INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY, VOL. XXXVII, 773–783 (1990)

How to Find a Saddle Point

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Abstract

This paper explains a method for finding saddle points on a multidimensional surface and shows how it may be used to define saddle-point seeking curves that have properties similar to well-known orthogonal trajectories. It is shown that a gradient extremal is a special case of one of these curves, and its chemical significance as the path, defined by local criteria, which starts from a stable structure and leads to a transition state, is discussed briefly in relation to the intrinsic reaction coordinate. It is emphasized that this theory gives a natural method for locating points that have Hessians of similar structure to those of transition states.

Introduction

In a recent paper [1], Hoffman et al. have explained how points on a potential surface, which correspond to stable structures, are linked by curves called gradient extremals. These unique curves follow streambeds that must pass through points on the surface, which correspond to transition states. Recently, a procedure, which follows these curves closely, has been applied by Ref. 2 to obtain a robust method for locating saddle points. In Ref. 3, a new *saddle point* algorithm was given that is based on *minimizing* an "image surface." It was shown how to apply this method to a potential surface, and simple examples were given to show its behavior. This paper explains the image surface theory in more detail, gives it a more theoretical basis, and shows how it may be used to calculate a gradient extremal. In fact, the image function algorithm may be thought of as a generalization of the gradient extremal method.

Gradient Extremals

The concept of the "mountaineer's algorithm" was described in Ref. 4. This defines an optimum ascent path as a path on a surface for which the gradient norm has a minimum on a given contour. This condition implies that at every point on the optimum ascent path that starts from a minimum the gradient vector is an eigenvector of the Hessian. This path is also called a gradient extremal. It is trivial to note that all stationary points and, in particular, saddle points must be on gradient extremals, because the zero vector always satisfies an eigenvalue equation trivially. This fact has been used in Refs. 1 and 2 to obtain a robust method for locating saddle points. However, there are disadvantages: exact second derivatives are needed to calculate points on the path, and, worse, this path must be followed accurately for the method to work. There is no reason to suppose that a gradient extremal is a direct path from a minimum to a saddle point; in fact, in general it is not. Also, it is necessary to start

 CCC 0020-7608/90/060773-11$04.00

the calculation of a gradient extremal at a point that is known to lie on it. This would usually be a stationary point, most likely a minimum. (The calculation of other points that lie on a gradient extremal, with no prior knowledge of positions of minima, would be as difficult as minimizing a function.)

Image Function Method

A novel method was described recently [3] for searching for saddle points on a multidimensional surface. This method assumes that the surface has analytic first and second derivatives and therefore may be approximated locally everywhere by a quadratic form. It is convenient to discuss this method in relation to quadratic forms. (Quadratic forms have a constant Hessian.) Consider such a quadratic approximation close to the origin:

$$f(\mathbf{x}) = f(0) + \mathbf{g}^T \cdot \mathbf{x} + \frac{1}{2}\mathbf{x}^T \cdot \mathbf{H} \cdot \mathbf{x},$$

where $\mathbf{g}$ is the vector of first derivatives at $\mathbf{x} = \mathbf{0}$, the superscript T denotes the transpose of a matrix or vector, and $\mathbf{H}$ is the matrix of second derivatives (Hessian matrix) also at $\mathbf{x} = \mathbf{0}$. By differentiating this approximation with respect to $\mathbf{x}$, and setting the first derivatives to zero, one obtains that $f(\mathbf{x})$ has a stationary point $\mathbf{x}^*$ at

$$\mathbf{x}^* = -\mathbf{H}^{-1} \cdot \mathbf{g},$$

with the optimum value of f given by

$$f_{\text{opt}} = f(\mathbf{x}^*) = f(0) - \frac{1}{2}\mathbf{g}^T \cdot \mathbf{H}^{-1} \cdot \mathbf{g}.$$

It is easier to discuss this stationary point in a representation of the quadratic approximation that has a diagonal Hessian matrix. If the directions of the coordinate axes are chosen to lie along principal axes, then the Hessian is diagonal. Such a representation in terms of principal axes of the quadratic form is found by computing the eigenvectors $\mathbf{u}_i$ of $\mathbf{H}$ and their eigenvalues λ_i, i.e.,

$$\mathbf{H} \cdot \mathbf{u}_i = \lambda_i \mathbf{u}_i.$$

Thus, the matrix representation of the linear transformation that diagonalizes $\mathbf{H}$, $\mathbf{U}$, has the eigenvectors $\mathbf{u}_i$, which form an orthonormal set, as its columns, and the transformed Hessian has the elements λ_i along its diagonal. In this principal axes representation, a general point $\mathbf{x}$ is transformed to

$$\mathbf{y} = \mathbf{U}^T \cdot \mathbf{x}$$

and the stationary point $\mathbf{y}^*$, which is given by

$$\mathbf{y}^* = \mathbf{U}^T \cdot \mathbf{x}^*$$

may be found alternatively from

$$y_i^* = -\left(\frac{g_i^p}{\lambda_i}\right),$$

where $\mathbf{g}^p$ is the gradient vector with respect to the principal axes representation

$$\mathbf{g}^p = \mathbf{U}^T \cdot \mathbf{g}.$$

If the i'th element of $\mathbf{g}^p$ and λ_i are both negated, it is obvious that all of the components of $\mathbf{y}^*$ remain unchanged. Thus, a related quadratic form, $\Phi(\mathbf{x})$, has the same stationary point as $f(\mathbf{x})$ if its i'th principal curvature and i'th principal gradient are both equal to minus those of $f(\mathbf{x})$. If $\mathbf{x}^*$ is a *minimum* on surface $f(\mathbf{x})$, then it will be a *saddle point* on surface $\Phi(\mathbf{x})$ and vice versa. Hence, if one wants to find a saddle point on f, one should minimize Φ. This is the essence of the image function method described in Ref. 3. For every *local* quadratic approximation, $f(\mathbf{x})$, to a multidimensional surface, one may use the above theory to find a *local* $\Phi(\mathbf{x})$ that has the same stationary point as $f(\mathbf{x})$ but a Hessian of different signature. The first derivatives of $\Phi(\mathbf{x})$ may be considered as the derivatives of the image of the multidimensional surface.

Thus, one may transform a multidimensional potential surface $f(\mathbf{x})$ such that its image $\Phi(\mathbf{x})$ has a minimum where $f(\mathbf{x})$ has a saddle. This transformation gives the first derivatives of $\Phi(\mathbf{x})$ at $\mathbf{x}$ and needs first and second derivatives of $f(\mathbf{x})$ to be defined and available at $\mathbf{x}$. In quantum mechanical studies of a potential surface, one wishes to find a transition-state saddle point at which the Hessian has all of its eigenvalues positive except one that is negative. Thus, for this problem, $\Phi(\mathbf{x})$ is defined by negating the *lowest* eigenvalue and its corresponding element of $\mathbf{g}^p$. Minimizing Φ means maximizing f along the principal curvature corresponding to the lowest eigenvalue and minimizing f in all the other directions. (This is what standard methods to find saddle points attempt to do by empirical, by trial and error means, and often by user intervention. The image function method achieves this naturally and does not need to know function values.) Note that at points that have equal lowest eigenvalues, there is a catastrophe because there is an infinity of eigenvectors with the lowest eigenvalue. (One must choose appropriate eigenvectors that resemble those at neighboring points to make the process continuous if one wishes to be able to give a proper mathematical definition of the path, but it is not necessary to do this to make the image function work.) Such a catastrophe point behaves rather like a stationary point of $\Phi(\mathbf{x})$. This pseudostationary point must resemble a saddle point of Φ locally because the Hessian of $\Phi(\mathbf{x})$ must have at least one negative eigenvalue there.

Although it may now seen straightforward to find a saddle point by trying to minimize $\Phi(\mathbf{x})$, one should note that only first and second derivatives of Φ are known and not function values. (There is never a *unique* Φ for a general function f; this is discussed in detail later.) If a standard optimization method that is based on the Hessian matrix, such as Newton's or the conjugate gradient methods, and that does not use function values were used to minimize Φ, it would be sure only to find a reducing path for Φ in a region where the Hessian of Φ is positive definite (where the Hessian of f has only one negative eigenvalue). It would not be able to distinguish between stationary points, and the route taken in the space of $\mathbf{x}$ on Φ would be exactly the same as that taken on f. This is because this kind of algorithm is based on the step

$$\Delta\mathbf{x} = -\mathbf{H}^{-1} \cdot \mathbf{g}$$

or equivalently

$$\Delta y_i = -\left(\frac{g_i^p}{\lambda_i}\right)$$

and negating numerator and denominator in the latter equation makes no effect on the optimizing path. ($\Delta \mathbf{x}$ means the change in $\mathbf{x}$ in an iteration.) A minimization routine that is able to distinguish minima from other stationary points but which does not use function values or the Hessian must be used; this is discussed later.

An example of a function that has a fairly simple image function is

$$f(\mathbf{x}) = \exp(-x_1^2) - \exp(-x_2^2),$$

where x_1 and x_2 are the components of $\mathbf{x}$. f has no mixed terms x_1x_2; therefore, its Hessian is a diagonal matrix. Its second derivatives (these are also the eigenvalues in this case) are

$$\lambda_1 = (4x_1^2 - 2)\exp(-x_1^2)$$
$$\lambda_2 = -(4x_2^2 - 2)\exp(-x_2^2);$$

therefore

$$\Phi(\mathbf{x}) = k - \exp(-x_1^2) - \exp(-x_2^2) \quad \text{if} \quad \lambda_1 < \lambda_2$$
$$= k + \exp(-x_1^2) + \exp(-x_2^2) \quad \text{if} \quad \lambda_2 < \lambda_1$$

where k is an arbitrary constant. Points for which the two eigenvalues are equal constitute pseudostationary points at $(\pm 1/\sqrt{2}, \pm 1/\sqrt{2})$. Near to the point $\mathbf{x} = 0$, λ_1 is negative and λ_2 is positive; hence, at the origin, f has a saddle point and Φ has a minimum, as expected.

Orthogonal Trajectories

A convenient technique for analyzing surfaces is to plot orthogonal trajectories [5]. These are curves that satisfy the differential equation

$$d\mathbf{x}/ds = -\nabla f,$$

where s parameterizes the curve and ∇ is the gradient operator. Each orthogonal trajectory cuts the contours of the surface at right angles. The minus sign means that as s increases on a trajectory the value of f decreases. For an example, consider the general N-dimensional quadratic surface:

$$f = a + \mathbf{g}^T \cdot \mathbf{x} + \frac{1}{2}\mathbf{x}^T \cdot \mathbf{H} \cdot \mathbf{x}$$
$$\nabla f = \mathbf{g} + \mathbf{H} \cdot \mathbf{x}$$

and, hence, the orthogonal trajectories are given by

$$\mathbf{x} = \sum_{i=1}^{i=N} A_i \mathbf{u}_i \exp(-\lambda_i s) - \mathbf{H}^{-1} \cdot \mathbf{g},$$

where A_i is an arbitrary constant, λ_i is the i'th eigenvector of $\mathbf{H}$, and $\mathbf{u}_i$ is its eigenvector. It is seen that for all $\mathbf{u}_i$ and for A_i the trajectories tend ($s \rightarrow \infty$) to the optimum point, $-\mathbf{H}^{-1} \cdot \mathbf{g}$ of f, only if all the eigenvalues are positive (i.e., $\mathbf{H}$ is positive definite). Hence, as is well known, one may search for minima of $f(\mathbf{x})$ by following its orthogonal trajectories. However, if $\mathbf{H}$ has one negative eigenvalue and the rest positive, suppose $\lambda_j < 0$, then unless $A_j = 0$, the trajectories cannot tend to the stationary point at $-\mathbf{H}^{-1} \cdot \mathbf{g}$, which in this case is a saddle point. Thus, trying to search for a saddle point by following an orthogonal trajectory is a very difficult task indeed and an optimization algorithm that attempts to follow these trajectories may be properly thought of as a minimization technique that can distinguish between stationary points.

From this analysis, a minimum of a function $f(\mathbf{x})$ may be found by repeating the steepest descent step:

$$\Delta\mathbf{x} = -\sigma\nabla f$$

for positive σ until convergence. (Again, Δ denotes the change of a quantity in an iteration interval.) For very small σ, the minimization path will approximate the orthogonal trajectories, and, generally, the algorithm can distinguish minima from other stationary points due to the above. If the image function, $\Phi(\mathbf{x})$, of $f(\mathbf{x})$ is found, then repeating the step

$$\Delta\mathbf{x} = -\sigma\nabla\Phi$$

for positive σ until convergence will produce paths that can *converge* only to a minimum of $\Phi(\mathbf{x})$, i.e., a saddle point of $f(\mathbf{x})$.

Dynamic Minimization Method

A more efficient minimization algorithm that can distinguish minima from other stationary points is Snyman's dynamic minimization method [3, 6, 7]. This method minimizes $f(\mathbf{x})$ by treating it as the potential energy of a particle of unit mass moving in a conservative force field. It calculates trajectories of the particle and monitors its kinetic energy. If the kinetic energy on a trajectory increases, then as total energy is conserved, the potential energy [function $f(\mathbf{x})$] must decrease. Since kinetic energy is nonnegative, unless one is at a minimum, there is always a trajectory on which $f(\mathbf{x})$ will decrease. Only trajectories of increasing kinetic energy are accepted, giving an efficient method that can distinguish minima from other stationary points and that does not use function values at all. The trajectories are found from integrating the equations of motion for the particle approximately. The force vector is given by minus the gradient vector; hence, the change in velocity is given by

$$\Delta\mathbf{v} = \nabla f(\mathbf{x})\,\Delta t$$

and the change in $\mathbf{x}$ by

$$\Delta\mathbf{x} = \mathbf{v}\Delta t$$

for positive time step Δt and where $\mathbf{v}$ is the particle's velocity. This method also adopts some heuristic steps [6, 7] that improve its performance. (This minimization scheme has been used successfully in a difficult geometry optimization problem [8]). Note that if $\mathbf{v} = 0$ is enforced at the start of each iteration, then the Snyman algorithm reduces to the steepest descent method with $\sigma = \Delta t^2$. It was shown in Ref. 3 that Snyman's algorithm applied to $\Phi(\mathbf{x})$ gives a very robust method for finding saddle points of $f(\mathbf{x})$, whose efficiency can be increased more by combining it with Newton's method [3] or the conjugate gradient method [9] when the gradients are small near to a saddle point of $f(\mathbf{x})$. It was also explained in Ref. 3 how the image function method may be applied to a chemical reaction potential surface to find transition-state geometries, giving a method for searching for regions, which have a Hessian matrix with only one negative eigenvalue, which is not based on trial and error.

The image transformation modifies the forces (gradients) so that the particle is *attracted* by the *saddle points* of $f(\mathbf{x})$ *in all directions* and is *repelled* by the *minima* of $f(\mathbf{x})$ *along the direction corresponding to the negated eigenvalue.*

Visualization of the Image Function for a General Function

Although it was stressed above that the image function is defined only locally, its first derivative vector is defined uniquely everywhere. (It can be defined uniquely for points at which the lowest eigenvalues of the Hessian of $f(\mathbf{x})$ are equal.) Therefore, it may be expected that one can generate contours for the image function approximately using approximate integration, i.e., from the step

$$\Delta\Phi = \nabla\Phi \cdot \Delta\mathbf{x}.$$

Figure 1 shows the contours of the Cerjan–Miller [3, 10] test function

$$f(\mathbf{x}) = (a - bx_2^2)x_1^2 \exp(-x_1^2) + \frac{1}{2}cx_2^2,$$

in which $a = c = 1$ and $b = 1.2$. x_1 and x_2 are the components of $\mathbf{x}$. $f(\mathbf{x})$ has a minimum at $(0, 0)$ and saddle points at $(\pm 1, 0)$. Figure 2 shows an attempt to construct a possible approximate global $\Phi(\mathbf{x})$ for this function starting with the arbitrary boundary condition $\Phi = 0$ at $(-1, 0)$. Broken-line contours denote negative values of Φ. This figure shows clearly that $(-1, 0)$ behaves like a minimum on the image surface and $(0, 0)$ behaves like a saddle point. It also shows some pseudostationary points where the eigenvalues of the Hessian of $f(\mathbf{x})$ are equal. [At $(\pm 1, \pm 0.948)$, $(0, \pm 0.645)$, and $(\pm 0.350, 0)$.] Although some of these seem to be surrounded by contours that are characteristic of minima or maxima, it can be verified that, in fact, they behave like saddle points by plotting more contours around them. The region close to $(1, 0)$ is almost flat, but again, by carrying out a more detailed calculation, it can be shown that this point behaves like a minimum on Φ.

It should be noted that numerical errors may be introduced by the approximate integration method and these can distort the picture. Also, the approximate values ob-

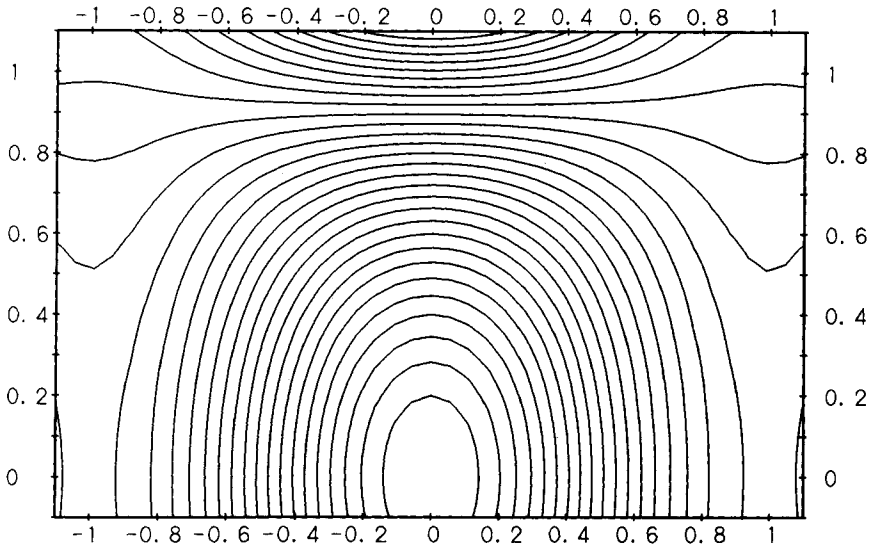

Figure 1. A contour map of the Cerjan–Miller test potential surface. This function has a minimum at $(0,0)$ and saddle points at $(\pm 1,0)$.

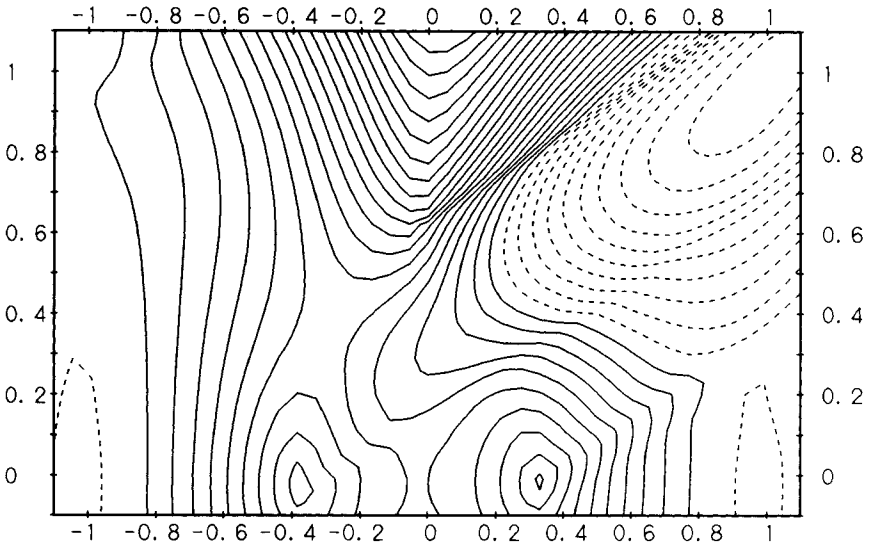

Figure 2. An attempt to find an approximate image function for the Cerjan–Miller function, using only its first derivatives. Solid lines show positive contours, and broken lines, negative contours. Note that the topology close to the stationary points at $(-1,0)$ and $(0,0)$ is what is expected. The image function has a minimum at $(-1,0)$, whereas the original function has a saddle point there. $(0,0)$ is a saddle point of the image function where the original function has a minimum. Pseudostationary points are present in the image function at $(\pm 1, 0.948)$, $(0, 0.645)$, and $(\pm 0.350, 0)$, where the Hessian of the Cerjan–Miller function has equal eigenvalues. These points are not found during a minimization of the image function because they must correspond to saddle points of the image function.

tained for Φ from the derivatives depend on the direction of $\Delta\mathbf{x}$. Generally, the directions chosen in the derivative table used to obtain the contour plot will be different from those chosen by the minimization algorithm. The minimization algorithm has never located a point in the broken-line region as a minimum of Φ. This misleading region in Figure 2 merely emphasizes that there is no global image function and that a visualization of one must be interpreted with great care!

Saddle-point Seeking Paths

To confirm that the method for obtaining the first derivatives for the image function really does transform minima to saddle points and vice versa, the "orthogonal trajectory step"

$$\Delta\mathbf{x} = -\sigma\nabla\Phi$$

was used to find saddle-point seeking curves for the surface

$$f = \frac{1}{2}(x_1x_2^2 - x_1^2x_2 + x_1^2 + 2x_2 - 3),$$

which was used in Ref. 1 to show gradient extremals. This function has two proper stationary points: saddle points at $(-0.87, 0.71)$ and $(3.13, 1.25)$. Otherwise, it is not bounded. The contours and saddle-point seeking paths are shown in Figure 3. Thick unbroken lines are contours of the function for positive f, broken lines are negative

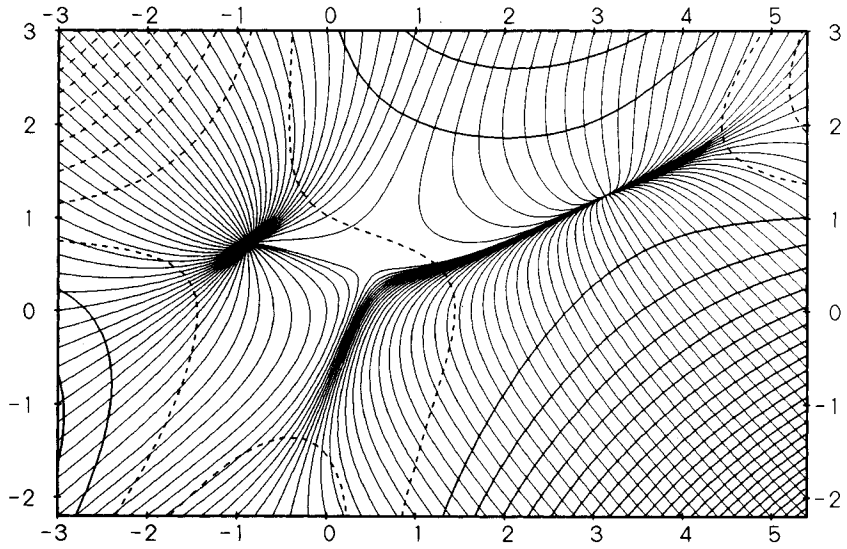

Figure 3. Saddle-point seeking paths for the surface of Hoffman et al. [1]. Thick lines denote positive contours and broken lines, negative contours. Thin lines show the saddle-point seeking paths, each of which was started from a point on the border of the diagram using the steepest descent algorithm on the image surface. These paths do not correspond to orthogonal trajectories because they each end at either of the two saddle points at $(-0.87, 0.71)$ or $(3.13, 1.25)$.

contours, and thin lines are the saddle-point seeking paths, which were started from points spaced equally at intervals of 0.2 on the border of the figure. (To obtain a neat figure, σ was given a value of 0.01 and each saddle-point seeking curve contains around 1000 points. If σ is 0.25, jagged curves that approximate the ones in the figure are found. These each contain around 30 points.) It is clearly seen that the paths finish at either of the saddle points. It shows that runs starting from any point can find a saddle point of the function.

The figure is very similar in appearance to a plot of orthogonal trajectories of a function, and, in fact, the saddle-point seeking paths are approximations of the orthogonal trajectories of the image function of f. These saddle-point seeking paths are seen to partition the space into catchment regions for both saddle points, just as orthogonal trajectories do for minima. There is a special saddle-point seeking curve that has all of its principal gradients equal to zero except the one corresponding to the negated eigenvalue. In the principal axis representation, the Hessian is diagonal; hence, its eigenvectors each have only one nonzero component and the principal gradient vector is an eigenvector. Transforming from the principal axis representation gives that the gradient vector is an eigenvector of the Hessian, and, therefore, this special saddle-point seeking curve is a gradient extremal. In fact, it is the reaction path [11] of the *image* function and could be calculated, using derivatives of Φ for a potential surface (instead of the derivatives of the potential surface itself), by an intrinsic reaction coordinate algorithm starting from a stable structure geometry. (It is important to note that the points on this path do not generally lie on the reaction path of the potential surface; i.e., this path is not the reverse of the reaction path. This would be true only for a reaction path that is a straight line [4].) A chemical reaction is likely to follow *the reaction path of the image function* if it is expected to choose a path that requires the least work to climb the hill *from a stable structure to a transition state*.

Conclusions

This paper has shown that a simple transformation may be applied to the first derivatives of a multidimensional function so that when these transformed derivatives are used in the steepest descent or in Snyman's minimization algorithm *only* a saddle point can be found. Saddle-point seeking curves are shown to exist that are similar in appearance to orthogonal trajectories but that are *attracted by saddle points*. As with orthogonal trajectories, these curves are seen in Figure 3 to partition the space into catchment regions. The problems involved in finding saddle points by using the image transformation are thus reduced to only those problems involved in finding minima.

Although this paper has considered only transition-state saddle points that have only one negative principal curvature, the method is applicable to any kind of saddle point. For an N-dimensional surface, there are, in general, $(N - 1)$ kinds of saddle point. For each kind of saddle point, an image transformation can be made to map it to a minimum. If the saddle point has M ($<N$) negative curvatures, then the relevant image transformation is defined by negating the lowest M Hessian eigenvalues and their corresponding principal gradients. Thus, there are $(N - 1)$ possible different sets of image function derivatives. (There is also the trivial image function $\Phi = -f$ that maps maxima to minima and vice versa.)

The gradient extremal is a special saddle-point seeking curve whose principal gradient vector has only one nonzero component. It uses only *local* criteria (local derivatives and local Φ) to define a unique path from a stable structure to a transition state. It is a reaction path on the image surface that has derivatives equal to the transformed derivatives at each point.

One shortcoming of the image method is that exact first and second derivatives are required (this is also true of the gradient extremal method [1, 2]), and it also needs eigenvalues and eigenvectors of the second derivative matrix for each point visited on a saddle-point seeking path. Its advantage over the gradient extremal method is that it may be started from *any* convenient starting point and it is not necessary to try to follow a gradient extremal at all.

At a first reading it may seem that the method would work well only in regions near to a saddle point. This has been shown not to be the case [3]. (In fact, a quadratically convergent method such as Newton's method must perform better than the image method does if started close enough to the required saddle point.) The performance of the image method is decided ultimately by the minimization method with which it is used. There can be no guarantee that the *desired* saddle point will be found — only that a saddle point of the *desired Hessian form* will be found. (This problem is similar to that encountered in the search for a global minimum, which is resolved by conducting several searches starting from different points and designating the global minimum as the lowest local minimum.) To be sure to find a particular saddle point, one must start from a point in its catchment region as shown in Figure 3. Such information is not usually available. The significant improvement, which the image method introduces, is that it defines paths naturally that lead from a region whose points have positive definite Hessians (for example) to a region whose points have transition-state-like Hessians (without using trial-and-error arguments that are based on prior knowledge of the potential surface). Although it may be argued that such paths are unpredictable on a multidimensional surface, they are made up of fundamental directions that lead from a general point to a region where Newton's, or the conjugate gradient method, or any other standard method can be expected to converge to a saddle point. In view of the fact that the recommended minimization method, Snyman's algorithm [6, 7], to be used in conjunction with the image method, is quick to move near to a local minimum but slow to converge to it, this new saddle-point seeking routine is best thought of as a method to find a suitable starting point from which a quadratically convergent algorithm can continue and be sure to locate the saddle point.

Acknowledgments

The calculations for the figures were carried out on the CONVEX C-201 computer at the Institute for Fundamental Chemistry. The author is indebted to The Japan Society for the Promotion of Science for the provision of a research fellowship.

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Received February 17, 1989
Accepted for publication July 21, 1989