Nord and Ruedenberg (HNR) [1] with changed parametrisation. We restrict ourselves to a Euclidean metric and to the two-dimensional (2D) case. Since it contains nearly all phenomena of PES paths of interest arising in real chemical systems and is already complicated. The N-dimensional problem has been outlined in [1], and a numerical procedure which traces a nonbifurcated N-dimensional GE has been recently proposed [4].

The aim of the present paper is a further elucidation of the conundrum of whether the rise of a valley succeeds or is flattened and disappears at the ends. In general, this happens in regions of the PES far away from stationary points (where bifurcations can emerge also [6]). Stable molecular vibrations need a convex bowl at the bottom of the PES, and a reaction goes over a SP. But before a chemical reaction starting in a bowl takes place the system first must be excited. It is possible that the reaction reaches very structured parts of the PES, in which case the valley may disappear somewhere in the mountains, the corresponding mode ceases to exist, its level ladder should end and its vibrational energy be redistributed into other modes. Hence, it is to be expected that changes in the PES valleys would be accompanied by strong changes of the spectroscopic behaviour of the molecule. It is therefore of great interest, to compute bifurcation points (BP) on a given PES and then to understand their influence on the spectrum of the molecule. The latter aim is the basis of a forthcoming paper by the author. The calculation of BPs is illustrated by some simple, but instructive, examples of analytic surfaces which give us the possibility of discussing the more abstract Basilevsky classification [7, 8] of BP's with simple solvable equations. We conclude the mathematical treatment with a discussion of the "strange" third GE of the HNR example [1] in the light of the Basilevsky classification [8]. We show how only a small change in a parameter of the PES makes a qualitative change in the BP character.

In a physical discussion we compare the quasilinear behaviour and internal energy redistribution which are consequences of PES valley bifurcations. The molecule HCN should be an interesting candidate for understanding bifurcations of valley paths.

2. Gradient extremals

We recall the definition of Hoffman, Nord and Ruedenberg (HNR) [1] (slightly modified):

A gradient extremal (GE) intersects every contour line in that point where the absolute value of the gradient is an extremal value compared to other gradient values on the same contour.

(Gradients are always perpendicular to the contour line.) We introduce the so called defect functional [5] for the gradient norm

$$\sigma(x, y) = \tfrac{1}{2}\|\mathrm{grad}\ U(x, y)\|^2 = \tfrac{1}{2}U_x^2 + \tfrac{1}{2}U_y^2 \qquad (1)$$

of the gradient (U_x, U_y) where $U(x, y)$ is the energy surface over a 2D configuration space $\boldsymbol{R}^2$. We use the standard partial derivative notation. The way to determine an extremal of the defect functional σ along a contour line of $U(x, y)$ is to search for solutions of

$$\boldsymbol{t} \cdot \mathrm{grad}\ \sigma = 0, \qquad (2)$$

where $\boldsymbol{t}$ is the unit tangent vector of the contour line $U(x, y) = \text{constant}$ or $y = \mathrm{cl}\,(x)$, and $\mathrm{grad}\ \sigma = \boldsymbol{H} \cdot \mathrm{grad}\ U$. (We use small initial letters of a contour line cl (x) for an explicit functional relation and capitals for corresponding implicit definitions). Equation (2) can be understood as a condensation of a formula for the direction derivative of the σ-functional along cl (x). The vector part of grad σ in directions other than $\boldsymbol{t}$ is cancelled by the scalar product with $\boldsymbol{t}$. Condition equation (2) remains in the assumed extremal condition along cl (x). In the 2D case we simply have

$$\boldsymbol{t} = (U_y, -U_x)/(2\sigma)^{1/2},$$

and we get from Eq. (2) the equation for a gradient extremal [1]

$$\mathrm{GE}\,(x, y) = U_{xy}(U_x^2 - U_y^2) + (U_{yy} - U_{xx})\,U_x U_y = 0. \qquad (3)$$

At first sight, Eq. (3) seems to be a differential equation [1], but here we have to differentiate the given energy $U = U(x, y)$ at any argument (x, y). The result at a point (x, y) is a value, zero or nonzero. The requirement for GE to be zero in Eq. (3) makes a (maybe implicit) functional relation of x and y, not a differential equation. Any couple (x, y) of the configuration plane can be tested in Eq. (3). In general only a subset of the plane will give a solution. But already in the 2D case it is not clear whether we get a 1D curve $y = \mathrm{ge}\,(x)$. We show this by a simple counterexample:

Example 1. The model energy is a paraboloid of rotation

$$U(x, y) = x^2 + y^2$$

We get $U_{xy} = 0$, $U_{xx} = 2$, $U_{yy} = 2$, and

$$\mathrm{GE}\,(x, y) = 0(4x^2 - 4y^2) + 0(4xy) = 0.$$

Every point (x, y) fulfils the GE equation. Thus, the whole plane is itself GE. At all points except the origin there are two eigenvector fields, one tangent to the profile parabola, the other tangent to the circle of revolution in a horizontal plane.

If we have a somewhat more complicated surface $U(x, y)$ we can assume that we get a 1D curve solving the GE condition equation (3). We emphasize that we look for curves $\mathrm{GE}\,(x, y) = 0$ or $y = \mathrm{ge}\,(x)$ in the (x, y)-plane. The valley floor path on the potential landscape then is the energy profile over this GE curve or, conversely, the GE is the projection of the valley floor on $U(x, y) = U(x, \mathrm{ge}\,(x))$ into the (x, y)-plane.

Properties of GE's are outlined [1]. (1) All stationary points are on GE because there $U_x = U_y = 0$. (2) Further we have the somewhat surprising behaviour that,