Eqs. (3), (11), and (16) we have

$$\frac{1}{\sqrt{\left(\frac{d\mathbf{q}}{dt'} \right)^T \left(\frac{d\mathbf{q}}{dt'} \right)}} \frac{d\mathbf{q}}{dt'} = \frac{d\mathbf{q}}{ds} = \frac{\mathbf{p}}{\sqrt{\mathbf{p}^T \mathbf{p}}}. \tag{21}$$

Equation (21) gives us the evolution of the tangent vector of the extremal curve. The equation for the evolution of the $\mathbf{p}$ vector is derived from the set of Eqs. (3), (4), (6), and (11),

$$\frac{1}{\sqrt{\left(\frac{d\mathbf{q}}{dt'} \right)^T \left(\frac{d\mathbf{q}}{dt'} \right)}} \frac{d\mathbf{p}}{dt'} = \frac{d\mathbf{p}}{ds} = \frac{\mathbf{H}\mathbf{g}}{\sqrt{\mathbf{g}^T \mathbf{g}}}. \tag{22}$$

Equations (21) and (22) are the canonical system of differential equations coming from the Euler–Lagrange differential equation (6) or, what is identical, the system of differential equations that characterizes the extremal curves of the Hamilton–Jacobi partial differential equation (16).[6] The proof of this assertion is given in Appendix B. Finally we accept that the above results are quite trivial since one recognizes that Eq. (21) is the tangent of the SD curve. However, we rewrite these equations in this manner to emphasize that the theory of Hamilton–Jacobi can not only be used to describe and analyze any SD curve and its field but also because it gives us the basis of the proposed algorithm to locate IRC paths explained below.

C. The second-order variational conditions

So far, we have only been studying the necessary first-order variational conditions of a curve to be extremal of the functional integral proposed in Eq. (4). It is interesting to analyze the necessary and sufficient second-order variational conditions to ensure that the extremal curves characterized by Eq. (9) minimize the functional (4). The second-order variational conditions are related to the weak Legendre condition,[6,26] and merely consist in analyzing the value and the corresponding sign of the determinant of the matrix, $\boldsymbol{\nabla}_{d\mathbf{q}/dt} \boldsymbol{\nabla}_{d\mathbf{q}/dt}^T F = \mathbf{F}_{d\mathbf{q}/dt, d\mathbf{q}/dt}$ along each point of the extremal curve, where $d\mathbf{q}/dt$ is the tangent of the extremal curve. If this determinant is non-negative, $\det|\mathbf{F}_{d\mathbf{q}/dt, d\mathbf{q}/dt}| \geqslant 0$, for all points of the curve, then this curve is an extremal satisfying the second-order necessary weak Legendre condition and possesses a minimum character in a neighborhood. On the other hand, if $\mathbf{F}_{d\mathbf{q}/dt, d\mathbf{q}/dt}$ is strictly positive, $\det|\mathbf{F}_{d\mathbf{q}/dt, d\mathbf{q}/dt}| > 0$, then we say that the extremal curve satisfies the second-order necessary weak strengthened Legendre condition with minimum character in a neighborhood. For the present case, the value of this determinant at each point of the extremal curve, the SD line, is obtained by substituting in Eq. (13) the value of the tangent vector given in Eq. (9),

$$\boldsymbol{\nabla}_{d\mathbf{q}/dt} \boldsymbol{\nabla}_{d\mathbf{q}/dt}^T F \Big|_{\frac{d\mathbf{q}}{dt} = \mathbf{g}} = \left(\mathbf{I} - \frac{\mathbf{g}\mathbf{g}^T}{\mathbf{g}^T \mathbf{g}} \right) = \mathbf{F}_{\mathbf{g},\mathbf{g}}. \tag{23}$$

From Eq. (23) we see that $\det \mathbf{F}_{\mathbf{g},\mathbf{g}} = 0$. This result means that the SD curve satisfies the necessary weak nonstrengthened Legendre condition and makes the integral functional (4) a minimum with respect to continuous comparison functions, $\mathbf{q}^*(t,\tau)$, with its continuous first derivatives in a neighborhood, i.e., as the parameter $\tau \to 0$ the curve $\mathbf{q}^*(t,\tau) \to \mathbf{q}(t)$ and the tangent $d\mathbf{q}^*(t,\tau)/dt \to d\mathbf{q}/dt$, the SD curve and its

tangent, respectively. A variation, $\mathbf{z}(t,\tau)=\mathbf{q}^*(t,\tau)-\mathbf{q}(t)$, which satisfies the previous two conditions as $\tau\to 0$, is called weak variation, and it means that the extremal curve $\mathbf{q}(t)$ is compared with curves that approximate $\mathbf{q}(t)$ in both slope as well as position. In the present problem, an extremal curve $\mathbf{q}(t)$ which minimizes the integral given in Eq. (4) with respect to all weak variations is called a weak minimum and as shown above satisfies the necessary weak Legendre condition.

The Legendre condition is still not sufficient to guarantee a minimum. To do so, we need to compare the extremal curve with all possible curves. These types of comparisons between an extremal curve with any other type of curves is the basis of the second-order variation strong condition of an extremal also known as the Weierstrass necessary condition.[26] The Weierstrass sufficient condition in the present problem is obtained if one ensures that the region of the PES containing the extremal curve under consideration (SD line) is covered by the type of field of extremal curves defined in Sec. II B. In other words, the extremal curve, SD line, can be embedded in the field of extremals, see below. With this consideration, the Weierstrass sufficient condition is formulated as follows:[26] we compare the values of the integral (4) evaluated on both the extremal curve, a SD line joining the points $\mathbf{q}_R$ and $\mathbf{q}(t)$, and an arbitrary curve $\mathcal{C}$ joining the same points in its neighborhood. The value of the integral (4) evaluated on this extremal curve is $J(\mathbf{q})$ according to the discussion of the preceding section. We denote by $\Delta V^{\mathcal{C}}_{R\to q}(\mathbf{q})$ the value of the integral (4) evaluated over the curve $\mathcal{C}$. By evaluating $J(\mathbf{q})$ as an integral along the path $\mathcal{C}$, as formulated in Eq. (20), the comparison of these values is now reduced to a comparison of the integrands alone. According to Sec. II B, the extremal curve, the SD line, is embedded in the field of extremals where the tangent of the extremals at each point of the region of the PES containing this extremal curve, $\mathbf{q}(t')$, and covered by this field is denoted by $d\mathbf{q}/dt'=\mathbf{g}[\mathbf{q}(t')]$. With these considerations, the difference between these values is

$$\begin{aligned}\Delta\left[\Delta V_{R\to q}\right]_{\mathcal{C}} &= \Delta V^{\mathcal{C}}_{R\to q}(\mathbf{q})-J(\mathbf{q})=\int_0^t\left[\sqrt{\mathbf{g}_{\mathcal{C}}^T\mathbf{g}_{\mathcal{C}}}\sqrt{(d\mathbf{q}_{\mathcal{C}}/dt')^T(d\mathbf{q}_{\mathcal{C}}/dt')}-\mathbf{g}_{\mathcal{C}}^T(d\mathbf{q}_{\mathcal{C}}/dt')\right]dt'\\ &=\int_0^t\left\{\left[1-\frac{\mathbf{g}_{\mathcal{C}}^T(d\mathbf{q}_{\mathcal{C}}/dt')}{\sqrt{\mathbf{g}_{\mathcal{C}}^T\mathbf{g}_{\mathcal{C}}}\sqrt{(d\mathbf{q}_{\mathcal{C}}/dt')^T(d\mathbf{q}_{\mathcal{C}}/dt')}}\right]\sqrt{\mathbf{g}_{\mathcal{C}}^T\mathbf{g}_{\mathcal{C}}}\sqrt{(d\mathbf{q}_{\mathcal{C}}/dt')^T(d\mathbf{q}_{\mathcal{C}}/dt')}\right\}dt'\\ &=\int_0^t\left\{\left[1-\frac{\mathbf{g}_{\mathcal{C}}^T(d\mathbf{q}_{\mathcal{C}}/dt')}{\sqrt{\mathbf{g}_{\mathcal{C}}^T\mathbf{g}_{\mathcal{C}}}\sqrt{(d\mathbf{q}_{\mathcal{C}}/dt')^T(d\mathbf{q}_{\mathcal{C}}/dt')}}\right]F(\mathbf{q}_{\mathcal{C}},d\mathbf{q}_{\mathcal{C}}/dt')\right\}dt'=\int_0^s\left[\sqrt{\mathbf{g}_{\mathcal{C}}^T\mathbf{g}_{\mathcal{C}}}-\mathbf{g}_{\mathcal{C}}^T(d\mathbf{q}_{\mathcal{C}}/ds')\right]ds',\end{aligned}\tag{24}$$

where the integration is taken along the curve $\mathcal{C}$, the gradient vector $\mathbf{g}_{\mathcal{C}}=\mathbf{g}(\mathbf{q}_{\mathcal{C}})$ and the vector $d\mathbf{q}_{\mathcal{C}}/dt'$ are the tangent vector of the field and the tangent vector of the curve $\mathcal{C}$ embedded in this field, respectively, and both tangents are evaluated at the point $\mathbf{q}_{\mathcal{C}}$, a point of the region of the PES covered by this field. To derive Eq. (24), Eqs. (4), (20), and (3) have been used. Equation (24) was first derived by Tachibana and Fukui.[9] The integrand of expression (24),

$$\begin{aligned}&E(\mathbf{q}_{\mathcal{C}},\mathbf{g}_{\mathcal{C}},d\mathbf{q}_{\mathcal{C}}/dt')\\ &\quad=\sqrt{\mathbf{g}_{\mathcal{C}}^T\mathbf{g}_{\mathcal{C}}}\sqrt{(d\mathbf{q}_{\mathcal{C}}/dt')^T(d\mathbf{q}_{\mathcal{C}}/dt')}-\mathbf{g}_{\mathcal{C}}^T(d\mathbf{q}_{\mathcal{C}}/dt')\\ &\quad=\left[1-\frac{\mathbf{g}_{\mathcal{C}}^T(d\mathbf{q}_{\mathcal{C}}/dt')}{\sqrt{\mathbf{g}_{\mathcal{C}}^T\mathbf{g}_{\mathcal{C}}}\sqrt{(d\mathbf{q}_{\mathcal{C}}/dt')^T(d\mathbf{q}_{\mathcal{C}}/dt')}}\right]F(\mathbf{q}_{\mathcal{C}},d\mathbf{q}_{\mathcal{C}}/dt'),\end{aligned}\tag{25}$$

which in this case is a function of the arguments $\mathbf{q}_{\mathcal{C}},\mathbf{g}_{\mathcal{C}}$ and $d\mathbf{q}_{\mathcal{C}}/dt'$, is known as Weierstrass E-function. Since for each point $\mathbf{q}_{\mathcal{C}}$ of the region of the PES covered by the field of extremals with tangent $\mathbf{g}_{\mathcal{C}}$ and for all possible values of the tangent vector $d\mathbf{q}_{\mathcal{C}}/dt'$, the Weierstrass E-function is nonnegative, $E(\mathbf{q}_{\mathcal{C}},\mathbf{g}_{\mathcal{C}},d\mathbf{q}_{\mathcal{C}}/dt')\geqslant 0$, then from the expression (24) we get $\Delta[\Delta V_{R\to p}]_{\mathcal{C}}\geqslant 0$ for all admissible curves $\mathcal{C}$ defined in the region of the PES covered by this field. This result means that $\Delta V^{\mathcal{C}}_{R\to q}(\mathbf{q})\geqslant J(\mathbf{q})$, and consequently the extremal curve, the SD line, connecting the points $\mathbf{q}_R$ and $\mathbf{q}(t)$, is actually a strong minimum. In particular, if we take all admissible curves $\mathcal{C}$ different from the SD curve, which means that $d\mathbf{q}_{\mathcal{C}}/dt'\neq\mathbf{g}_{\mathcal{C}}$, then we have a proper strong minimum since in this case $\Delta V^{\mathcal{C}}_{R\to q}(\mathbf{q})>J(\mathbf{q})$.

The Legendre conditions are related with the Weierstrass E-function through the expression

$$\begin{aligned}&E(\mathbf{q}_{\mathcal{C}},\mathbf{g}_{\mathcal{C}},d\mathbf{q}_{\mathcal{C}}/dt')\\ &\quad=\tfrac{1}{2}(d\mathbf{q}_{\mathcal{C}}/dt'-\mathbf{g}_{\mathcal{C}})^T\left[\boldsymbol{\nabla}_{d\mathbf{q}/dt}\,\boldsymbol{\nabla}^T_{d\mathbf{q}/dt}F\right]_{d\mathbf{q}/dt=\mathbf{g}^*_{\mathcal{C}}}(d\mathbf{q}_{\mathcal{C}}/dt'-\mathbf{g}_{\mathcal{C}}),\end{aligned}\tag{26}$$

where the matrix $\boldsymbol{\nabla}_{d\mathbf{q}/dt}\boldsymbol{\nabla}^T_{d\mathbf{q}/dt}F$ is that given in Eq. (13) and $\mathbf{g}^*_{\mathcal{C}}=\mathbf{g}_{\mathcal{C}}+\theta(d\mathbf{q}_{\mathcal{C}}/dt'-\mathbf{g}_{\mathcal{C}})$, with $0<\theta<1$. The proof of Eq. (26) is given in Appendix C. Since the matrix $[\boldsymbol{\nabla}_{d\mathbf{q}/dt}\boldsymbol{\nabla}^T_{d\mathbf{q}/dt}F]_{d\mathbf{q}/dt=\mathbf{g}^*_{\mathcal{C}}}$ is a projector with respect to the vector $\mathbf{g}^*_{\mathcal{C}}$, from Eq. (13) and (26) we see that, $E(\mathbf{q}_{\mathcal{C}},\mathbf{g}_{\mathcal{C}},d\mathbf{q}_{\mathcal{C}}/dt')>0$, if the vector $(d\mathbf{q}_{\mathcal{C}}/dt'-\mathbf{g}_{\mathcal{C}})$ is orthogonal to the vector $\mathbf{g}^*_{\mathcal{C}}$, otherwise $E(\mathbf{q}_{\mathcal{C}},\mathbf{g}_{\mathcal{C}},d\mathbf{q}_{\mathcal{C}}/dt')=0$. Finally, using Eq. (24)–(26), we obtain

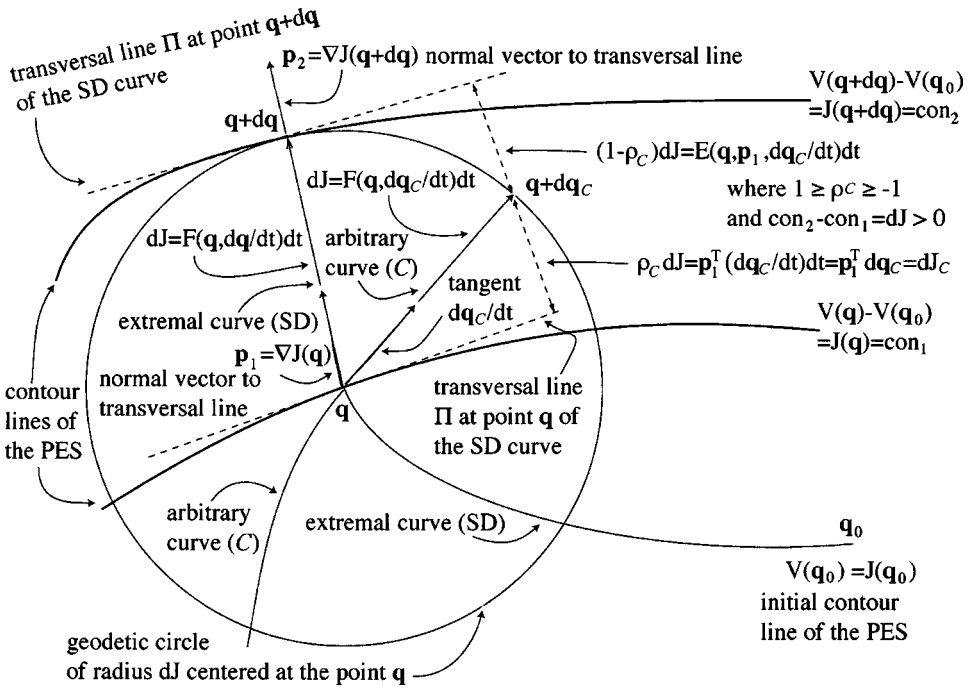

FIG. 1. The main scheme of the variational problem given in Eq. (4). See text for a detailed discussion.

$$\Delta[\Delta V_{R\to q}]_{\mathcal{C}} = \Delta V^{\mathcal{C}}_{R\to q}(\mathbf{q}) - J(\mathbf{q})$$
$$= \int_0^t E(\mathbf{q}_C, \mathbf{g}_C, d\mathbf{q}_C/dt')dt'$$
$$= \frac{1}{2}\int_0^t \left\{(d\mathbf{q}_C/dt' - \mathbf{g}_C)^T[\nabla_{d\mathbf{q}/dt}\nabla^T_{d\mathbf{q}/dt}F]_{d\mathbf{q}/dt=\mathbf{g}^*_C} \times (d\mathbf{q}_C/dt' - \mathbf{g}_C)\right\}dt'. \quad (27)$$

Then the Weierstrass sufficient condition for an extremal curve to be minimal can be formulated, as Eq. (27), to be positive with the possibility to embed the extremal curve joining the two points, $\mathbf{q}(0)$ and $\mathbf{q}(t)$, in the field of extremals. Equation (27) will be used in the following section.

The basic point in the theory of sufficient conditions just exposed and used above is the possibility of embedding the extremal curve under consideration in a field. If the endpoints of the extremal curve are not too far, i.e., small t parameter, then it can always be embedded in a field. We remember that a field is defined by the set of extremal curves cutting the surface Π transversally.[6] The set of extremal curves emerging from a central point will constitute a field up to its envelope or conjugate points to the central point. The first point at which neighboring extremal curves all starting at the same central point intersect is called conjugate point with respect to the central point. In the envelope or conjugate points the set of extremals does not cut Π transversally. In the present problem, the SD curves, emerging from the point $\mathbf{q}_R$, which is a stationary point character minimum, intersect for the first time at the stationary points of the PES character saddle points and maxima. These types of stationary point are the conjugate points $\mathbf{q}_{\mathrm{CP}}$ with respect to central point $\mathbf{q}_R$. The above discussion about second-order sufficient conditions is now reduced to the consideration that in the region of the PES containing the SD curve, the extremal curve $\mathbf{q}(t')$, emerging from the point $\mathbf{q}_R$, is a minimum if in the region $0<t'<t$, where $\mathbf{q}_R=\mathbf{q}(0)$ and $\mathbf{q}(t)=\mathbf{q}$, a conjugate point of $\mathbf{q}_R$ does not exist, and Eq. (27) is positive definite in this interval of integration. If the interval of integration $0<t'<t$ contains $t_{\mathrm{CP}}, 0<t_{\mathrm{CP}}<t$, where $\mathbf{q}(t_{\mathrm{CP}})=\mathbf{q}_{\mathrm{CP}}$ is a conjugate point with respect to the central point $\mathbf{q}_R$, then the extremal curve $\mathbf{q}(t')$ is not a minimum provided that the Weierstrass E-function defined in Eq. (26) is positive definite, $E(\mathbf{q}_C, \mathbf{g}_C, d\mathbf{q}_C/dt') \geqslant 0$, along the extremal curve.[26] The conjugate point $\mathbf{q}_{\mathrm{CP}}$ can be a stationary point character saddle point or maximum in the PES. However, for saddle points with one negative eigenvalue, known as first-order saddle points (FOSPs), only one SD curve emerging form the central point $\mathbf{q}_R$ arrives at this type of stationary points. As a consequence, the first-order saddle points are not conjugate points with respect to the central point $\mathbf{q}_R$, a stationary point with character minimum in the PES. This result is proved from a rigorous mathematical point of view in Appendix D using the Jacobi equation associated to the variational problem under consideration.[26]

Finally in Fig. 1 we show the basic scheme of all the concepts just exposed for the present variational problem. The explanation of this figure is the following. A SD curve starting at the point $\mathbf{q}_0$ of the PES transverses the contour lines $V(\mathbf{q})-V(\mathbf{q}_0)=\mathrm{const}=\mathrm{con}_1$ and $V(\mathbf{q}+d\mathbf{q})-V(\mathbf{q}_0)=\mathrm{const}=\mathrm{con}_2$ at the points $\mathbf{q}$ and $\mathbf{q}+d\mathbf{q}$, respectively. The normal vector of the transversal line, Π, at the point $\mathbf{q}$ is $\mathbf{p}_1=\nabla_{\mathbf{q}}J(\mathbf{q})=\nabla_{\mathbf{q}}V(\mathbf{q})=\mathbf{g}_1$, whereas the normal vector of the transversal line, Π, at the point $\mathbf{q}+d\mathbf{q}$ is $\mathbf{p}_2=\nabla_{\mathbf{q}}J(\mathbf{q}+d\mathbf{q})=\nabla_{\mathbf{q}}V(\mathbf{q}+d\mathbf{q})=\mathbf{g}_2$, J being the solution of the eiconal equation (16). These transversal lines are tangent to the contour lines. The difference between the contour lines con_1 and con_2 is denoted by dJ, which is the infinitesimal geodetic distance evaluated on the SD curve using Eq. (10), between the points $\mathbf{q}$ and $\mathbf{q}+d\mathbf{q}$. The tangent vector of the SD curve at the point $\mathbf{q}$ is $d\mathbf{q}/dt$, and $d\mathbf{q}_C/dt$ denotes the tangent vector at the point $\mathbf{q}$ of another arbitrary curve $\mathcal{C}$ passing through this point.

The geodetic distance dJ is taken as a radius of a circle centered at point $\mathbf{q}$, this circle is known as the geodetic circle. In this circle the equality, $dJ=F(\mathbf{q},d\mathbf{q}/dt)dt=[\mathbf{p}_1^T\mathbf{p}_1]^{1/2}[(d\mathbf{q}/dt)^T(d\mathbf{q}/dt)]^{1/2}dt=F(\mathbf{q},d\mathbf{q}_\mathcal{C}/dt)dt=[\mathbf{p}_1^T\mathbf{p}_1]^{1/2}\times[(d\mathbf{q}_\mathcal{C}/dt)^T(d\mathbf{q}_\mathcal{C}/dt)]^{1/2}dt$, is satisfied. The SD path connecting the points $\mathbf{q}$ and $\mathbf{q}+d\mathbf{q}$ is one of the radial curves of this circle. Notice that $dJ>0$, because $dt>0$ and $F(\mathbf{q},d\mathbf{q}/dt)$ defined in expression (4) is positive definite and due to Eq. (21), the value of the geodetic distance is $dJ=\mathbf{p}_1^T\mathbf{p}_1dt$. Furthermore, comparing the normal vector of the Π line at the point $\mathbf{q}+d\mathbf{q}$, we see that it coincides with the radius vector of the geodetic circle at $\mathbf{q}+d\mathbf{q}$, consequently both the contour line con_2 and the geodetic circle are tangential to each other at that point. The above construction can be extended to all geodetic circles of radius dJ with centers on the contour line con_1. As a consequence of these results we say that the contour line $\text{con}_2=J(\mathbf{q}+d\mathbf{q})=\text{con}_1+dJ$ with $dJ>0, J(\mathbf{q}+d\mathbf{q})$ being a solution of the Hamilton–Jacobi equation (16), is an envelope line of the all possible geodetic circles of radius dJ centered on the contour line con_1.

In fact the above results only show that the geodetic circles are tangential to the contour line con_2. Now we need to prove that the line con_2 is an envelope line of these circles, in others words, the geodetic circles lie entirely on one side of the contour line con_2 apart from the points of tangential contact with it. We will show that this construction gives us a geometrical meaning to both the Weierstrass E-function, Eq. (25), and the Weierstrass necessary condition, Eq. (24).

To prove the above question, we consider an arbitrary curve $\mathcal{C}$ connecting the points $\mathbf{q}$ and $\mathbf{q}+d\mathbf{q}_\mathcal{C}$ such that $F(\mathbf{q},d\mathbf{q}_\mathcal{C}/dt)dt=dJ$. As a consequence the point $\mathbf{q}+d\mathbf{q}_\mathcal{C}$ lies on the geodetic circle of radius dJ, as shown in Fig. 1, and now we need to prove that this point lies on the same side of the contour line con_2 as does the point $\mathbf{q}$. We apply the differential form of the Hilbert's invariant integral, given in Eq. (19), to the arbitrary curve $\mathcal{C}$ joining the points $\mathbf{q}$ and $\mathbf{q}+d\mathbf{q}_\mathcal{C}$, resulting in $dJ_\mathcal{C}=\mathbf{p}_1^Td\mathbf{q}_\mathcal{C}=\mathbf{p}_1^T(d\mathbf{q}_\mathcal{C}/dt)dt=\mathbf{p}_1^T(d\mathbf{q}_\mathcal{C}/dt)\times\{[\mathbf{p}_1^T\mathbf{p}_1]^{1/2}[(d\mathbf{q}_\mathcal{C}/dt)^T(d\mathbf{q}_\mathcal{C}/dt)]^{1/2}\}^{-1}F(\mathbf{q},d\mathbf{q}_\mathcal{C}/dt)dt=\rho_\mathcal{C}F(\mathbf{q},d\mathbf{q}_\mathcal{C}/dt)dt=\rho_\mathcal{C}dJ$. Clearly the values of $\rho_\mathcal{C}$ are in the domain $-1\leqslant\rho_\mathcal{C}\leqslant 1$. Taking into account the values of $\rho_\mathcal{C}$ and that $\text{con}_2-\text{con}_1=dJ>0$, the point $\mathbf{q}+d\mathbf{q}_\mathcal{C}$ lies on the contour line $\text{con}_1+dJ_\mathcal{C}=\text{con}_1+\rho_\mathcal{C}dJ$, not shown in the figure, such that $\text{con}_2\geqslant\text{con}_1+\rho_\mathcal{C}dJ$. Consequently the point $\mathbf{q}+d\mathbf{q}_\mathcal{C}$ lies on the same side of the contour line con_2 as does the point $\mathbf{q}$.

Finally, from Eq. (25) we see that the Weierstrass E-function takes the form $dJ-dJ_\mathcal{C}=F(\mathbf{q},d\mathbf{q}_\mathcal{C}/dt)dt-\rho_\mathcal{C}F(\mathbf{q},d\mathbf{q}_\mathcal{C}/dt)dt=(1-\rho_\mathcal{C})dJ=E(\mathbf{q},\mathbf{p}_1,d\mathbf{q}_\mathcal{C}/dt)dt$, which is non-negative everywhere as proved in Sec. II C, specifically after Eq. (24). These results show that for the variational problem under consideration, defined in Eq. (4), where the functional $F(\mathbf{q},d\mathbf{q}/dt)$ is non-negative, the contour line con_2 is an envelope line of the geodetic circles centered on the contour line con_1.[26] The above construction of solutions as envelopes of the present variational problem is exactly the same as that used in the Fermat–Huyghens principle for the construction of wave fronts in the propagation of light,[26] as is already explained in the Sec. II B.

III. THE WEIERSTRASS SUFFICIENT CONDITION AS A TOOL TO LOCATE THE IRC CURVE

A. Background of the algorithm

The above results about the variational nature of the SD curve open the possibility to use a variety of algorithms to integrate this type of curves and specifically the IRC curve line. We present in this section a way to deal with the calculation of the IRC line. The IRC curve is a SD curve line in mass weighted coordinates connecting two minima in the PES, namely, $\mathbf{q}_R$ and $\mathbf{q}_P$, through a first-order saddle point $\mathbf{q}_{\text{FOSP}}$.[11] Taking into account both the definition of IRC and the concept of centered field discussed in Sec. II, the IRC path can be seen as a SD curve composed by two SD lines, each one being an extremal curve of one of the fields of extremals centered or emerging from the minima $\mathbf{q}_R$ and $\mathbf{q}_P$, and both ending in a common point $\mathbf{q}_{\text{FOSP}}$. The $\mathbf{q}_{\text{FOSP}}$ point is not a conjugate point either for the SD line emerging from the $\mathbf{q}_R$ point or for the SD line emerging from the $\mathbf{q}_P$ point. These two centered fields are identical, because for each field the corresponding $\mathbf{p}$ vector of this field is a function of the corresponding geodetic distance $J,\mathbf{p}=\nabla_\mathbf{q}J$, as explained in the preceding section, and this function J should satisfy the same Hamilton–Jacobi equation (16). As a consequence for both the centered fields the vector of these fields is $\mathbf{p}=\mathbf{g}(\mathbf{q})$. The geodetic distance from the central point $\mathbf{q}_R$ ($\mathbf{q}_P$) to the variable end point $\mathbf{q}_{\text{FOSP}}$ is denoted by $J_R(\mathbf{q}_{\text{FOSP}})$ [$J_P(\mathbf{q}_{\text{FOSP}})$].

We propose to use the Weierstrass sufficient condition, discussed in the preceding section, as a way to obtain the IRC curve. Since the IRC curve is composed by two extremal curves, SD curves, each one being an extremal belonging to one of the centered fields and for both fields the field vector is $\mathbf{p}=\mathbf{g}(\mathbf{q})$, then the Weierstrass sufficient condition for the IRC curve given in Eq. (27) becomes

$$\begin{aligned}\Delta[\Delta V_{R\to P}]_\mathcal{C}&=\Delta[\Delta V_{R\to q_{\text{FOSP}}}]_\mathcal{C}-\Delta[\Delta V_{P\to q_{\text{FOSP}}}]_\mathcal{C}\\&=[\Delta V^\mathcal{C}_{R\to q_{\text{FOSP}}}-J_R(\mathbf{q}_{\text{FOSP}})]-[\Delta V^\mathcal{C}_{P\to q_{\text{FOSP}}}-J_P(\mathbf{q}_{\text{FOSP}})]=\int_0^t E(\mathbf{q}_\mathcal{C},\mathbf{g}_\mathcal{C},d\mathbf{q}_\mathcal{C}/dt')dt'-\int_{t_f}^t E(\mathbf{q}_\mathcal{C},\mathbf{g}_\mathcal{C},d\mathbf{q}_\mathcal{C}/dt')dt'\\&=\int_0^{t_f}E(\mathbf{q}_\mathcal{C},\mathbf{g}_\mathcal{C},d\mathbf{q}_\mathcal{C}/dt')dt'=\int_0^{t_f}\left[\sqrt{\mathbf{g}_\mathcal{C}^T\mathbf{g}_\mathcal{C}}\sqrt{(d\mathbf{q}_\mathcal{C}/dt')^T(d\mathbf{q}_\mathcal{C}/dt')}-\mathbf{g}_\mathcal{C}^T(d\mathbf{q}_\mathcal{C}/dt')\right]dt',\end{aligned}\tag{28}$$

where t_f is the value of the independent variable t' in the origin of the field centered in $\mathbf{q}_P$, in other words, $\mathbf{q}_P=\mathbf{q}(t_f)$. From Eq. (28) it is clear that $\Delta[\Delta V_{R\to P}]_{\mathcal{C}}\geqslant 0$. According to the discussion of preceding section, the sufficiency condition for the IRC path is achieved since it is a SD curve, $\mathbf{q}(t')$, connecting the points $\mathbf{q}_R=\mathbf{q}(0)$ and $\mathbf{q}_P=\mathbf{q}(t_f)$ of the PES if in the interval $0<t'<t_f$, a conjugate point with respect to both points $\mathbf{q}_R$ and $\mathbf{q}_P$ does not exist. This shows clearly that the IRC is an extremal curve of the functional given in Eq. (4) with character strong minimum in a neighborhood.

Minimizing the $\Delta[\Delta V_{R\to P}]_{\mathcal{C}}$ function given in Eq. (28) with respect to the parameters that characterize a given arbitrary $\mathcal{C}$ curve connecting the fixed end points $\mathbf{q}_R$ and $\mathbf{q}_P$ of the PES, iteratively, we will find the near SD curve to this $\mathcal{C}$ curve. The curve $\mathcal{C}$ is assumed to satisfy the differential equation $d\mathbf{q}_{\mathcal{C}}(t')/dt'|_{t'=t}=\mathbf{f}[\mathbf{q}_{\mathcal{C}}(t)]$, where $0\leqslant t\leqslant t_f$ and $\mathbf{f}$ is a vector of a field vector. This curve $\mathcal{C}$ is represented as a polygonal line or a chain line defined in the region of the PES under consideration and connecting the points $\mathbf{q}_R$ and $\mathbf{q}_P$ and the vector $\mathbf{f}=\Delta\mathbf{q}_{\mathcal{C}},\Delta\mathbf{q}_{\mathcal{C}}$ being the difference vector between two consecutive vertex points of the chain. The minimization of the $\Delta[\Delta V_{R\to P}]_{\mathcal{C}}$ function has the effect of transforming the curve $\mathcal{C}$ into another curve such that the field vector $\mathbf{f}$ at each point of this new curve coincides as much as possible with the field vector $\mathbf{g}$, which is the field vector of the field of extremals of the functional given in Eq. (4). This is the basis of the proposed algorithm to find the SD curve connecting the stationary points character minimum of the PES, $\mathbf{q}_R$ and $\mathbf{q}_P$. The resulting SD curve is the IRC path if conjugate points do not exist in this curve, in others words, if the SD curve does not contain stationary points character saddle point with more that one negative eigenvalue, as shown in Appendix D.

The basis of the algebraic process of the proposed algorithm is the following: first we approximate the integral (28) by using a set of $n+1$ points of an arbitrary curve $\mathcal{C}$,

$$\begin{aligned}\Delta[\Delta V_{R\to P}]_{\mathcal{C}} &= \int_0^{t_f} E(\mathbf{q}_{\mathcal{C}},\mathbf{g}_{\mathcal{C}},d\mathbf{q}_{\mathcal{C}}/dt')dt' \\ &= \int_0^{t_f}\Big[\sqrt{\mathbf{g}_{\mathcal{C}}^T\mathbf{g}_{\mathcal{C}}}\sqrt{(d\mathbf{q}_{\mathcal{C}}/dt')^T(d\mathbf{q}_{\mathcal{C}}/dt')} \\ &\quad -\mathbf{g}_{\mathcal{C}}^T(d\mathbf{q}_{\mathcal{C}}/dt')\Big]dt' \\ &\approx \sum_{i=1}^{n-1}\left(\sqrt{\mathbf{g}_{\mathcal{C}i}^T\mathbf{g}_{\mathcal{C}i}}\sqrt{\Delta\mathbf{q}_{\mathcal{C}i}^T\Delta\mathbf{q}_{\mathcal{C}i}}-\mathbf{g}_{\mathcal{C}i}^T\Delta\mathbf{q}_{\mathcal{C}i}\right) \\ &= \sum_{i=1}^{n-1} E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i}) \\ &= \{\Delta[\Delta V_{R\to P}]_{\mathcal{C}}\}_{\text{approx}}, \end{aligned} \tag{29}$$

where $\{\mathbf{q}_{\mathcal{C}i}\}_{i=0}^{n}$ denotes a set of $n+1$ position vectors of the arbitrary $\mathcal{C}$ curve, $\Delta\mathbf{q}_{\mathcal{C}i}=\mathbf{q}_{\mathcal{C}i+1}-\mathbf{q}_{\mathcal{C}i}$, and $\mathbf{g}_{\mathcal{C}i}=\mathbf{g}(\mathbf{q}_{\mathcal{C}i})$ is the gradient vector evaluated a the point $\mathbf{q}_{\mathcal{C}i}$. Notice that this set of selected position vectors is the point vertices of the chain that represents the curve $\mathcal{C}$. The point vectors $\mathbf{q}_{\mathcal{C}0}=\mathbf{q}_R$ and $\mathbf{q}_{\mathcal{C}n}=\mathbf{q}_P$ do not appear in the evaluation of $\{\Delta[\Delta V_{R\to P}]_{\mathcal{C}}\}_{\text{approx}}$ function, because they are the fixed initial and final points of this curve, respectively, and their gradient vectors are zero, $\mathbf{g}_R=\mathbf{g}(\mathbf{q}_{\mathcal{C}0})=\mathbf{g}_P=\mathbf{g}(\mathbf{q}_{\mathcal{C}n})=\mathbf{0}$. Now, we expand the function $\{\Delta[\Delta V_{R\to P}]_{\mathcal{C}}\}_{\text{approx}}$ up to first order in a Taylor series with respect to the parameters that characterize the arbitrary curve $\mathcal{C}$,

$$\begin{aligned}&\{\Delta[\Delta V_{R\to P}]_{\mathcal{C}'}\}_{\text{approx}} \\ &\quad=\{\Delta[\Delta V_{R\to P}]_{\mathcal{C}}\}_{\text{approx}} \\ &\qquad+\sum_{i=1}^{n-1}(\mathbf{q}_{\mathcal{C}'i}-\mathbf{q}_{\mathcal{C}i})^T\Big[\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\Big|_{\mathcal{C}}\Big],\end{aligned} \tag{30}$$

where $\mathcal{C}'$ is other arbitrary curve and $\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})$ is the Weierstrass E-gradient vector evaluated in the position vectors that characterize the curve $\mathcal{C}$. The explicit form of the Weierstrass E-gradient vector is

$$\begin{aligned}&\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i}) \\ &\quad=\sqrt{\Delta\mathbf{q}_{\mathcal{C}i}^T\Delta\mathbf{q}_{\mathcal{C}i}}\mathbf{H}_{\mathcal{C}_i}\left(\frac{\mathbf{g}_{\mathcal{C}i}}{\sqrt{\mathbf{g}_{\mathcal{C}i}^T\mathbf{g}_{\mathcal{C}i}}}-\frac{\Delta\mathbf{q}_{\mathcal{C}i}}{\sqrt{\Delta\mathbf{q}_{\mathcal{C}i}^T\Delta\mathbf{q}_{\mathcal{C}i}}}\right) \\ &\qquad-\left[\sqrt{\mathbf{g}_{\mathcal{C}i-1}^T\mathbf{g}_{\mathcal{C}i-1}}\left(\frac{\mathbf{g}_{\mathcal{C}i-1}}{\sqrt{\mathbf{g}_{\mathcal{C}i-1}^T\mathbf{g}_{\mathcal{C}i-1}}}-\frac{\Delta\mathbf{q}_{\mathcal{C}i-1}}{\sqrt{\Delta\mathbf{q}_{\mathcal{C}i-1}^T\Delta\mathbf{q}_{\mathcal{C}i-1}}}\right)\right. \\ &\qquad\left.-\sqrt{\mathbf{g}_{\mathcal{C}i}^T\mathbf{g}_{\mathcal{C}i}}\left(\frac{\mathbf{g}_{\mathcal{C}i}}{\sqrt{\mathbf{g}_{\mathcal{C}i}^T\mathbf{g}_{\mathcal{C}i}}}-\frac{\Delta\mathbf{q}_{\mathcal{C}i}}{\sqrt{\Delta\mathbf{q}_{\mathcal{C}i}^T\Delta\mathbf{q}_{\mathcal{C}i}}}\right)\right],\end{aligned} \tag{31}$$

where the matrix $\mathbf{H}_{\mathcal{C}i}=\mathbf{H}(\mathbf{q}_{\mathcal{C}i})$ is the Hessian matrix at the point $\mathbf{q}_{\mathcal{C}i}$. The first term of the right-hand side of Eq. (31) involves a Hessian matrix, however, this term can be simplified because the curve $\mathcal{C}$ is embedded in a gradient vector field, the field of extremal curves corresponding to the variational problem given in the expression (4). Taking into account this consideration, the term $\mathbf{H}_{\mathcal{C}i}\Delta\mathbf{q}_{\mathcal{C}i}$ is transformed into $\mathbf{H}_{\mathcal{C}i}\Delta\mathbf{q}_{\mathcal{C}i}=\mathbf{H}_{\mathcal{C}i}(\mathbf{q}_{\mathcal{C}i+1}-\mathbf{q}_{\mathcal{C}i})\approx\Delta\mathbf{g}_{\mathcal{C}i}=\mathbf{g}_{\mathcal{C}i+1}-\mathbf{g}_{\mathcal{C}i}$, where the equality is achieved when the point $\mathbf{q}_{\mathcal{C}i+1}$ of the curve $\mathcal{C}$ is within the quadratic expansion of the PES centered in $\mathbf{q}_{\mathcal{C}i}$. The other term, $\mathbf{H}_{\mathcal{C}i}\mathbf{g}_{\mathcal{C}i}$, is the gradient variation vector along the SD curve running through the point $\mathbf{q}_{\mathcal{C}i}$, see Eq. (22). As a consequence, $\mathbf{H}_{\mathcal{C}i}\mathbf{g}_{\mathcal{C}i}\approx(\mathbf{g}_i^*-\mathbf{g}_{\mathcal{C}i})/\tau_i$, $\mathbf{g}_i^*$ being the gradient vector of a point close to the point $\mathbf{q}_{\mathcal{C}i}$ and situated on the SD curve that links this point and the $\mathbf{q}_{\mathcal{C}i}$ point and τ_i the distance between these two points. With these two approximations Eq. (31) is transformed into the expression

$$\begin{aligned}&\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i}) \\ &\quad\approx\frac{\sqrt{\Delta\mathbf{q}_{\mathcal{C}i}^T\Delta\mathbf{q}_{\mathcal{C}i}}}{\sqrt{\mathbf{g}_{\mathcal{C}i}^T\mathbf{g}_{\mathcal{C}i}}}\frac{(\mathbf{g}_i^*-\mathbf{g}_{\mathcal{C}i})}{\tau_i}-\Delta\mathbf{g}_{\mathcal{C}i} \\ &\qquad-\left[\sqrt{\mathbf{g}_{\mathcal{C}i-1}^T\mathbf{g}_{\mathcal{C}i-1}}\left(\frac{\mathbf{g}_{\mathcal{C}i-1}}{\sqrt{\mathbf{g}_{\mathcal{C}i-1}^T\mathbf{g}_{\mathcal{C}i-1}}}-\frac{\Delta\mathbf{q}_{\mathcal{C}i-1}}{\sqrt{\Delta\mathbf{q}_{\mathcal{C}i-1}^T\Delta\mathbf{q}_{\mathcal{C}i-1}}}\right)\right. \\ &\qquad\left.-\sqrt{\mathbf{g}_{\mathcal{C}i}^T\mathbf{g}_{\mathcal{C}i}}\left(\frac{\mathbf{g}_{\mathcal{C}i}}{\sqrt{\mathbf{g}_{\mathcal{C}i}^T\mathbf{g}_{\mathcal{C}i}}}-\frac{\Delta\mathbf{q}_{\mathcal{C}i}}{\sqrt{\Delta\mathbf{q}_{\mathcal{C}i}^T\Delta\mathbf{q}_{\mathcal{C}i}}}\right)\right].\end{aligned} \tag{32}$$

Notice that in Eq. (32) only gradient and position vectors are involved. Either Eq. (31) or Eq. (32) is the basic expressions for the proposed algorithm. Equation (32) should be used for large molecular systems.

Finally we have to impose the sufficiency conditions on the algorithm. These sufficiency conditions consist in avoiding the existence of higher order saddle points and maxima in the region of the PES where the search to locate the IRC path is focused. Since these types of stationary points possess higher potential energy with respect to first-order saddle points, during the location process the condition of lower energy at each step is imposed. This restriction is imposed by assuring that at each point vertex of the new $\mathcal{C}'$ curve the corresponding value of the potential energy is lower than or equal to the corresponding point vertex of the previous $\mathcal{C}$ curve.

B. Algorithm description

The minimization scheme of the function $\{\Delta[\Delta V_{R\to P}]_{\mathcal{C}}\}_{\text{approx}}$ is carried out by using a Newton–Raphson method solved in a Krylov subspace and its complementary subspace. This method has been employed by Brooks *et al.*[28,29] for both finding minima and locating the IRC curve in the PES. However, there is an important difference with respect to the algorithm proposed by these authors, namely, their objective function is different from that used in the present algorithm which is $\{\Delta[\Delta V_{R\to P}]_{\mathcal{C}}\}_{\text{approx}}$ defined in Eq. (29). We recall that this function is related through the calculus of variations with the exact definition of the SD path given in Eq. (1). This function and its derivatives with respect to the position coordinates, given in the expressions either (31) or (32), are well defined. In addition, using this function and the corresponding derivatives we avoid complicated iterative numerical procedures as those that appear in the algorithm described by the above authors.[29] The grounds and basic equations of the present method are explained in Appendix E. Now we outline the algorithm.

At the initial iteration, $\mu=1$, a guess curve $\mathcal{C}_0$ is defined by a set of $n+1$ point vectors. Normally, this $\mathcal{C}_0$ curve is a straight line. The vectors $\mathbf{q}_0$ and $\mathbf{q}_n$ correspond to the stationary points character minima in the PES related with the geometry structure associated with the reactants and products, respectively. These two vectors are fixed during all the optimization processes. The rest of $n-1$ points, $\{\mathbf{q}_{\mathcal{C}_0 i}\}_{i=1}^{n-1}$, correspond to the vertices of the chain representation of the curve $\mathcal{C}_0$ and are selected in such a way that they are equidistant. The Weierstrass E-gradient vector, $\boldsymbol{\nabla}_{\mathbf{q}_{\mathcal{C}i}} E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i}, \mathbf{g}_{\mathcal{C}i}, \Delta\mathbf{q}_{\mathcal{C}i})|_{\mathcal{C}=\mathcal{C}_0}$, for each point vertex, $i=1,\ldots,n-1$, is computed by using either Eq. (31) or Eq. (32). Taking these gradient vectors as direction vectors, a new set of $n-1$ point vertex is computed through the equation

$$\mathbf{q}_{\mathcal{C}_1 i} = \mathbf{q}_{\mathcal{C}_0 i} + \eta_i \left[\boldsymbol{\nabla}_{\mathbf{q}_{\mathcal{C}i}} E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i}, \mathbf{g}_{\mathcal{C}i}, \Delta\mathbf{q}_{\mathcal{C}i})|_{\mathcal{C}=\mathcal{C}_0}\right] \quad \forall\ i, i=1,\ldots,n-1, \tag{33}$$

where the vector $\mathbf{q}_{\mathcal{C}_1 i}$ corresponds to the new position vector of the vertex i of the new curve $\mathcal{C}_1$, and the scale factor η_i is selected in such a way that $V(\mathbf{q}_{\mathcal{C}_1 i}) < V(\mathbf{q}_{\mathcal{C}_0 i})$. After the evaluation of all new vertex points a reparametrization of the new curve $\mathcal{C}_1$ may be necessary to ensure that the vertex points do not cluster. A very simple scheme has been adopted here: when the length of two consecutive segments of this new curve, $\Delta\mathbf{q}_{\mathcal{C}_1 i}$ and $\Delta\mathbf{q}_{\mathcal{C}_1 i+1}$, have a ratio larger than a given threshold, say 0.7, the central point $\mathbf{q}_{\mathcal{C}_1 i+1}$ is moved along its tangent to center it. Finally, the Weierstrass E-gradient vector $\boldsymbol{\nabla}_{\mathbf{q}_{\mathcal{C}i}} E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i}, \mathbf{g}_{\mathcal{C}i}, \Delta\mathbf{q}_{\mathcal{C}i})|_{\mathcal{C}=\mathcal{C}_1}$ for each vertex point, $i=1,\ldots,n-1$, of the new curve $\mathcal{C}_1$ is computed. If the convergence criteria is not satisfied for each vertex point, then the rectangular matrices, $\mathbf{R}_i^{(1)}$ and $\mathbf{G}_i^{(1)}$ for $i=1,\ldots,n-1$, are built and stored according to the expressions (E2) and (E7), respectively, and iteration *2* begins, otherwise the converged curve $\mathcal{C}_1$ is the chain representation of the IRC path between the points $\mathbf{q}_R$ and $\mathbf{q}_P$.

At the μ^{th} iteration, for $\mu>1$, the Newton–Raphson method described in Appendix E is applied. In this case and for each vertex point i, we have, the position vector $\mathbf{q}_{\mathcal{C}_{\mu-1} i}$, the Weierstrass E-gradient vector $\boldsymbol{\nabla}_{\mathbf{q}_{\mathcal{C}i}} E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i}, \mathbf{g}_{\mathcal{C}i}, \Delta\mathbf{q}_{\mathcal{C}i})|_{\mathcal{C}=\mathcal{C}_{\mu-1}}$, and the rectangular matrices $\mathbf{R}_i^{(\mu-1)}$ and $\mathbf{G}_i^{(\mu-1)}$. The set of equations (E11), (E5), and (E12) is solved and the new position vector $\mathbf{q}_{\mathcal{C}_\mu i}$ of the new curve $\mathcal{C}_\mu$ is then computed by a slight modification of Eq. (E13),

$$\mathbf{q}_{\mathcal{C}_\mu i} = \mathbf{q}_{\mathcal{C}_{\mu-1} i} + \eta_i \left[\mathbf{A}_i^{(\mu-1)}(\mathbf{q}_{\mathcal{C}_\mu i} - \mathbf{q}_{\mathcal{C}_{\mu-1} i}) + \mathbf{B}_i^{(\mu-1)}(\mathbf{q}_{\mathcal{C}_\mu i} - \mathbf{q}_{\mathcal{C}_{\mu-1} i})\right], \tag{34}$$

where the factor η_i plays the same role as explained in the iteration $\mu=1$. After the evaluation of all new vertex points, a reparametrization of the new curve $\mathcal{C}_\mu$ may be necessary to ensure that vertex points do not cluster and this is done by using the same procedure as reported in the iteration $\mu=1$. The set of Weierstrass E-gradient vectors, $\boldsymbol{\nabla}_{\mathbf{q}_{\mathcal{C}i}} E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i}, \mathbf{g}_{\mathcal{C}i}, \Delta\mathbf{q}_{\mathcal{C}i})|_{\mathcal{C}=\mathcal{C}_\mu}$, for $i=1,\ldots,n-1$, of the new curve $\mathcal{C}_\mu$ is computed. If the convergence criteria is not satisfied for each vertex point then we update and store the new rectangular matrices, $\mathbf{R}_i^{(\mu)}$ and $\mathbf{G}_i^{(\mu)}$ for $i=1,\ldots,n-1$, and the new iteration $(\mu+1)^{\text{th}}$ begins, otherwise the converged curve $\mathcal{C}_\mu$ is the chain representation of the IRC path between the points $\mathbf{q}_R$ and $\mathbf{q}_P$.

To introduce stability in this minimization algorithm just described, in the evaluation of the Weierstrass E-gradient vector, $\boldsymbol{\nabla}_{\mathbf{q}_{\mathcal{C}i}} E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i}, \mathbf{g}_{\mathcal{C}i}, \Delta\mathbf{q}_{\mathcal{C}i})|_{\mathcal{C}=\mathcal{C}_\mu}$, using either Eq. (31) or Eq. (32), the current gradient vector $\mathbf{g}_{\mathcal{C}_\mu i}$ of the point vortex $\mathbf{q}_{\mathcal{C}_\mu i}$ is replaced by the vector $(\mathbf{g}_{\mathcal{C}_\mu i+1}+\mathbf{g}_{\mathcal{C}_\mu i})/2$, which is the average gradient vector of the segment vector $\Delta\mathbf{q}_{\mathcal{C}_\mu i}=\mathbf{q}_{\mathcal{C}_\mu i+1} - \mathbf{q}_{\mathcal{C}_\mu i}$. In addition, if the angle between the resulting averaged gradient vector $\mathbf{g}_{\mathcal{C}_\mu i}$ and the vector $\Delta\mathbf{q}_{\mathcal{C}_\mu i}$ is outside the range $[\pi/2, -\pi/2]$, then the sign of $\Delta\mathbf{q}_{\mathcal{C}_\mu i}$ vector has to be changed accordingly.

In the present implementation of the algorithm, the Weierstrass E-Hessian matrix, $\boldsymbol{\nabla}_{\mathbf{q}_{\mathcal{C}i}} \boldsymbol{\nabla}_{\mathbf{q}_{\mathcal{C}i}}^T E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i}, \mathbf{g}_{\mathcal{C}i}, \Delta\mathbf{q}_{\mathcal{C}i})|_{\mathcal{C}=\mathcal{C}_\mu}$, is taken as the unit matrix.

C. Locating the IRC curve on a symmetric potential energy surface

The above proposed integration technique has been applied to find the IRC curve of the surface equation, $V(x,y) = 2(x^2-2)^2+[(x-y)^2-1]^2+4(1-x^2-y^2)^2+[(x+y)^2-1]^2$, which is shown in Fig. 2. The gray arrows are the gradient vectors of the field. As explained in the previous sections,

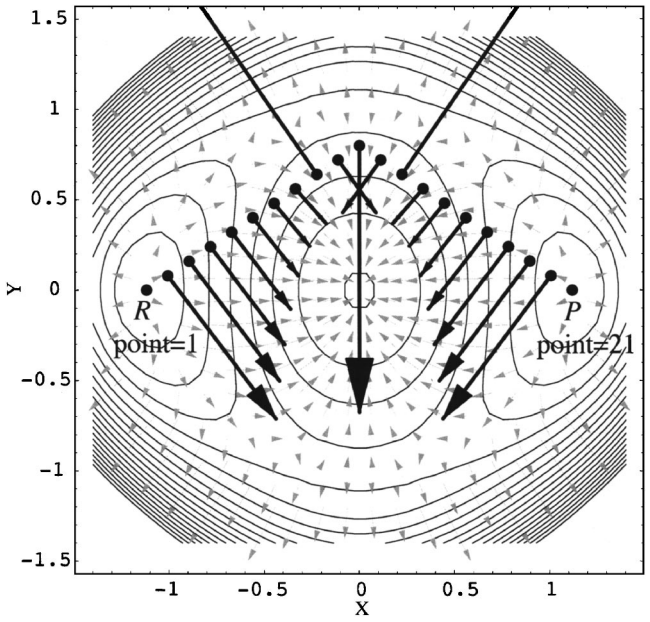

FIG. 2. Representation of the PES of Sec. III C. The solid lines are some contours of the potential energy. The light solid arrows are some selected gradients of the field, which are the vectors of the field **p** of the proposed variational problem defined in Eq. (4). The dark dots are the set of *21* points of the initial curve. The point *R* is labeled as *1* and the point *P* as *21*. The bold faced arrows are the Weierstrass *E*-gradient vectors $\boldsymbol{\nabla}_{\mathbf{q}i}E_{\text{approx}}(\mathbf{q}_i,\mathbf{g}_i,\Delta\mathbf{q}_i)|_{\mathcal{C}_{(R\to P)}}$ associated with the points of the initial curve.

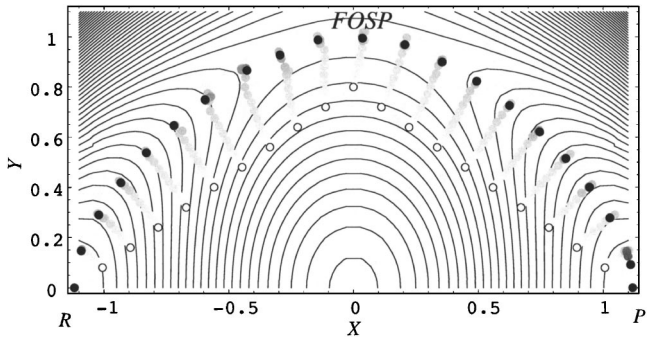

FIG. 3. Evolution of the algorithm to find the IRC curve line based on the minimization of the Weierstrass *E*-function, as defined in Eq. (29), for the PES given in Fig. 2. The solid lines are some contours of the potential energy. The white open dots are the set of *21* points of the initial guess curve. The dark dots indicate the final converged position of the *21* points. In this final position, all points are located in the IRC curve. The IRC curve line follows the sequence of stationary points: $R\to\text{FOSP}\to\text{P}$. The gradient faced points indicate the behavior of the algorithm during the minimization process.

these gradient vectors are the tangent vectors of the SD curves and these curves define the field of extremals. Due to the symmetry of the surface, only two SD paths are the IRC curves. These two paths follow the sequence of stationary points $R\to\text{FOSP}\to P$, and correspond to the SD paths connecting *R* and *P*, such that the integral given in Eq. (4) evaluated on this curve has the lowest value. This surface is challenging because it presents a maximum, which is an attractor of the SD lines. The algorithm has to make sure that it converges to the SD line that passes through FOSP. For the sake of simplicity, in this section we have dropped the subscript $\mathcal{C}$ in the $\mathbf{q}_i,\mathbf{g}_i$, and $\Delta\mathbf{q}_i$ vectors.

The set of open dots defines a broken line, which is the initial guess curve, $\mathcal{C}(R\to P)$. This initial curve is characterized by $n=21$ points, where the points $\mathbf{q}_1=\mathbf{q}_R$ and $\mathbf{q}_{21}=\mathbf{q}_P$ are fixed and the rest of the points are allowed to move. The bold faced arrows correspond to the set of *19* vectors, $\boldsymbol{\nabla}_{\mathbf{q}i}E_{\text{approx}}(\mathbf{q}_i,\mathbf{g}_i,\Delta\mathbf{q}_i)|_{\mathcal{C}_{(R\to P)}}$ for $i=2,\ldots,20$, of the initial curve $\mathcal{C}(R\to P)$. The direction of these vectors is different depending on the point, and for points *9* and *13* a decrease of the Weierstrass *E*-function would imply an increase of potential energy. Therefore the η_i factors applied to the points where $\mathbf{g}_i^T[\boldsymbol{\nabla}_{\mathbf{q}i}E_{\text{approx}}(\mathbf{q}_i,\mathbf{g}_i,\Delta\mathbf{q}_i)|_{\mathcal{C}_{(R\to P)}}]<0$ for $i=2,\ldots,20$ are chosen positive and vice versa. In this manner the new set of generated points will possess lower potential energy. Finally, the algorithm converges in the way that all *21* points are located in the IRC curve. This final position is represented by a set of dark dots in Fig. 3.

As is conventional in many minimization procedures, we take some steps as steepest descent, until we get close to the quadratic region, by using Eq. (33). In this example, *10* steps were taken this way. This procedure also allows to generate a set of matrices, $\mathbf{R}_i^{(\mu)}$ and $\mathbf{G}_i^{(\mu)}$, as defined in Eqs. (E2) and (E7), respectively, for $i=2,\ldots,20$. At every Newton–Raphson step and for each $\mathbf{q}_i$ point, we first evaluate the new position due to the space spanned by the set of difference positions using Eqs. (E11) and (E5). If the new point implies a descent $V(x,y)$, then it is accepted, otherwise the Newton–Raphson step is rejected and a steepest descent step is taken. Finally the variation due to the complementary subspace is computed through Eq. (E12) and properly scaled by η_i to guarantee a descent effect in the function $E_{\text{approx}}(\mathbf{q}_i,\mathbf{g}_i,\Delta\mathbf{q}_i)|_{\mathcal{C}_{(R\to P)}}$.

For the sake of completeness, we have compared the present method with the nudged elastic band method[17,18] (NEB) with a tangent vector defined as $\Delta\mathbf{q}_i=\mathbf{q}_{i+1}-\mathbf{q}_i$ for $i=2,\ldots,20$ on the current curve $\mathcal{C}(R\to P)$. In such a case the algorithm is unstable and, as expected, leads to kinks.[18] We are aware that corrections to this are possible,[18] but this comparison was only done to show that the method presented here does not suffer from this problem and is stable even with a crude tangent estimation.

The convergence of this method has also been tested. Figure 4 shows the decrease in the function $\{\Delta[\Delta V_{R\to P}]_{\mathcal{C}}\}_{\text{approx}}$ defined in Eq. (29), being $\mathcal{C}(R\to P)$, the current curve, for the Newton–Raphson algorithm described here and a quenched velocity Verlet as the one used in NEB.[17,18] It has to be mentioned that each quenched velocity Verlet step involves a single gradient evaluation for each point, whereas the Newton–Raphson step may involve several gradient evaluations to choose the correct η_i of Eq. (34). However, we have seen that the number of gradient evaluations is, on average, close to *1.5* per point, or even less when we get closer to the optimized path.

The use of the approximate Weierstrass *E*-gradient vector, through Eq. (32), is also surprising, because its convergence behavior is excellent until very close to converged IRC path (Fig. 4). At that point, a more accurate gradient would be needed to decrease the value of the function $\{\Delta[\Delta V_{R\to P}]_{\mathcal{C}}\}_{\text{approx}}$. Equation ((32)) is therefore useful to get

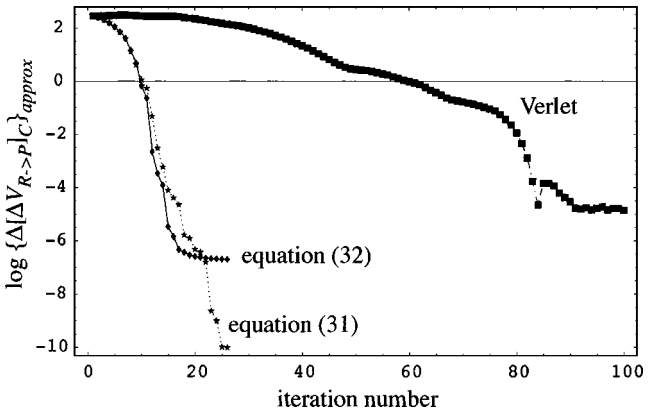

FIG. 4. The behavior of $\log\{\Delta[\Delta V_{R\to P}]_C\}_{\text{approx}}$, defined in Eq. (29), vs *iteration number*, during the minimization process of the Weierstrass *E*-function, for the example discussed in Fig. 2 and 3. See the text for more details.

pretty accurate paths that can then be refined by increasing the number of points in the discretization or with conventional transition state searches.

It is also worth pointing out that the reparametrization of the current $\mathcal{C}(R\to P)$ is only necessary during the initial steps, because the Weierstrass *E*-gradient vector, evaluated by using Eq. (31), once we are close to the final SD curve, is perpendicular to this curve. This is also true for the perpendicular force used in the NEB method, but the difference is that Eq. (31) corresponds to a gradient vector of a certain objective function while the NEB projection makes its force nonconservative.

Certainly a number of authors have also worked on the convergence of NEB or similar chain-of-states methods such as that used in the proposed algorithm.[19–21,23,29] Vanden-Eijden *et al.*[19] and Wales *et al.*[21] implemented a Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimizer type,[30] both achieving superlinear convergence. We have also commented briefly on the differences and similarities of the recent NEB improved algorithm described in Ref. 29. The NEB method has also been coupled to Car–Parrinello molecular dynamics[23] for better convergence with density functional theory calculations. All of these methods outperform the steepest descent minimization of the original NEB method that we, and the other reported authors, have used for comparison. It would surely be interesting to compare all of them but this is beyond the scope of this work. Indeed, the algorithm presented in this paper was mainly formulated to prove and to show the potential applications of a correct description of IRC method via Hamilton–Jacobi theory. A computationally less expensive formulation of the method would be desirable and is part of our future work, nevertheless, we would like to stress that the described algorithm represents an improvement of the original NEB method.

IV. CONCLUSIONS

The calculus of variations and specifically the Fermat variational principle can be used as a tool to study the nature of the IRC model and to establish new algorithms to evaluate this type of path. From this point of view, the IRC paths are extremal curves of a Fermat variational principle. The Hamilton–Jacobi equation associated with this Fermat variational principle has been derived, resulting in a very simple expression. As in the normal calculus of variations, from the derived eiconal equation we obtain the associated characteristic system of equations of the IRC curve. The analysis of the second-order variation permits to establish the strong minimum character of the IRC path and from this analysis to propose new algorithm to locate IRC curves.

ACKNOWLEDGMENTS

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APPENDIX A: ALTERNATIVE DERIVATION OF THE HAMILTON–JACOBI EQUATION FOR THE EXTREMAL CURVES OF THE TYPE SD LINE

In this appendix we establish the connection between Eq. (16) and the Hamilton–Jacobi equation or, in others words, we show that Eq. (16) plays the role of a Hamilton–Jacobi equation. To prove this assertion, the basic idea is to deal with homogeneous functional with respect to the argument $d\mathbf{q}/dt$, but of degree greater than one, because in this case it is possible to apply the Legendre transformation and then to derive in the standard way the corresponding Hamilton–Jacobi equation.[6,26] In addition this new homogeneous functional should be related to the functional of expression (4). To this aim, we first choose the function $\mathbf{q}(x)$ such that variation of the integral

$$I(\mathbf{q}) = \int_0^{x'} S\left(\mathbf{q}, \frac{d\mathbf{q}}{dx}\right) dx = \int_0^{x'} \mathbf{g}^T\mathbf{g}\left(\frac{d\mathbf{q}}{dx}\right)^T\left(\frac{d\mathbf{q}}{dx}\right) dx \qquad \text{(A1)}$$

with respect to this function vanishes. The variable x is proportional to the variable t of variational problem (4) in the way that $dx = F(\mathbf{q}, d\mathbf{q}/dt)dt$, where both t and $F(\mathbf{q}, d\mathbf{q}/dt)$ are those given in expression (4). We note that the functional $S(\mathbf{q}, d\mathbf{q}/dx)$ of Eq. (A1) is homogeneous of degree two with respect to the argument $d\mathbf{q}/dx$. The extremal curves $\mathbf{q}(x)$ of the variational problem (A1) satisfy the Euler–Lagrange differential equation

$$\boldsymbol{\nabla}_{\mathbf{q}} S - \frac{d}{dx}(\boldsymbol{\nabla}_{d\mathbf{q}/dx} S) = \mathbf{0}. \qquad \text{(A2)}$$

The tangent of these extremal curves is $d\mathbf{q}/dx = \mathbf{g}/(\mathbf{g}^T\mathbf{g})$. Due to the homogeneity of the S functional, it satisfies the relation

$$S = -S + \left(\frac{d\mathbf{q}}{dx}\right)^T (\boldsymbol{\nabla}_{d\mathbf{q}/dx} S). \qquad \text{(A3)}$$

Differentiating Eq. (A3) with respect to x and using Eq. (A2), we conclude that the functional S becomes constant along an extremal curve $\mathbf{q}(x)$, because $dS/dx = 0$. In other words, $S = \text{const} = 1$ along an extremal curve. With this result, Eq. (A2) can be transformed into the following way:

$$\frac{1}{2\sqrt{S}}\left[\nabla_{\mathbf{q}}S-\frac{d}{dx}\nabla_{d\mathbf{q}/dx}S\right]+\frac{1}{4}\frac{\nabla_{d\mathbf{q}/dx}S}{S}\frac{dS}{dx}$$
$$=\frac{1}{2\sqrt{S}}\nabla_{\mathbf{q}}S-\frac{d}{dx}\left(\frac{1}{2\sqrt{S}}\nabla_{d\mathbf{q}/dx}S\right)$$
$$=\frac{dt}{dx}\left[\nabla_{\mathbf{q}}F-\frac{d}{dt}(\nabla_{d\mathbf{q}/dt}F)\right]=\mathbf{0}. \tag{A4}$$

Since, $dt/dx=1/F(\mathbf{q},d\mathbf{q}/dt)\neq 0$, any extremal curve satisfying Eq. (A2) also satisfies Eq. (6). Consequently the Hamilton–Jacobi equation of the variational problem (A1) is related with the Hamilton–Jacobi equation of the variational problem (4). To prove this assertion, first we derive the Hamilton–Jacobi equation for the variational problem (A1). Since S is an homogeneous functional of degree two with respect to the argument $d\mathbf{q}/dx$, or in other words, $\det[\nabla_{d\mathbf{q}/dx}\nabla^T_{d\mathbf{q}/dx}S]=2\mathbf{g}^T\mathbf{g}\neq 0$, except in stationary points, we can use the Legendre transformation. Defining the vector $\mathbf{p}^*$ as

$$\mathbf{p}^*=\nabla_{d\mathbf{q}/dx}S=2\mathbf{g}^T\mathbf{g}\frac{d\mathbf{q}}{dx} \tag{A5}$$

and substituting in the right-hand side of Eq. (A3), the expression of the vector $d\mathbf{q}/dx$ as a function of $\mathbf{p}^*$ obtained from Eq. (A5), we get the transformed Legendre function of S, namely,

$$L(\mathbf{q},\mathbf{p}^*)=\frac{1}{4}\frac{(\mathbf{p}^*)^T\mathbf{p}^*}{\mathbf{g}^T\mathbf{g}}. \tag{A6}$$

We emphasize that the left-hand side of Eq. (A3) is equal to the transformed Legendre function $L(\mathbf{q},\mathbf{p}^*)$ and, as a consequence, in this case $L(\mathbf{q},\mathbf{p}^*)=S(\mathbf{q},d\mathbf{q}/dx)$. If $J^*(\mathbf{q},x)$ is the geodetic distance corresponding to the variational problem (A1), then its total differential form, whose general formula is given in Eq. (10), now reads

$$dJ^*(\mathbf{q},x)=(\nabla_{d\mathbf{q}/dx}S)^Td\mathbf{q}+\left[S-(\nabla_{d\mathbf{q}/dx}S)^Td\mathbf{q}/dx\right]dx$$
$$=\mathbf{p}^*d\mathbf{q}-L(\mathbf{q},\mathbf{p}^*)dx=(\nabla_{\mathbf{q}}J^*)^Td\mathbf{q}+\left(\frac{\partial J^*}{\partial x}\right)dx, \tag{A7}$$

where Eqs. (A3) and (A5) have been used. From Eq. (A7) we have $\mathbf{p}^*=\nabla_{\mathbf{q}}J^*(\mathbf{q},x)$ and

$$\frac{\partial J^*(\mathbf{q},x)}{\partial x}=-L(\mathbf{q},\nabla_{\mathbf{q}}J^*)=-\frac{1}{4}\frac{(\nabla_{\mathbf{q}}J^*)^T\nabla_{\mathbf{q}}J^*}{\mathbf{g}^T\mathbf{g}}. \tag{A8}$$

In the derivation of expression (A8), expression (A6) has been used. Equation (A8) is the Hamilton–Jacobi formula of the variational problem (A1). Since the right-hand side of Eq. (A8) is independent of x, a solution of this partial differential equation is $J^*(\mathbf{q},x)=\mathcal{C}x+2J(\mathbf{q})$, where $\mathcal{C}$ is a constant. Using the fact that $L(\mathbf{q},\mathbf{p}^*)=1$, we have $\mathcal{C}=-1$ and as a result we obtain Eq. (16).

APPENDIX B: THE CHARACTERISTIC SYSTEM OF DIFFERENTIAL EQUATIONS OF THE HAMILTON–JACOBI EQUATION (16)

Let us assume that $J(\mathbf{q})$ is the geodetic distance function and a solution of the partial differential equation (16); then we want to characterize the field of extremals such that these extremal curves transverse all families of contour line surfaces, $J(\mathbf{q})=\text{const}$, as explained in Sec. II B. Now we define a field vector $\mathbf{p}$ in the region of the PES considered by the equation

$$\mathbf{p}=\nabla_{\mathbf{q}}J(\mathbf{q}). \tag{B1}$$

Substituting Eq. (B1) in Eq. (16) we have

$$\frac{\mathbf{p}^T\mathbf{p}}{\mathbf{g}^T\mathbf{g}}=1. \tag{B2}$$

Now we use the family of curves defined by the ordinary differential equation (14),

$$\frac{1}{\sqrt{\left(\frac{d\mathbf{q}}{dt'}\right)^T\left(\frac{d\mathbf{q}}{dt'}\right)}}\frac{d\mathbf{q}}{dt'}=\frac{d\mathbf{q}}{ds}=\frac{\mathbf{p}}{\sqrt{\mathbf{p}^T\mathbf{p}}}, \tag{B3}$$

where the vectors $\nabla_{\mathbf{q}}J(\mathbf{q})$ and $\mathbf{g}$ that appear on the right-hand side of Eq. (14) are substituted by the vector $\mathbf{p}$ by using Eqs. (B1) and (B2), respectively. Equation (3) has also been used to change the independent variable t'. The vector $\mathbf{p}$ becomes a function of the independent variable t' along the curve characterized by the system of differential equations (B3). By differentiation of the vector $\mathbf{p}$ with respect to this independent variable t', we obtain

$$\frac{1}{\sqrt{\left(\frac{d\mathbf{q}}{dt'}\right)^T\left(\frac{d\mathbf{q}}{dt'}\right)}}\frac{d\mathbf{p}}{dt'}=\left[\nabla_{\mathbf{q}}\nabla^T_{\mathbf{q}}J(\mathbf{q})\right]\frac{d\mathbf{q}}{dt'}\frac{1}{\sqrt{\left(\frac{d\mathbf{q}}{dt'}\right)^T\left(\frac{d\mathbf{q}}{dt'}\right)}}. \tag{B4}$$

By differentiation of the partial differential equation (16) with respect to $\mathbf{q}$, and after some trivial rearrangements we obtain the identity

$$\left[\nabla_{\mathbf{q}}\nabla^T_{\mathbf{q}}J(\mathbf{q})\right]\frac{\mathbf{p}}{\sqrt{\mathbf{p}^T\mathbf{p}}}-\mathbf{H}\frac{\mathbf{g}}{\sqrt{\mathbf{g}^T\mathbf{g}}}=\mathbf{0}. \tag{B5}$$

Finally using Eqs. (B3)–(B5) and (3), we get

$$\frac{1}{\sqrt{\left(\frac{d\mathbf{q}}{dt'}\right)^T\left(\frac{d\mathbf{q}}{dt'}\right)}}\frac{d\mathbf{p}}{dt'}=\frac{d\mathbf{p}}{ds}=\mathbf{H}\frac{\mathbf{g}}{\sqrt{\mathbf{g}^T\mathbf{g}}}. \tag{B6}$$

Thus Eqs. (B3) and (B6) or Eqs. (21) and (22) characterize a family of curves as extremal curves and correspond to the characteristic system of differential equations associated to the partial differential equation (16) and consequently these extremal curves are the extremals of the variational problem given in Eq. (4).

APPENDIX C: PROOF OF EQ. (26)

The functional $F(\mathbf{q},d\mathbf{q}/dt')$ defined in Eq. (4) can be expanded with respect to the argument $d\mathbf{q}/dt'$ using a Tay-

lor's series up to first order with the remainder around the point $d\mathbf{q}/dt'=\mathbf{g}$, the tangent of the extremal curves of the field of extremals,

$$F(\mathbf{q}_C,d\mathbf{q}_C/dt') = F(\mathbf{q}_C,\mathbf{g}_C) + (d\mathbf{q}_C/dt' - \mathbf{g}_C)^T\boldsymbol{\nabla}_{d\mathbf{q}/dt'} \times F(\mathbf{q}_C,d\mathbf{q}/dt')|_{d\mathbf{q}/dt'=\mathbf{g}_C} + \tfrac{1}{2}(d\mathbf{q}_C/dt' - \mathbf{g}_C)^T[\boldsymbol{\nabla}_{d\mathbf{q}/dt'}\boldsymbol{\nabla}^T_{d\mathbf{q}/dt'}F(\mathbf{q}_C,d\mathbf{q}/dt')]_{d\mathbf{q}/dt'=\mathbf{g}^*_C} \times (d\mathbf{q}_C/dt' - \mathbf{g}_C), \quad \text{(C1)}$$

where the vector $\mathbf{g}^*_C=\mathbf{g}_C+\theta(d\mathbf{q}_C/dt'-\mathbf{g}_C)$ with $0<\theta<1$, $\mathbf{q}_C$ is a point of the region of the PES covered by the field of extremal curves, the SD lines emerging from the fixed point $\mathbf{q}_R$, $d\mathbf{q}_C/dt'$ is the tangent vector of an arbitrary curve C embedded in this field of extremals at the point $\mathbf{q}_C$ and the gradient vector $\mathbf{g}_C=\mathbf{g}(\mathbf{q}_C)$ is the tangent vector of the extremal curve also called tangent of the field at this point $\mathbf{q}_C$. Now we rearrange Eq. (C1) as follows:

$$F(\mathbf{q}_C,d\mathbf{q}_C/dt') - F(\mathbf{q}_C,\mathbf{g}_C) - (d\mathbf{q}_C/dt' - \mathbf{g}_C)^T\boldsymbol{\nabla}_{d\mathbf{q}/dt'} \times F(\mathbf{q}_C,d\mathbf{q}/dt')|_{d\mathbf{q}/dt'=\mathbf{g}_C} = \tfrac{1}{2}(d\mathbf{q}_C/dt' - \mathbf{g}_C)^T \times [\boldsymbol{\nabla}_{d\mathbf{q}/dt'}\boldsymbol{\nabla}^T_{d\mathbf{q}/dt'}F(\mathbf{q}_C,d\mathbf{q}/dt')]_{d\mathbf{q}/dt'=\mathbf{g}^*_C}(d\mathbf{q}_C/dt' - \mathbf{g}_C). \quad \text{(C2)}$$

Substituting in the left-hand side of Eq. (C2) the expressions for $F(\mathbf{q}_C,d\mathbf{q}_C/dt')$ and $\boldsymbol{\nabla}_{d\mathbf{q}/dt'}F(\mathbf{q}_C,d\mathbf{q}/dt')$, which are given in the Eqs. (4) and (11), respectively, and after some trivial rearrangements we get

$$\sqrt{\mathbf{g}^T_C\mathbf{g}_C}\sqrt{(d\mathbf{q}_C/dt')^T(d\mathbf{q}_C/dt')} - \mathbf{g}^T_C(d\mathbf{q}_C/dt') = \tfrac{1}{2}(d\mathbf{q}_C/dt' - \mathbf{g}_C)^T[\boldsymbol{\nabla}_{d\mathbf{q}/dt'}\boldsymbol{\nabla}^T_{d\mathbf{q}/dt'} \times F(\mathbf{q}_C,d\mathbf{q}/dt')]_{d\mathbf{q}/dt'=\mathbf{g}^*_C}(d\mathbf{q}_C/dt' - \mathbf{g}_C). \quad \text{(C3)}$$

Finally, substituting Eq. (C3) in Eq. (25) we obtain Eq. (26).

APPENDIX D: ANALYTICAL REPRESENTATION OF CONJUGATE POINTS BELONGING TO SD LINE, PROOF THAT A SD CURVE CONNECTING BOTH A MINIMUM AND A FIRST-ORDER SADDLE POINT IN THE PES AND EMBEDDED IN A CENTERED FIELD OF SD CURVES DOES NOT CONTAIN CONJUGATE POINTS

The origin of the concept of conjugate points of a field of extremal curves is related to the following question: given an extremal curve $\mathbf{q}(t')$, i.e., a curve satisfying Eq. (6), and the varied curve $\mathbf{q}^*(t')=\mathbf{q}(t')+\mathbf{z}(t')$, which conditions have to be imposed on $\mathbf{z}(t')$ such that the varied curve $\mathbf{q}^*(t')$ is also an extremal curve satisfying Eq. (6)? To answer this question first we substitute the curve $\mathbf{q}^*(t')=\mathbf{q}(t')+\mathbf{z}(t')$ into the Euler–Lagrange equation (6)

$$\boldsymbol{\nabla}_{\mathbf{q}}F(\mathbf{q}+\mathbf{z},d\mathbf{q}/dt'+d\mathbf{z}/dt') - \frac{d}{dt'}[\boldsymbol{\nabla}_{d\mathbf{q}/dt'}F(\mathbf{q}+\mathbf{z},d\mathbf{q}/dt'+d\mathbf{z}/dt')] = \mathbf{0}. \quad \text{(D1)}$$

Second, taking into account that $\mathbf{q}(t')$ is also a solution of the Euler–Lagrange equation (6), using Taylor's series and neglecting infinitesimal order higher than one with respect to both $\mathbf{z}(t')$ and $d\mathbf{z}(t')/dt'$, and finally combining terms, we obtain the linear differential equation

$$\frac{d}{dt'}\left[(\boldsymbol{\nabla}_{d\mathbf{q}/dt'}\boldsymbol{\nabla}^T_{d\mathbf{q}/dt'}F)\frac{d\mathbf{z}(t')}{dt'}\right] - \left[(\boldsymbol{\nabla}_{\mathbf{q}}\boldsymbol{\nabla}^T_{\mathbf{q}}F) - \frac{d}{dt'}(\boldsymbol{\nabla}_{\mathbf{q}}\boldsymbol{\nabla}^T_{d\mathbf{q}/dt'}F)\right]\mathbf{z}(t') = \mathbf{0}. \quad \text{(D2)}$$

Equation (D2) is the Jacobi equation[26] of the variational problem given in expression (4). The Jacobi equation, except for infinitesimals of order higher than one with respect to $\mathbf{z}(t')$ and $d\mathbf{z}(t')/dt'$, is the linear differential equation satisfied by the difference between two neighboring or infinitely close extremal curves. Given two neighboring extremal curves, $\mathbf{q}^*(t')$ and $\mathbf{q}(t')$, of a centered field of extremals, emerging from the same initial point, $\mathbf{q}_R=\mathbf{q}(0)$, the difference vector function, $\mathbf{z}(t')=\mathbf{q}^*(t')-\mathbf{q}(t')$, satisfying Eq. (D2) is a nonzero solution of Jacobi equation within an infinitesimal order higher than one relative to $\mathbf{z}(t')$ and $d\mathbf{z}(t')/dt'$. In the present case, N solutions of the Jacobi equation (D2) exist, N being the dimension of $\mathbf{q}$ vector. The set of initial conditions for each one of these N solutions of the Jacobi equation (D2) are obtained as follows: the initial point is the central point, $\mathbf{q}(0)=\mathbf{q}_R$, and the vector difference $\mathbf{z}(0)$ is a set equal to the zeroed vector, $\mathbf{z}(0)=\mathbf{0}$, whereas its first derivative with respect to t', $d\mathbf{z}(t')/dt'|_{t'=0}=\mathbf{1}$, where $\mathbf{1}^T=(1_1,\ldots,1_N)$.

Given an extremal curve $\mathbf{q}(t')$ the point $\mathbf{q}_{CP}=\mathbf{q}(t_{CP})$ is said to be a conjugate point to the central point of the field $\mathbf{q}_R=\mathbf{q}(0)$, if at $\mathbf{q}_{CP}=\mathbf{q}(t_{CP})$ the difference $\mathbf{q}^*(t_{CP})-\mathbf{q}(t_{CP})$, $\mathbf{q}^*(t')$ being a neighboring extremal curve emerging from the same initial point $\mathbf{q}_R=\mathbf{q}(0)$, is an infinitesimal of order higher than one relative to $\mathbf{z}(t_{CP})$ and $d\mathbf{z}(t')/dt'|_{t'=t_{CP}}$.

Now, we apply these results to the SD curve emerging from the $\mathbf{q}_R$ point that arrives to the first-order saddle point $\mathbf{q}_{FOSP}$. Substituting the integrand $F(\mathbf{q},d\mathbf{q}/dt')$, given in expression (4), into Eq. (D2), after some rearrangement we obtain the corresponding Jacobi equation for the variational problem (4),

$$-\mathbf{g}^T\mathbf{g}\mathbf{P}\frac{d^2\mathbf{z}(t')}{dt'^2} - \sqrt{\mathbf{g}^T\mathbf{g}}\left(\frac{\mathbf{g}^T\mathbf{H}\mathbf{g}}{\mathbf{g}^T\mathbf{g}}(\mathbf{I}+\mathbf{Q}) - \mathbf{H}\mathbf{Q} - \mathbf{Q}\mathbf{H}\right)\frac{d\mathbf{z}(t')}{dt'} + (\mathbf{H}\mathbf{P}\mathbf{H} - \mathbf{H}\mathbf{P}\mathbf{H}\mathbf{Q} - \mathbf{H}\mathbf{Q}\mathbf{H}\mathbf{P} - \mathbf{P}\mathbf{H}\mathbf{Q}\mathbf{H} - \mathbf{Q}\mathbf{H}\mathbf{P}\mathbf{H})\mathbf{z}(t') = \mathbf{0}, \quad \text{(D3)}$$

where $\mathbf{I}$ is the unit matrix, $\mathbf{g}$ is the gradient vector, and $\mathbf{H}$ is the Hessian matrix at the point $\mathbf{q}$ of the SD curve, the matrices $\mathbf{P}$ and $\mathbf{Q}$ are the projectors, $\mathbf{P}=\mathbf{I}-\mathbf{g}\mathbf{g}^T/(\mathbf{g}^T\mathbf{g})$, and $\mathbf{Q}=\mathbf{g}\mathbf{g}^T/(\mathbf{g}^T\mathbf{g})$, respectively. In the derivation of Eq. (D3) only the quadratic terms in the expansion of the PES around the point $\mathbf{q}$ have been considered. As a consequence the whole integration of the Jacobi equation from $\mathbf{q}_R=\mathbf{q}(0)$ to $\mathbf{q}_{FOSP}=\mathbf{q}(t)$ associated to a SD curve is carried out by stepwise quadratic approximation, using Eq. (D3). Notice that $t'=0$ at the $\mathbf{q}_R$ point and $t'=t$ at the $\mathbf{q}_{FOSP}$ point. The vector $\mathbf{z}(t')$ and its derivatives with respect to t' are expressed as a linear combination of the eigenvectors of the Hessian matrix $\mathbf{H}$,

namely, $\mathbf{z}(t')=\mathbf{V}\mathbf{a}(t')$, $d\mathbf{z}(t')/dt'=\mathbf{V}\mathbf{a}'(t')$, and $d^2\mathbf{z}(t')/dt'^2=\mathbf{V}\mathbf{a}''(t')$, $\mathbf{V}$ being the matrix defined by the set of orthonormal eigenvectors of the $\mathbf{H}$ matrix. When the SD curve arrives at the first-order saddle point $\mathbf{q}_{\mathrm{FOSP}}$, then around this point in the direction of the SD curve, the gradient vector can be approximated as $\mathbf{g}\approx\mathcal{C}\mathbf{v}_{TV}$, where $\mathbf{v}_{TV}$ is the column vector of the $\mathbf{V}$ matrix corresponding to the normalized eigenvector of the Hessian matrix with negative eigenvalue and $\mathcal{C}$ a small scalar taking the value $\mathcal{C}=0$ at the first-order saddle point.[31] With these considerations, at the first-order saddle point, $\mathbf{q}(t)=\mathbf{q}_{\mathrm{FOSP}}$, the first two terms of Eq. (D3) vanish. On the other hand, since at the first-order saddle point the matrix $\mathbf{P}=\mathbf{I}-\mathbf{v}_{TV}\mathbf{v}_{TV}^T$ and the matrix $\mathbf{Q}=\mathbf{v}_{TV}\mathbf{v}_{TV}^T$, then the terms, $\mathbf{PHQ}=\mathbf{QHP}=\mathbf{O}$, $\mathbf{O}$ being the zeroed matrix. As a consequence the remainder term of Eq. (D3) is $\mathbf{HPHV}\mathbf{a}(t)=\mathbf{0}$. Since we are interested in the SD curve that arrives at the first-order saddle point, we multiply from the left the remaining term by both $\mathbf{v}_{TV}\mathbf{v}_{TV}^T$ and $\mathbf{I}-\mathbf{v}_{TV}\mathbf{v}_{TV}^T$ resulting in $[\mathbf{a}(t)]_{\mathrm{TV}}\neq 0$ and $[\mathbf{a}(t)]_i=0\ \forall\ i=1,N$ and $i\neq TV$, respectively. Taking into account the initial conditions, $\mathbf{z}(0)=\mathbf{0}$ and $d\mathbf{z}(t')/dt'|_{t'=0}\neq\mathbf{0}$, and invoking the continuous dependences of the solution of Eq. (D3) with respect to these initial conditions, then $\mathbf{a}(t)\neq\mathbf{0},\mathbf{a}'(t)\neq\mathbf{0}$, and $\mathbf{a}''(t)\neq\mathbf{0}$. Consequently, the solution of Eq. (D3) related with the SD curve that arrives at the first-order saddle point, $\mathbf{q}_{\mathrm{FOSP}}=\mathbf{q}(t)$, from the minimum point, $\mathbf{q}_R=\mathbf{q}(0)$, is such that $\mathbf{z}(t)\neq\mathbf{0}, d\mathbf{z}(t')/dt'|_{t'=t}\neq\mathbf{0}$ and $d^2\mathbf{z}(t')/dt'^2|_{t'=t}\neq\mathbf{0}$, by invoking the transformation $\mathbf{z}(t')=\mathbf{V}\mathbf{a}(t'), d\mathbf{z},(t')/dt'=\mathbf{V}\mathbf{a}'(t')$, and $d^2\mathbf{z}(t')/dt'=\mathbf{V}\mathbf{a}''(t')$ at $t'=t$. This result shows that the first-order saddle point is not a conjugate point with respect to the central point $\mathbf{q}_R$, a stationary point character minimum in the PES.

APPENDIX E: MATHEMATICAL BASIS OF THE NEWTON–RAPHSON METHOD SOLVED IN BOTH A KRYLOV SUBSPACE AND ITS COMPLEMENTARY SUBSPACE USED IN THE MINIMIZATION OF THE FUNCTION GIVEN IN EQ. (29)

In this appendix we derive the set of equations of the Newton–Raphson algorithm to be applied in the minimization of the function given in Eq. (29) with respect to the parameters that characterize the arbitrary $\mathcal{C}$ curve to locate a SD curve. The Newton–Raphson equations are projected and solved in both a Krylov subspace and its complementary subspace. The Krylov subspace is generated during the minimization process. This method has been reviewed several times and used in different contexts.[28,29,32–34]

At the $(\mu+1)^{\mathrm{th}}$ iteration of the minimization process, $\mu>1$, the current curve is denoted by $\mathcal{C}_\mu$, the point vector of the vertex i by $\mathbf{q}_{\mathcal{C}_\mu i}$, and the Weierstrass E-gradient vector by $\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\mathrm{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\nabla\mathbf{q}_{\mathcal{C}i})|_{\mathcal{C}=\mathcal{C}_\mu}$. The dimension of these two vectors is N. The Weierstrass E-gradient vector can be evaluated by either Eq. (31) or Eq. (32). There exists a set of μ vectors $\{\mathbf{q}_{\mathcal{C}_v i}\}_{v=1}^{\mu}$ and the corresponding Weierstrass E-gradients $\{\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\mathrm{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})|_{\mathcal{C}=\mathcal{C}_v}\}_{v=1}^{\mu}$ for each point vertex i. We define the matrix $\mathbf{A}_i^{(\mu)}$ which is a projector onto the subspace defined by the vector differences $\{(\mathbf{q}_{\mathcal{C}_v i})-\mathbf{q}_{\mathcal{C}_\mu i}\}_{v=1}^{\mu-1}$. The matrix $\mathbf{B}_i^{(\mu)}$ corresponds to the projector onto the complementary subspace. Both $\mathbf{A}_i^{(\mu)}$ and $\mathbf{B}_i^{(\mu)}$ are the matrices of dimension $N\times N$. These matrices have the following properties: $\mathbf{A}_i^{(\mu)}+\mathbf{B}_i^{(\mu)}=\mathbf{I}, \mathbf{A}_i^{(\mu)}\mathbf{A}_i^{(\mu)}=\mathbf{A}_i^{(\mu)}, \mathbf{B}_i^{(\mu)}\mathbf{B}_i^{(\mu)}=\mathbf{B}_i^{(\mu)}$, and $\mathbf{A}_i^{(\mu)}\mathbf{B}_i^{(\mu)}=\mathbf{O}$, where $\mathbf{I}$ is the $N\times N$ identity matrix and $\mathbf{O}$ is the $N\times N$ zeroed matrix. The explicit form of the $\mathbf{A}_i^{(\mu)}$ matrix is

$$\mathbf{A}_i^{(\mu)}=\mathbf{R}_i^{(\mu)}\left[\left(\mathbf{R}_i^{(\mu)}\right)^T\left(\mathbf{R}_i^{(\mu)}\right)\right]^{-1}\left(\mathbf{R}_i^{(\mu)}\right)^T, \tag{E1}$$

where $\mathbf{R}_i^{(\mu)}$ is a rectangular matrix of dimension $N\times(\mu-1)$ whose column vectors are defined by vector differences between the current and the previous position vectors,

$$\mathbf{R}_i^{(\mu)}=\left[(\mathbf{q}_{\mathcal{C}_1 i}-\mathbf{q}_{\mathcal{C}_\mu i}),\ldots,(\mathbf{q}_{\mathcal{C}_{\mu-1} i}-\mathbf{q}_{\mathcal{C}_\mu i})\right]. \tag{E2}$$

The set of column vectors that defines the $\mathbf{R}_i^{(\mu)}$ rectangular matrix is assumed to be linearly independent.

The application of the Newton–Raphson method to minimize the function $\{\Delta[\Delta V_{R\to P}]_{\mathcal{C}}\}_{\mathrm{approx}}$, defined in Eq. (29), at the point i for the iteration μ, results in the following expression:

$$\left[\nabla_{\mathbf{q}_{\mathcal{C}i}}\nabla_{\mathbf{q}_{\mathcal{C}i}}^T E_{\mathrm{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}\right](\mathbf{q}_{\mathcal{C}_{\mu+1}i}-\mathbf{q}_{\mathcal{C}_\mu i}) = -\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\mathrm{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}, \tag{E3}$$

where $\mathbf{q}_{\mathcal{C}_{\mu+1}i}$ is the position vector of the vertex i of the new curve $\mathcal{C}_{\mu+1}$, and the matrix $\nabla_{\mathbf{q}_{\mathcal{C}i}}\nabla_{\mathbf{q}_{\mathcal{C}i}}^T E_{\mathrm{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})|_{\mathcal{C}=\mathcal{C}_\mu}$ is the Weierstrass E-Hessian matrix evaluated in the point vertex i of the curve $\mathcal{C}_\mu$. Using the above projectors and their properties, Eq. (E3) can be rearranged as

$$\begin{aligned}\mathbf{B}_i^{(\mu)}(\mathbf{q}_{\mathcal{C}_{\mu+1}i}-\mathbf{q}_{\mathcal{C}_\mu i}) = &-\left[\nabla_{\mathbf{q}_{\mathcal{C}i}}\nabla_{\mathbf{q}_{\mathcal{C}i}}^T E_{\mathrm{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}\right]^{-1}\\ &\times\Big\{\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\mathrm{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}\\ &+\left[\nabla_{\mathbf{q}_{\mathcal{C}i}}\nabla_{\mathbf{q}_{\mathcal{C}i}}^T E_{\mathrm{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}\right]\\ &\times\mathbf{A}_i^{(\mu)}(\mathbf{q}_{\mathcal{C}_{\mu+1}i}-\mathbf{q}_{\mathcal{C}_\mu i})\Big\}.\end{aligned} \tag{E4}$$

From Eq. (E4) we see that if we know the variation of the position vector within the current Krylov subspace, $\mathbf{A}_i^{(\mu)}(\mathbf{q}_{\mathcal{C}_{\mu+1}i}-\mathbf{q}_{\mathcal{C}_\mu i})$, then we can compute the variation of the position vector in the corresponding complementary subspace $\mathbf{B}_i^{(\mu)}(\mathbf{q}_{\mathcal{C}_{\mu+1}i}-\mathbf{q}_{\mathcal{C}_\mu i})$. If we define the vector $\mathbf{c}_i^{(\mu)}$ of dimension $\mu-1$ as

$$\mathbf{R}_i^{(\mu)}\mathbf{c}_i^{(\mu)}=\mathbf{A}_i^{(\mu)}(\mathbf{q}_{\mathcal{C}_{\mu+1}i}-\mathbf{q}_{\mathcal{C}_\mu i}) \tag{E5}$$

and we multiply Eq. (E4) from the left by $\mathbf{A}_i^{(\mu)}$, we obtain

$$\begin{aligned}\mathbf{0} = &\mathbf{A}_i^{(\mu)}\left[\nabla_{\mathbf{q}_{\mathcal{C}i}}\nabla_{\mathbf{q}_{\mathcal{C}i}}^T E_{\mathrm{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}\right]^{-1}\\ &\times\Big\{\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\mathrm{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}\\ &+\left[\nabla_{\mathbf{q}_{\mathcal{C}i}}\nabla_{\mathbf{q}_{\mathcal{C}i}}^T E_{\mathrm{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}\right]\mathbf{R}_i^{(\mu)}\mathbf{c}_i^{(\mu)}\Big\}.\end{aligned} \tag{E6}$$

Now, the action of the Weierstrass E-Hessian matrix $\nabla_{\mathbf{q}_{\mathcal{C}i}}\nabla_{\mathbf{q}_{\mathcal{C}i}}^T E_{\mathrm{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})|_{\mathcal{C}=\mathcal{C}_\mu}$ on the $\mathbf{R}_i^{(\mu)}$ matrix is approximated as follows:

$$\left[\nabla_{\mathbf{q}_{\mathcal{C}i}}\nabla^T_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}\right]\mathbf{R}_i^{(\mu)}$$
$$\approx\Big[\Big(\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_1}$$
$$-\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}\Big),\ldots,$$
$$\times\Big(\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_{\mu-1}}$$
$$-\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}\Big)\Big]=\mathbf{G}_i^{(\mu)}. \tag{E7}$$

The $\mathbf{G}_i^{(\mu)}$ matrix is a rectangular matrix of dimension $N\times(\mu-1)$ defined by the set of vector differences between the current and previous Weierstrass E-gradient vectors. Multiplying Eq. (E6) from the left by $(\mathbf{R}_i^{(\mu)})^T$ and substituting Eq. (E7), we obtain

$$\mathbf{0}^{(\mu)}=\left(\mathbf{R}_i^{(\mu)}\right)^T\left[\nabla_{\mathbf{q}_{\mathcal{C}i}}\nabla^T_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}\right]^{-1}$$
$$\times\left\{\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}+\mathbf{G}_i^{(\mu)}\mathbf{c}_i^{(\mu)}\right\}, \tag{E8}$$

where $\mathbf{0}^{(\mu)}$ is a zeroed vector of dimension $\mu-1$. To solve Eq. (E8), first we define the matrix

$$\mathbf{D}_i^{(\mu)}=\left(\mathbf{R}_i^{(\mu)}\right)^T\left[\nabla_{\mathbf{q}_{\mathcal{C}i}}\nabla^T_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}\right]^{-1}\mathbf{G}_i^{(\mu)} \tag{E9}$$

and the vector

$$\mathbf{e}_i^{(\mu)}=\left(\mathbf{R}_i^{(\mu)}\right)^T\left[\nabla_{\mathbf{q}_{\mathcal{C}i}}\nabla^T_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}\right]^{-1}$$
$$\times\ \nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}. \tag{E10}$$

Notice that the dimensions of the $\mathbf{D}_i^{(\mu)}$ matrix and the $\mathbf{e}_i^{(\mu)}$ vector are $(\mu-1)\times(\mu-1)$ and $(\mu-1)$ respectively. With the above definitions, the solution of Eq. (E8) is

$$\mathbf{c}_i^{(\mu)}=-\left[\left(\mathbf{D}_i^{(\mu)}\right)^T\left(\mathbf{D}_i^{(\mu)}\right)\right]^{-1}\left(\mathbf{D}_i^{(\mu)}\right)^T\mathbf{e}_i^{(\mu)}. \tag{E11}$$

Substituting the resulting value of the $\mathbf{c}_i^{(\mu)}$ vector in Eq. (E5) we obtain $\mathbf{A}_i^{(\mu)}(\mathbf{q}_{\mathcal{C}_{\mu+1}i}-\mathbf{q}_{\mathcal{C}_\mu i})$ vector. Using the set of equations (E4), (E5), and (E7), we obtain an expression to compute the term $\mathbf{B}_i^{(\mu)}(\mathbf{q}_{\mathcal{C}_{\mu+1}i}-\mathbf{q}_{\mathcal{C}_\mu i})$,

$$\mathbf{B}_i^{(\mu)}(\mathbf{q}_{\mathcal{C}_{\mu+1}i}-\mathbf{q}_{\mathcal{C}_\mu i})$$
$$=-\left[\nabla_{\mathbf{q}_{\mathcal{C}i}}\nabla^T_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}\right]^{-1}$$
$$\times\left\{\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})\big|_{\mathcal{C}=\mathcal{C}_\mu}+\mathbf{G}_i^{(\mu)}\mathbf{c}_i^{(\mu)}\right\}. \tag{E12}$$

Finally, taking the vector $\mathbf{A}_i^{(\mu)}(\mathbf{q}_{\mathcal{C}_{\mu+1}i}-\mathbf{q}_{\mathcal{C}_\mu i})$ and the vector $\mathbf{B}_i^{(\mu)}(\mathbf{q}_{\mathcal{C}_{\mu+1}i}-\mathbf{q}_{\mathcal{C}_\mu i})$, evaluated from Eq. (E12), we obtain the position vector of the vertex i of the new curve $\mathcal{C}_{\mu+1}$,

$$\mathbf{q}_{\mathcal{C}_\mu i}+\mathbf{A}_i^{(\mu)}(\mathbf{q}_{\mathcal{C}_{\mu+1}i}-\mathbf{q}_{\mathcal{C}_\mu i})+\mathbf{B}_i^{(\mu)}(\mathbf{q}_{\mathcal{C}_{\mu+1}i}-\mathbf{q}_{\mathcal{C}_\mu i})$$
$$=\mathbf{q}_{\mathcal{C}_\mu i}+(\mathbf{q}_{\mathcal{C}_{\mu+1}i}-\mathbf{q}_{\mathcal{C}_\mu i})=\mathbf{q}_{\mathcal{C}_{\mu+1}i}. \tag{E13}$$

In standard applications of the above method, the Weierstrass E-Hessian matrix $\nabla_{\mathbf{q}_{\mathcal{C}i}}\nabla^T_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})|_{\mathcal{C}=\mathcal{C}_\mu}$, which appears in Eq. (E11), through the $\mathbf{D}_i^{(\mu)}$ matrix and the $\mathbf{e}_i^{(\mu)}$ vector, and in Eq. (E12), is normally taken as a unit matrix or as a diagonal matrix.

As a summary the algorithm at the $(\mu+1)^{\text{th}}$ iteration, and for each point vertex i, only needs the position vector $\mathbf{q}_{\mathcal{C}_\mu i}$, the Weierstrass E-gradient vector $\nabla_{\mathbf{q}_{\mathcal{C}i}}E_{\text{approx}}(\mathbf{q}_{\mathcal{C}i},\mathbf{g}_{\mathcal{C}i},\Delta\mathbf{q}_{\mathcal{C}i})|_{\mathcal{C}=\mathcal{C}_\mu}$, and the matrices $\mathbf{R}_i^{(\mu)}$ and $\mathbf{G}_i^{(\mu)}$, defined in the expression (E2) and (E7), respectively. With these vectors and matrices solve the set of equations (E11), (E5), and (E12), and finally using Eq. (E13) compute the new position vector $\mathbf{q}_{\mathcal{C}_{\mu+1}i}$.

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