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The Variational Nature of the Gentlest Ascent Dynamics and the Relation of a Variational Minimum of a Curve and the Minimum Energy Path

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Abstract It is shown that the path described by the gentlest ascent dynamics to find transition states [W. E and X. Zhou, Nonlinearity 24, 1831 (2011)] is an example of a quickest nautical path for a given stationary wind or current, the so-called Zermelo navigation variational problem. In the present case the current is the gradient of the potential energy surface. The result opens the possibility to propose new curves based on Zermelo's theory for two tasks: locate transition states and define reaction paths. The relation between a minimal variational character, that some former reaction pathways possess, and the minimum energy path is discussed.

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1 introduction

The concept of the reaction path (RP) is one of the concepts most widely used in the chemical community. The RP is a continuous curve on the potential energy surface (PES) joining two minimums through a first index saddle point (SP) or transition state. More accurately, it is a continuous curve which monotonically ascends from a minimum to the SP and monotonically descends from the SP to the other minimum. If the RP is located in a deep valleys valley floor then the RP is named minimum energy path (MEP). Many types of curves satisfy the RP requirement and can be used as its

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representation[1]. The first curve proposed for this purpose was the steepest descent[2,3], which is still the most used model curve. Other curves defined as possible RP, to name a few, are the gradient extremals (GE)[4–7], the distinguished reaction coordinate[8], or more mathematical, the Newton trajectory (NT)[9,10], and more recently the gentlest ascent dynamics (GAD)[11]. All these curves have their advantages and inconveniences for the use as an RP representation.

Despite many RPs commonly being geodesic curves on a surface[12], each type of the RP curve has different mathematical fundaments. For this reason each RP has its own evolution on the PES to reach a first index SP from the minimum. The properties and features of some RP curves mentioned above are variational in nature, like the steepest descent[13,14], gradient extremals[15], and the distinguished reaction coordinate also known as NT[16]. An attempt to reach the variationality of the GAD curve model is reported in reference[17] based on the concept of the image function. However this result is not general since it is applicable only to quadratic regions of the PES.

In this paper, first we report a proof of the variational character of the GAD curves. We consider a system with N degrees of freedom represented by a point vector $\mathbf{x} \in \mathbb{R}^N$. Curves in the $\mathbb{R}^N$ are usually characterized by $\mathbf{x}(t)$ with a parameter t. The potential energy is described by the PES function, $V(\mathbf{x})$. The concept of the GAD model is that of a dynamical system. The solution curves of the GAD equations[11] evolve from a point close to a minimum to an SP on the PES. The GAD model is based on the gradient field of the PES, $\mathbf{g}(\mathbf{x}) = \nabla_{\mathbf{x}} V(\mathbf{x})$, and a normalized control vector, $\mathbf{w}$. Used is also the Hessian matrix, $\mathbf{H}(\mathbf{x}) = \nabla_{\mathbf{x}} \mathbf{g}^T(\mathbf{x})$. The control vector itself is generated on the path, point by point, by a continuous version of the power method for finding the eigenvector of the Hessian matrix which belongs to the smallest eigenvalue. The study of this control vector $\mathbf{w}$ is the aim of this paper.

The first GAD equation for the tangent or velocity vector $\dot{\mathbf{x}}$ of a GAD curve is the sum of the reverse (negative) gradient plus two times an effect of the control vector, $\mathbf{w}$, shorten with the projection on the gradient

$$\dot{\mathbf{x}} = -\mathbf{g} + 2\left(\mathbf{w}^T\mathbf{g}\right)\mathbf{w} = -[\mathbf{I} - 2\mathbf{w}\mathbf{w}^\mathbf{T}]\mathbf{g} \tag{1}$$

if we assume that the $\mathbf{w}$-vector is a normalized vector. $(\mathbf{w}^T\mathbf{g})$ is the scalar product. Geometrically, matrix $[\mathbf{I}-2\mathbf{w}\mathbf{w}^\mathbf{T}]$ is a mirror transformation at the mirror line through $\mathbf{w}$. Note that $(\mathbf{w}\mathbf{w}^T)$ is a dyadic product matrix. The vector $\mathbf{w}(t)$ depends on the curve parameter, t. Finding the variational bases of this model is, in general, difficult. We address this issue by finding the optimal geodesic distance[18] functional, F, for the control of the search, that generates a curve subject to the constraints

(a) the gradient field cannot be controlled,

(b) the control is executed by the normalized vector, $\mathbf{w}$, which is here generated by the power method to find the eigenvector with lowest eigenvalue of the Hessian, $\mathbf{H}$, thus

$$\dot{\mathbf{w}} = -[\mathbf{I} - \mathbf{w}\mathbf{w}^T]\mathbf{H}\mathbf{w} \tag{2}$$

where the matrix $[\mathbf{I} - \mathbf{w}\mathbf{w}^T]$ is the projection orthogonal to the control vector $\mathbf{w}$.

The behavior of some GAD curves is shown in Fig.1 on a 2D toy potential[19]. The GAD is the counterpart of a well-known classical navigation problem posed and solved by Zermelo[20,21]:

"May be it is given the present location of a ship in the sea, with a given current distribution characterized by a location dependent vector field. One desires to find the optimal control of the ship so as to reach the destination in the shortest possible time."

Back to GAD: the gradient vector field of the PES function can be thought of as representing the current of the sea, which we cannot change, whereas the normalized vector $\mathbf{w}$ determines the control.

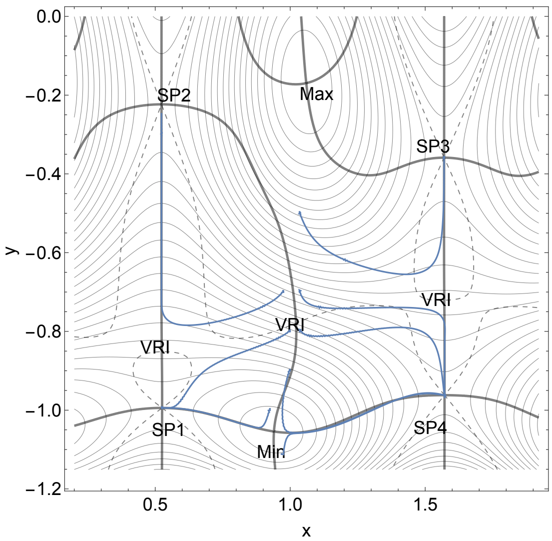

Fig. 1 Some GAD curves (Eq.(1), blue) on a two-dimensional toy potential[19]. The thin dashes mark the borderline between valleys and ridges. The thick black curves are gradient extremals[4,5]. The control vector, **w**, is throughout the first eigenvector, calculated by Eq.(2). The initial points for all GADs are from the strip x≈ 1, and $-0.5 > y > -1.1$. All GADs finish at SPs of index one going along the gradient extremals at least. GADs from the minimum go only to the SP1 and to the SP4. VRI is valley-ridged inflection point.

The destination is the next SP of the PES. We recall that the set of coupled first order ordinary differential equations, Eqs. (1) and (2), constitute the basic expressions of the GAD model[11,17]. In Section II we introduce the variational approach with a Randers metric[22]. In Sections III and IV we use the Euler equations of the approach, where in Section V we use the ansatz of a Mayer variational problem. The general case of GAD for the search of saddles of any index is treated in Section VI. Section VII concludes the paper; here we also compare different RP curves and their variational character as well as their relation to a MEP definition. Thus, taking into account the results on the variational character of the GAD curves and the well known variationality of other curves used as representation of reaction paths, we discuss the relation between a minimum variational character and the minimum energy path (MEP). We think that the present paper can be of interest for both, the community of researchers which are interested in the exploration of the PES, as well as the researchers from the control theory community.

2 The variational approach

We now understand Eq. (1) as a variational problem with control vector **w**, a Zermelo problem. The gradient of the PES plays the role of the wind or the current distribution which we cannot influence. The length of the control vector is given by the double projection of the gradient onto the vector **w** itself. With reference ⟦23⟧ (Eqs. (23)-(27) there) we can translate Eq. (1) into a functional $F(\mathbf{x}, \dot{\mathbf{x}})$

with Randers metric

$$F(\mathbf{x},\dot{\mathbf{x}}) = \frac{\sqrt{\left(\dot{\mathbf{x}}^T\mathbf{g}\right)^2 + \dot{\mathbf{x}}^T\dot{\mathbf{x}}\left[\left(2\mathbf{w}^T\mathbf{g}\right)^2 - \mathbf{g}^T\mathbf{g}\right]} + \dot{\mathbf{x}}^T\mathbf{g}}{\left[\left(2\mathbf{w}^T\mathbf{g}\right)^2 - \mathbf{g}^T\mathbf{g}\right]} \ . \tag{3}$$

The expression is simplified if we introduce the matrix

$$\mathbf{M} = \frac{1}{D^2}\mathbf{g}\mathbf{g}^T + \frac{1}{D}\mathbf{I} \tag{4}$$

and the vector

$$\mathbf{m} = \frac{1}{D}\mathbf{g} \ . \tag{5}$$

$\mathbf{I}$ is the unit matrix and $D = \left[(2\mathbf{w}^T\mathbf{g})^2 - \mathbf{g}^T\mathbf{g}\right]$ is a real number. Thus we have

$$F(\mathbf{x},\dot{\mathbf{x}}) = \sqrt{\dot{\mathbf{x}}^T\mathbf{M}\dot{\mathbf{x}}} + \mathbf{m}^T\dot{\mathbf{x}} \ . \tag{6}$$

The solution curves of the GAD problem could then found by working out the geodesics of the metric. This type of a metric was introduced by Randers in his study of gravitation and electromagnetism[24]. Note that such a metric is non-Riemannian because of the linear term $\mathbf{m}^T\dot{\mathbf{x}}$.

To address such a type of a navigation problem in the calculus of variations[18, 21, 25], one requires the concept of a geodesic distance. It has to be a concept of a distance that depends not only on the location but also on the direction of the tangent of the path. Specifically, for a given curve, $\mathbf{x}(t)$ with any curve parameter t in the configuration space, we consider an integral of the form

$$\mathfrak{I}(\mathbf{x}) = \int_{t_0}^{t_f} F(\mathbf{x},\dot{\mathbf{x}})dt \tag{7}$$

for a positive functional F. t_0 is a fixed initial value for the parameter t, but t_f is an unspecified final value of this parameter. F is assumed to be homogeneous of first degree in $\dot{\mathbf{x}}$, $F(\mathbf{x},\lambda\dot{\mathbf{x}}) = \lambda F(\mathbf{x},\dot{\mathbf{x}})$ for any $\lambda > 0$, so that $\mathfrak{I}$ is independent of the choice of the parameter t along $\mathbf{x}(t)$. The functional, $F(\mathbf{x},\dot{\mathbf{x}})$, includes for each point $\mathbf{x}$ of the configuration space a distance in the tangential space. The Randers metric (6) fulfills this. The initial point $\mathbf{x}(t_0)$ in integral (7) is a minimum. It is carried into the final point $\mathbf{x}(t_f)$ which is a saddle point (SP) of index one. (For a numerical curve following along Eq. (1), the $\mathbf{x}(t_0)$ is to move out of the minimum to realize $\mathbf{g} \neq \mathbf{0}$, and the final convergence at the SP is also bad[26]). The variational approach is to find a minimum of $\mathfrak{I}$ for a variation of different curves $\mathbf{x}(t)$.

Evidence of metric ansatz (3)

Following Carathéodory[21] we formulate the GAD model as a case of a positive definite variational problem. We have to prove that the functional $F(\mathbf{x},\dot{\mathbf{x}})$ is always defined for all line elements which can go through a point. The line elements, $(\mathbf{x},\mathbf{g})$, are the points $\mathbf{x}$ which describe the position on the PES, and the gradients, $\mathbf{g}$, considered as a flow, which vary from point to point. The $\mathbf{w}$-vector in Eq. (1) controls the navigation on the PES and forms an angle β with the gradient vector at each point $\mathbf{x}$. We use generally by $\mathbf{x}(t)$ the coordinates of an arbitrary path where t is the parameter that characterizes the curve. If we specialize $\mathbf{x}(t)$ to a GAD curve fulfilling Eq. (1) then we may observe that we can understand the metric Eq. (3) as a positive solution of the quadratic equation

$$\left(\dot{\mathbf{x}} + \mathbf{g}F\right)^T\left(\dot{\mathbf{x}} + \mathbf{g}F\right) = \left(2\mathbf{w}^T\mathbf{g}F\right)^2 \tag{8}$$

if such a root exists. The equation is, at the other hand, the scalar product of the following equation with itself

$$\frac{1}{F}\dot{\mathbf{x}}+\mathbf{g}=2\big(\mathbf{w}^T\mathbf{g}\big)\mathbf{w}=2(\mathbf{w}\mathbf{w}^T)\mathbf{g} \tag{9}$$

if we assume that the **w**-vector is a normalized vector. Since $F=1$ this is Eq. (1), the GAD approach for a differential equation. Thus, the Randers metric Eq. (6) and Eq. (1) are equivalent to describe a GAD curve.

We still discuss the question of the existence of F in Eq. (3). We again assume that we are on a GAD curve $\mathbf{x}(t)$. γ is the angle formed by the vectors $\dot{\mathbf{x}}$ and $\mathbf{g}$ and β is the angle formed by the vectors $\mathbf{w}$ and $\mathbf{g}$. Using the angles in the scalar products then the functional $F\left(\mathbf{x},\dot{\mathbf{x}}\right)$ in Eq. (3) takes the form

$$F(\mathbf{x},\dot{\mathbf{x}})=\frac{\sqrt{\dot{\mathbf{x}}^T\dot{\mathbf{x}}}}{\sqrt{\mathbf{g}^T\mathbf{g}}}\left[\frac{cos\gamma+\sqrt{cos^2\gamma+(4cos^2\beta-1)}}{4cos^2\beta-1}\right]. \tag{10}$$

Since tangent $\dot{\mathbf{x}}$ is that given in Eq. (1) then it holds $\dot{\mathbf{x}}^T\dot{\mathbf{x}}=\mathbf{g}^T\mathbf{g}$. Also we consider that $\mathbf{g}^T\dot{\mathbf{x}}=\sqrt{\dot{\mathbf{x}}^T\dot{\mathbf{x}}}\sqrt{\mathbf{g}^T\mathbf{g}}cos\gamma=\left(\mathbf{g}^T\mathbf{g}\right)cos\gamma$. Multiplying Eq. (1) from the left by $\mathbf{g}^T$ we obtain $\mathbf{g}^T\dot{\mathbf{x}}=\mathbf{g}^T\mathbf{g}\left(2cos^2\beta-1\right)$. Equating both equations for $\mathbf{g}^T\dot{\mathbf{x}}$ we obtain that it holds everywhere on a GAD curve

$$cos\gamma=2cos^2\beta-1\ . \tag{11}$$

With the relation $\left(4cos^2\beta-1\right)=2\left(2cos^2\beta-1\right)+1=2cos\gamma+1$ we can substitute the expression in Eq. (10) and we have $F\left(\mathbf{x},\dot{\mathbf{x}}\right)=1$ for all angles. Note that the putative singularity in the denominator, $(4cos^2\beta-1)$, for $\beta=\pm(60^o+k\,\pi)$ or $\beta=\pm(120^o+k\,\pi)$ at $k=0,1$ cancels out. We result that for a GAD curve, $\mathbf{x}(t)$, the variational integral (7) reduces to

$$\Im=\int_{t_0}^{t_f}1dt=t_f-t_0\ . \tag{12}$$

3 The Hamiltonian and the first canonical Euler equation

Note that the matrix $\mathbf{M}$ and the vector $\mathbf{m}$ are functions of $\mathbf{x}$ and $\mathbf{w}$. If we differentiate Eq. (6) with respect to $\dot{\mathbf{x}}$, we have $\nabla_{\dot{\mathbf{x}}}F=\frac{\mathbf{M}}{\sqrt{\dot{\mathbf{x}}^T\mathbf{M}\dot{\mathbf{x}}}}\dot{\mathbf{x}}+\mathbf{m}=\mathbf{y}$. $\mathbf{y}$ is the vector of canonical coordinates. The Hamiltonian corresponding to this type of metric, F, is $2H\left(\mathbf{x},\mathbf{y}\right)=\left(\mathbf{y}-\mathbf{m}\right)^T\mathbf{M}^{-1}\left(\mathbf{y}-\mathbf{m}\right)-1=0$. Working in this way one needs to compute the inverse of the matrix $\mathbf{M}$ which is tedious, see APPENDIX A. A way to avoid this calculation is that proposed by Zermelo: We obtain by differentiation of Eq. (8) with respect to $\dot{\mathbf{x}}$

$$\big(\mathbf{I}+\mathbf{y}\mathbf{g}^T\big)(\dot{\mathbf{x}}+\mathbf{g}F)=\big(2\mathbf{w}^T\mathbf{g}\big)^2F\mathbf{y}\ . \tag{13}$$

By a simple algebraic manipulation we get that the eigenvalue equation for $\mathbf{y}$ holds

$$\big(\mathbf{I}+\mathbf{y}\mathbf{g}^T\big)\mathbf{y}=\big(1+\mathbf{y}^T\mathbf{g}\big)\mathbf{y}=\omega\mathbf{y}\ . \tag{14}$$

We can try to solve Eq. (13) for $(\dot{\mathbf{x}}+\mathbf{g}F)$. We obtain the following equivalent equation

$$\omega(\dot{\mathbf{x}}+\mathbf{g}F)=\big(2\mathbf{w}^T\mathbf{g}\big)^2F\mathbf{y}. \tag{15}$$

Therefore, since $\mathbf{w}^T\mathbf{g}\neq 0$, we can write using Eq. (9)

$$\mathbf{w}\omega=\big(2\mathbf{w}^T\mathbf{g}\big)\,\mathbf{y}\ . \tag{16}$$

If we insert the $\mathbf{y}$-vector into the expression of ω given in Eq. (14), then we obtain that $\omega = 2$ constant throughout, and $\mathbf{y}^T\mathbf{g} = 1$. The Eq. (16) can be expressed as a scalar function of $\mathbf{w}^T\mathbf{g}$. Moreover, it follows that

$$0 = \left(2\mathbf{w}^T\mathbf{g}\right)^2\mathbf{y}^T\mathbf{y} - \omega^2 = \left(2\mathbf{w}^T\mathbf{g}\right)^2\mathbf{y}^T\mathbf{y} - \left(1+\mathbf{y}^T\mathbf{g}\right)^2 \ . \tag{17}$$

We obtain that we can choose a quadratic function of the $\mathbf{y}$-vector as the Hamiltonian function

$$H(\mathbf{x},\mathbf{y}) = \frac{1}{2}[(2\mathbf{w}^T\mathbf{g}(\mathbf{x}))^2\ (\mathbf{y}^T\mathbf{y}) - (1+\mathbf{y}^T\mathbf{g}(\mathbf{x}))^2] \tag{18}$$

where the control vector is assumed to be locally fixed.

According to the general formulas of the calculus of variation[18,21], it is $\dot{\mathbf{x}} = \lambda\nabla_{\mathbf{y}}H(\mathbf{x},\mathbf{y})$, and we have

$$\dot{\mathbf{x}} = \lambda\Big(\left(2\mathbf{w}^T\mathbf{g}\right)^2\mathbf{y} - \omega\mathbf{g}\Big) \ . \tag{19}$$

It is now

$$F = (\nabla_{\dot{\mathbf{x}}}F)^T\dot{\mathbf{x}} = \mathbf{y}^T\dot{\mathbf{x}} = \lambda\Big(\left(2\mathbf{w}^T\mathbf{g}\right)^2\mathbf{y}^T\mathbf{y} - \omega\mathbf{y}^T\mathbf{g}\Big). \tag{20}$$

With the help of Eqs. (14) and (17), we obtain from this

$$F = \lambda\big(\omega^2 - \omega\,(\omega-1)\big) = \lambda\omega. \tag{21}$$

Since by assumption $F > 0$, λ must be always positive since ω is positive equal two. The possibility to decide either a given line element is positive or negative regular is to calculate the $\mathfrak{E}$-function or the Weierstrass error function[21], a function related with the derivative of the functional F with respect to $\dot{\mathbf{x}}$ at fixed $\mathbf{x}$, and a second direction $\dot{\mathbf{x}}'$ obtaining

$$\begin{aligned} &\mathfrak{E}(\mathbf{x},\dot{\mathbf{x}},\dot{\mathbf{x}}') = F(\mathbf{x},\dot{\mathbf{x}}') - (\nabla_{\dot{\mathbf{x}}}F(\mathbf{x},\dot{\mathbf{x}}))^T\dot{\mathbf{x}}' = F(\mathbf{x},\dot{\mathbf{x}}') - \mathbf{y}^T\dot{\mathbf{x}}' = \lambda'\omega' - \\ &\lambda'\mathbf{y}^T\left(\left(2\mathbf{w}'^T\mathbf{g}\right)^2\mathbf{y}' - \omega'\mathbf{g}\right) = \lambda'\omega' - \lambda'\left(\left(2\mathbf{w}'^T\mathbf{g}\right)^2\mathbf{y}^T\mathbf{y}' - \omega'\mathbf{y}^T\mathbf{g}\right) = \\ &\lambda'\omega' - \lambda'\left(\left(2\mathbf{w}'^T\mathbf{g}\right)^2\mathbf{y}^T\mathbf{y}' - \omega'\omega + \omega'\right) = \lambda'\left(\omega'\omega - \left(2\mathbf{w}'^T\mathbf{g}\right)^2\mathbf{y}^T\mathbf{y}'\right) \end{aligned} \tag{22}$$

where we have used that $\mathbf{y}^T\mathbf{g} = \omega - 1$. Now we substitute Eq. (16) in this expression and obtain the final expression

$$\mathfrak{E}(\mathbf{x},\dot{\mathbf{x}},\dot{\mathbf{x}}') = \lambda'\omega'\omega\left(1 - \mathbf{w}^T\mathbf{w}'\frac{\mathbf{w}'^T\mathbf{g}}{\mathbf{w}^T\mathbf{g}}\right) = \lambda'\omega'\omega\left(1 - cos\alpha\frac{cos\beta'}{cos\beta}\right) \ . \tag{23}$$

α is the angle formed by the vectors $\mathbf{w}'$ and $\mathbf{w}$. The expression in the parenthesis is always ≥ 0. The line elements are therefore all strong; they are positive since $\lambda'\omega' > 0$ and $\omega = 2$. The only line elements which form an exception are the *anomalous* line elements for which $\mathbf{w}^T\mathbf{g} = 0$. These line elements lie on the limit curves for the stationary field of extremals. In the general case, it is conceivable that an extremal passes through such a line element and that the $\mathfrak{E}$-function has either different signs on each side of this point or the same sign.

For many purposes it is more convenient to introduce ν as a parameter, whereby we set $F = \lambda\omega = 1$. Moreover, if we replace the $\mathbf{y}$-vector by its value from Eq. (16), then the canonical equation become especially simple. Namely, instead of Eq. (19), we obtain Eq. (1) in the form

$$\frac{d\mathbf{x}}{d\nu} = -\big(\mathbf{I} - 2\mathbf{w}\mathbf{w}^T\big)\mathbf{g} \ . \tag{24}$$

Of course, it is not surprising that we obtain back Eq. (1) from the first canonical equation, because Eq. (1) was the start relation for the approach (3) and (8).

4 The second canonical Euler equation

According to the second fundamental equation of the calculus of variations, it is $\dot{\mathbf{y}} = -\lambda \nabla_{\mathbf{x}} H(\mathbf{x}, \mathbf{y})$, and we obtain the extremals of the problem by adding to Eq. (19)

$$\dot{\mathbf{y}} = -\lambda\big(4\big(\mathbf{w}^T\mathbf{g}\big)\big(\mathbf{y}^T\mathbf{y}\big)\mathbf{H}\mathbf{w} - \omega\mathbf{H}\mathbf{y}\big) \tag{25}$$

where we recall that the bold $\mathbf{H}$ is the Hessian of the PES. For a solution we have to use initial values $(\mathbf{x}_0, \mathbf{y}_0)$ for which the Hamiltonian $H = 0$ holds in Eq. (17). Now we extend the property of the control vector $\mathbf{w}$ from being fixed to be a function of t (or ν). The purpose is to transform the expression for $\dot{\mathbf{y}}$ which tells us how the control vector, $\mathbf{w}$, changes with respect to t (or ν) since this is the second basic element of the GAD problem. The second canonical Euler equation, Eq. (25), gives us this opportunity because both, the $\mathbf{y}$-vector and the control vector $\mathbf{w}$, are related through Eq. (16). We substitute Eq. (16) in the right hand side of Eq. (25)

$$\dot{\mathbf{y}} = -\frac{\lambda\omega^2}{2\mathbf{w}^T\mathbf{g}}\mathbf{H}\mathbf{w}. \tag{26}$$

On the other hand, we differentiate Eq. (16) with respect to t taking into account that $d\omega/dt = 0$ since $\omega = 2$,

$$\dot{\mathbf{y}} = \frac{\omega}{2\mathbf{w}^T\mathbf{g}}\left[\mathbf{I} - \frac{\mathbf{w}\mathbf{g}^T}{\mathbf{w}^T\mathbf{g}}\right]\dot{\mathbf{w}} - \frac{2\omega}{\left(2\mathbf{w}^T\mathbf{g}\right)^2}\mathbf{w}\left(\mathbf{w}^T\dot{\mathbf{g}}\right). \tag{27}$$

To avoid the explicit calculation of $\dot{\mathbf{g}}$ in the direction of the $\mathbf{w}$ vector, we use that $d\omega/dt = 0 = \dot{\mathbf{y}}^T\mathbf{g} + \mathbf{y}^T\dot{\mathbf{g}}$, where from this result the next relation holds, $-\dot{\mathbf{y}}^T\mathbf{g} = \mathbf{y}^T\dot{\mathbf{g}}$. We substitute in this expression Eq. (16) and Eq. (26). The resulting expression for $\mathbf{w}^T\dot{\mathbf{g}}$ is substituted into Eq. (27), resulting in

$$\dot{\mathbf{y}} = \frac{\omega}{2\mathbf{w}^T\mathbf{g}}\left[\mathbf{I} - \frac{\mathbf{w}\mathbf{g}^T}{\mathbf{w}^T\mathbf{g}}\right]\dot{\mathbf{w}} - \frac{2\lambda\omega^2}{\left(2\mathbf{w}^T\mathbf{g}\right)^2}\mathbf{w}\left(\mathbf{g}^T\mathbf{H}\mathbf{w}\right) . \tag{28}$$

Finally, Eq. (26) is equated with Eq. (28), obtaining

$$\frac{\omega}{2\mathbf{w}^T\mathbf{g}}\left[\mathbf{I} - \frac{\mathbf{w}\mathbf{g}^T}{\mathbf{w}^T\mathbf{g}}\right]\dot{\mathbf{w}} - \frac{2\lambda\omega^2}{\left(2\mathbf{w}^T\mathbf{g}\right)^2}\mathbf{w}\left(\mathbf{g}^T\mathbf{H}\mathbf{w}\right) = -\frac{\lambda\omega^2}{2\mathbf{w}^T\mathbf{g}}\mathbf{H}\mathbf{w} . \tag{29}$$

Multiplying both sides from the left by the projector $\left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right]$ we obtain

$$\left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right]\dot{\mathbf{w}} = -\lambda\omega\left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right]\mathbf{H}\mathbf{w}. \tag{30}$$

Finally, setting $\lambda\omega = 1$ and using the idem potency of the projector $\left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right]$ (see APPENDIX B) we get the result

$$\frac{d\mathbf{w}}{d\nu} = -\big[\mathbf{I} - \mathbf{w}\mathbf{w}^T\big]\mathbf{H}\mathbf{w} . \tag{31}$$

The equation is derived from the Hamiltonian (17) for which only Eq. (1) and the variational integral (7) are used. The equation (31) contains the variation of the GAD control vector (see Eq. (2)). It forms with Eq. (24) a system which permits to find all variational extremals of the GAD problem. If we have calculated the vectors $\mathbf{x}$ and $\mathbf{w}$ as functions of ν, then we can determine the $\mathbf{y}$ from Eq. (16) without further integration.

According to Eqs. (24) and (31), every GAD extremal is unique determined by its initial values $\mathbf{x}_0, \mathbf{w}_0$. In the case of $\mathbf{w}$ is an eigenvector of $\mathbf{H}$, Eq. (31) is stationary: the change of $\mathbf{w}$ is zero. The approach (31) is an eigenvector following method[27–31] along the direction of the eigenvector which belongs to the smallest eigenvalue. This case that $\mathbf{w_0}$ is the 'smallest' eigenvector of $\mathbf{H}$ forms the optimal control case, other directions $\mathbf{w_0}$ show by a successive application of Eq. (31) a convergence toward the optimal control curve. Along a calculation, the direction of $\mathbf{w}$ is turned into the corresponding eigenvector direction, and the GAD curve confluences to the optimal GAD curve. It is similar to the steepest descent, where all curves, which follow a steepest descent, confluent into the valley floor pathway.
The proof has to go on by the Pontryagin Maximum Principle[25,32,33].

5 Another proof based on the method of Lagrangian multipliers

In this section we want to present the problem (3) to (7) as a Mayer variational problem[21]. We have been seen before that in a gradient distribution field the search of a stationary point is identical to a problem of the calculus of variations with control. As in the previous section the search or motion on the PES can be represented by defining the coordinates, $\mathbf{x}$, as a function of a parameter t or ν. However, not all such functions represent a "drivable" path, since the condition of Eq. (9) must always be fulfilled, now rewritten as,

$$\frac{1}{\dot{\nu}}\dot{\mathbf{x}} = -\mathbf{g} + 2\left(\mathbf{w}^T\mathbf{g}\right)\mathbf{w} \ . \tag{32}$$

ν is any curve parameter with $t = t(\nu)$. The path is used in the form $\mathbf{x}(t) = \mathbf{x}(t(\nu))$.

The necessary and sufficient condition for each point of the path to correspond to at least one driving direction $\mathbf{w}$, under its application the path is guided, is

$$(\dot{\mathbf{x}} + \dot{\nu}\mathbf{g})^T(\dot{\mathbf{x}} + \dot{\nu}\mathbf{g}) - \left(2\mathbf{w}^T\mathbf{g}\right)^2\dot{\nu}^2 = 0 \ . \tag{33}$$

On the other hand, the integral that should be minimized has the form

$$\Im = \int_{t_0}^{t_f}\dot{\nu}dt \ . \tag{34}$$

We trade a Mayer problem[21] in which we set $F = \dot{\nu}$ and Eq. (33) plays the role of a constraint with Lagrangian multiplier, μ

$$2M(\mathbf{x}, \dot{\mathbf{x}}, \dot{\nu}) = 2\dot{\nu} + \mu\left[(\dot{\mathbf{x}} + \dot{\nu}\mathbf{g})^T(\dot{\mathbf{x}} + \dot{\nu}\mathbf{g}) - \left(2\mathbf{w}^T\mathbf{g}\right)^2\dot{\nu}^2\right] \ . \tag{35}$$

We search a curve $\mathbf{x}(t)$ for which M is stationary. With new canonical coordinates we have

$$\mathbf{y}_\mathbf{x} = \nabla_{\dot{\mathbf{x}}}M(\mathbf{x}, \dot{\mathbf{x}}, \dot{\nu}) = \mu(\dot{\mathbf{x}} + \dot{\nu}\mathbf{g}) \ , \tag{36}$$

$$y_\nu = \nabla_{\dot{\nu}}M(\mathbf{x}, \dot{\mathbf{x}}, \dot{\nu}) = 1 + \mu\left[\mathbf{g}^T(\dot{\mathbf{x}} + \dot{\nu}\mathbf{g}) - \left(2\mathbf{w}^T\mathbf{g}\right)^2\dot{\nu}\right] \ . \tag{37}$$

If we set as an abbreviation another variable ω than above

$$\omega = \mu\dot{\nu} \ , \tag{38}$$

then we have

$$\left(2\mathbf{w}^T\mathbf{g}\right)^2\omega = 1 - y_\nu + \mathbf{g}^T\mathbf{y}_\mathbf{x} \ , \tag{39}$$

and comparing Eqs. (38), (36) and (33) yields the zero of the following Hamiltonian function

$$2H(\mathbf{x},\mathbf{y_x},\dot{\nu}) = \mathbf{y_x}^T\,\mathbf{y_x} - (2\mu\,\mathbf{w}^T\mathbf{g}(\mathbf{x}))^2\dot{\nu}^2 = 0 \tag{40}$$

being equivalent to the Hamiltonian

$$2H(\mathbf{x},\mathbf{y_x},y_\nu) = \mathbf{y_x}^T\,\mathbf{y_x} - \frac{1}{(2\,\mathbf{w}^T\mathbf{g}(\mathbf{x}))^2}(1-y_\nu+\mathbf{g}(\mathbf{x})^T\mathbf{y_x})^2 = 0\ . \tag{41}$$

The differential equations for the extremals of the problem are $\dot{\mathbf{x}} = \lambda\nabla_{\mathbf{y_x}}H$, they read

$$\dot{\mathbf{x}} = \lambda\left(\mathbf{y_x} - \omega\mathbf{g}\right)\ , \tag{42}$$

which is nothing else Eq.(36) with $\lambda = 1/\mu$. It holds per definition

$$\dot{\nu} = \lambda\omega\ , \tag{43}$$

The Hamiltonian (41) does not depend on ν, it is a function of y_ν only. We differentiate the Hamiltonian with respect to $\mathbf{x}$, resulting

$$2\nabla_{\mathbf{x}}H\left(\mathbf{x},\mathbf{y_x},y_\nu\right) = -4\left(2\mathbf{w}^T\mathbf{g}\right)\mathbf{H}\mathbf{w}\omega^2 - 2\left(2\mathbf{w}^T\mathbf{g}\right)^2\omega\nabla_{\mathbf{x}}\omega\ . \tag{44}$$

Now, we differentiate both sides of Eq. (39) with respect to $\mathbf{x}$ and obtain $4\left(2\mathbf{w}^T\mathbf{g}\right)\mathbf{H}\mathbf{w}\omega + \left(2\mathbf{w}^T\mathbf{g}\right)^2\nabla_{\mathbf{x}}\omega = \mathbf{H}\mathbf{y_x}$. We multiply this equation by ω, and we rearrange this to $2\left(2\mathbf{w}^T\mathbf{g}\right)\mathbf{H}\mathbf{w}\omega^2 + \left(2\mathbf{w}^T\mathbf{g}\right)^2\omega\nabla_{\mathbf{x}}\omega = \omega\mathbf{H}\mathbf{y_x} - 2\left(2\mathbf{w}^T\mathbf{g}\right)\mathbf{H}\mathbf{w}\omega^2$. We substitute this expression into Eq. (44) and have $\nabla_{\mathbf{x}}H\left(\mathbf{x},\mathbf{y_x},y_\nu\right) = -\omega\left(\mathbf{H}\mathbf{y_x} - 2\left(2\mathbf{w}^T\mathbf{g}\right)\mathbf{H}\mathbf{w}\omega\right)$. Since $\dot{\mathbf{y}}_\mathbf{x} = -\lambda\nabla_{\mathbf{x}}H\left(\mathbf{x},\mathbf{y_x},y_\nu\right)$ we get

$$\dot{\mathbf{y}}_\mathbf{x} = \lambda\omega\left(\mathbf{H}\mathbf{y_x} - 2\omega\left(2\mathbf{w}^T\mathbf{g}\right)\mathbf{H}\mathbf{w}\right)\ , \tag{45}$$

and

$$\dot{y}_\nu = 0\ . \tag{46}$$

Here, the bold $\mathbf{H}$ is again the Hessian matrix of the PES.

First, we know that ω cannot vanish at any regular point of a path. That is, because of Eq. (40) with $\mu\dot{\nu} = \omega$ it would follow from $\omega = 0$ that the $\mathbf{y_x}$ vector must also vanish, and then all $\dot{\mathbf{x}}$ and all $\dot{\mathbf{y}}_\mathbf{x}$ vectors are equal zero. Second, we note that a monotonically increasing function of the parameter t must always be chosen for ν. We can therefore choose the parameter by setting $\nu = t$, $\dot{\nu} = \lambda\omega = 1$. We then obtain by comparison of Eq. (1) with Eq. (42):

$$-\mathbf{g} + 2\left(\mathbf{w}^T\mathbf{g}\right)\mathbf{w} = \frac{1}{\omega}\left(\mathbf{y_x} - \omega\mathbf{g}\right)\ . \tag{47}$$

It follows from this and from Eq. (38) that

$$\mathbf{y_x} = 2\omega\ \left(\mathbf{w}^T\mathbf{g}\right)\mathbf{w}\ , \tag{48}$$

$$1 - y_\nu = 2\omega\ \left(\mathbf{w}^T\mathbf{g}\right)^2\ . \tag{49}$$

If we insert all these values in the previous canonical equations, then we obtain

$$\dot{\mathbf{x}} = -\left(\mathbf{I} - 2\mathbf{w}\mathbf{w}^T\right)\mathbf{g}\ , \tag{50}$$

$$\dot{\mathbf{y}}_\mathbf{x} = -\omega\left(2\mathbf{w}^T\mathbf{g}\right)\mathbf{H}\mathbf{w}\ . \tag{51}$$

In fact, the Hamiltonian function H is an integral of the canonical differential equations. We must always choose the initial conditions such that the equation $H = 0$ is identically fulfilled.
We differentiate Eq. (48) with respect to t

$$\dot{\mathbf{y}}_{\mathbf{x}} = 2\left[\dot{\omega}\left(\mathbf{w}^T\mathbf{g}\right) + \omega\left(\dot{\mathbf{w}}^T\mathbf{g} + \mathbf{w}^T\dot{\mathbf{g}}\right)\right]\mathbf{w} + 2\omega\left(\mathbf{w}^T\mathbf{g}\right)\dot{\mathbf{w}} \ . \tag{52}$$

The term $\left(\dot{\mathbf{w}}^T\mathbf{g} + \mathbf{w}^T\dot{\mathbf{g}}\right)$ is eliminated by first differentiating Eq. (49) with respect to t and second taking into account Eq. (46), resulting that $2\omega\left(\dot{\mathbf{w}}^T\mathbf{g} + \mathbf{w}^T\dot{\mathbf{g}}\right) = -\dot{\omega}\left(\mathbf{w}^T\mathbf{g}\right)$. Substituting this expression in Eq. (52) and equating the resulting expression with Eq. (51), we obtain

$$\dot{\omega}\left(\mathbf{w}^T\mathbf{g}\right)\mathbf{w} + 2\omega\left(\mathbf{w}^T\mathbf{g}\right)\dot{\mathbf{w}} = -2\omega\left(\mathbf{w}^T\mathbf{g}\right)\mathbf{H}\mathbf{w} \ . \tag{53}$$

Multiplying both sides from the left by $\mathbf{w}^T$ and since $\mathbf{w}^T\mathbf{w} = 1$ and from this $\mathbf{w}^T\dot{\mathbf{w}} = 0$ we have

$$\dot{\omega} = -2\omega\left(\mathbf{w}^T\mathbf{H}\mathbf{w}\right) \ . \tag{54}$$

Multiplying again both sides of Eq. (53) from the left by the projector $\left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right]$ and using the idem potency of this projector (see APPENDIX B) we get the result

$$\dot{\mathbf{w}} = -\left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right]\mathbf{H}\mathbf{w} \ . \tag{55}$$

It is the proposed approach (2) for the control vector, see ref.[11]. For given initial conditions, Eqs. (50) and (55) permit to find the vectors $\mathbf{x}$ and $\mathbf{w}$ as functions of t or ν. In the present case we determine the function $\omega(t)$ by a quadrature from Eq. (54). We can then uniquely calculate the vector $\mathbf{y}_{\mathbf{x}}$ and y_ν with the help of Eqs. (48) and (49), respectively. We emphasize that Eqs. (50) and (55) are again the basic equations of the GAD model, Eqs. (1) and (2).

For a given pathway, ω is determined except for a constant factor; the same likewise holds of $\mathbf{y}_{\mathbf{x}}$ and $1 - y_\nu$. The integration of Eq. (54) leads to

$$\omega(t) = \omega(t_0)\, exp\left(-2\int_{t_0}^{t}\left(\mathbf{w}^T\mathbf{H}\mathbf{w}\right)dt\right) \ . \tag{56}$$

According to this equation if $\omega(t_0) > 0$ then $\omega(t)$ will be positive otherwise will be negative. As in Section 3 we must still distinguish the extremals into maximals and minimals. For this purpose we investigate again the $\mathfrak{E}$-function or the Weierstrass error function calculated here most readily from its original definition. We shall consider a solution $S(\mathbf{x}, \nu)$ of the partial differential equation

$$H\left(\mathbf{x}, \mathbf{y}_{\mathbf{x}}, y_\nu\right) = H\left(\mathbf{x}, S_{\mathbf{x}}, S_\nu\right) = 0 \ , \tag{57}$$

being, $\mathbf{y}_{\mathbf{x}} = \nabla_{\mathbf{x}} S = S_{\mathbf{x}}$ and $y_\nu = \partial S/\partial\nu = S_\nu$, and an arbitrary line element

$$\dot{\mathbf{x}}' = -\mathbf{g} + 2\left(\mathbf{g}^T\mathbf{w}'\right)\mathbf{w}' \ , \tag{58}$$

$$\dot{\nu}' = 1 \ . \tag{59}$$

Then the $\mathfrak{E}$-function has the value[21]

$$\begin{aligned}&\mathfrak{E}\left(\mathbf{x}, \dot{\mathbf{x}}, \dot{\nu}, \dot{\mathbf{x}}', \dot{\nu}'\right) = \left(\mathbf{y}_{\mathbf{x}}^T\dot{\mathbf{x}} + y_\nu\dot{\nu}\right) - \left(\mathbf{y}_{\mathbf{x}}^T\dot{\mathbf{x}}' + y_\nu\dot{\nu}'\right) = 1 + \mathbf{y}_{\mathbf{x}}^T\left(\mathbf{I} - 2\mathbf{w}'\mathbf{w}'^T\right)\mathbf{g} - y_\nu = \\ &\omega\left[1 - \mathbf{w}^T\mathbf{w}'\tfrac{\mathbf{g}^T\mathbf{w}'}{\mathbf{g}^T\mathbf{w}}\right]\left(2\mathbf{g}^T\mathbf{w}\right)^2\end{aligned} \tag{60}$$

where we have used the $\mathbf{y}_{\mathbf{x}}$-vector and the value y_ν of the Eqs. (48) and (49) that hold for the family of extremals that transversally intersects our solution $S(\mathbf{x}, \nu) = constant$.

The minimal or maximal character of the extremal under investigation also depends of the sign of ω. However, ω is calculated only up to the constant factor $\omega(t_0)$ for a given extremal. Consequently, it appears that the above criteria on the minimal or maximal character is illusory, since for the integration of the canonical differential equations, we are still free to choose the sign of $\omega(t_0)$ for every prescribed extremal. On the other hand, common sense tells us that a given extremal cannot simultaneously be a maximal and a minimal. The solution of this difficulty consists in the fact that ω must have a completely determined sign if it is to be possible to construct a complete figure which contains the given extremals. That is, we can always find a solution $S(\mathbf{x},\nu)$ of the differential equation $H=0$ where, in an extremal element to be determined as positive or negative regular, the derivative of S_ν vanishes[21]. $(1-y_\nu)$ is positive in a certain neighborhood of this point. According to Eq. (49) ω must thus have the same sign as $2\left(\mathbf{w}^T\mathbf{g}\right)^2$ which is always positive. Instead of Eq. (60), we can therefore write

$$\mathfrak{E}(\mathbf{x},\dot{\mathbf{x}},\dot{\mathbf{x}}') = 2\left[1-\mathbf{w}^T\mathbf{w}'\frac{\mathbf{g}^T\mathbf{w}'}{\mathbf{g}^T\mathbf{w}}\right] = 2\left[1-cos\alpha\frac{cos\beta'}{cos\beta}\right] \tag{61}$$

and obtain in this way the same result given in Eq. (23) of Section 3 taking $\omega=2$ and $\lambda'\omega'=1$. As noted in Section 3, the only line elements forming an exception here are the *anomalous* line elements for which $\mathbf{g}^T\mathbf{w}=0$ or that is the same $cos\beta=0$. These anomalous line elements lie on the limit curves for a stationary field[21]. In the general case, it is conceivable that an extremal passes through such a line element and that the Weierstrass error function, $\mathfrak{E}$, has different signs on each side of this point. Already for Eq. (16) we had excluded the case $\mathbf{g}^T\mathbf{w}=0$ under the development of the Hamiltonian.

6 The general case

The general case of GAD model was already proposed by E and Zhou in the original article[11], see also reference[17]. GAD can be extended to handle higher index saddle points. For a vector space spanned by k direction vectors, let $\mathbf{W}=\left[\mathbf{w}_1|\cdots|\mathbf{w}_k\right]$, where each $\mathbf{w}_i$ represents a unit normed direction vector such that $\mathbf{w}_i^T\mathbf{w}_j=\delta_{i,j}$ for $1\leqslant i,j\leqslant k$. In this manner $\mathbf{W}^T\mathbf{W}=\mathbf{I}_k$, being $\mathbf{I}_k$ the unit matrix of dimension k. Notice that $k<N$ otherwise GAD coincides with the steepest-ascent method[17]. Then, index-k saddle points of the energy surface $V(\mathbf{x})$ are stable fixed points or attractors of the following dynamical system,

$$\dot{\mathbf{x}} = -\left[\mathbf{I}-2\mathbf{W}\mathbf{W}^T\right]\mathbf{g} = -\mathbf{g}+2\mathbf{W}\mathbf{k} \tag{62}$$

$$\dot{\mathbf{W}} = -\left[\mathbf{I}-\mathbf{W}\mathbf{W}^T\right]\mathbf{H}\mathbf{W}\ . \tag{63}$$

In Eq. (62) the $\mathbf{k}$-vector has the expression $\mathbf{k}=\mathbf{W}^T\mathbf{g}$ with dimension k and it is assumed that $\mathbf{k}\neq\mathbf{0}_k$; otherwise the general GAD is merely the steepest-descent model. An element of this vector is $\mathbf{k}_i=\mathbf{w}_i^T\mathbf{g}$. The procedure to proof the variational nature of the general GAD model is identical to that reported in Sections 2, 3, and 4. With this in mind we rewrite Eq. (9) in the following manner

$$\frac{1}{F}\dot{\mathbf{x}}+\mathbf{g} = 2\mathbf{W}\mathbf{k}\ . \tag{64}$$

In the same way as in Section 2, Eq. (64) allows us to calculate the functional F as a real, especially positive root of the equation

$$\left(\dot{\mathbf{x}}+\mathbf{g}F\right)^T\left(\dot{\mathbf{x}}+\mathbf{g}F\right) = 4\left(\mathbf{k}^T\mathbf{k}\right)F^2 \tag{65}$$

if such a root exists. Now we want to operate with canonical coordinates. For this purpose we differentiate Eq. (65) with respect to $\dot{\mathbf{x}}$ and we set $\mathbf{y}=\nabla_{\dot{\mathbf{x}}}F$ like in Section 3

$$\left(\mathbf{I}+\mathbf{y}\mathbf{g}^T\right)\left(\dot{\mathbf{x}}+\mathbf{g}F\right) = 4\left(\mathbf{k}^T\mathbf{k}\right)F\mathbf{y}\ . \tag{66}$$

Using Eqs. (14) and (64), Eq. (66) is transformed to an explicit expression for the $\mathbf{y}$-vector,

$$\omega \mathbf{W}\mathbf{k} = 2\left(\mathbf{k}^T\mathbf{k}\right)\mathbf{y} \ . \tag{67}$$

Multiplying Eq. (67) from the left by $\mathbf{g}^T$ we obtain $\omega = 2\mathbf{g}^T\mathbf{y}$. Since $\omega = 1 + \mathbf{g}^T\mathbf{y}$, we conclude that $\mathbf{g}^T\mathbf{y} = 1$ as in Section 3. From this equation for the $\mathbf{y}$-vector it follows that,

$$0 = 4\big(\mathbf{k}^T\mathbf{k}\big)\big(\mathbf{y}^T\mathbf{y}\big) - \omega^2 = 4\big(\mathbf{k}^T\mathbf{k}\big)\big(\mathbf{y}^T\mathbf{y}\big) - \big(1 + \mathbf{y}^T\mathbf{g}\big)^2 = 2H(\mathbf{x},\mathbf{y}) \ . \tag{68}$$

Here we have taken into account that $\mathbf{k}^T\mathbf{k} \neq 0$. As occurs in Section 3 we can choose a quadratic function of the $\mathbf{y}$-vector for the Hamiltonian function, $H(\mathbf{x},\mathbf{y})$. Proceeding along the theory of calculus of variations[18, 21] we compute $\dot{\mathbf{x}} = \lambda\nabla_{\mathbf{y}}H(\mathbf{x},\mathbf{y})$, and we have

$$\dot{\mathbf{x}} = \lambda\big(4\big(\mathbf{k}^T\mathbf{k}\big)\mathbf{y} - \omega\mathbf{g}\big) \ . \tag{69}$$

Using the expression for $\mathbf{y}^T\mathbf{g} = \omega - 1$ and Eq. (68) we can write
$F = (\nabla_{\dot{\mathbf{x}}}F)^T\dot{\mathbf{x}} = \mathbf{y}^T\dot{\mathbf{x}} = \lambda\big(4\big(\mathbf{k}^T\mathbf{k}\big)\big(\mathbf{y}^T\mathbf{y}\big) - \omega\mathbf{y}^T\mathbf{g}\big) = \lambda\big(\omega^2 - \omega\left(\omega - 1\right)\big) = \lambda\omega$. λ must be always positive since ω is positive equal to two in order to ensure the assumption that $F > 0$, the same reason which is used in Section 3. From these results we derive the expression of the $\mathfrak{E}$-function or the Weierstrass error function[21],

$$\begin{aligned}
&\mathfrak{E}(\mathbf{x},\dot{\mathbf{x}},\dot{\mathbf{x}}') = F(\mathbf{x},\dot{\mathbf{x}}') - (\nabla_{\dot{\mathbf{x}}}F(\mathbf{x},\dot{\mathbf{x}}))^T\dot{\mathbf{x}}' = F(\mathbf{x},\dot{\mathbf{x}}') - \mathbf{y}^T\dot{\mathbf{x}}' = \lambda'\omega' - \\
&\lambda'\mathbf{y}^T\left(4\left(\mathbf{k}'^T\mathbf{k}'\right)\mathbf{y}' - \omega'\mathbf{g}\right) = \lambda'\omega' - \lambda'\left(4\left(\mathbf{k}'^T\mathbf{k}'\right)\mathbf{y}^T\mathbf{y}' - \omega'\mathbf{y}^T\mathbf{g}\right) = \\
&\lambda'\omega' - \lambda'\left(\tfrac{\mathbf{k}^T\mathbf{W}^T\mathbf{W}'\mathbf{k}'}{\mathbf{k}^T\mathbf{k}}\omega'\omega - \omega'\omega + \omega'\right) = \lambda'\omega'\omega\left(1 - \tfrac{\mathbf{k}^T\mathbf{W}^T\mathbf{W}'\mathbf{k}'}{\mathbf{k}^T\mathbf{k}}\right) = \\
&\lambda'\omega'\omega\left(1 - cos\alpha\left(\tfrac{\mathbf{k}'^T\mathbf{k}'}{\mathbf{k}^T\mathbf{k}}\right)^{1/2}\right) \ .
\end{aligned} \tag{70}$$

α is the angle formed by the vectors $\mathbf{W}\mathbf{k}$ and $\mathbf{W}'\mathbf{k}'$. As in Section 3 the line elements are therefore all strong; positive or negative and $\lambda'\omega' > 0$ and $\omega = 2$. The only line elements which form an exception are the *anomalous* line elements for which $\mathbf{k} = \mathbf{0}_k$. These line elements lie on the limit curves for the stationary field of extremals. In the general case, it is conceivable that an extremal passes through such a line element and that the $\mathfrak{E}$-function has either different signs on each side of this point or the same sign.

Following the procedure outlined in Section 3 we introduce the ν parameter that makes $F = \lambda\omega = 1$ and we substitute in Eq. (69) the $\mathbf{y}$-vector taken from Eq. (67) resulting the Eq. (62) in the form,

$$\frac{d\mathbf{x}}{d\nu} = -\big(\mathbf{I} - 2\mathbf{W}\mathbf{W}^T\big)\mathbf{g} \ . \tag{71}$$

Where the definition of the $\mathbf{k}$-vector has been taken into account. The second canonical equation of the calculus of variations is obtained through the evaluation of $\dot{\mathbf{y}} = -\lambda\nabla_{\mathbf{x}}H(\mathbf{x},\mathbf{y})$, and we obtain the extremals of the problem by adding it to Eq. (69)

$$\dot{\mathbf{y}} = -\lambda\big(4\big(\mathbf{y}^T\mathbf{y}\big)\mathbf{H}\mathbf{W}\mathbf{k} - \omega\mathbf{H}\mathbf{y}\big) \ , \tag{72}$$

where again the matrix $\mathbf{H}$ is the Hessian of the potential function, $V(\mathbf{x})$. Following the reasoning of Section 4 we say that for a solution of Eqs. (69) and (72) we have to use initial values $(\mathbf{x}_0, \mathbf{y}_0)$ for which the Hamiltonian $H = 0$ holds. Now we work with the property that the matrix of control vectors $\mathbf{W}$ is a function of t (or ν). As in Section 4 the purpose is to transform the expression for $\dot{\mathbf{y}}$ which tells us how the matrix control vectors, $\mathbf{W}$, changes with respect to t (or ν) since this is the second basic element of the general GAD problem. The second canonical Eq. (72), gives us this opportunity because both, the $\mathbf{y}$-vector and the matrix control vectors $\mathbf{W}$, are related through Eq. (67). We substitute Eq. (67) in the right hand side of Eq. (72),

$$\dot{\mathbf{y}} = -\frac{\lambda\omega^2}{2\mathbf{k}^T\mathbf{k}}\mathbf{HWk} \ . \tag{73}$$

On the other hand, first we differentiate Eq. (67) with respect to t taking into account that $d\omega/dt = 0$ since $\omega = 2$, and second we substitute in it Equations 67 and 73,

$$\dot{\mathbf{W}}\mathbf{k} + \mathbf{W}\dot{\mathbf{k}} = 2\frac{\mathbf{k}^T\dot{\mathbf{k}}}{\mathbf{k}^T\mathbf{k}}\mathbf{Wk} - \lambda\omega\mathbf{HWk} \ . \tag{74}$$

Since we are interested in an expression that gives how the matrix control vectors, $\mathbf{W}$, changes with respect to t (or ν), we multiply Eq. (74) from the left by the projector $\left[\mathbf{I} - \mathbf{W}\mathbf{W}^T\right]$,

$$\left\{\left[\mathbf{I} - \mathbf{W}\mathbf{W}^T\right]\left(\dot{\mathbf{W}} + \lambda\omega\mathbf{HW}\right)\right\}\mathbf{k} = \mathbf{0} \ . \tag{75}$$

As explained in the beginning of this Section the vector $\mathbf{k} \neq \mathbf{0}_k$ this implies that the term into the brackets, $\{\cdots\}$, of Eq. (75) is zero and this term into the brackets can be rearranged as follows,

$$\left[\mathbf{I} - \mathbf{W}\mathbf{W}^T\right]\dot{\mathbf{W}} = -\lambda\omega\left[\mathbf{I} - \mathbf{W}\mathbf{W}^T\right]\mathbf{HW} \ . \tag{76}$$

Finally, setting $\lambda\omega = 1$ and using the idem potency of the projector $\left[\mathbf{I} - \mathbf{W}\mathbf{W}^T\right]$ (see APPENDIX B) we get the result,

$$\frac{d\mathbf{W}}{d\nu} = -\left[\mathbf{I} - \mathbf{W}\mathbf{W}^T\right]\mathbf{HW} \ . \tag{77}$$

We finish this Section like Section 4: Eq. (77) contains the variation of the GAD matrix control vectors. It forms with Eq. (71) a system which permits to find all extremals of the general GAD problem. If we have calculated the vector $\mathbf{x}$ and matrix $\mathbf{W}$ as functions of ν, then we can determine the $\mathbf{y}$-vector from Eq. (67) without further integration. According to Eqs. (71) and (77), every general GAD extremal curve is unique determined by the initial values $\mathbf{x}_0, \mathbf{W}_0$. Note that for $k = 1$ all equations derived in this Section reduce to these derived in Sections 3 and 4.

7 Discussion and conclusion

7.1 Analysis of the GAD curve based on its variational nature

If we fix the point $\mathbf{x}$ and let vary the normalized control vector, $\mathbf{w}$, then we obtain all possible directions of progress of an extremal GAD curve when it starts at the point $\mathbf{x}$. Compare scheme 2 of ref.[34]: the curve described by the end points of the vector $d\mathbf{x}/d\nu$ is a circle of radius $|\mathbf{g}|$ with center at $\mathbf{x}$. The direction is given by $\mathbf{w}$: for $\mathbf{w} \,||\, \mathbf{g}$ we step from $\mathbf{x}$ to $\mathbf{x} + \mathbf{g}$, for $\mathbf{w} \perp \mathbf{g}$ we step from $\mathbf{x}$ to $\mathbf{x} - \mathbf{g}$, (this was excluded in our development, see Eq. (16)) and for $\angle(\mathbf{w}, \mathbf{g}) = \pm 45^o$ we step from $\mathbf{x}$ orthogonal to $\mathbf{g}$. The right hand side of Eq. (24) is a mirror transformation of $\mathbf{g}$ at the mirror line, $\mathbf{w}$.

Let us consider a special pair of initial point and control vector, $(\mathbf{x}_0, \mathbf{w}_0)$, for which $\mathbf{g}_0^T\mathbf{w}_0 = 0$, thus $cos\beta = 0$. If we integrate Eqs. (24) and (31) with this condition, then we obtain the steepest-descent curve, which can be represented as the limit curve of the GAD problem: it never comes to the SP. Thus the steepest-descents are line elements, which have no place in the classification as positive or negative regular line elements of the present variational problem. They are anomalous line elements of the problem, see the discussion that follows Eq. (23) in Section 3 and the last paragraph of Section 5.

We conclude that the GAD concept describes curves that are extremals of a variational problem with a Randers metric. These curves extremalize the integral functional of Eq. (7) where F is that given in Eq. (3). Along the GAD curve holds $F(\mathbf{x}, \dot{\mathbf{x}}) = 1$, but if the parameter that characterizes the GAD curve is the arc-length, s, then $F(\mathbf{x}, d\mathbf{x}/ds) = 1/\sqrt{(\mathbf{g}^T\mathbf{g})}$ (see APPENDIX A). The variational problem falls in the category of a variational theory with optimal control.[25] All GAD numerical curves which use the system of coupled first order ordinary differential equations (24) and (31) are attracted by the first index saddle points (SPs); and they are repelled from the minimums of the PES. An imagination gives the Fig. 1 in the Introduction. For a proof see the appendix B of the work of Samanta and E [26]. It follows the result that any GAD curve is the extremal path from an initial minimum point $\mathbf{x}_0$ of the PES to the point $\mathbf{x}_{final}$ (a previously unknown first index saddle point) , if the initial control vector is the first eigenvector to the smallest eigenvalue. We note that every GAD curve confluents anywhere to a gradient extremal where the gradient of the PES is an eigenvector of the Hessian. We find that at the converged point the unite control vector $\mathbf{w}$ remains on this eigenvector of the Hessian matrix. There tends Eq. (31) to zero.

7.2 Proposed reaction curves based on the model of Zermelo's problem

So far we have presented, proved and analyzed the variational nature of the GAD curves. With these results we propose in this subsection a new curve that can be used as a reaction path but is restricted to the general requirements of Zermelo's problem. For this aim the curve is subject to the set of constraints exposed in Section 1 but the control vector is generated by another form. With these considerations we propose a curve where its tangent is given by the expression

$$\dot{\mathbf{x}} = -\mathbf{g} + f(\phi, \mathbf{x}, \mathbf{w})\,\mathbf{w}\ . \tag{78}$$

As before the control vector, $\mathbf{w}$, is assumed to be normalized. The function $f(\phi, \mathbf{x}, \mathbf{w})$ is a continuous and differentiable function with respect to $\mathbf{x}$ and ϕ is a constant. To delimit the function $f(\phi, \mathbf{x}, \mathbf{w})$, we should organize that if the control vector, $\mathbf{w}$, is associated to the uphill direction of the evolution of the curve then the general expression should be one that minimizes the potential energy in the subspace orthogonal to the $\mathbf{w}$-vector and maximizes it along the $\mathbf{w}$ direction, like in the GAD case. May be the most general form is of the type

$$\begin{aligned}\dot{\mathbf{x}} &= -\left(\mathbf{I} - \mathbf{w}\mathbf{w}^T\right)\mathbf{g} + \phi'\mathbf{w}\mathbf{w}^T\mathbf{g} = -\left(\mathbf{I} - (1+\phi')\,\mathbf{w}\mathbf{w}^T\right)\mathbf{g} \\ &= -\mathbf{g} + (1+\phi')\left(\mathbf{w}^T\mathbf{g}\right)\mathbf{w} = -\mathbf{g} + \phi\left(\mathbf{w}^T\mathbf{g}\right)\mathbf{w}\ .\end{aligned} \tag{79}$$

Thus $f(\phi, \mathbf{x}, \mathbf{w}) = \phi\mathbf{w}^T\mathbf{g}$ with ϕ larger than one. The ansatz corresponds with $\phi = 2$ to the GAD curve. The behavior of the kind of curves is shown in Fig.2 by examples. For the example PES, with lower values of $\phi < 2$ the TPs climbs uphill the PES, and an end for usefull ϕ constants is ≈ 1.2. For lower values the TP disappears and the curve does not find the SP.

With the same procedure exposed in the Sections 2-4 we derive the second canonical equation that governs the evolution of the control vector, $\mathbf{w}$. The functional $F(\mathbf{x}, \dot{\mathbf{x}})$ now is

$$F(\mathbf{x}, \dot{\mathbf{x}}) = \frac{\sqrt{\left(\dot{\mathbf{x}}^T\mathbf{g}\right)^2 + \dot{\mathbf{x}}^T\dot{\mathbf{x}}\left[f(\phi, \mathbf{x}, \mathbf{w})^2 - \mathbf{g}^T\mathbf{g}\right]} + \dot{\mathbf{x}}^T\mathbf{g}}{\left[f(\phi, \mathbf{x}, \mathbf{w})^2 - \mathbf{g}^T\mathbf{g}\right]} \tag{80}$$

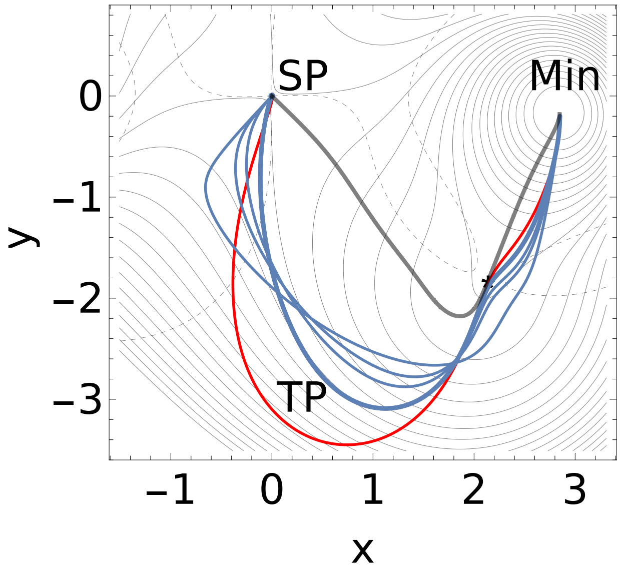

Fig. 2 Curves (blue with $\phi \geq 2$, red with $\phi = \sqrt{2}$) to Eq.(78) with $f(\phi, \mathbf{x}) = \phi\, \mathbf{g}^T \mathbf{w}$. Start is at minimum. The bold curve is the GAD curve with $\phi = 2$, the other blue curves are to $\phi = 3, 4$, and 10. The control vector is calculated by Eq.(85). The surface is a modified NFK case[35,36]. The * marks a quasi-shoulder, and the thin dashes mark the borderline between valleys and ridges. For comparison the GE is given (thick black curve) which is here the valley floor pathway between SP and Min.

The form of the element D appearing in Eqs. (4) and (5) is $D = f\left(\phi, \mathbf{x}, \mathbf{w}\right)^2 - \mathbf{g}^T \mathbf{g}$. In the remainder of the section we drop the dependence of f to abbreviate the expressions. Starting from Eq. (78) and using the same reasoning exposed from Eq. (13) to Eq. (16) the resulting equivalent expression to Eq. (16) for the GAD curve is

$$f \mathbf{y} = \omega \mathbf{w} \tag{81}$$

From Eq. (81) and remembering that $\omega = 1 + \mathbf{y}^T \mathbf{g}$, we obtain $\omega = f\left(\mathbf{g}^T \mathbf{y}\right) / \left(\mathbf{g}^T \mathbf{w}\right)$, if $\mathbf{g}^T \mathbf{w} \neq 0$ and $\mathbf{y}^T \mathbf{g} = \left(\mathbf{w}^T \mathbf{g} / \left(f - \mathbf{w}^T \mathbf{g}\right)\right)$. The Hamiltonian function is

$$2H\left(\mathbf{x}, \mathbf{y}\right) = f^2 \mathbf{y}^T \mathbf{y} - \omega^2 = 0 \tag{82}$$

obtained from Eq. (81). As in Section 3 we compute $\dot{\mathbf{x}} = \lambda \nabla_{\mathbf{y}} H(\mathbf{x}, \mathbf{y})$ for the first canonical equation of the extremal. It results $\dot{\mathbf{x}} = \lambda \left(f^2 \mathbf{y} - \omega \mathbf{g}\right)$. Substituting in this expression the $\mathbf{y}$-vector from Eq. (81), and taking $\lambda\omega = 1$ we get the expression of the tangent of the curve, Eq. (78). We note also that the functional F if evaluated on these curves takes the value $F = \left(\nabla_{\mathbf{x}} F\right)^T \dot{\mathbf{x}} = \mathbf{y}^T \dot{\mathbf{x}} = \lambda\omega = 1$ as for the GAD curve. Following the same procedure described in Section 4, we derive the second canonical equation $\dot{\mathbf{y}} = -\lambda \nabla_{\mathbf{x}} H(\mathbf{x}, \mathbf{y})$. Adding this to the first canonical equation, the corresponding extremals of the present problem are obtained

$$\dot{\mathbf{y}} = -\lambda \left(\mathbf{y}^T \mathbf{y} f \nabla_{\mathbf{x}} f - \omega \mathbf{H} \mathbf{y}\right) \ . \tag{83}$$

Using Eqs. (78) and (81) and that $\dot{f} = \left(\nabla_{\mathbf{x}} f\right)^T \dot{\mathbf{x}} + \left(\nabla_{\mathbf{w}} f\right)^T \dot{\mathbf{w}}$ instead of Eq. (83) we write

$$\dot{\omega} \mathbf{w} - \omega \frac{\left(\nabla_{\mathbf{x}} f\right)^T \dot{\mathbf{x}}}{f} \mathbf{w} + \omega \left[\mathbf{I} - \frac{\mathbf{w} \left(\nabla_{\mathbf{w}} f\right)^T}{f}\right] \dot{\mathbf{w}} = -\lambda \omega^2 \left(\nabla_{\mathbf{x}} f - \mathbf{H} \mathbf{w}\right) \ . \tag{84}$$

Since the control vector, $\mathbf{w}$, is a normalized vector and that $\lambda\omega = 1$ we first multiply Eq. (84) from the left by the projector $\left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right]$ obtaining the expression for $\dot{\mathbf{w}}$

$$\dot{\mathbf{w}} = -\left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right]\left(\nabla_{\mathbf{x}} f - \mathbf{H}\mathbf{w}\right) \tag{85}$$

where the idem potency property of the projector has been used (see APPENDIX B) and the term with $\dot{\omega}$ desapears. This last expression forms with Eq. (78) a system of coupled first order ordinary differential equations which permits all the extremals to be found if the initial values are given, $(\mathbf{x}_0, \mathbf{w}_0)$. Now multiplying from the left Eq. (84) by the $\mathbf{w}^T$ vector and using that $\mathbf{w}^T\dot{\mathbf{w}} = 0$ due to normalization, using $\lambda\omega = 1$ and the definition of $\dot{f}$ given above we get

$$\frac{\dot{\omega}}{\omega} = \frac{\dot{f}}{f} - \left(\mathbf{w}^T\nabla_{\mathbf{x}} f - \mathbf{w}^T\mathbf{H}\mathbf{w}\right) . \tag{86}$$

For a given extremal, ω is determined except for a constant factor. The integration of Eq. (86) leads to,

$$\omega(t) = \omega(t_0)\frac{f_t}{f_0} exp\left(-\int_{t_0}^{t}\left(\left(\nabla_{\mathbf{x}} f\right)^T\mathbf{w} - \mathbf{w}^T\mathbf{H}\mathbf{w}\right)dt\right) . \tag{87}$$

where f_0 and f_t is the function f evaluated at t_0 and t, respectively. According to this Eq. (87) since $\omega(t_0)/f_0 > 0$ then $\omega(t)/f_t$ will be positive in the same way as explained for the GAD curve in Section 5.

Finally, whether a given line element is positive or negative regular is decided by analyzing the $\mathfrak{E}$-function or the Weierstrass error function[21], compare Section 3. Proceeding in the same way we have that $\mathfrak{E} = F(\mathbf{x}, \dot{\mathbf{x}}') - \mathbf{y}^T\dot{\mathbf{x}}' = \lambda'\omega'\omega\left(1 - (f'/f)\,\mathbf{w}^T\mathbf{w}'\right) = \lambda'\omega'\omega\left(1 - (f'/f)\,cos\alpha\right)$ where $f' = f(\phi, \mathbf{x}, \mathbf{w}')$ and α is the angle formed by the vectors $\mathbf{w}$ and $\mathbf{w}'$. Since $\lambda'\omega' = 1$ and the expression in the parenthesis is always ≥ 0, and it disappears only for $\alpha = 0$, we say that the line elements are all strong, positive or negative regular according as $\omega > 0$ or $\omega < 0$, but according to Eq. (87) this occurs if $\omega(t_0) > 0$ or $\omega(t_0) < 0$, respectively. In the present case the anomalous line element occurs when $f = 0$. Thus a curve with tangent of the form given in Eq. (78) extremalizes an integral functional like that of Eq. (7) where the functional $F(\mathbf{x}, \dot{\mathbf{x}})$, see Eq. (80), is homogeneous of degree one with respect to the $\dot{\mathbf{x}}$ argument.

7.3 The relation between the variational nature of a curve and the minimum energy path

The RP concept is based on the definition of a curve located on a PES, which is monotonically increasing in potential energy from the reactant minimum to the SP and monotonically decreasing from this point to the product minimum. Many geodesic curves (geodesic in a certain sense) satisfy this definition and for this reason there is a set of curves proposed as RP. The most widely used curves for this purpose, already mentioned in the Section 1, are the steepest descent[2,3,37], the gradient extremals[4–7], the distinguished reaction coordinate[8], and its new version, the Newton trajectory (NT) [9,10], and the GAD curve[11]. The common fact of these curves is that all of them are of variational nature, but the question emerges: How this property ensures that the curves satisfy the RP definition or even more the restricted definition of a MEP? An RP curve fulfills the category of a MEP if the whole curve is located on a valley floor of the PES. We here find that there does not exist a relation between the variational property of a curve, and that the curve satisfies the MEP requirement. Even more, that the curve satisfies the general definition of an RP. The RP definition can be formulated as follows: it is the curve for that holds in the interval $t_0 < t < t_{SP}$ the inequality

$dV(\mathbf{x}(t))/dt = \mathbf{g}^T\dot{\mathbf{x}} > 0$ and for the interval $t_{SP} < t < t_f$ the inequality $dV(\mathbf{x}(t))/dt = \mathbf{g}^T\dot{\mathbf{x}} < 0$. On the other hand the MEP requirement can be formulated saying that a curve is located in a valley if at each point the projected Hessian matrix in the subspace orthogonal to the gradient of this point is positive definite. This is equivalent to evaluate the value of the quotient $\mathbf{g}^T\mathbf{A}\mathbf{g}/\mathbf{g}^T\mathbf{g}$, where $\mathbf{A}$ is the adjoint matrix of the Hessian matrix[38], the so-called desingularized inverse of the Hessian.

The steepest-descent/ascent curve is the curve that at each point follows the gradient of the PES. This curve is variational and extremalizes the integral functional[13, 14]

$$\Im(\mathbf{x}) = \int_{t_0}^{t} F(\mathbf{x}, \dot{\mathbf{x}})\, dt = \int_{t_0}^{t} \sqrt{(\mathbf{g}^T\mathbf{g})}\sqrt{(\dot{\mathbf{x}}^T\dot{\mathbf{x}})}dt = \int_{s_0}^{s} \sqrt{(\mathbf{g}^T\mathbf{g})}ds \tag{88}$$

where s is the arc-length and, like for the GAD curve, F is a functional homogeneous of degree one with respect to the argument $\dot{\mathbf{x}}$. The second variation indicates that only the steepest-descent/ascent curve that joints two minimums of the PES through an SP minimizes the integral functional of Eq. (88). This special curve, so-called intrinsic reaction coordinate (IRC)[2], always satisfies the RP definition, but the second variation[13] does not imply that the curve should be fully located in a valley deep, see a counter example elsewhere[36]. The second variation is not related with the MEP condition above mentioned. We conclude that the gradient curve of the type IRC is always an RP but can be or not be an MEP. This depends on the shape of the PES.

A gradient extremal curve was proposed as an RP some time ago[4, 5]. Its definition can be described assuming first that we are on a "valley ground" of the PES with $\mathbf{g}(\mathbf{x}) \neq \mathbf{0}$. The GE curve is defined by the condition that the norm of the gradient is stationary at each point of this curve with respect to the variations of $\mathbf{x}$ within the equipotential hypersurface, $V(\mathbf{x}) = \nu$. At each point of a GE curve it is satisfied the eigenvalue equation

$$\mathbf{H}(\mathbf{x})\,\mathbf{g}(\mathbf{x}) = h(\mathbf{x})\,\mathbf{g}(\mathbf{x}) \tag{89}$$

where h is the eigenvalue of the Hessian matrix and the gradient is its corresponding eigenvector. The demonstration of the variational nature of these type of curves was formulated in ref. [15] (see also references therein), with

$$\begin{aligned} \Im(\mathbf{x}) &= \textstyle\int_{t_0}^{t} \left[F(\mathbf{x}, t') - h(\mathbf{x})\, G(\mathbf{x}, t')\right] dt' \\ &= \textstyle\int_{t_0}^{t} \left[1/2\mathbf{g}^T(\mathbf{x}(t'))\,\mathbf{g}(\mathbf{x}(t')) - h(\mathbf{x}(t'))\,(V(\mathbf{x}(t')) - \nu)\right] dt' \ . \end{aligned} \tag{90}$$

Within the theory of the calculus of variations, this problem is classified as a Bolza variational problem which is related to a Lagrangian multipliers problem[21]. The GE curve extremalizes the integral functional given in Eq. (90) and in its evolution it transverses the set of equipotential surfaces. The variation of the potential energy as the curve evolves is done by the expression, $dV(\mathbf{x}(s))/ds = t_g\sqrt{\mathbf{g}^T\mathbf{g}}$, being t_g the cosine of the angle formed by the GE tangent and the gradient vector[15]. At a point where it happens $t_g = 0$, the GE shows a turning point. After this TP the curve changes the sign of its energy variation. We note that around the turning point the quotient $\mathbf{g}^T\mathbf{A}\mathbf{g}/\mathbf{g}^T\mathbf{g}$ preserves the sign[15]. For this reason a GE curve can lost the RP condition in a valley[19, 6]. However, if the GE curve joins two minimums of the PES and if it does not have on this sub-arc turning points, then this GE curve describes an RP with the category MEP[15]. A GE curve joining two minimums of the PES minimizes the integral functional of Eq. (90) if and only if it does not have on this sub-arc turning points. Otherwise other arbitrary curves joining the same two minimums lower the value of the integral functional (90) [15]. We conclude that GE curves joining two minimums of the PES and do not have turning points in between, minimize the functional (90), and satisfy the RP definition and the MEP requirement. In this case the model of GE curves has a direct relation between variationality, RP and MEP definitions. Unfortunately, the GE curves do not cover all the PES, in other words, a GE curve does not exist at every point of the PES. There can be parts of a reaction valley of a PES where no continuous GE exists[39,12]. A well known example is the MB potential where no GE connects the global minimum and the next SP[38]. Sometimes GEs show an 'avoided crossing' [6,40].

The distinguished reaction coordinate[8], or its new reformulation, the NT[9,10], are model curves which are often used to locate SPs. They are curves that can be used as representation of an RP. The variational nature of the curves was studied in ref.[16]. It corresponds to a problem where the functional only depends on the arguments, coordinates and the parameter that characterizes the curve

$$\Im\left(\bar{\mathbf{x}}\right) = \int_{x_{rc}^{0}}^{x_{rc}} F\left(\bar{\mathbf{x}}, x'_{rc}\right) dx'_{rc} = \int_{x_{rc}^{0}}^{x_{rc}} V\left(\bar{\mathbf{x}}, x'_{rc}\right) dx'_{rc} \tag{91}$$

where the $\bar{\mathbf{x}}$-vector is the coordinate vector $\mathbf{x}$ without the x_{rc} component. It can be shown[38,16] that the curve which extremalizes the functional integral (91) is the curve which satisfies the Branin equation[41]

$$d\mathbf{x}/dt = \pm\mathbf{A}\left(\mathbf{x}\right)\mathbf{g}\left(\mathbf{x}\right) \tag{92}$$

where $t = x_{rc}$. The formalization of the RP definition, in the present model, takes the form $dV\left(\mathbf{x}\left(t\right)\right)/dt = \mathbf{g}^T\dot{\mathbf{x}} = \pm\mathbf{g}^T\mathbf{A}\mathbf{g}$, where Eq. (92) has been used. If $det\mathbf{A}$ is positive definite along the whole NT curve joining two minimums of the PES then this curve is an RP and it also has the category of an MEP, because for this model curve both RP and MEP formulation coincide. In addition, in ref.[16] is shown that the second variation of the integral functional (91) is positive definite if the NT curve satisfies the inequality $\mathbf{g}^T\mathbf{A}\mathbf{g} > 0$ which is noting more than the MEP requirement. Thus for the NT model coincides the minimum variational condition with the MEP condition. However, if the NT has a turning point or a valley-ridged inflection point (VRI) then the minimum variational character is lost[16] and the RP and the MEP conditions are not satisfied. An NT curve can be started at any point of the PES.

The variational character of the GAD curve model has been studied in the previous Sections 2-6. When the RP formalization is applied we have $dV\left(\mathbf{x}\left(t\right)\right)/dt = \mathbf{g}^T\dot{\mathbf{x}} = -\mathbf{g}^T\mathbf{g} + 2\left(\mathbf{w}^T\mathbf{g}\right)^2 = -\mathbf{g}^T\mathbf{g}\left(1 - 2cos^2\beta\right)$ where Eq. (1) has been applied. It holds $dV\left(\mathbf{x}\left(t\right)\right)/dt > 0$ if $1 \leqslant cos\beta < 1/\sqrt{2}$ or if $-1/\sqrt{2} > cos\beta \geqslant -1$. When these conditions are satisfied for the sub-arc of the GAD curve joining a minimum and an SP of the PES then this GAD curve satisfies the RP definition. However, the RP requirement is lost when $cos\beta = \pm 1/\sqrt{2}$ which is the turning point condition of the GAD curve model[17]. After this point $dV\left(\mathbf{x}\left(t\right)\right)/dt < 0$ until the SP is reached. In the singular case when the GAD curve decreases in potential energy and it holds $dV\left(\mathbf{x}\left(t\right)\right)/dt = -\mathbf{g}^T\mathbf{g} < 0$, than it follows a steepest descent curve. As noted in Section 3, this occurs when the GAD curve is an anomalous curve, if it is a line element liying on the limit of curves for the stationary field of extremals. There is also a relation between MEP requirement and the GAD minimization or maximization variational character, see Eq. (23) of Section 3 or Eq. (61) of Section 5. For this reason a GAD curve is an RP if it has not a turning point. Otherwise it may not achieve the category of the MEP, and this requirement should be analyzed posteriorly after the curve has been integrated.

In Fig. 3 we show a GAD curve (in blue). The GAD curve starts near the minimum (MIN) with the $\mathbf{w}$-vector being the eigenvector to the smaller eigenvalue. It directly finds the 'minimum energy path' to the quasi-shoulder, then it exhausts the next valley up to a region where the valley floor ends. There it goes back over a turning point (TP) and finds the SP, at least. Note that the direct pathway

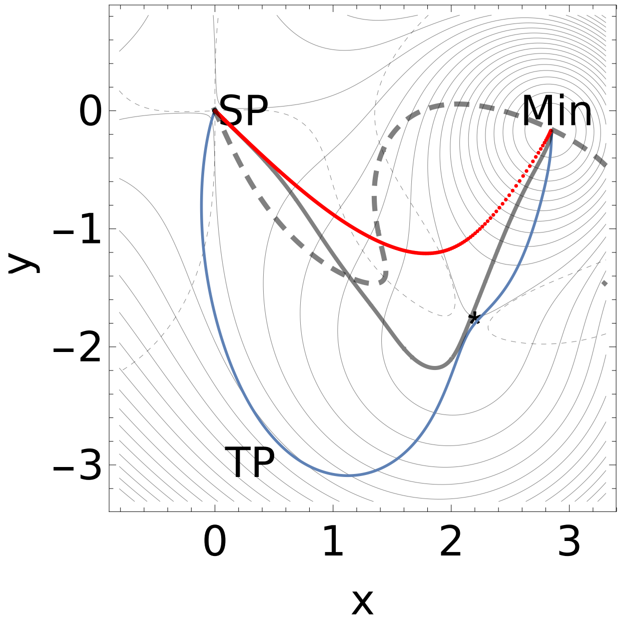

Fig. 3 A GAD curve (blue) by Eq.(1) on a two-dimensional toy potential. The control vector is throughout the first eigenvector, calculated by Eq.(2). The surface is a modified NFK case[35,36]. The * marks a quasi-shoulder, and the thin dashes mark the borderline between valleys and ridges. TP is the turning point of the GAD curve. For comparisons are given: the valley GE by a bold faced black curve, the IRC by a red curve, and an NT by a dashed black curve. Note that the IRC starts near the SP, but the GAD starts near the Min.

from Min to SP would here go along the second eigenvector direction. By the way, the IRC (red), the steepest descent from SP, goes here across the convex promontory between SP and minimum[36]. Further curves are the valley gradient extremal (GE) which exhaustes here the valley ground pathway, and an NT which has two TPs on the convexity border.

Finally, for the theory of reaction pathways: if a GAD curve does not have a turning point (compare the contrast in Fig. 3) on its travel from the minimum point to the first index saddle point, this GAD is an RP falling in the category of an MEP, otherwise even it is not an RP because after the turning point the energy of the curve decreases until it reaches the first index saddle point[17]. But the behavior of the energy does not play any role for the GAD system. Only the gradient, the Hessian, and the control vector count for the development of the GAD curve.

For the curve based on Zermelo's problem model introduced in Section 7.2 the RP formulation takes the form $dV(\mathbf{x}(t))/dt = \mathbf{g}^T\dot{\mathbf{x}} = -\mathbf{g}^T\mathbf{g}\left(1 - \left(f/\sqrt{\mathbf{g}^T\mathbf{g}}\right) cos\beta\right)$, where Eq. (78) has been used. It is $dV(\mathbf{x}(t))/dt > 0$ when $1 < \left(f/\sqrt{\mathbf{g}^T\mathbf{g}}\right) cos\beta$ and in this situation this curve is an RP. But if $\left(f/\sqrt{\mathbf{g}^T\mathbf{g}}\right) cos\beta = 1$ the curve loses the RP condition. It is the turning point of this type of curve, see Fig. 2. The remainder is similar to the GAD curve model or should be analyzed in detail for each f.

APPENDIX A

In this Appendix we calculate the inverse to matrix $\mathbf{M}$ defined in Eq. (4). It has the spectral decomposition $\mathbf{M} = \frac{1}{D}\left(\frac{\mathbf{g}^T\mathbf{g}}{D}+1\right)\frac{\mathbf{g}\mathbf{g}^T}{\mathbf{g}^T\mathbf{g}} + \frac{1}{D}\left[\mathbf{I} - \frac{\mathbf{g}\mathbf{g}^T}{\mathbf{g}^T\mathbf{g}}\right]$ and the inverse is evaluated to

$$\mathbf{M}^{-1} = D\left(\frac{\mathbf{g}^T\mathbf{g}}{D}+1\right)^{-1}\frac{\mathbf{g}\mathbf{g}^T}{\mathbf{g}^T\mathbf{g}} + D\left[\mathbf{I} - \frac{\mathbf{g}\mathbf{g}^T}{\mathbf{g}^T\mathbf{g}}\right] \ . \tag{93}$$

This inverse exists if $D \neq 0$. Now, we use the Hamilton expression $2H(\mathbf{x},\mathbf{y}) = (\mathbf{y}-\mathbf{m})^T \mathbf{M}^{-1}(\mathbf{y}-\mathbf{m}) - 1 = 0$ and we compute $\dot{\mathbf{x}}$ from the Hamilton equation, namely, $\dot{\mathbf{x}} = \lambda\nabla_{\mathbf{y}} H(\mathbf{x},\mathbf{y}) = \lambda\mathbf{M}^{-1}(\mathbf{y}-\mathbf{m})$. From this expression we derive the $\mathbf{y}$ vector such that $\dot{\mathbf{x}}$ is that given in Eq. (1). More specifically $\lambda\mathbf{y} = \mathbf{M}\dot{\mathbf{x}} + \lambda\mathbf{m} = -\mathbf{M}\left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right]\mathbf{g} - \lambda\mathbf{m}$. After some rearrangement we obtain $\frac{(2\mathbf{w}^T\mathbf{g})}{2}\mathbf{y} = \mathbf{w}$ which is just the Eq. (16) with $\omega = 2$. Substituting this value for the $\mathbf{y}$ vector in the above equation $\dot{\mathbf{x}} = \lambda\nabla_{\dot{\mathbf{x}}} H(\mathbf{x},\mathbf{y}) = \lambda\mathbf{M}^{-1}(\mathbf{y}-\mathbf{m})$ you will obtain Eq. (1) as expected.

The Randers Hamiltonian of the present problem is, see above $2H(\mathbf{x},\mathbf{y}) = 0 = \mathbf{y}^T\mathbf{M}^{-1}\mathbf{y} - 2\mathbf{y}^T\mathbf{M}^{-1}\mathbf{m} - \left(1 - \mathbf{m}^T\mathbf{M}^{-1}\mathbf{m}\right)$. We can evaluate the term which is independent on the $\mathbf{y}$ vector, namely, $\left(1 - \mathbf{m}^T\mathbf{M}^{-1}\mathbf{m}\right) = 1 - \frac{1}{4cos^2\beta}$. This implies that the term depending on the $\mathbf{y}$ vector has an upper-bound $\mathbf{y}^T\mathbf{M}^{-1}(\mathbf{y}-2\mathbf{m}) \leqslant 3/4$.

Let us still define $\dot{\mathbf{x}} = d\mathbf{x}/dt$ and the arc-length $ds = \sqrt{\dot{\mathbf{x}}^T\dot{\mathbf{x}}}dt = \lambda dt$ in the usual manner. From these definitions we have, $\dot{\mathbf{x}} = \sqrt{\dot{\mathbf{x}}^T\dot{\mathbf{x}}}d\mathbf{x}/ds = \lambda d\mathbf{x}/ds$. Note that $\lambda > 0$. We take the property that the functional $F(\mathbf{x},\dot{\mathbf{x}})$ is of degree one with respect to the $\dot{\mathbf{x}}$ argument. With this fact at hand we have, $F(\mathbf{x},\dot{\mathbf{x}})\,dt = \left(\sqrt{\dot{\mathbf{x}}^T\mathbf{M}\dot{\mathbf{x}}} + \mathbf{m}^T\dot{\mathbf{x}}\right)dt = \left(\sqrt{\lambda^2\,(d\mathbf{x}/ds)^T\,\mathbf{M}\,(d\mathbf{x}/ds)} + \lambda\mathbf{m}^T\,(d\mathbf{x}/ds)\right)dt = F(\mathbf{x}, d\mathbf{x}/ds)\,\lambda dt = F(\mathbf{x}, d\mathbf{x}/ds)\,ds$, where the matrix $\mathbf{M}$ and the vector $\mathbf{m}$ are defined in Eqs. (4) and (5) respectively. This result implies that the Zermelo integral or Zermelo geodetic distance through the GAD curve has $(energy/length)^{-1}\,length$ as units.

A special property of the Randers functional $F(\mathbf{x},\dot{\mathbf{x}})$ is the following: if we change $\dot{\mathbf{x}}$ by $-\dot{\mathbf{x}}$ then $F(\mathbf{x},\dot{\mathbf{x}}) \neq F(\mathbf{x},-\dot{\mathbf{x}})$, due to the linear term in contrast to a Riemann metric.

APPENDIX B

In this Appendix we explain the idem potency - trick to avoid $\left(\mathbf{I} - \mathbf{w}\mathbf{w}^T\right)$ at the left hand side of Eq. (30). Let us assume that the matrix $\mathbf{S}$ collects a set of $(N-1)$ orthonormal linear independent vectors which are orthogonal to the $\mathbf{w}$ vector. We can write $\left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right] = \left[\mathbf{S}\mathbf{S}^T\right]$. Since by construction $\mathbf{S}^T\mathbf{S} = \mathbf{I}$ we can write $\left[\mathbf{S}\mathbf{S}^T\right]\left[\mathbf{S}\mathbf{S}^T\right] = \left[\mathbf{S}\mathbf{S}^T\right]$, which is equivalent to write, $\left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right]\left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right] = \left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right]$. From these results, we can write $\left[\mathbf{S}\mathbf{S}^T\right]\left\{\dot{\mathbf{w}} + \lambda\omega\left[\mathbf{I} - \mathbf{w}\mathbf{w}^T\right]\mathbf{H}\mathbf{w}\right\} = \mathbf{O}$. Since $\mathbf{S}$ is formed by linear independent vectors then the term into the brackets, $\{\cdots\}$, is zero and the second GAD equation emerges.

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