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Gradient extremals

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Gradient extremals on N-dimensional energy hypersurfaces $V = V(x_1 \cdots x_N)$ are curves defined by the condition that the gradient ∇V is an eigenvector of the hessian matrix $\nabla\nabla V$. For variations which are restricted to any $(N-1)$ dimensional hypersurface $V(x_1 \cdots x_N) = V_0 =$ constant, the absolute value of the gradient ∇V is an extremum at those points where a gradient extremal intersects this surface. In many, though not all, cases gradient extremals go along the bottom of a valley or along the crest of a ridge. The properties of gradient extremals are discussed through a detailed differential analysis and illustrated by an explicit example. Multidimensional generalizations of gradient extremals are defined and discussed.

Key words: Potential energy surfaces — Reaction paths

1. Introduction

In the adiabatic approximation, the reactive rearrangement of a chemical system leading from a stable reactant configuration through an activated transition complex to a stable product configuration is described by a motion of the representative system point on the energy hypersurface from one minimum over a saddlepoint to another minimum. The valleys leading from the reactants up to the transition saddle and down to the products are the reaction channels and, in zeroth approximation, the system point is perceived as following a reaction path which is imagined to run along the floors of these valleys.

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The customary approach to defining such a lowest-energy path consists of taking it to be the union of the two lines of steepest descent leading from the saddlepoint, to the two minima. The definition is unambiguous since exactly one steepest descent line originates in either downhill direction at the saddlepoint. It starts out in the direction of that eigenvector of the hessian (the matrix of second derivatives) which corresponds to the one negative eigenvalue, and it ends at a minimum.

This choice has the shortcoming that one must start at the saddlepoint and proceed to the minimum. It is not possible to find the floor of the valley, if defined in this manner, without prior knowledge of the saddlepoint. This is so because, away from this point, there exist no *local* properties which distinguish this steepest descent line from other steepest descent lines. For example, at a minimum there are infinitely many steepest descent lines entering parallel to that eigenvector of the hessian which corresponds to its smallest eigenvalue, while only one steepest descent line comes into the minimum parallel to every other eigenvector of the hessian. Under "normal" conditions one might expect the steepest descent line originating from the saddlepoint to be among the manifold mentioned first, but that does not have to be the case.

Intuitively one would expect that it should also be possible to find one's way from a minimum through a valley up to a saddlepoint by using only *local* criteria for staying on the "floor" of a valley. Any such procedure must be based on the differential behavior of the surface, because differential properties can be ascertained for any point on such a path independent of any other point so that one can follow the path in any direction, from the saddlepoint to the minimum or vice versa. In 1974, when faced with the problem of finding saddlepoints on *ab initio* energy surfaces, the authors formulated such a procedure in an unpublished manuscript and discussed it with a number of colleagues. This material is contained in Sect. 2.1 below. Subsequently the authors were disappointed when in numerical tests the shapes of the resulting curves, which they called gradient extremals, sometimes differed markedly from what they intuitively expected [1].

Pancir [2] and Basilevsky and Shamov [3] have priority in writing about this subject. Their publications came to the authors' attention in 1982. The approach of Basilevsky and Shamov is similar to ours: it is based on an extremum principle, which they call the "mountaineer's algorithm" and, from this extremum principle, it is deduced that the gradient is an eigenvector of the hessian on the resulting curves. This eigenvalue equation had been considered earlier by Pancir, although not in connection with an extremum principle but while searching for a definition of a reaction path. In this context gradient extremals suffer from the same shortcomings as general steepest descent curves: they are not invariant under coordinate transformations and they are defined without reference to the kinetic energy. Nonetheless, the lack of a true physical meaning and the metric ambiguity do not detract from the fact that gradient extremals represent unique curves between stationary points which can be followed in any direction, e.g. from a minimum to a saddle.

Sections 2.3 and 2.4 furnish an analysis of some of the unusual properties of gradient extremals which, to our knowledge, have not been previously discussed.

An instructive example is examined in Sect. 3. Multidimensional generalizations of gradient extremals are developed in Sect. 4.

2. Gradient extremals

2.1. Definition and differential equation

We begin by asking: "Which place would a person walking in a valley tend to consider as the valley floor?" If we define a "floor line" in terms of its intersections with the contour lines running around the valley, then the following answer seems reasonable:

> *A floor line intersects every contour line in that point where the gradient is smallest in absolute value compared to other gradient values on the same contour.*

(All gradients are, of course, perpendicular to the contour line). This is to say that the floor line intersects any contour in that point where moving perpendicular to the contour produces a minimal change in height, i.e. where equidistant contours are spaced farthest apart, i.e. where the valley is "least steep". Basilevsky and Shamov call this the mountaineer's algorithm.

Let us apply this idea to a surface $V = f(x) = f(x_1 \cdots x_M)$. For convenience, we introduce the term *contour subspace* to denote the *nonlinear* $(M-1)$ dimensional subspace (hypersurface) defined by the condition $f(x) = V =$ constant (there exists thus a contour subspace for every contour). In generalization of the considerations in the preceding paragraph, let us then look for those points in a contour subspace where the absolute value of the gradient, $|\nabla f|$, is *extremal.* Lines which *connect* such points on *different* contour subspaces we shall call *gradient extremals.* They intersect the contour subspaces in points where $(\nabla f)^2$ is an extremum.

Clearly at any such point the condition

$$(\boldsymbol{c} \cdot \nabla)(\nabla f)^2 = \sum_i c_i(\partial/\partial x_i) \sum_j (\partial f/\partial x_j)^2 = 0 \tag{2.1}$$

must be satisfied *for any vector* **c** *lying in the* $(M-1)$ *dimensional linear space that is tangent to the contour subspace at that point.* Hence the projection of $\nabla(\nabla f)^2$ onto this tangent space must vanish and we must have

$$(\boldsymbol{P} \cdot \nabla)(\nabla f \cdot \nabla f) = \sum_j P_{ij}(\partial/\partial x_j)(\nabla f)^2 = 0, \tag{2.2}$$

where $\boldsymbol{P}$ is the projecting matrix onto the tangent subspace. Since this contour tangent space is perpendicular to the gradient ∇f, we can write

$$P_{ij} = \delta_{ij} - P^0_{ij}, \tag{2.3}$$

with P^0_{ij} being the projector onto the direction of the gradient. The projectors $\boldsymbol{P}$ and $\boldsymbol{P}^0$ are explicitly defined in the Appendix Eqs. (A.2) and (A.3). The condition given in Eq. (2.2) can now be rewritten by using differential identities, as shown in the Appendix eqs. (A.5) to (A.9), and this leads to the equation

$$\sum_j H_{ij}(x)g_j(x) = \lambda(x)g_i(x), \tag{2.4}$$

which must hold for every point on a gradient extremal. Here $\boldsymbol{g}(x)$ and $\boldsymbol{H}(x)$ are the gradient and the hessian of $f(x)$ at point x:

$$g_i(x) = (\partial f/\partial x_i), \qquad H_{ij}(x) = (\partial f^2/\partial x_i\, \partial x_j), \tag{2.5}$$

and $\lambda(x)$ is defined in Eq. (A.7) of the Appendix, which can be written as

$$\lambda(x) = \sum_{ij} H_{ij}g_i g_j / \sum_i g_i^2. \tag{2.6}$$

Thus, a *gradient extremal is a locus of points where the gradient of* $f(x)$ *is an eigenvector of the hessian of* $f(x)$. This result can also be obtained by finding the extremum of $(\nabla f)^2$ under the constraint that $f(x) = V = \text{constant}$, i.e. $\nabla\{(\nabla f)^2 - 2\lambda f\} = 0$ with λ being a Lagrangian multiplier.

Several properties of gradient extremals are immediate. First: that Eq. (2.4) indeed determines a curve can be seen as follows. Suppose that $\boldsymbol{U}(x)$ is the orthogonal matrix which diagonalizes the hessian matrix $\boldsymbol{H}(x)$ at the point x, so that

$$\boldsymbol{U}^{\dagger}(x)\boldsymbol{H}(x)\boldsymbol{U}(x) = \boldsymbol{h}(x), \tag{2.7}$$

where $\boldsymbol{h}(x)$ is diagonal, then the αth row of $\boldsymbol{U}$ namely $\{U_{j\alpha}\}$ is the eigenvector of $\boldsymbol{H}$ with eigenvalue h_α. Thus for the gradient $\boldsymbol{g}$ to be parallel to this eigenvector, it is necessary and sufficient that $\boldsymbol{g}$ be orthogonal to all other eigenvectors of the hessian, which implies

$$\sum_j g_j U_{jk} = \sum_j g_j(x)\, U_{jk}(x) = 0, \quad \text{for all } k \neq \alpha. \tag{2.8}$$

These $(M-1)$ equations are linearly independent since $\boldsymbol{U}$ is orthogonal and they define a one-dimensional curve in the total M-dimensional space. It is also apparent that there are M essentially different curves of this kind, corresponding to the M different eigenvectors of $\boldsymbol{H}$. Any one of these curves can, moreover, come in several pieces.

Secondly, it is apparent that all *stationary points* on the surface $V = f(x)$ (minima, maxima, saddlepoints) lie on gradient extremals. This must be so because, at these points $(\nabla f)^2$ is an *absolute* minimum, namely $(\nabla f)^2 = 0$.

Thirdly, it can be seen that only at stationary points can two or more gradient extremals cross each other with a non-zero angle of intersection. This follows, because, in general, each of the gradient extremals, intersecting at a given point, requires the gradient to be parallel to a different eigenvector of the hessian. Since the latter are however orthogonal, this is clearly impossible unless $(\nabla f)^2 = 0$, implying a stationary point. This reasoning does not prove that the gradient extremals themselves intersect at right angles. However we shall see below that, in fact, they do. It follows that, at a stationary point in an M dimensional parameter space, M gradient extremals intersect at right angles, each being tangent to one of the M orthogonal eigenvectors of the Hessian.

2.2. Classification of gradient extremals

Gradient extremals can be classified according to two considerations which we shall first illustrate for the case of a function of two variables $V=f(x,y)$.

The first question is how $f(x,y)$ changes when one moves away from a point on the gradient extremal *in a direction perpendicular to the gradient.* If the ground rises, i.e. $f(x,y)$ increases, then we are in a *valley*; if the ground falls, i.e. $f(x,y)$ decreases, then we are on a *ridge*. Since, perpendicular to ∇f, the directional first derivatives of f vanish, this change is characterized by the *sign of the eigenvalue* λ' *of the hessian which belongs to the eigenvector which is orthogonal to the gradient.*

The second consideration pertains to the *variation* of $(\nabla f)^2$ *in the contour subspace.* So far we have tacitly assumed that Eq. (2.4) implies a *minimum* of $(\nabla f)^2$, indicating points of gentlest slope. This equation encompasses, however, also the cases that $(\nabla f)^2$ is a maximum or a saddlepoint in the contour subspace. A maximum yields a point of steepest slope which corresponds to geographic formations known as cliffs and cirques, depending on the sign of λ'.

Thus, when the second order terms determine the behavior of f on a gradient extremal, we have the four cases listed in the following table

Variation of $(\nabla f)^2$ in contour subspace	Variation of $f(x)$ perpendicular to ∇f Uphill ($\lambda'>0$)	Downhill ($\lambda'<0$)
Minimum	Valley	Ridge
Maximum	Cirque	Cliff

Contour lines illustrating the four cases are shown in Fig. 1.

In more than two dimensions there exists a greater variety of cases, but the analysis is still based on the same two types of considerations. The increment of $f(x)$ perpendicular to the gradient is now determined by the eigenvalues belonging to all eigenvectors perpendicular to the gradient (which corresponds to the first eigenvector with the eigenvalue λ). These can be obtained as the eigenvalues of the *reduced* hessian

$$\hat{H}_{ij} = H_{ij} - \lambda P^0_{ij} \tag{2.9}$$

where P^0_{ij} is the projector on the eigenvector $\nabla f/|\nabla f|$, as defined in Eq. (A.2). Using the projector $\boldsymbol{P}$ (see Eq. A.3), and the gradient extremal condition (A.9),

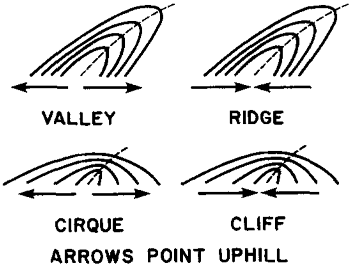

Fig. 1. Contours (*solid lines*) and gradient extremals (*dotted lines*) for a valley, a ridge, a cirque and a cliff

one can write the matrix (2.9) also in the form

$$\hat{\boldsymbol{H}} = \boldsymbol{P} \cdot (\nabla\nabla f) \cdot \boldsymbol{P} = \boldsymbol{P} \cdot (\nabla\nabla f) = (\nabla\nabla f) \cdot \boldsymbol{P}. \tag{2.9a}$$

The type of extremum *within the contour space*, on the other hand, is now determined by the eigenvalues of the matrix of second derivatives within that subspace, namely

$$\boldsymbol{H}^c = (\boldsymbol{P} \cdot \nabla)(\boldsymbol{P} \cdot \nabla)(\nabla f)^2/2. \tag{2.10}$$

This can be simplified by the manipulations derived in the Appendix. The result, Eq. (A.18), can be expressed as follows

$$\boldsymbol{H}^c = \boldsymbol{P} \cdot (\boldsymbol{T} \cdot \boldsymbol{g}) \cdot \boldsymbol{P} + \boldsymbol{H} \cdot (\boldsymbol{H} - \lambda \boldsymbol{I}) \tag{2.11}$$

$$H^c_{ij} = \sum_{rst} T_{rst} g_r P_{si} P_{tj} + \sum_r H_{ir} H_{rj} - \lambda H_{ij} \tag{2.11a}$$

where T_{rst} is the matrix of *third* derivatives:

$$T_{rst}(x) = \partial^3 f / \partial x_r \, \partial x_s \, \partial x_t. \tag{2.12}$$

From the spectral decomposition of $\boldsymbol{H}$ it is apparent that, in Eq. (2.11), one can make the substitution:

$$\boldsymbol{H} \cdot (\boldsymbol{H} - \lambda \boldsymbol{I}) = \hat{\boldsymbol{H}} \cdot (\hat{\boldsymbol{H}} - \lambda \boldsymbol{I}), \tag{2.13}$$

because λ is the eigenvalue which is omitted in $\hat{\boldsymbol{H}}$. The eigenvalues of the matrix (2.13) are $h_n(h_n - \lambda)$, if h_n are the eigenvalues of $\boldsymbol{H}$ different from $h_1 = \lambda$.

An "absolute valley" would be characterized by the matrices $\boldsymbol{H}$ *and* $\boldsymbol{H}^c$ both being positive definite. A "normal" reaction channel would be expected to have this character.

2.3. *Tangential direction of gradient extremals*

Intuitively it is extremely tempting to expect that one would move in the direction of the gradient (∇f) if one advances along the gradient extremal, i.e. that the gradient (∇f), in addition to being an eigenvector of the hessian, is also tangent to the gradient extremal itself. If this were so, then the gradient extremals would be a special class of steepest descent lines.

Such is not the case however. In general the tangent to a gradient extremal forms a finite angle with the gradient ∇f.

This can be seen as follows. If $\boldsymbol{t}(x)$ is the unit vector tangent to the gradient extremal at a point (x), then $(\boldsymbol{t} \cdot \nabla)$ is the derivative in the direction of this tangent. Since Eq. (2.2) is valid on the entire gradient extremal, we have therefore

$$(\boldsymbol{t} \cdot \nabla)(\boldsymbol{P} \cdot \nabla)(\nabla f)^2/2 = 0. \tag{2.14}$$

If we decompose $\boldsymbol{t}$ and ∇ into their components parallel and perpendicular to the gradient ∇f, viz.

$$\boldsymbol{t} = \boldsymbol{t}_\parallel + \boldsymbol{t}_\perp, \tag{2.15a}$$

$$\nabla = (\boldsymbol{P}^0 \cdot \nabla) + (\boldsymbol{P} \cdot \nabla), \tag{2.15b}$$

then we have

$$(\boldsymbol{t} \cdot \nabla) = \boldsymbol{t}_\parallel \cdot \boldsymbol{P}^0 \cdot \nabla + \boldsymbol{t}_\perp \cdot \boldsymbol{P} \cdot \nabla. \tag{2.15c}$$

Inserting this decomposition into Eq. (2.14), we obtain

$$t_{\parallel} \cdot \boldsymbol{A} + \boldsymbol{t}_{\perp} \cdot \boldsymbol{B} = 0, \tag{2.16}$$

where the matrices $\boldsymbol{A}$, $\boldsymbol{B}$ are given by

$$\boldsymbol{A} = (\boldsymbol{P}^0 \cdot \nabla)(\boldsymbol{P} \cdot \nabla)(\nabla f)^2/2, \tag{2.17}$$

$$\boldsymbol{B} = (\boldsymbol{P} \cdot \nabla)(\boldsymbol{P} \cdot \nabla)(\nabla f)^2/2. \tag{2.18}$$

These are calculated in the Appendix and, according to Eqs. (A.17), (A.18), can be written as

$$\boldsymbol{A} = \boldsymbol{P}^0 \cdot [(\nabla\nabla\nabla f) \cdot (\nabla f)] \cdot \boldsymbol{P} = \boldsymbol{P}^0 \cdot (\boldsymbol{T} \cdot \boldsymbol{g}) \cdot \boldsymbol{P} \tag{2.19}$$

$$\begin{aligned} \boldsymbol{B} &= \boldsymbol{P} \cdot [(\nabla\nabla\nabla f) \cdot (\nabla f)] \cdot \boldsymbol{P} - (\nabla\nabla f) \cdot (\nabla\nabla f - \lambda \boldsymbol{I}) \\ &= \boldsymbol{P} \cdot (\boldsymbol{T} \cdot \boldsymbol{g}) \cdot \boldsymbol{P} - \boldsymbol{H} \cdot (\boldsymbol{H} - \lambda \boldsymbol{I}) = \boldsymbol{H}^c. \end{aligned} \tag{2.20}$$

Equation (2.16) shows that $\boldsymbol{t}$ has a component $\boldsymbol{t}_{\perp} = \boldsymbol{t}_{\parallel} \cdot \boldsymbol{A}\boldsymbol{B}^{-1}$ perpendicular to the gradient ∇f. This component vanishes only if the matrix $\boldsymbol{A}$ vanishes. This is, in fact, the case at the stationary points where $\boldsymbol{g} = \nabla f = 0$. It follows, therefore, that, *at a stationary point, gradient extremals are parallel to steepest descent lines and intersect each other at right angles.* Another case where $\boldsymbol{t}_{\perp}$ vanishes is at points where $\boldsymbol{T} = (\nabla\nabla\nabla f)$ vanishes.

On the other hand, *it is possible that a gradient extremal is perpendicular to the gradient and thus tangent to the contour subspace*! According to Eq. (2.16) this somewhat surprising situation occurs whenever an eigenvalue of $\boldsymbol{B}$ vanishes. According to the discussion in Sect. 2.2, such a change in sign occurs when the character of the gradient extremal changes, say from valley to cirque or from a ridge to a cliff.

3. Two-dimensional case

3.1. Differential relations

The derived equations assume a simple form for a two-dimensional space of variables. Here the condition (2.2) can be replaced by

$$(\boldsymbol{e} \cdot \nabla)(\nabla f)^2/2 = \boldsymbol{e} \cdot (\nabla\nabla f) \cdot (\nabla f) = 0, \tag{3.1}$$

where $\boldsymbol{e}$ denotes the unit vector perpendicular to the gradient and tangent to the contour line. In the present case we have an explicit form for $\boldsymbol{e}$, namely

$$\boldsymbol{e} = \{(\partial f/\partial y), -(\partial f/\partial x)\}/[(\partial f/\partial x)^2 + (\partial f/\partial y)^2]^{1/2}. \tag{3.2}$$

Insertion of $\boldsymbol{e}$ and ∇f into (3.1) yields the equation

$$f_{xy}(f_x^2 - f_y^2) + (f_{yy} - f_{xx})f_x f_y = 0, \tag{3.3}$$

where standard partial derivative notation has been used. Eq. (3.3) is the differential equation for the gradient extremals. It is also readily derived from the general Eq. (2.8).

For any point on these curves the eigenvalues of the hessian are given by the expressions

$$\lambda = (\nabla f \cdot \nabla\nabla f \cdot \nabla f)/(\nabla f)^2$$
$$= (f_{xx}f_x^2 + 2f_{xy}f_xf_y + f_{yy}f_y^2)/(f_x^2+f_y^2), \tag{3.4}$$

and

$$\lambda' = (\boldsymbol{e} \cdot \nabla f \cdot \boldsymbol{e})$$
$$= (f_{xx}f_y^2 - 2f_{xy}f_xf_y + f_{yy}f_y^2)/(f_x^2+f_y^2), \tag{3.5}$$

the former corresponding to the direction of ∇f and the latter to the direction of $\boldsymbol{e}$. According to the discussion in Section 2, the sign of λ' determines whether one has a valley (cirque) or a ridge (cliff).

The distinction between a valley (ridge) and a cirque (cliff), i.e. whether $(\nabla f)^2$ is a minimum or maximum in the contour subspace depends on the sign of the second derivative of $(\nabla f)^2$ in that subspace, viz.,

$$\lambda'' = (\boldsymbol{e} \cdot \nabla)(\boldsymbol{e} \cdot \nabla)(\nabla f)^2/2. \tag{3.6}$$

From this equation one obtains

$$\lambda'' = \lambda_1'' + \lambda_2'' \tag{3.7}$$

with

$$\lambda_1'' = [\nabla(\nabla f)^2/2] \cdot [(\boldsymbol{e} \cdot \nabla)\boldsymbol{e}],$$
$$\lambda_2'' = \boldsymbol{e} \cdot [\nabla\nabla(\nabla f)^2/2] \cdot \boldsymbol{e},$$

where the differentiations do not act beyond the square brackets. Further differential manipulations yield

$$\lambda_1'' = -(\boldsymbol{e} \cdot \nabla\nabla f \cdot \boldsymbol{e})(\nabla f \cdot \nabla\nabla f \cdot \nabla f)/(\nabla f)^2,$$
$$\lambda_2'' = \boldsymbol{e} \cdot (\nabla\nabla\nabla f \cdot \nabla f) \cdot \boldsymbol{e} + (\boldsymbol{e} \cdot \nabla\nabla f) \cdot (\nabla\nabla f \cdot \boldsymbol{e}),$$

whence, by virtue of Eqs. (3.4) and (3.5),

$$\lambda_1'' = -\lambda\lambda', \tag{3.8a}$$
$$\lambda_2'' = \boldsymbol{e} \cdot (\nabla\nabla\nabla f \cdot \nabla f) \cdot \boldsymbol{e} + (\lambda')^2. \tag{3.8b}$$

Inserting these results in Eq. (3.7), one finally has

$$\lambda'' = \lambda'(\lambda' - \lambda) + \boldsymbol{e} \cdot (\nabla\nabla\nabla f \cdot \nabla f) \cdot \boldsymbol{e}, \tag{3.9}$$

where

$$\boldsymbol{e} \cdot (\nabla\nabla\nabla f \cdot \nabla f) \cdot \boldsymbol{e} = (f_{xxx}f_y + f_{yyy}f_x)f_xf_y + f_{xxy}f_y(f_y^2 - 2f_x^2) + f_{xyy}f_x(f_x^2 - 2f_y^2). \tag{3.10}$$

These equations are in agreement with the more general equations (2.11), (2.12), (2.13).

The signs of λ' and λ'' characterize the gradient extremal as follows:

$\lambda' > 0$, $\lambda'' > 0$ is a valley, $\lambda' > 0$, $\lambda'' < 0$ is a cirque,

$\lambda' < 0$, $\lambda'' > 0$ is a ridge, $\lambda' < 0$, $\lambda'' < 0$ is a cliff.

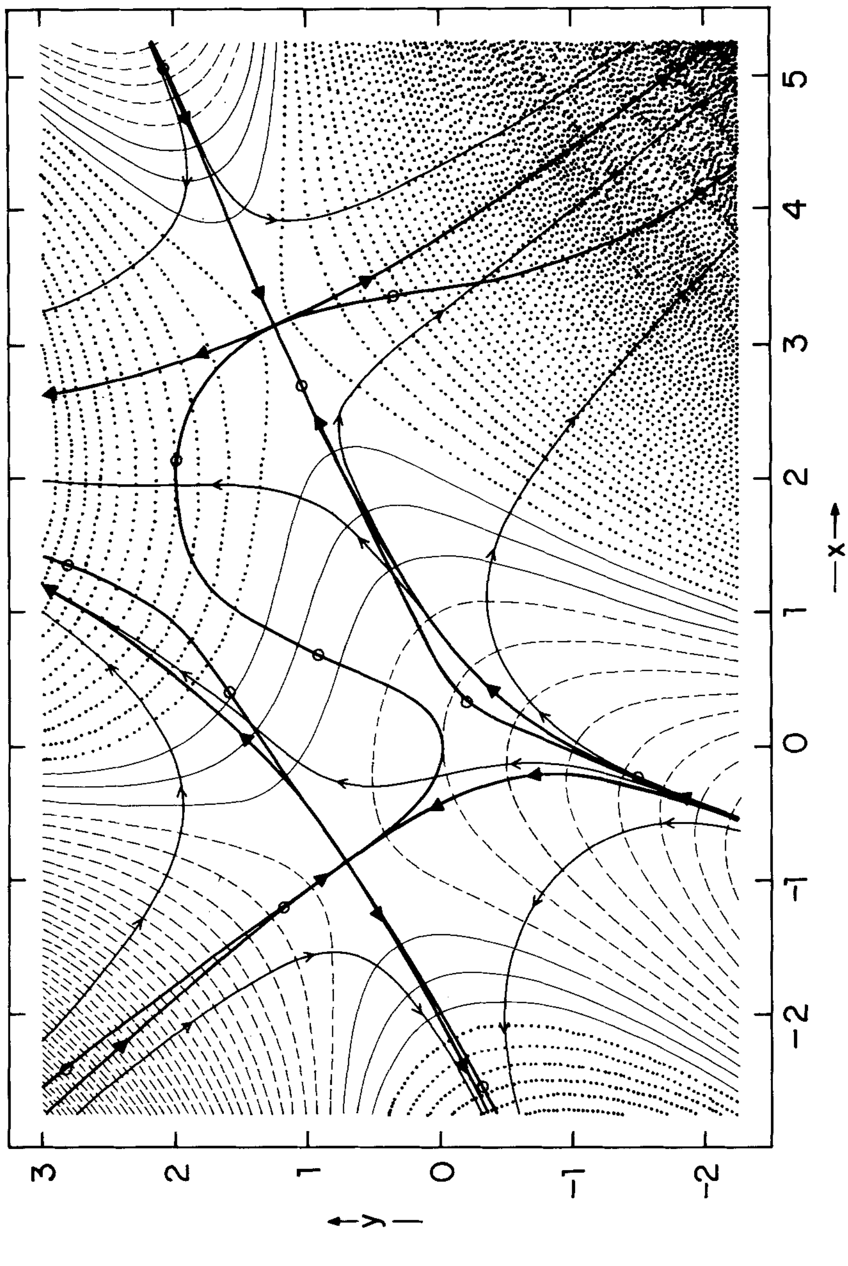

Fig. 2. The energy surface $f=(xy^2-yx^2+x^2+2y-3)/2$. *Dashed lines*: contours for $f \leq -1$. *Dotted lines*: contours for $f \geq 1$. *Solid lines* (without symbols): contours $f=-0.5$, 0, $+0.5$. *Curves* with *arrows*: orthogonal trajectories. *Fat curves* with *fat arrows*: orthogonal trajectories passing through saddlepoints. *Curves* with *circles*: gradient extremals

3.2. Illustrative example

In order to illustrate the discussed relationships we consider the surface

$$f(x, y) = (xy^2 - yx^2 + x^2 + 2y - 3)/2. \quad (3.11)$$

Its contour lines are displayed in Fig. 2 as the curves which are not marked by symbols. Some orthogonal trajectories are also drawn. They are characterized by arrows. Four of these orthogonal trajectories pass through the two saddlepoints, S_1 at $(x = -0.872, y = 0.7105)$ and S_2 at $(x = 3.135, y = 1.249)$, and these are drawn as fat lines. On all trajectories the arrows point in the uphill direction. This implies that the values of the dashed contours lie below $f(S_1)$ and that the values of the dotted contours lie above $f(S_2)$. Also one has $f(S_2) > f(S_1)$. There are three contours with values between $f(S_1)$ and $f(S_2)$ and they are drawn as solid lines. Of these, the one in the middle corresponds to $f(x, y) = 0$. The increment between adjacent contours is $\Delta f = 0.5$. The dashed contours outline three valleys. The dotted contours outline three ridges. The area between S_1 and S_2 is a relatively flat transition region.

There are three gradient extremals, which are drawn as lines with open circles on them. Two of them, one going through S_1, the other through S_2, both in a SW to NE direction, are quite similar to two corresponding orthogonal trajectories. The third gradient extremal is the curved line starting in the upper left and ending in the lower right. Its behavior differs greatly from that of any orthogonal trajectory.

The properties of these gradient extremals are elucidated by an examination of the eigenvalues defined in the preceding Section. Fig. 3 exhibits the eigenvalue plots for the two gradient extremals which are similar to orthogonal trajectories.

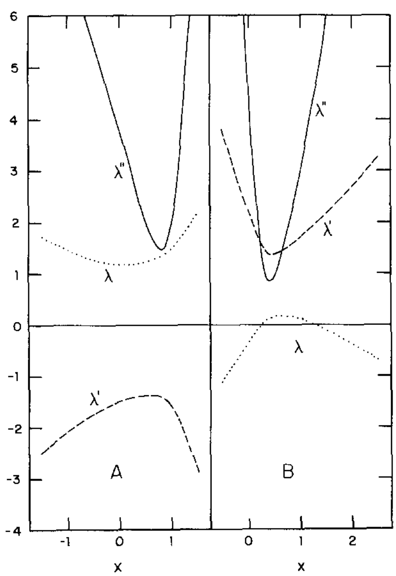

Fig. 3. Eigenvalues (Eqs. (3.4), (3.5), (3.9)) for the gradient extremals which pass through one saddlepoint only

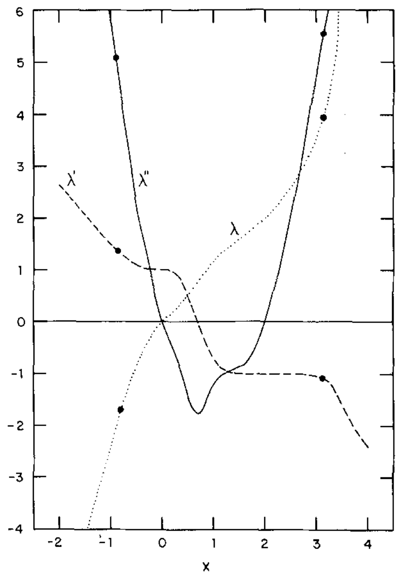

Fig. 4. Eigenvalues (Eqs. (3.4), (3.5), (3.9)) for the gradient extremal passing through both saddlepoints. The latter are indicated by *heavy dots*

Figure 3A corresponds to the gradient extremal passing through the saddlepoint S_1. It is seen that $\lambda' < 0$ and $\lambda'' > 0$ for the entire curve, indicating that it follows a ridge. Figure 3B corresponds to the gradient extremal passing through the saddlepoint S_2. Here we have $\lambda' > 0$, $\lambda'' > 0$, indicating that it follows a valley. Both inferences agree with the contourplot of Fig. 2.

Figure 4 exhibits the eigenvalues for the doubly curved third gradient extremal which is dissimilar to any orthogonal trajectory. At the upper left of Fig. 2 the curve clearly starts out as a valley, which is confirmed by the eigenvalues $\lambda' > 0$, $\lambda'' > 0$. At the point $(x = 0, y = 0)$ the curves becomes tangent to the contour $f = -3/2$. It is here that λ'' vanishes, in agreement with the general theory, and changes sign. From here on λ'' is negative and the curve follows a *cirque* (λ' is still positive). As the curve traverses the flat middle plateau, the cirque flattens out and turns into a cliff at the point $(x = 0.685,\ y = 0.920)$, where λ' vanishes and becomes negative. A little further on, at the point $(x = 2, y = 2)$ the curve becomes tangent to the contour $f = 5/2$ and here λ'' vanishes again and turns back to being positive. From here on out this gradient extremal follows a ridge.

4. Multidimensional generalization of gradient extremals

It is possible to define the gradient extremals in a slightly different manner which lends itself to a natural, multidimensional generalization of these curves.

Consider the expansion of the surface $V = f(x)$ around an arbitrary point $x^0 = (x_1^0 \cdots x_N^0)$ to second order in the cartesian displacements $\xi_i(x_i - x_i^0)$, viz.

$$V = V^0 + \sum_i g_i^0 \xi_i + \sum_{ij} H_{ij}^0 \xi_i \xi_j / 2. \tag{4.1}$$

We introduce new displacement coordinates $q_1, q_2, \ldots q_N$ at the same point x^0, which are related to the ξ_i by an orthogonal transformation

$$\xi_i = \sum_n^N U^0_{in} q_n, \qquad q_n = \sum_i^N \xi_i U^0_{in}, \tag{4.2}$$

so that

$$V = V^0 + \sum_n g_n q_n + \sum_{nm} h_{nm} q_n q_m / 2. \tag{4.3}$$

We now define the orthogonal matrix U^0_{in} by the following two sets of conditions:

(i) The gradient ∇f lies in the direction of q_1 so that

$$g_2 = g_3 = \cdots = g_N = 0; \tag{4.4}$$

(ii) The second order terms are diagonal in the displacements $q_2, q_3 \ldots q_N$, so that $h_{nm} = 0$ when $n, m > 2$ and $n \neq m$; i.e.

$$h = \begin{pmatrix} h_{11} & h_{12} & h_{13} & h_{14} & \cdot & \cdot & h_{1N} \\ h_{21} & h_{22} & 0 & 0 & \cdot & \cdot & 0 \\ h_{31} & 0 & h_{33} & 0 & \cdot & \cdot & 0 \\ h_{41} & 0 & 0 & h_{44} & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ h_{N1} & 0 & 0 & 0 & \cdot & \cdot & h_{NN} \end{pmatrix} \tag{4.5}$$

Since these are $N(N-1)/2$ conditions in total, there exists a unique set of such displacements q_n at any point $(x^0_1 - x^0_N)$ in configuration space and the coefficients g_1, h_{1n} and h_{nn} are thus defined as functions everywhere in that space.

The gradient extremals can now be obtained by requiring that the functions $h_{1n} (n \geq 2)$ all vanish, viz.

$$h_{12} = h_{13} = h_{14} = \cdots = h_{1N} = 0. \tag{4.6}$$

These are $(N-1)$ equations whose relations determine curves in configuration space which manifestly have the property that the gradient is an eigenvector of the hessian.

From this point of view we can generalize the concept of the gradient extremal by requiring that only $(N-n)$ of the coefficient functions h_{1m} vanish, for example

$$h_{1,n+1} = h_{1,n+2} = h_{1,n+3} = \cdots h_N = 0 \tag{4.7}$$

where $n>3$, so that e.g. for $n=4$:

$$\boldsymbol{h}=\begin{pmatrix} h_{11} & h_{12} & h_{13} & h_{14} & 0 & 0 & \cdot & \cdot & 0 \\ h_{21} & h_{22} & 0 & 0 & 0 & 0 & \cdot & \cdot & 0 \\ h_{31} & 0 & h_{33} & 0 & 0 & 0 & \cdot & \cdot & 0 \\ h_{41} & 0 & 0 & h_{44} & 0 & 0 & \cdot & \cdot & 0 \\ 0 & 0 & 0 & 0 & h_{55} & 0 & \cdot & \cdot & 0 \\ 0 & 0 & 0 & 0 & 0 & h_{66} & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & 0 & 0 & 0 & \cdot & \cdot & h_{NN} \end{pmatrix} \tag{4.8}$$

These conditions define a *n-dimensional surface* in configurational space which has the property that, at each of its points, the gradient of V lies in the linear subspace spanned by n eigenvectors of the hessian of V. It is apparent that this surface is also defined by the equations (2.8) *when the equations for* $k=1,2,\ldots n$ *are omitted from that set.*

It also is clear that any m-dimensional surface, with $m\leq n$, formed by a subset of m of the n eigenvectors, lies totally imbedded in the n-dimensional surface. In particular, the gradient extremals lie totally within higher dimensional surfaces or they intersect such surfaces only at extremal points. In general, the intersection of two surfaces is itself a surface of lower dimension.

5. Appendix

5.1. *Differential relations pertaining to gradient extremals*

1. The projection of an arbitrary vector $\boldsymbol{a}$ in the direction of the gradient ∇f is written as

$$\boldsymbol{P}^0\cdot\boldsymbol{a}=\boldsymbol{a}\cdot\boldsymbol{P}^0=\left\{\sum_j P^0_{ij}a_j\right\}, \tag{A.1}$$

where the projection matrix is

$$P^0_{ij}=(\partial f/\partial x_i)(\partial f/\partial x_j)/\sum_k(\partial f/\partial x_k)^2 \tag{A.2}$$

$$\boldsymbol{P}^0=[(\nabla f)\times(\nabla f)]/[(\nabla f)\cdot(\nabla f)]. \tag{A.2a}$$

Consequently the matrix

$$P_{ij}=\delta_{ij}-P^0_{ij}, \tag{A.3}$$

generates the projection in the linear space that is tangent to the contour subspace. Clearly:

$$\boldsymbol{P}^0\cdot\nabla f=\nabla f,\qquad \boldsymbol{P}\cdot\nabla f=0. \tag{A.4}$$

2. For the derivatives of the central quantity $(\nabla f)\cdot(\nabla f)/2=(\nabla f)^2/2$ we obtain

$$\nabla(\nabla f)^2/2=(\nabla\nabla f)\cdot(\nabla f)=\left\{\sum_j(\partial^2 f/\partial x_i\,\partial x_j)(\partial f/\partial x_j)\right\}. \tag{A.5}$$

The expression (A.5) can be decomposed in a projection parallel and perpendicular to ∇f. These are

$$(\boldsymbol{P}^0\cdot\nabla)(\nabla f)^2/2=\boldsymbol{P}^0\cdot(\nabla\nabla f)\cdot(\nabla f)=\lambda(\nabla f), \tag{A.6}$$

where λ has been *defined* as

$$\lambda = (\nabla f) \cdot (\nabla\nabla f) \cdot (\nabla f)/(\nabla f)^2 \tag{A.7a}$$

$$\lambda = \boldsymbol{P}^0 : (\nabla\nabla f) = (\nabla\nabla f) : \boldsymbol{P}^0. \tag{A.7b}$$

Consequently

$$(\boldsymbol{P} \cdot \nabla)(\nabla f)^2/2 = (\nabla\nabla f) \cdot (\nabla f) - \lambda(\nabla f). \tag{A.8}$$

Gradient extremals are defined by the condition that the expression (A.8) vanishes:

$$(\nabla\nabla f) \cdot (\nabla f) = \lambda(\nabla f). \tag{A.9}$$

3. In order to analyze higher derivatives, we begin by calculating $\nabla\lambda(x)$. Because of the gradient extremal condition (A.9) some cancellation occurs in the calculation of $\nabla\lambda$, and one obtains

$$\nabla f = \nabla\{(\nabla f) \cdot (\nabla\nabla f) \cdot (\nabla f)/(\nabla f)^2\},$$

$$= [(\nabla f) \cdot (\nabla\nabla\nabla f) \cdot (\nabla f)]/(\nabla f)^2, \tag{A.10a}$$

$$= (\nabla\nabla\nabla f) : \boldsymbol{P}^0 = \boldsymbol{P}^0 : (\nabla\nabla\nabla f), \tag{A.10b}$$

from which follows also

$$(\nabla\lambda)_k(\nabla f)_l = \{(\nabla\nabla\nabla f) \cdot (\nabla f) \cdot \boldsymbol{P}^0\}_{kl}. \tag{A.11}$$

4. Now for the second derivatives of $(\nabla f)^2/2$. From Eq. (A.6) we find

$$\nabla_k(\boldsymbol{P}^0 \cdot \nabla)_l(\nabla f)^2/2 = \nabla_k\lambda(\nabla f)_l = (\nabla\lambda)_k(\nabla f)_l + \lambda(\nabla\nabla f)_{kl},$$

whence by virtue of Eq. (A.11)

$$\nabla_k(\boldsymbol{P}^0 \cdot \nabla)_l(\nabla f)^2/2 = \{(\nabla\nabla\nabla f) \cdot (\nabla f) \cdot \boldsymbol{P}^0\}_{kl} + \lambda(\nabla\nabla f)_{kl}. \tag{A.12}$$

From Eq. (A.8) we find

$$\nabla_k(\boldsymbol{P} \cdot \nabla)_l(\nabla f)^2/2 = \nabla_k\{(\nabla\nabla f) \cdot \nabla f - \lambda(\nabla f)\}_l$$

$$= \{(\nabla\nabla\nabla f) \cdot (\nabla f) - (\nabla\lambda)(\nabla f) + (\nabla\nabla f) \cdot (\nabla\nabla f - \lambda\boldsymbol{I})\}_{kl},$$

whence by virtue of (A.11) and (A.3)

$$\nabla_k(\boldsymbol{P} \cdot \nabla)_l(\nabla f)^2/2 = \{(\nabla\nabla\nabla f) \cdot (\nabla f) \cdot \boldsymbol{P} + (\nabla\nabla f) \cdot (\nabla\nabla f - \lambda\boldsymbol{I})\}_{kl}. \tag{A.13}$$

Equations (A.12) and (A.13) are in accord with

$$\nabla\nabla(\nabla f)^2/2 = (\nabla\nabla\nabla f) \cdot (\nabla f) + (\nabla\nabla f) \cdot (\nabla\nabla f). \tag{A.14}$$

From (A.12) follows furthermore

$$(\boldsymbol{P}^0 \cdot \nabla)(\boldsymbol{P}^0 \cdot \nabla)(\nabla f)^2/2 = \boldsymbol{P}^0(\nabla\nabla\nabla f) \cdot \nabla f \cdot \boldsymbol{P}^0 + \lambda\boldsymbol{P}^0 \cdot (\nabla\nabla f),$$

whence by virtue of (A.5)

$$(\boldsymbol{P}^0 \cdot \nabla)(\boldsymbol{P}^0 \cdot \nabla)(\nabla f)^2/2 = \boldsymbol{P}^0 \cdot (\nabla\nabla\nabla f) \cdot (\nabla f) \cdot \boldsymbol{P}^0 + \lambda^2\boldsymbol{P}^0. \tag{A.15}$$

Applying $\boldsymbol{P}^0$ to Eq. (A.14) we find

$$(\boldsymbol{P}^0 \cdot \nabla)\nabla(\nabla f)^2/2 = \boldsymbol{P}^0 \cdot (\nabla\nabla\nabla f) \cdot (\nabla f) + \boldsymbol{P}^0 \cdot (\nabla\nabla f) \cdot (\nabla\nabla f),$$

whence by virtue of Eqs. (A.6) and (A.9)

$$(\boldsymbol{P}^0 \cdot \nabla)\nabla(\nabla f)^2/2 = \boldsymbol{P}^0 \cdot (\nabla\nabla\nabla f) \cdot (\nabla f) + \lambda^2\boldsymbol{P}^0. \tag{A.16}$$

We thus have the four relations

$$\nabla\nabla(\nabla f)^2/2 = (\nabla\nabla\nabla f) \cdot (\nabla f) + (\nabla\nabla f) \cdot (\nabla\nabla f), \tag{A.14}$$

$$\nabla(\boldsymbol{P}^0 \cdot \nabla)(\nabla f)^2/2 = (\nabla\nabla\nabla f) \cdot (\nabla f) \cdot \boldsymbol{P}^0 + \lambda(\nabla\nabla f), \tag{A.12}$$

$$(\boldsymbol{P}^0 \cdot \nabla)\nabla(\nabla f)^2/2 = \boldsymbol{P}^0 \cdot (\nabla\nabla\nabla f) \cdot (\nabla f) + \lambda^2\boldsymbol{P}^0, \tag{A.16}$$

$$(\boldsymbol{P}^0 \cdot \nabla)(\boldsymbol{P}^0 \cdot \nabla)(\nabla f)^2/2 = \boldsymbol{P}^0 \cdot (\nabla\nabla\nabla f) \cdot (\nabla f) \cdot \boldsymbol{P}^0 + \lambda^2\boldsymbol{P}^0. \tag{A.15}$$

By combining Eqs. (A.15) and (A.16) and taking into account Eq. (A.3), we find furthermore

$$(\boldsymbol{P}^0 \cdot \nabla)(\boldsymbol{P} \cdot \nabla)(\nabla f)^2/2 = \boldsymbol{P}^0 \cdot [(\nabla\nabla\nabla f) \cdot (\nabla f)] \cdot \boldsymbol{P} \tag{A.17}$$

By combining Eqs. (A.12), (A.14), (A.15), (A.16) and taking into account Eq. (A.3), we find also

$$(\boldsymbol{P}\cdot\nabla)(\boldsymbol{P}\cdot\nabla)(\nabla f)^2/2=\boldsymbol{P}\cdot(\nabla\nabla\nabla f)\cdot(\nabla f)\cdot\boldsymbol{P}+(\nabla\nabla f)\cdot(\nabla\nabla f-\lambda\boldsymbol{I}). \tag{A.18}$$

Subtracting Eq. (A.17) from Eq. (A.18) yields again (A.13).

References

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