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The Variational Structure of Gradient Extremals

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ABSTRACT: The gradient extremals can be taken as a representation of reaction paths. We prove that this type of curve possesses a variational nature. We report the conditions such that these curves have the character of a minimal curve. Finally we discuss the relations between the points of these curves being turning points with respect to other special points of the potential energy surface, like the valley-ridge inflection points.

1. INTRODUCTION

The potential energy surface (PES) is the basic tool of the mechanistic and dynamical studies of the chemical reactivity. Some reactions with a diradical character approach the extreme case where the flatness of some regions of the PES precludes the definite assignment of distinct minima, saddle points (SPs), and lowest-energy pathways on the way from a reactant to several products. An example is the PES associated with the mechanism of the rearrangement vinylcyclopropane—cyclopentene.[1] In these examples the non-intrinsic reaction coordinate (IRC) pathways emerge. The IRC is the most widely used curve to represent a reaction path (RP). The dynamic behavior of these reactions has been studied by several authors observing a deviation from that predicted by the well-known transition-state theory (TST) which is a statistical, dynamical theory.[2−5] For these reactions the RP matched by the bulk of trajectories joining the reactant and product regions is different from the IRC pathway.[6] As a starting point, we explain this behavior. One hypothesizes a PES such that an utter flat intermediate region has one entrance and two exits. It is quite unlikely that a particular entrance will be dynamically coupled with equal strength to the two exits, even when the symmetry properties of the PES would appear to make the two exits equivalent.[2] We associate this dynamical situation with the mechanism that a reagent A can go to two products B and C. We explain this nonsymmetric rearrangement bifurcation, A → B and A → C, in terms of the PES model saying that in between the two SPs of the entrance to this region there exists a nonsymmetrical bifurcation implying that there is not a monkey SP.[7] An example of this PES may be represented by the function

$$V(x, y) = \frac{1}{3}(x^3 - 3xy^2) - \pi(x - y) + \frac{1}{40}\left(\left(x + \frac{7}{4}\right)^4 + y^4\right) \tag{1}$$

This PES has two adjacent first-order SPs. In the left panel of Figure 1, the PES of eq 1 is depicted. There are two SPs, which we name the SP_{ab} for the pathway from A to B and SP_{bc} for the pathway from B to C. By inspection of the two SPs, we note that SP_{ab} is higher in energy units than SP_{bc}. In this PES, the SPs may be nodes of a RP, however, from the left minimum A to the minimum C top right, no direct steepest descent (SD) exists, or anything that is equivalent to an IRC path. The SD from the two SPs leads to the minimum B at the right bottom. The fat curves in the right panel of Figure 1 are gradient extremals (GE).[8−18] The combination of the GE branches from minimum A to SP_{ab}, further to SP_{bc}, and then further to minimum C can be seen as a static model of a RP, which indeed connects the two minimums A and C. This is a non-IRC path and matches the cloud of dynamic trajectories that, starting in the minimum A, end in the region associated with the minimum C, see Figure 2. In the left panel of Figure 2 we show a set of classical trajectories at a given time. The starting point of the trajectories is the minimum A. At this time, some of them reside in the initial region, but a big portion of these trajectories are located in the region associated to the minimum B. A subset of a few trajectories crosses the region of the transition state SP_{bc} arriving to the region of the minimum C. The classical trajectories were computed using a code described in ref 19. In the central and right panels we show two different times of a Gaussian wave packet propagation on the same PES. At the initial time the Gaussian wave packet is centered in the region of the minimum A. In the central panel it is shown the time that an important portion of the Gaussian wave packet is located in the region of the PES where not only the valley bifurcates but also the wave packet spreads in this region. In the right panel we show the behavior of this quantum propagation after a long time. An important portion of the Gaussian wave packet resides in the region of the minimum A, whereas the reminder resides mainly in the bifurcation region, around the minimum B, but a small part resides in the region of the minimum C. As in classical simulation, the transformation from A to B is favored before A to C. For this example we can say that the IRC is the curve representing the RP being more favored according to the classical and quantum dynamic models, whereas the GE curve represents the RP being less favored according to these models.

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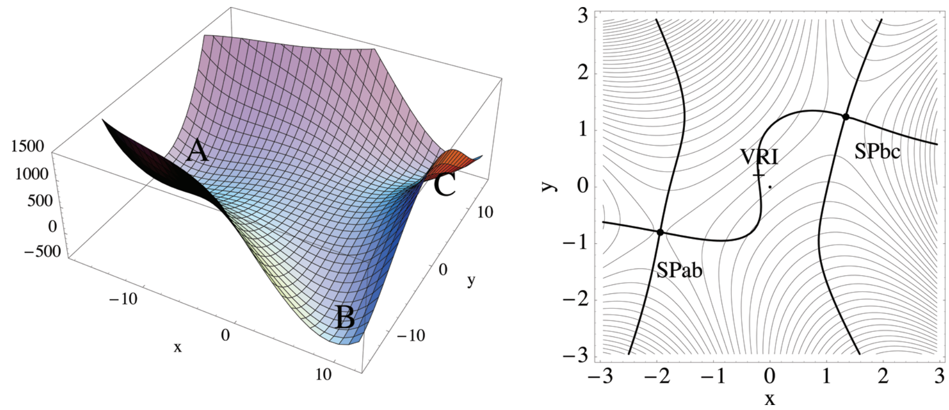

Figure 1. Left panel: PES associated to the mechanism of the reaction A → B + C. The mechanism for this reaction consists of two elementary reactions, namely, A → B and A → C. Each product is associated with different minimums in the PES. Right panel: GE in the enlarged center of the left panel. VRI: The valley from minimum B separates into two valleys over the SPs and a ridge between. The VRI point is crossed by the GE, which connects the two adjacent SPs.

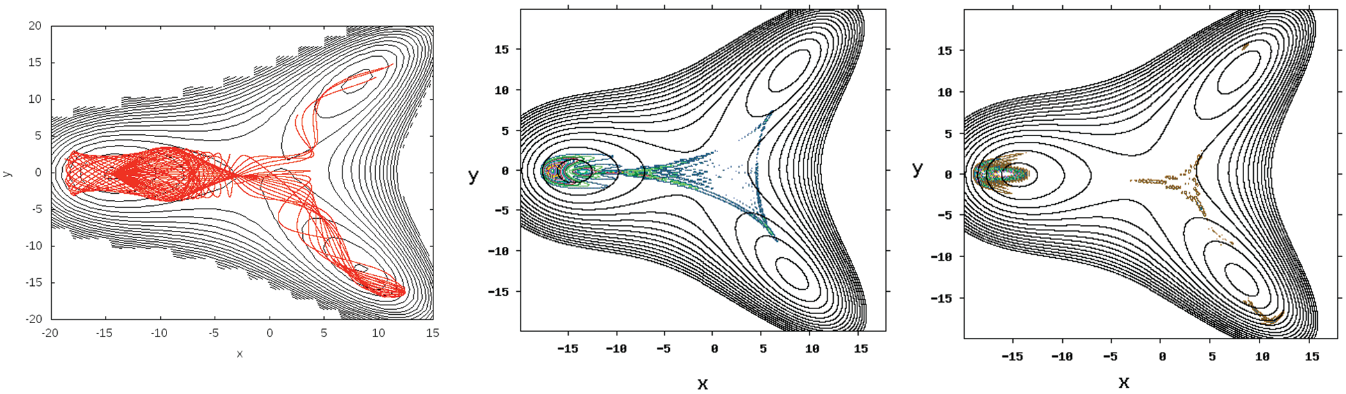

Figure 2. Left panel: A representative set of exact classical trajectories on the PES given in eq 1. A static RP, which is represented by a curve, can be understood as the curve that matches the average position of the cloud of trajectories after a long time. The IRC can be seen as an approximation to the average position of the set of trajectories that goes from the minimum A to B, whereas the GE curve is the approximation from A to the minimum C. Central panel: Quantum propagation of a Gaussian wave packet at the time that spreads into the bifurcation region of the PES. Notice that an important portion of the Gaussian wave packet resides in the region of the minimum A. Right panel: The propagation of the Gaussian wave packet at a latter time. Portions of the wave packet reside in the bifurcation region and the minimums as well. The portion of wave packet in the minimum B is bigger than that the minimum C.

The quantum propagation was computed using the MCTDH program.[20−22] From the classical dynamic theory, the RP model, which always is represented by a curve, can be envisaged as the curve that matches in the best way the average in position of the cloud of trajectories after a long time. In the present case, both the IRC and the GE play this role, because both match the average of the two different clouds of trajectories after a long time.[23] From a quantum point of view this relation between quantum dynamics and RP model is more difficult. However, in some cases we can say that the curve representing a RP can be seen as the curve that matches in the best way the maximum of the square of the wave function with respect to the position after a long time.[24]

Nevertheless, in the present study we are interested in the variational properties of the GE curves. The GEs are curves that usually run along valley floors or ridges of a PES. More rigorously and specifically speaking, the GEs of a PES, $V(\mathbf{q})$, are defined as the curves, $\mathbf{q}(t)$, where t is the curve parameter, which cuts at each point a member of the isopotential hypersurfaces of this PES, $V(\mathbf{q}(t)) = v(t)$, and the square of the gradient norm, $\nabla_{\mathbf{q}}{}^{T}V(\mathbf{q})\nabla_{\mathbf{q}}V(\mathbf{q}) = \mathbf{g}(\mathbf{q})^{T}\mathbf{g}(\mathbf{q})$, is stationary at each point of this curve in respect of the variations of $\mathbf{q}$ within the member of isopotential hypersurfaces that is cut by the curve at this point.[11,16] Because one can use GEs as model reaction pathways, we treat this kind of curves in this letter. We note that also another sort of curves, Newton trajectories (NT),[25−29] is well adapted to the connection of adjacent SPs, compare refs 30 and 31 and references therein.

As explained before in studies on dynamics of chemical reactions, examples of nonstatistical dynamical behavior in large organic systems involve cases in which transient intermediates occupy plateau regions or at best shallow minimums on the PES.

These regions are accessible by GEs, and due to this fact, a GE can be seen as a representation of some average of a representative ensemble of classical trajectories.

In principle it is plausible to believe that intermediates in deeper minimums show some statistical behavior due to the higher density of vibrational states at energies near their exit channels. A rapid intramolecular vibrational energy redistribution should often be present. But examples of this kind suggest that nonstatistical dynamics can persist even in these cases.

The RP model is roughly defined as a curve in the coordinate space, which connects two minimums by passing the SP, the transition structure (TS) of a PES. If the RP curve is totally confined in a valley floor, then the RP takes the category of a minimum energy path (MEP). It is a secondary question, how a RP ascends to the SP and descends from it to a minimum. This looseness makes a variety of RP definitions possible, the most widely used being the IRC, the NT and the GE type of curves. A parametrization t of the RP curve $\mathbf{q}(t) = (q_1(t), \ldots, q_N(t))^T$ is called reaction coordinate. In the last years the use of the variational theory of calculus of variations in the analysis and derivation of the different type of curves satisfying the features of the RP model has been reviewed.[31−46] The variational analysis of a RP curve representation provides, at least from a mathematical point of view, the nature and the features of the associated curves to this representation, like the extremal properties do, and what type of curves satisfy the minimum conditions. As noted before, the GE model has been studied in detail by the works of Ruedenberg and Jensen,[17,18] however in this article we present a study based on the theory of calculus of variations[47] to give the grounds and features of this type of curve.

In this article we analyze the variational nature of the GE curves and their implications. Also the tangent of a GE curve is derived through a perturbation method widely used in quantum mechanics. The characterization of a GE curve as a maximum or minimum is reported. The relation between special points of the GE curve in respect of special points of the PES is discussed. Finally some conclusions are given.

2. LAGRANGE−BOLZA VARIATIONAL PROBLEM AS A THEORETICAL BASIS OF THE GE CURVES

2.1. The First-Order Variational Condition. We show here that, in contrast to a remark in ref 44, the GE curves are extremal curves that belong to the problem of the theory of calculus of variations called Lagrangian or Bolza problem.[48,49] Briefly, within the possible generalizations of the simplest problems in the calculus of variations, one of the most important is the well-known problem of Lagrange and its generalizations, the so-called Bolza problem. In this type of variational problem, the extremal curve affording a stationary value to the fundamental integral is required to satisfy certain subsidiary conditions. The same requirements are also imposed on the curves of comparison being necessary to evaluate and analyze the necessary and sufficient extremal conditions.

The definition of a GE curve implies that as the curve evolves, the hypersurface v changes as a function of t, the parameter that characterizes the curve. In order to formulate the present problem, it is important to take into account that the arguments of the functional are subject to the boundary conditions and an additional condition. These conditions refer to the entire course of the arguments of the functional leading to an essential modification of the Euler differential equations. We are facing a variational problem with a finite subsidiary condition. The specific formulation consists in making the integral

$$I(\mathbf{q}) = \int_{t_0}^{t'} F(t, \mathbf{q})\mathrm{d}t = \int_{t_0}^{t'} 1/2\mathbf{g}^T\mathbf{g}\mathrm{d}t \tag{2}$$

stationary in comparison to curves $\mathbf{q}(t)$ which satisfy in addition to the boundary conditions, $\mathbf{q}(t_0)$, $\mathbf{q}(t')$, a subsidiary condition of the form

$$G(t, \mathbf{q}) = V(\mathbf{q}(t)) - v(t) = 0 \tag{3}$$

where as before $\mathbf{g} = \nabla_\mathbf{q}V(\mathbf{q}(t))$. Geometrically speaking, we want to determine a curve $\mathbf{q}(t)$ lying on the PES by the extremal requirement. This problem can be formulated in a more compact form in the following way:

$$\begin{aligned} I(\mathbf{q}) &= \int_{t_0}^{t'} L(t, \mathbf{q})\mathrm{d}t = \int_{t_0}^{t'} [F(t, \mathbf{q}) - \lambda(\mathbf{q}(t))G(t, \mathbf{q})]\mathrm{d}t \\ &= \int_{t_0}^{t'} \{1/2\mathbf{g}^T\mathbf{g} - \lambda(\mathbf{q}(t))[V(\mathbf{q}(t)) - v(t)]\}\mathrm{d}t \end{aligned} \tag{4}$$

where λ is the Lagrangian multiplier which depends on t through $\mathbf{q}$. The extremal curve satisfies the following set of equations at each point

$$\mathbf{Hg} - [V(\mathbf{q}) - v]\nabla_\mathbf{q}\lambda(\mathbf{q}) - \lambda(\mathbf{q})\mathbf{g} = \mathbf{0} \tag{5}$$

where we have dropped the dependence on t and $\mathbf{H} = \nabla_\mathbf{q}\,\mathbf{g}^T$ is the Hessian matrix at the point $\mathbf{q}$ of the PES. Equation 5 is the resulting Euler−Lagrange equation of the variational problem (eq 4). Substituting eq 3 into eq 5 we get

$$\mathbf{Hg} - \lambda(\mathbf{q})\mathbf{g} = \mathbf{0} \tag{6}$$

It means that the gradient is an eigenvector of the Hessian. It is the "coining" property of GEs. To eliminate the Lagrange multiplier $\lambda(\mathbf{q})$ from eq 6, we first multiply it from the right by $\mathbf{g}^T/\mathbf{g}^T\mathbf{g}$ and its transposed form from the left by $\mathbf{g}/\mathbf{g}^T\mathbf{g}$, subtracting and taking into account that $\mathbf{H} = \mathbf{H}^T$, we obtain

$$\mathbf{H}\frac{\mathbf{gg}^T}{\mathbf{g}^T\mathbf{g}} - \frac{\mathbf{gg}^T}{\mathbf{g}^T\mathbf{g}}\mathbf{H} = \mathbf{HP} - \mathbf{PH} = \mathbf{O} \tag{7}$$

where $\mathbf{P}$ is the projector onto the $\mathbf{g}$ subspace and $\mathbf{O}$ is the zero matrix. This equation is necessary but not sufficient; it must be combined with the auxiliary condition that the eigenvector is normal

$$(\mathbf{g}|\mathbf{g}|^{-1})^T(\mathbf{g}|\mathbf{g}|^{-1}) = 1 \tag{8}$$

where $|\mathbf{g}| = (\mathbf{g}^T\mathbf{g})^{1/2}$. Multiplying this condition from the left by $\mathbf{g}\,|\mathbf{g}|^{-1}$ and from the right by $\mathbf{g}^T\,|\mathbf{g}|^{-1}$, we get

$$\frac{\mathbf{gg}^T}{\mathbf{g}^T\mathbf{g}}\frac{\mathbf{gg}^T}{\mathbf{g}^T\mathbf{g}} = \mathbf{PP} = \mathbf{P} = \frac{\mathbf{gg}^T}{\mathbf{g}^T\mathbf{g}} \tag{9}$$

The condition 9 is called idempotency being characteristic of the projectors like $\mathbf{P}$ introduced in eq 7. We emphasize that eqs 7 and 9 are equivalent to the eq 6 and the normalization condition, (eq 8). Finally, from eq 9 we have, $\mathbf{O} = \mathbf{P} - \mathbf{PP} = (\mathbf{I} - \mathbf{P})\,\mathbf{P}$, where $\mathbf{I}$ is the unity matrix and $(\mathbf{I} - \mathbf{P})$ is the projector that projects to the orthogonal subspace of the subspace spanned by the $\mathbf{g}$ vector. If we multiply eq 7 from the left by $(\mathbf{I} - \mathbf{P})$ and from the right by $\mathbf{g}$ we obtain, using the last equality

$$(\mathbf{I} - \mathbf{P})\mathbf{HPg} = \left(\mathbf{I} - \frac{\mathbf{gg}^T}{\mathbf{g}^T\mathbf{g}}\right)\mathbf{Hg} = \mathbf{0} \tag{10}$$

Equations 9 and 10 are equivalent to eq 6 and the normalization condition, (eq 8). Equation 6 plus the normalization condition (eq 8) or eqs 7 and 9 or eqs 10 and 9 are equivalent forms to provide the necessary and sufficient conditions for the stationarity of the functional (eq 4). In ref 17, eq 10 was used as the starting point to implicitly obtain the curve solution, $\mathbf{q}(t)$, the GE.

2.2. Tangent Derivation of the Extremal Curve, GE, from an Application of Perturbation Theory. In the variational problem (eq 4), the integrand does not involve the tangent argument, $\mathbf{t} = d\mathbf{q}/dt$. Thus, the set of Euler–Lagrange equations reduces to the simple form given in eqs 6 and 8 or their equivalent form 7 and 9. Either of these two sets of equations determines the GE curve $\mathbf{q} = \mathbf{q}(t)$ implicitly. We note that in this case the boundary values, $\mathbf{q}_0 = \mathbf{q}(t_0)$ and $\mathbf{q}_f = \mathbf{q}(t_f)$, cannot be prescribed arbitrarily if the problem should have a solution.[47] On the contrary, one has to look for a solution starting at a $\mathbf{q}_0$ and take the value $\mathbf{q}_f$ from there. The tangent vector, $\mathbf{t}$, is necessary to integrate the curve but it does not appear in the expression. Here we use the perturbation theory due to McWeeny which is widely used in quantum mechanics[50] to implicitly derive the tangent of the GE from the eqs 7 and 9. First we assume that the current point, $\mathbf{q} = \mathbf{q}(t)$, is located on a GE, so that the eqs 7 and 9 are satisfied.

The basic idea is to start at a point located on a GE in the absence of any first-order variation in $\mathbf{q}$ and to seek the necessary first-order changes in the gradient to maintain the GE condition when the perturbation in $\mathbf{q}$ is applied. In this manner the first-order variation in the gradient due to the first-order perturbation in $\mathbf{q}$ is the tangent of the GE. With eq 7, the problem of perturbation theory merely consists of restoring the GE condition when, due to a perturbation or variation in $\mathbf{q}$, $\mathbf{H} \to \mathbf{H} + \Delta\mathbf{H}$, and other quantities, change accordingly. This problem is easily solved using the properties of projection operators.

Let us assume that all quantities appearing in eqs 7 and 9 can be expanded in powers of a perturbation parameter t, so that

$$\mathbf{H} = \mathbf{H}_0 + (t - t_0)\frac{d}{dt}\mathbf{H}\bigg|_{\mathbf{q}=\mathbf{q}_0} + (t - t_0)^2\frac{1}{2}\frac{d^2}{dt^2}\mathbf{H}\bigg|_{\mathbf{q}=\mathbf{q}_0} + \ldots = \mathbf{H}_0 + (t - t_0)\mathbf{H}_0^{(1)} + (t - t_0)^2\mathbf{H}_0^{(2)} + \ldots \tag{11a}$$

$$\mathbf{P} = \mathbf{P}_0 + (t - t_0)\frac{d}{dt}\mathbf{P}\bigg|_{\mathbf{q}=\mathbf{q}_0} + (t - t_0)^2\frac{1}{2}\frac{d^2}{dt^2}\mathbf{P}\bigg|_{\mathbf{q}=\mathbf{q}_0} + \ldots = \mathbf{P}_0 + (t - t_0)\mathbf{P}_0^{(1)} + (t - t_0)^2\mathbf{P}_0^{(2)} + \ldots \tag{11b}$$

where $\mathbf{H}_0$ and $\mathbf{P}_0$ are the unperturbed Hessian and projector matrices evaluated at the point $\mathbf{q}_0 = \mathbf{q}(t_0)$ belonging to the extremal curve. From the eqs 7, 11a, and 11b separating the orders, it follows readily that

$$(\mathbf{H}_0\mathbf{P}_0^{(1)} + \mathbf{H}_0^{(1)}\mathbf{P}_0) - (\mathbf{P}_0\mathbf{H}_0^{(1)} + \mathbf{P}_0^{(1)}\mathbf{H}_0) = \mathbf{O} \tag{12}$$

will determine the first-order change in $\mathbf{P}_0$ with the auxiliary equation

$$\mathbf{P}_0\mathbf{P}_0^{(1)} + \mathbf{P}_0^{(1)}\mathbf{P}_0 = \mathbf{P}_0^{(1)} \tag{13}$$

which arises from eq 9. This auxiliary condition requires that $\mathbf{P}_0^{(1)}$ be of the form

$$\frac{d\mathbf{P}}{dt}\bigg|_{\mathbf{q}=\mathbf{q}_0} = \mathbf{P}_0^{(1)} = (\mathbf{I} - \mathbf{P}_0)\mathbf{M}_0\mathbf{P}_0 + \mathbf{P}_0\mathbf{M}_0^T(\mathbf{I} - \mathbf{P}_0) \tag{14}$$

where the matrix $\mathbf{M}_0$ is

$$\mathbf{M}_0 = \mathbf{H}_0\left(\frac{d\mathbf{q}}{dt}\bigg|_{\mathbf{q}=\mathbf{q}_0}\right)(\mathbf{g}_0^T\mathbf{g}_0)^{-1}\mathbf{g}_0^T = \mathbf{H}_0\mathbf{t}_0(\mathbf{g}_0^T\mathbf{g}_0)^{-1}\mathbf{g}_0^T \tag{15}$$

where $\mathbf{g}_0$ and $\mathbf{t}_0$ are the gradient and the tangent vectors evaluated at $\mathbf{q}_0 = \mathbf{q}(t_0)$, respectively. The form of the $\mathbf{M}_0$ matrix results from the application of the directional derivative, $d/dt = [\nabla_{\mathbf{q}}](d\mathbf{q}/dt) = [\nabla_{\mathbf{q}}]\mathbf{t}$, on the normalized gradient vector, being $\nabla_{\mathbf{q}}^T = (\partial/\partial q_1, \ldots, \partial/\partial q_N)$. On substituting eq 14 in eq 12 and multiplying from the left and right by $(\mathbf{I} - \mathbf{P}_0)$ and $\mathbf{P}_0$, respectively, we obtain

$$(\mathbf{I} - \mathbf{P}_0)\mathbf{H}_0(\mathbf{I} - \mathbf{P}_0)\mathbf{M}_0\mathbf{P}_0 - (\mathbf{I} - \mathbf{P}_0)\mathbf{M}_0\mathbf{P}_0\mathbf{H}_0\mathbf{P}_0 + (\mathbf{I} - \mathbf{P}_0)\mathbf{H}_0^{(1)}\mathbf{P}_0 = \mathbf{O} \tag{16}$$

where we have noted that $\mathbf{H}_0\mathbf{P}_0 - \mathbf{P}_0\mathbf{H}_0 = \mathbf{O}$ and that $(\mathbf{I} - \mathbf{P}_0)\mathbf{P}_0 = \mathbf{O}$. The eq 16 incorporates all quantities and completely determines the first-order change in $\mathbf{P}_0^{(1)}$, which in turn determines the tangent vector, $\mathbf{t}_0$, of the gradient extremal at $\mathbf{q}_0$.

A solution is obtained most conveniently by multiplying eq 16 from the right by $\mathbf{g}_0\,|\mathbf{g}_0|^{-1}$, then we have

$$\left(\mathbf{I} - \frac{\mathbf{g}_0\mathbf{g}_0^T}{\mathbf{g}_0^T\mathbf{g}_0}\right)\left[\langle\mathbf{F}_0\mathbf{g}_0\rangle + \mathbf{H}_0^2 - \frac{\mathbf{g}_0^T\mathbf{H}_0\mathbf{g}_0}{\mathbf{g}_0^T\mathbf{g}_0}\mathbf{H}_0\right]\mathbf{t}_0 = \mathbf{0} \tag{17}$$

where we have applied that $(\mathbf{I} - \mathbf{P}_0)\mathbf{H}_0\mathbf{P}_0 = \mathbf{O}$, since $\mathbf{q}_0$ is a point of the GE. $\mathbf{F}_0$ is the third energy derivative tensor with respect to $\mathbf{q}$ evaluated at $\mathbf{q}_0$. The $\langle\mathbf{F}_0\mathbf{g}_0\rangle$ symbolism is used to indicate a square matrix that is a contracted product of a three-index array with a vector yielding a two-index array; thus,

$$\langle\mathbf{F}_0\mathbf{g}_0\rangle_{ij} = \sum_{k=1}^{N}(\mathbf{F}_0)_{ijk}g_k^0 \tag{18}$$

where g^0_k is the k element of the $\mathbf{g}_0$ vector. The term $\langle\mathbf{F}_0\mathbf{g}_0\rangle$ arises from the last term of the left-hand side part of eq 16, that is

$$\mathbf{H}_0^{(1)}\mathbf{g}_0 = \left(\frac{d}{dt}\mathbf{H}\bigg|_{\mathbf{q}=\mathbf{q}_0}\right)\mathbf{g}_0 = \langle\mathbf{F}_0\mathbf{t}_0\rangle\mathbf{g}_0 = \langle\mathbf{F}_0\mathbf{g}_0\rangle\mathbf{t}_0 \tag{19}$$

where the directional derivative and eq 18 have been used. The eq 17 was derived for the first time by Sun and Rudenberg.[17] We represent the projector $(\mathbf{I} - \mathbf{P}_0) = \mathbf{V}_0\,\mathbf{V}_0^T$ being $\mathbf{V}_0$ a rectangular matrix of dimension $N \times (N-1)$ containing the $N-1$ eigenvectors of $\mathbf{H}_0$ orthonormal to $\mathbf{g}_0\,|\mathbf{g}_0|^{-1}$ and the tangent vector as $\mathbf{t}_0 = \mathbf{g}_0\,|\mathbf{g}_0|^{-1}\,e_g^0 + \mathbf{V}_0\,\mathbf{e}_{N-1}^0$, where $\mathbf{e}_{N-1}^0$ is a vector of dimension $N-1$. Substituting this in eq 17 we obtain after multiplying from the left by $\mathbf{V}_0^T$

$$-\mathbf{V}_0^T\langle\mathbf{F}_0\mathbf{g}_0\rangle\frac{\mathbf{g}_0}{|\mathbf{g}_0|}e_g^0 = \mathbf{V}_0^T\left[\langle\mathbf{F}_0\mathbf{g}_0\rangle + \mathbf{H}_0^2 - \frac{\mathbf{g}_0^T\mathbf{H}_0\mathbf{g}_0}{\mathbf{g}_0^T\mathbf{g}_0}\mathbf{H}_0\right]\mathbf{V}_0\mathbf{e}_{N-1}^0 \tag{20}$$

Notice that $\mathbf{V}_0^T\,\mathbf{H}_0\,\mathbf{V}_0 = {}^D\mathbf{H}_0^{N-1} = \{h_{ij}^0\quad\delta_{ij}\}_{i,j=1}^{N-1}$, $\mathbf{V}_0^T\,\mathbf{H}_0\,\mathbf{g}_0/|\mathbf{g}_0|^{-1} = \mathbf{0}_{N-1}$ and $\mathbf{V}_0^T\quad\mathbf{V}_0 = \mathbf{I}_{N-1}$ because we are in a point of a GE. The vector $\mathbf{0}_{N-1}$ is the zero vector of dimension $N-1$, while $\mathbf{I}_{N-1}$ is the unitary matrix of dimension $(N-1) \times (N-1)$. When the determinant of the square matrix of the right-hand side part of eq 20 is different from zero, then the vector $\mathbf{e}^0_{N-1}$ is obtained as a function of e^0_g, and the latter is evaluated by a normalization of the vector $\mathbf{e}_0^T = (e^0_g, (\mathbf{e}^0_{N-1})^T)$. This completely determines $\mathbf{t}_0$ the tangent vector of the GE at $\mathbf{q}_0$.

2.3. Special Points of GE Curves. We analyze the form of the solutions of the eq 20. In case that the determinant of the square matrix appearing on the right-hand side part of eq 20 is equal zero, a careful analysis of this equation should be taken into account to evaluate $\mathbf{e}_0$. For a deeper analysis of this situation see refs 17 and 18. Such points where the gradient extremal has a $\det(\mathbf{V}_0^T[<\mathbf{F}_0\mathbf{g}_0> + \mathbf{H}_0^2 - \lambda_0\mathbf{H}_0]\mathbf{V}_0) = 0$ being $\lambda_0 = \mathbf{g}_0^T\mathbf{H}_0\mathbf{g}_0/(\mathbf{g}_0^T\mathbf{g}_0)$ can be either a turning point (TP), a point where the curve touches the isopotential energy contour tangentially, or a bifurcation point (BP), a point where two GEs cross. The structure of the tangent vector $\mathbf{e}_0$ is obtained in these points by transforming the eq 20 in the set of coordinates that diagonalizes the square matrix appearing on the right-hand side part of this equation,

$$\mathbf{V}_0^T\left[\langle \mathbf{F}_0\mathbf{g}_0\rangle + \mathbf{H}_0^2 - \frac{\mathbf{g}_0^T\mathbf{H}_0\mathbf{g}_0}{\mathbf{g}_0^T\mathbf{g}_0}\mathbf{H}_0\right]\mathbf{V}_0 = \mathbf{V}_0^T\mathbf{C}_0\mathbf{V}_0 = \mathbf{U}_0\mathbf{C}_D^0\mathbf{U}_0^T \tag{21}$$

Where $\mathbf{U}_0$ is the unitary matrix of dimension $(N-1) \times (N-1)$ such that it diagonalizes the $\mathbf{V}_0^T\mathbf{C}_0\mathbf{V}_0$ matrix and $\mathbf{C}_D^0 = \{c^0_{ij}, \delta_{ij}\}_{i,j=1}^{N-1}$, then eq 20 is transformed to

$$\mathbf{b}_0 e_g^0 = \mathbf{C}_D^0\mathbf{w}_0 \tag{22}$$

being $\mathbf{b}_0 = -\mathbf{U}_0^T\mathbf{V}_0^T\langle\mathbf{F}_0\mathbf{g}_0\rangle\mathbf{g}_0|\mathbf{g}_0|^{-1}$, and $\mathbf{w}_0 = \mathbf{U}_0^T\mathbf{e}^0_{N-1}$, both vectors of dimension $N-1$. As explained above, if $\det(\mathbf{V}_0^T\mathbf{C}_0\mathbf{V}_0) \neq 0$ then the tangent vector in the original coordinates is $\mathbf{t}_0 = e_g^0(\mathbf{g}_0\,|\mathbf{g}_0|^{-1} + \mathbf{V}_0\mathbf{U}_0(\mathbf{C}^0_D)^{-1}\mathbf{b}_0)$, where e_g^0 is computed by a normalization of $\mathbf{t}_0$ vector. If $\det(\mathbf{V}_0^T\mathbf{C}_0\mathbf{V}_0) = 0$, then at least one element of the diagonal matrix $\mathbf{C}_D^0$ is equal zero. Let us assume that $c_{ii}^0 = 0$, then if the i element of the $\mathbf{b}_0$ vector, b_i^0, is different from zero, the solution of eq 22 plus the normalization condition implies that $e_g^0 = 0$ and $\mathbf{w}_0^T = (0_1, ..., 1_i, ..., 0_{N-1})$, and from this, the tangent takes the following form $\mathbf{e}_0^T = (e_g^0, (\mathbf{e}_{N-1})^T) = (0, \mathbf{w}_0^T\mathbf{U}_0^T) = (0, (\mathbf{u}_i^0)^T)$, where $\mathbf{u}_i^0$ is the i column vector of the $\mathbf{U}_0$ matrix. The resulting normalized tangent vector in the original coordinates is $\mathbf{t}_0 = \mathbf{V}_0\mathbf{u}_i^0$, where it does not have the component in the eigenvector pointing in the same direction to the gradient vector, thus $e_g^0 = 0$. Due to this fact, at this point the GE does not cross the isopotential energy contour. It touches tangentially this isopotential contour. This point is a TP for this GE, and we say that the curve is characteristic at this point.[51,52] An example of two TPs is the PES depicted in Figure 1. The points at ∼(−0.25, −0.80) and ∼(0.0, 1.0) are TPs of the central GE curve.

In case that both $c_{ii}^0 = 0$ and $b_i^0 = 0$, then eq 22 plus the normalization condition gives two solutions: one is that which touches the isopotential energy contour being the expression of the tangent the same as the one given above. The second solution is that which crosses the isopotential energy contour. In this case $\mathbf{w}_0^T = e_g^0(c^0_{11}/b^0_1, ..., 0_i, ..., c^0_{N-1N-1}/b^0_{N-1})$ and from this the tangent $\mathbf{e}_0$ takes the form $\mathbf{e}_0^T = (e_g^0, (\mathbf{e}_{N-1}{}^0)^T) = e_g^0\,(1, \mathbf{w}_0^T\mathbf{U}_0^T)$, where e_g^0 is computed by a normalization of $\mathbf{e}_0$ vector. The resulting normalized tangent vector in the original coordinates takes the form $\mathbf{t}_0 = e_g^0\,(\mathbf{g}_0|\mathbf{g}_0|^{-1} + \mathbf{V}_0\mathbf{U}_0\mathbf{w}_0)$. The GE curve with this tangent is a noncharacteristic curve at this point, it transverses the isopotential energy contour because $e_g^0 \neq 0$. Since in a point where both $c_{ii}^0 = 0$ and $b_i^0 = 0$, two GE curves coincide at this point one with tangent $\mathbf{t}_0 = \mathbf{V}_0\mathbf{u}_i^0$ and the other with tangent $\mathbf{t}_0 = e_g^0\,(\mathbf{g}_0|\mathbf{g}_0|^{-1} + \mathbf{V}_0\mathbf{U}_0\mathbf{w}_0)$, this point is called bifurcation point (BP) for this type of GE curves. It is interesting to notice that the structure of eq 20 is very close to the basic equation to integrate Newton Trajectory curves as one can see by an inspection of eq (31) of ref 31, see also refs 29 and 53. The basic differences between both equations lie in that the vector of the left-hand side part of eq 20 depends on the Hessian matrix rather than a contracted product of a three-index array with the gradient vector and that the square matrix of the right-hand side part is only a function of the Hessian matrix.

An example of a GE bifurcation is shown in Figure 3, on the well-known Müller–Brown PES (mb-PES).[54] At point ∼(0.06, 2.06) a bifurcation of the GE curve takes place. Note that the two eigenvalues of the Hessian matrix at this node

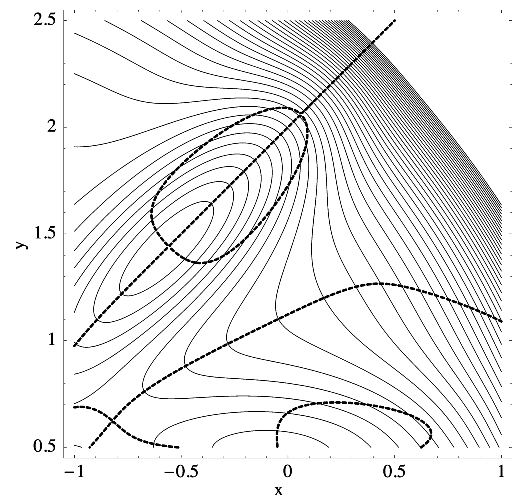

Figure 3. GE curves (fat dashes) on the mb-PES.

$$\mathbf{H}(0.06\quad 2.06) = \begin{pmatrix} 1902.96 & -389.644 \\ -389.644 & 1902.96 \end{pmatrix}$$

are totally different: they are 1513.31 and 2292.6. By the way, the GE curve starting orthogonally to the minimum valley meets itself at the BP. There is also its TP at the slope of the bowl.

Now we show by an example that a degeneracy of eq 6 involving the eigenvector that points in the same direction to the gradient vector does not affect the behavior of the actual GE curve. Let us assume that on a point at the GE curve the Hessian is degenerated, but $\det(\mathbf{H}) \neq 0$, and one of the degenerated eigenvectors coincides with the gradient direction at this point. Nevertheless, the derivation of the tangent of the curve due to Ruedenberg's formula, eq 17, is true and the GE curve behaves 'normally'. In Figure 4 we again demonstrate this with the mb-PES. We again show the GE curves of Figure 3 and the level lines of two eigenvalues: The value of each of them is equal to 313.1 units. The two systems cross exactly at the GE curve near the deep minimum. There the GE curve does not show any anomaly.

Finally, we say that the perturbational method due to McWeeny[50] has been used until now to derive the well-known tangent vector that characterizes the GE curve. Using the same method one can evaluate the first-order gradient correction through the GE curve, $\mathbf{g}(\mathbf{q}(t))$. For this task, first we insert

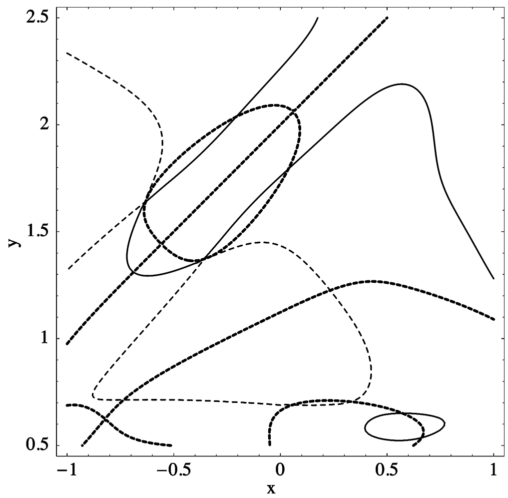

Figure 4. GE curves (fat dashes) and two level lines of eigenvalues (continuous line and thin dashes) at exactly 313.1 units. The two level lines cross on the GE curve.

eq 15 into eq 16, multiply the equation from the right of the resulting expression by $\mathbf{g}_0\,|\mathbf{g}_0|^{-1}$, and assume that $\mathbf{q}_0$ is a point on a GE curve,

$$\begin{aligned}\mathbf{g}(\mathbf{q}(t)) &\approx (\mathbf{P}_0 + (t - t_0)\mathbf{P}_0^{(1)})\mathbf{g}_0\,|\mathbf{g}_0|^{-1}\\ &= \mathbf{g}_0\,|\mathbf{g}_0|^{-1} + (t - t_0)\mathbf{V}_0\mathbf{V}_0^T\mathbf{H}_0\mathbf{t}_0\,|\mathbf{g}_0|^{-1}\\ &= (\mathbf{g}_0 + (t - t_0)\mathbf{V}_0\mathbf{V}_0^T\mathbf{H}_0(\mathbf{g}_0\,|\mathbf{g}_0|^{-1}e_g^0\\ &\quad + \mathbf{V}_0\mathbf{e}_{N-1}^0))|\mathbf{g}_0|^{-1}\\ &= (\mathbf{g}_0 + (t - t_0)\mathbf{V}_0\,{}^D\mathbf{H}_0^{N-1}\mathbf{e}_{N-1}^0)|\mathbf{g}_0|^{-1}\\ &= (\mathbf{g}_0 + (t - t_0)\sum_{i=1}^{N-1}\mathbf{v}_i^0 h_{ii}^0(e_{N-1}^0)_i)|\mathbf{g}_0|^{-1}\end{aligned} \tag{23}$$

where we have taken that $(\mathbf{I} - \mathbf{P}_0) = \mathbf{V}_0\mathbf{V}_0^T$ and $\mathbf{v}_i^0$ and $(e_0^{N-1})_i$ are the $\mathbf{i}$ column vector and the i element of the $\mathbf{V}_0$ matrix and the $\mathbf{e}_0^{N-1}$ vector, respectively. Notice that due to the structure of this particular perturbation problem, it is irrelevant that the eigenvector which points in the same direction like the gradient vector be degenerate or not in respect of the others eigenvectors of the Hessian matrix, since the division by differences between eigenvalues does not appear as it usually appears in the application of perturbation methods. In the same way, one has the corresponding expression to compute the first-order eigenvector correction to each eigenvector of the subset, $\{\mathbf{v}_i^0\}_{i=1}^{N-1}$. Because $\mathbf{I} = \mathbf{P}_0 + (\mathbf{I} - \mathbf{P}_0) = \mathbf{P}_0 + \mathbf{Q}_0$ then $-\,\mathrm{d}\mathbf{Q}_0/\mathrm{d}t = \mathrm{d}\mathbf{P}_0/\mathrm{d}t = -\mathbf{Q}_0^{(1)} = {}_0\mathbf{P}^{(1)}$. Substituting $\mathbf{g}(\mathbf{q}(t))$ by $\mathbf{v}_i(\mathbf{q}(t))$, $\mathbf{P}_0$ by $\mathbf{Q}_0$, $\mathbf{P}_0^{(1)}$ by $-\mathbf{Q}_0^{(1)}$ and $\mathbf{g}_0$ by $\mathbf{v}_i^0$ in eq 23, we obtain the desired expression. The projector $\mathbf{Q}_0$ is represented by $\mathbf{V}_0\mathbf{V}_0^T$.

2.4. The Extremal Sufficient Conditions. Conjugate Points of GE Curves. The set of Euler differential eqs 6 is a necessary condition for an extremum. However, a particular extremal curve satisfying the boundary conditions can furnish an actual extremal, let us say with the character of a minimum, only if it satisfies certain additional necessary conditions that take the form of inequalities, normally denoted as $\delta^2 I \geq 0$. The formulation of such inequalities together with their refinement into sufficient conditions is an important part of the theory of calculus of variations.[47,55] To prove this we first replace in the integral $I(\mathbf{q})$ of eq 4, the argument $\mathbf{q}$ by $\mathbf{q}_C(t,\varepsilon) = \mathbf{q}(t) + \varepsilon\,\mathbf{p}(t)$, being ε a small number. The curve $\mathbf{q}(t)$ must be an extremal and $\mathbf{q}_C(t,\varepsilon)$ is an arbitrary curve both satisfying the eq 3. The functions $\mathbf{p}(t)$ are variations of the extremal curve $\mathbf{q}(t)$ and satisfy the equation:

$$P(t, \mathbf{p}) = \mathbf{p}^T\nabla_{\mathbf{q}}G(t, \mathbf{q}) = \mathbf{p}^T\nabla_{\mathbf{q}}V(\mathbf{q}) = \mathbf{p}^T\mathbf{g} = 0 \tag{24}$$

with $\mathbf{p}(t_0) = \mathbf{0}$. In this way the comparison curves satisfy the subsidiary condition. Second, we expand $I(\mathbf{q})$ by the Taylor theorem until the second order in ε

$$\begin{aligned}H(\varepsilon) &= I(\mathbf{q} + \varepsilon\mathbf{p})\\ &= I(\mathbf{q}) + \varepsilon\delta I(\mathbf{q}, \mathbf{p}) + \frac{\varepsilon^2}{2}\delta^2 I(\mathbf{q}, \mathbf{p}) + O(\varepsilon^2)\end{aligned} \tag{25}$$

Since $I(\mathbf{q})$ is stationary for the extremal curve $\mathbf{q}(t)$, $\mathrm{d}H(\varepsilon)/\mathrm{d}\varepsilon\,|_{\varepsilon=0} = \delta I(\mathbf{q},\mathbf{p})$ vanishes, where the Euler–Lagrange eq 6 follows. A necessary condition for a minimum is $d^2H(\varepsilon)/d^2\varepsilon|_{\varepsilon=0} = \delta^2 I(\mathbf{q},\mathbf{p}) \geq 0$. The derivative $\delta^2 I(\mathbf{q},\mathbf{p})$ is expressible in the form

$$\begin{aligned}\delta^2 I(\mathbf{q}, \mathbf{p}) &= \int_{t_0}^{t'}\mathbf{p}^T[\nabla_{\mathbf{q}}\nabla_{\mathbf{q}}^T L(t, \mathbf{q})]\mathbf{p}\mathrm{d}t\\ &= \int_{t_0}^{t'}\mathbf{p}^T[\langle\mathbf{Fg}\rangle + \mathbf{H}^2 - \lambda\mathbf{H}]\mathbf{p}\mathrm{d}t = \int_{t_0}^{t'}\mathbf{p}^T\mathbf{C}\mathbf{p}\mathrm{d}t\end{aligned} \tag{26}$$

where we have dropped the dependence on t. This integral is evaluated along the GE and λ is just that given in eq 6. The condition $\delta^2 I(\mathbf{q},\mathbf{p}) \geq 0$ implies a problem of Lagrange in the $t\mathbf{p}$-space of precisely the same type as the original problem in the $t\mathbf{q}$ space. The integral to be minimized is $\delta^2 I(\mathbf{q},\mathbf{p})$, and the equation of the condition corresponding to eq 3 is the eq 24. To this $t\mathbf{p}$ problem we apply the Euler–Lagrange equation. The condition 24 can be introduced without the use of the multiplier rule if we consider that $\mathbf{p}(t) = (\mathbf{I} - \mathbf{P})\,\mathbf{m}(t)$, where $\mathbf{m}(t)$ is a vector of dimension N. We represent the projector $(\mathbf{I} - \mathbf{P}) = \mathbf{V}\mathbf{V}^T$ being as before $\mathbf{V}$, the matrix of dimension $N \times (N{-}1)$ containing the set of $N{-}1$ eigenvectors of $\mathbf{H}$ orthogonal to the $\mathbf{g}|\mathbf{g}|^{-1}$ vector. With this consideration we write $\mathbf{p}(t) = \mathbf{V}\mathbf{V}^T\mathbf{m}(t) = \mathbf{V}\mathbf{n}(t)$, being $\mathbf{n}(t)$ a vector of length $N{-}1$. Substituting this form of $\mathbf{p}(t)$ vector in eq 26 we have,

$$\delta^2 I(\mathbf{q}, \mathbf{p}) = \int_{t_0}^{t'}\mathbf{p}^T\mathbf{C}\mathbf{p}\mathrm{d}t = \int_{t_0}^{t'}\mathbf{n}^T\mathbf{V}^T\mathbf{C}\mathbf{V}\mathbf{n}\mathrm{d}t = \delta^2 I(\mathbf{q}, \mathbf{n}) \tag{27}$$

where we have again dropped the dependence on t. From eq 27 we conclude that the GE will extremalize the integral (eq 4) with a minimization character if it applies along the curve $\det(\mathbf{V}^T\mathbf{C}\mathbf{V}) \geq 0$.

More concisely, the minimum value of the integral of eq 26, or equivalently eq 27, defines the accessory problem of the variational problem under consideration. This variational $t\mathbf{p}$ problem of eq 26, which is the same variational $t\mathbf{n}$ problem of eq 27, is solved by the application of the Euler–Lagrange equations on the functional integral 27. These Euler–Lagrange equations are known as Jacobi equations of the accessory variational problem.[56] The accessory problem 27 affects the existence of extreme values of the fundamental integral (eq 4). The application of the Euler–Lagrange equation on the integral functional 27 results in the next expression:

$$\mathbf{V}^T\mathbf{CVn} = \mathbf{0}_{N-1} \tag{28}$$

If $\det(\mathbf{V}^T\mathbf{CV}) \neq 0$ along the GE between t_0 and t', then the unique solution of eq 28 is $\mathbf{n}(t) = \mathbf{0}_{N-1}$, which implies $\mathbf{p}(t) = \mathbf{Vn}(t) = \mathbf{0}$. From this we infer that the integral $\delta^2 I(\mathbf{q,p})$, or, that is, the same like $\delta^2 I(\mathbf{q,n})$, vanishes if $\mathbf{n}$ is the solution of the Jacobi eq 28, which possesses zero at $t = t_0$. In addition if $\det(\mathbf{V}^T\mathbf{CV}) > 0$ ($\det(\mathbf{V}^T\mathbf{CV}) < 0$) along this interval, then the GE curve extremalizes the integral (eq 4) with the character of a minimum (maximum). The value of integral (eq 4) evaluated using a different path, $\mathbf{q}_C(t,\varepsilon)$, is higher (lower) than that evaluated on the GE path $\mathbf{q}(t)$. If $\det(\mathbf{V}^T\mathbf{CV}) = 0$ at any point of the GE curve, say $t = t_1$, then the procedure is close to that which follows eq 21. We diagonalize the matrix $\mathbf{V}^T\mathbf{CV}$ of Jacobi eq 28 at this point. As before, let $\mathbf{U}$ be the unitary matrix of dimension $(N-1) \times (N-1)$, such that $\mathbf{V}^T\mathbf{CV} = \mathbf{UC}_D\mathbf{U}^T$, where $\mathbf{C}_D = \{c_{ij}\delta_{ij}\}_{i,j=1}^{N-1}$, then eq 28 is transformed to

$$\mathbf{C}_D\mathbf{z} = \mathbf{0}_{N-1} \tag{29}$$

being $\mathbf{z}(t_1) = \mathbf{U}^T\mathbf{n}(t_1)$. Because $\det(\mathbf{V}^T\mathbf{CV}) = 0$, then at least one element of $\mathbf{C}_D$ diagonal matrix is equal zero. Let us assume that $c_{ii} = 0$ then two solutions of the $\mathbf{z}(t_1)$ vector exist both of the form $\mathbf{z}(t_1)^T = (0_1, ..., z_i, ..., 0_{N-1})$, one with $z_i = 0$ and other with $z_i \neq 0$. In the first case $\mathbf{p}(t_1) = \mathbf{Vn}(t_1) = \mathbf{VUz}(t_1) = \mathbf{0}$ and in the second case $\mathbf{p}(t_1) = \mathbf{Vn}(t_1) = \mathbf{VUz}(t_1) = \mathbf{Vu}_i z_i \neq \mathbf{0}$, where $\mathbf{u}_i$ is the i column vector of the $\mathbf{U}$ matrix. This result implies that in a point of the GE curve, $\mathbf{q}(t_1)$, so that $\det(\mathbf{V}^T\mathbf{CV}) = 0$ there exist two solutions of the Jacobi eq 28, namely, $\mathbf{p}(t_1) = \mathbf{0}$ and $\mathbf{p}(t_1) \neq \mathbf{0}$, making the value of the integrand of eq 27 equal to zero at this point of the GE curve, $\mathbf{q}(t_1)$. According to the discussion that follows eq 20, a point of the GE curve so that $\det(\mathbf{V}^T\mathbf{CV}) = 0$ can be either a TP or a BP. In the case of a TP, the two solutions of eq 29, namely, $\mathbf{p}(t_1) = \mathbf{0}$ and $\mathbf{p}(t_1) \neq \mathbf{0}$ coincide with the GE curve since in the last case the structure $\mathbf{p}(t_1)$ is equal to the structure of the tangent vector $\mathbf{t}$ at this point. The same occurs for the BP, because for $\mathbf{p}(t_1) = \mathbf{0}$ the arbitrary curve $\mathbf{q}_C(t_1)$ coincides with both GE curves that meet at this point. The other solution, $\mathbf{p}(t_1) \neq \mathbf{0}$, the resulting arbitrary curve coincides with the GE curve that at the BP touches tangentially the isopotential contour hypersurface, since the form of the vector $\mathbf{p}(t_1)$ is the same to the tangent vector $\mathbf{t}$ of this GE curve. For this reason in these cases both solutions of eq 29 make the integrand of eq 27 equal zero at this point.

Once the value of the integral $\delta^2 I(\mathbf{q,p})$ has been evaluated along a GE curve, we now explore the effect of the existence on the GE curve of a point so that $\det(\mathbf{V}^T\mathbf{CV}) = 0$. Let us assume a GE curve starting at the point $\mathbf{q}_0 = \mathbf{q}(t_0)$ being this point a stationary point with the character of a minimum of the PES and ending at a first-order SP located at $\mathbf{q}_f = \mathbf{q}(t_f)$. At the point $\mathbf{q}_1 = \mathbf{q}(t_1)$ with $t_0 < t_1 < t_f$ of this GE curve is the $\det(\mathbf{V}^T\mathbf{CV}) = 0$ but at each point of the subarc within t_0 and t_1 is the $\det(\mathbf{V}^T\mathbf{CV}) > 0$. Let the point be a turning point for the GE under consideration, and after this turning point, the GE enters into a region where $\det(\mathbf{V}^T\mathbf{CV}) < 0$ until the last point $\mathbf{q}_f$. Notice that $\mathbf{C}$ is a continuous matrix function on $\mathbf{q}$. In this case we say that one can find an arbitrary curve, not necessarily a GE curve, joining the points $\mathbf{q}_0$ and $\mathbf{q}_f$ such that the integral (eq 4) takes a lower value in respect of the initial GE curve. In Figure 5, being equivalent to Figure 1 of the ref 17, exists two GE paths joining the points M2 and TP1 as well as the points M2 and TP2.

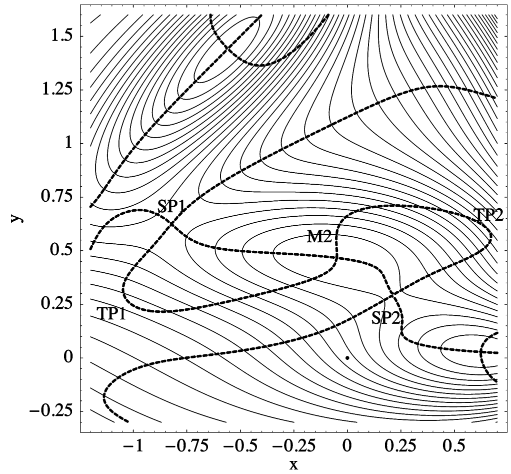

Figure 5. GE curves (fat dashes) on the mb-PES between SP1, minimum M2, and SP2 as well as turning points TP1 and TP2.

The value of the integral (eq 4) for the GE curve that coincides with the IRC path has a lower value in respect of the GE curve that evolves through the TP located at ∼(−1.00, 0.25). The preceding explanation is supported by numerical results calculated with the Mathematica program.[57] At point ∼(−0.5, 0.5) on the direct GE path between the minimum M2 and TS1 of the mb-PES, the value of $\det(\mathbf{V}^T\mathbf{CV}) = 1.0 \times 10^6$ is greater than zero. Notice that in the present case, since mb-PES is a two-dimensional PES, the $\mathbf{V}$ matrix is in fact a vector of dimension two, $\mathbf{v}^T = (v_x, v_y)$ and due to this fact, $\mathbf{V}^T\mathbf{CV} = \mathbf{v}^T\mathbf{Cv}$, is already a number; in other words, $\det(\mathbf{V}^T\mathbf{CV}) = \mathbf{v}^T\mathbf{Cv}$. In contrast, the value at the point ∼(−1.00, 0.25) on the GE path that goes through the mountains $\mathbf{v}^T\mathbf{Cv} = -200.00$, it is less than zero.

The same argument can be used if the $\mathbf{q}_1$ point is a BP. If the branch that achieves the point $\mathbf{q}_f$ after the BP enters into a region where $\det(\mathbf{V}^T\mathbf{CV}) < 0$ until the last point $\mathbf{q}_f$ then, as before, one can find an arbitrary curve, which is not necessarily a GE curve, so that the integral (eq 4) takes a lower value in respect of the original GE curve. The conclusion is: A point on a GE curve so that $\det(\mathbf{V}^T\mathbf{CV}) = 0$ reminds us of a Jacobi conjugate point of the curves that extremalizes the functional integral where the tangent argument appears explicitly.[55,56] We say that these points of the GE curve are like Jacobi conjugate points if they represent a change on the sign of the determinant of the $\mathbf{V}^T\mathbf{CV}$ matrix function in the evolution of the curve. Notice that the existence of Jacobi conjugate points in a curve extremalizing a functional integral where the tangent argument appears explicitly implies that the functional integral of the corresponding accessory problem cannot be reduced to a quadratic functional. From this follows that the value of the original functional integral evaluated using any curve can be lower than that of the value of the extremal curve.[55] In the present variational problem the accessory variational problem is already quadratic. Thus the existence of Jacobi-like conjugate points does not imply that the accessory problem can be reduced in a quadratic form. In the present case, these points may represent a change of sign of the quadratic functional $\mathbf{n}^T\mathbf{V}^T\mathbf{CVn}$, therefore it follows that from this point any curve can reduce the functional integral of eq 4. We emphasize that the Jacobi conjugate point concept takes its full complete relevance when the extremal curves under consideration form a field of extremals, like SD curves.[39] The GE curves do not form a field of extremals in the PES region. There exist N GE curves only if the dimension of the PES is N. Nevertheless, we say that TP and BP points of a GE arc curve in some aspects resemble the original Jacobi conjugate point concept, and due to this fact, we say that these points can be seen as Jacobi-like conjugate points.

3. RELATION BETWEEN TPs OF A GE CURVE AND VALLEY-RIDGE INFLECTION POINTS

Regarding Figure 1, a valley-ridge inflection point (VRI) emerges in the GE subarc that goes from the TP located at the point ~(−0.2, −0.6) and to the TP located at the point ~(0.0, 1.0). The VRI point is related to the existence of a bifurcation in the PES. The VRI is a feature of the PES and does not always have relations with the nature of the curve.[58] In Figure 4 of the mb-PES, looking at the GE subarc being orthogonally to the GE RP at the minimum M2, which goes from the TP1 located at the point ~(−1.00, 0.25) to the TP2 located at the point ~(0.6, 0.6), a point of this subarc is the minimum M2. This GE subarc is orthogonal to the GE RP at the stationary point, M2. As before, a stationary point is a feature of the PES and does not always have relations to the nature of the curve going through it. However the most important is a possible relation between TPs of a GE and VRIs of the PES. In Figure 5 of ref 59 is shown the TPs of the different GEs and the VRI points of the mb-PES. With this observation, we enunciate the next proposition.

A GE touches at its TP, $\mathbf{q}(t_{TP})$, a isopotential hypersurface of the full PES. At other GE points, it crosses a family of isopotential hypersurfaces transversally. We may assume that at $\mathbf{q}(t_{TP})$ and the next points $\mathbf{q}(t)$ of the GE, with $t_{TP} < t$, the family of isopotential hypersurfaces is pseudoconvex with the pseudoconvexity index:[60]

$$\mu = \frac{\mathbf{g}^T\mathbf{A}\mathbf{g}}{\mathbf{g}^T\mathbf{g}} > 0 \text{ (or vice versa)} \tag{30}$$

If along the GE the index μ changes the sign then there is a VRI point. In eq 30 the $\mathbf{A}$ matrix is the adjoint matrix of the Hessian matrix $\mathbf{H}$, and it satisfies the relation, $\mathbf{AH} = \mathbf{I}\det(\mathbf{H})$.

The proof of the proposition is the following: At the transition point of the GE through the contour valley-ridge, we have to find a zero eigenvector of the Hessian matrix lying in the tangential plane of the corresponding isopotential hypersurface. Because this point belongs to a GE, the gradient is an eigenvector of the Hessian matrix, and due to this fact, the gradient vector is orthogonal to the eigenvector with null eigenvalue. This is nothing more that the definition of a VRI point.[60] Notice that it is not necessary that a TP point of the GE curve exists before the GE transverses a contour valley-ridge inflection. In Figure 5 of ref 59 exists an isolated VRI point on a GE curve, but no TP of this GE exists near to this VRI point. On the other hand, there can be two consecutive TPs of a GE without a VRI point in between, see again Figure 5 of ref 59.

Finally we remark that if a GE having a VRI point in a subarc, then it does not imply that in this subarc $\det(\mathbf{V}^T\mathbf{CV}) \geq 0$ holds, or vice versa. In other words, the VRI point does not affect the extremal character of the subarc. Let us assume a GE subarc without TP lifting a valley region with $\det(\mathbf{V}^T\mathbf{CV})) \geq 0$ and entering in a ridge region through a VRI point, where in this new region the GE has $\det(\mathbf{V}^T\mathbf{CV})) \geq 0$. This result is a direct consequence of the discussion of Section2.4.

4. DISCUSSION, SUMMARY, AND CONCLUSION

The GE curve can be used to determine the TS and intermediates of any reaction mechanism starting at the reactant minimum. Examples are demonstrated for methyleneimine ($H_2C{=}NH$) computed using a CASSCF calculation,[13] the electrocyclic reaction of cyclobutene to butadiene,[9] or the formation of amino-acetonitrile.[61] As reported in the Introduction Section, the GE path is also a type of curve that can be used as a representation of a RP in the cases that fail the IRC as a representation. Due to the importance of this type of path, we have proved the variational nature of the GE path. GEs are curves where the norm of the gradient has a local extremum on isopotential hypersurfaces of the PES, $V(\mathbf{q}(t)) = v(t)$. An example is discussed in ref 53, where the IRC is going down across a ridge, but the GE represents the MEP which is parallel nearby. The PES of that example is a modified PES of an alanine dipeptide rearrangement.[62] The GE paths are extremal curves of a variational problem that is formulated in expression (eq 4). The tangent of this type of curves has been derived using the perturbation theory due to McWeeny that is widely used in quantum mechanics. In addition their extremal sufficient conditions are studied and reported being summarized as follows. If the curve starts at a minimum of the PES with $\det(\mathbf{V}^T\mathbf{CV}) > 0$, with eq 27, and ends at a first-order stationary point, the extremal curve achieves its condition of a minimal curve. However, if this curve has a TP or a BP, then from this point to the end point may be $\det(\mathbf{V}^T\mathbf{CV}) < 0$, and the GE curve looses its minimum character, see Figure 1. If $\det(\mathbf{V}^T\mathbf{CV}) < 0$ from the TP to the end point, then other curves exist. Not necessarily a GE curve joins the initial and final point so that the integral (eq 4) takes a lower value. The TP and the BP of a GE curve can be seen as a Jacobi conjugate point of this type of curves. Nevertheless, this equivalence should be taken carefully since the GE curves do not form a field of curves covering the PES region as occurs with the SD curves or with NTs. In the later cases the concept of Jacobi conjugate points takes its important relevance. The missing "field" property may be an advantage of the GE calculation. In ref 30 was found a VRI point of the ring closure of the allyl radical, however that point is located after a small ring-opening. The search with NT failed because it was done in the false direction. But a search of the minimal GE along the minimum valley of the allyl radical found that point. The VRI points are important on PESs where the RP bifurcates.[58] The relation between the VRI points and the GE curve is also analyzed. VRIs are the type of points related to the curve which leaves a valley region and enters into a ridge region of the PES, or vice versa. The behavior of the GE path can be used as a way to take information on the topology of the PES region where the reaction mechanism takes place.[63]

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Notes

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