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An algorithm for determining dynamically defined reaction paths (DDRP)*

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Summary. A numerically stable and well-parallelizable curve variational algorithm is described for determining tangent curves of vector fields between two given stationary points. In particular, the method is suitable for finding reaction paths and saddle points on potential energy hypersurfaces (PHS). The stability of the procedure is illustrated by an artificial mathematical function, showing phases of following the reaction on the PHS.

Key words: Potential energy hypersurface – Reaction path – Saddle point – IRC

1 Introduction

Many fundamental subjects and problems of modern chemistry (reaction kinetics, reaction mechanisms, chemical reactivity, vibrational spectroscopy, stability and conformation of molecules, etc.) are closely related to the concept of potential energy hypersurfaces (PHS) [1–7]. The calculation and analysis of (multidimensional) PHSs is a rather difficult and time-consuming task, therefore mathematical and computational techniques (methods and procedures, algorithms and programs) that may facilitate this task are of particular significance.

A large number of PHS studies [8–15] uses the concept of reaction path (RP). Without going into any details of the various definitions we mention only three main distinctions referring to RP: the minimum energy RP (MERP) [16], the steepest descent (SD) way [17] and the intrinsic reaction coordinate (IRC) [18, 19]. Many other definitions and descriptions of the RP can be found in the literature. Some of them involve higher derivatives of the functional with respect of the abstract reaction parameter, the reaction coordinate (RC is a parameter for the actual geometrical changes taken place in the reactants and products in

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* Dedicated to Professor Zoltán G. Szabó, the great teacher and scientist in reaction kinetics and in many other fields of physical chemistry, on his 84th birthday.

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time during the reaction, from the beginning to the end). However, any definition can be transcribed into the form of tangent curves of vector fields in an appropriately selected new configurational space.

Most earlier works – due to the limited capacities of computer hardware – concentrated on the calculation of certain points of special importance along the RP. Such critical points of the PHS [20] are the minima corresponding to stable molecular configurations (e.g. equilibrium structures of reactants and products) and the saddle point (SP) associated with the transition state (TS) of a chemical reaction or conformational change that occur along the RP connecting the minima. Using the SD procedure of Ishida et al. [21], Ruedenberg and coworkers [22–25] gave spectacular representations of segments of PHS of various chemical reactions, including even bifurcating transition regions. Some of the methods [26] aiming the determination of the whole RP have been based upon issuing approximating SD paths from some critical points. These kinds of approach are globally very unstable [27] since small changes in the starting direction at a hyperbolic stationary point may cause unpredictable changes. On the other hand, such methods are not well-parallelizable.

In previous papers [28, 29] we gave the theoretical background of a global procedure for searching the SDRP and external points of the PHS in Cartesian coordinates. This renders it possible to make use of parallel and vector processor facilities. In the present paper – joined with the abstract mathematical considerations [29] – we are going to give a procedure and an algorithm determining tangent curves of vector fields between two given stationary points (where the fields vanish). The *a priori* existence of such tangent curves is not at all certain, however we can show by a careful analysis of the proofs of Theorem 2.1 in [28] that under not too restrictive conditions on the structure of domains of attraction [30] ("catchment regions" of Mezey [31, 32]) starting from almost any arbitrary curve connecting two given stationary points we can construct a tangent curve of the vector field by using a numerically stable curve variational method. Another paper [33] shows how to implement this procedure and algorithm in the form of a computer program which is designed to facilitate the determination of equilibrium and SP geometries from energy and energy derivative data and to help in the optimal choice of the successive PHS points at which further calculations would be performed. This procedure can also be used to follow the RP along the PHS (i.e. gradient-following or SD path on a surface) which has been expressed in terms of suitable mass-weighted internal coordinates [34] transformed to Cartesian coordinates and vice versa. Moreover, the general vector field version of the procedure is suitable in treating the coordinate independent RP calculations [10, 35]. A next paper [36] will illustrate the usage of the procedure on a simple chemical reaction system, by applying the MNDO semiempirical quantum chemical method for obtaining the energy functional.

2 Algorithm

Let $V: \mathbb{R}^n \to \mathbb{R}^n$ be a continuous vector field on $\mathbb{R}^n$. We call the points where the field V vanishes the *singularities* of V and we write S_V for their set. In accordance with the usual interpretation of IRC in terms of the gradient field of the potential function, we call a curve $t \mapsto c(t)$ in $\mathbb{R}^n$ an *IRC of the vector field* V if the endpoints of c are singularities of V and the one sided derivatives $(d^+/dt)\, c(t)$, $(d^-/dt)\, c(t)$ exist and are parallel to V everywhere on the domain of c.

For the maximal solution of the initial value problem:

$$\frac{d}{dt}y(t) = V(y(t)); \qquad y(0) = x \tag{1}$$

we shall write $\exp(tV)(x) := y(t)$. The transformation $\exp(V)$ is called the *exponential* of the vector field V. Notice that the exponential of V is not necessarily defined on the whole manifold $\mathbb{R}^n$ but only on the domain:

$$D_V := \{x : (1) \text{ has solution on } [0, 1]\}.$$

For any $x \in S_V$ the figure

$$A_{x,V} := \left\{ z : z \in \bigcap_{t>0} D_{tV}, x = \lim_{t\to\infty} \exp(tV)(x) \right\}$$

is called the catchment region of the singular point x of the vector field V.

In [28] we have essentially proved the following.

Theorem. *Suppose V is an analytic vector field on $\mathbb{R}^n$ with the following properties*
(i) V has only finitely many singular points,
(ii) the catchment regions of the singularities of V cover the whole $\mathbb{R}^n$,
(iii) around every singularity, the vector field V has a non-degenerate linear image in some analytic chart (i.e. the singularities of V are of Siegel type).

Then, given any piecewise analytic curve $c : [0, 1] \to \mathbb{R}^n$ changing catchment region only finitely many times, the curves $c^t := \exp(tV)(c)$ are well-defined for all t and, for $t \to \infty$ they converge uniformly with arc length proportional reparametrization on [0, 1] *to an* IRC *of the vector field V.*

We have a control also over the asymptotic behaviour of all the derivatives of the curves c^t. Namely, for every $t \geqslant 0$ there exists a partition $0 = \alpha_0(t) < \alpha_1(t) < \cdots < \alpha_N(t) = 1$ of the interval $[0, 1]$ and for each $i = 1, \ldots, N$ there exists an analytic reparametrization $p_i^t : [0, T_i(t)] \to [\alpha_{i-1}^t, \alpha_i^t]$ of the interval $[\alpha_{i-1}^t, \alpha_i^t]$ onto some interval $[0, T_i(t)]$ where $T_i(t) \to \infty$ and $c_{i-1}^t(T_{i-1}(t)) = c_i^t(0) \to y_i$ for some stationary point y_i of the field V as $t \to \infty$ such that all the derivatives of the reparametrized subcurves $C_i^t := c_i^t(p_i^t)$ converge locally uniformly for $t \to \infty$.

It seems to be very hard to calculate effective convergence estimates along the lines of the proof of the Theorem. In practical cases, one can give suitable estimates for uniform convergence from the behaviour of a small number of exponential curves of the field V. On the other hand, the existence of the described control over the derivatives ensures that numerical methods based on the Theorem can be very stable. Although the techniques of the proof of the Theorem based heavily upon manipulations with Taylor coefficients, such coefficients do not occur at all in the final result. This makes it possible to construct algorithms requiring only values of the vector field from a "black box". Moreover, it may be expected that one has convergence at least in Hausdorff distance for the curves c^t even when replacing the analyticity of V with some finite smoothness condition (as e.g. continuously differentiability). It seems also that the assumption that the stationary points of the field V should be of Siegel type and should only form a finite family can be weakened. Indeed, this condition played only a simplifying role in the proof of the Theorem. However, it is crucial that the catchment regions of the singular points of V should cover the whole space $\mathbb{R}^n$. If we consider the case of the gradient field of the potential function of some system of atoms, this condition fails in most cases since the potential function vanishes in exponential order towards infinity. It is not hard to bypass a difficulty of such kind: given a sphere $D := \{x \in \mathbb{R}^n : \|x\| < R\}$ where we are interested for the IRC of the potential surface, we can perturb the potential function by a polynomial having very small values and derivatives on D and tending rapidly to infinity outside of D. Or alternatively, instead of modifying the potential function, we may project the points of the curves c^t lying outside of D onto the boundary of D. Alternative techniques for the same purpose are also described in ref. [37].

The strategy for determining IRC suggested by the Theorem is seemingly very simple: since in most practical cases the catchment regions of the given vector field admit piecewise smooth boundaries, starting from a polygon (or some piecewise smooth curve c^0, one only has to calculate the curve c^t for a sufficiently large value of t in order to obtain a suitable uniform approximation of some IRC. Notice that the IRC obtained may pass through several stationary points of the field V. Thus this method is suitable in constructing IRC between reactants and products even if the chemical processes involve several critical configurations (corresponding to SPs on the PHS). A series of numerical procedures relies heavily upon the assumption of the existence of only one critical configuration in course of the reaction. While this assumption is very plausible in case of a small molecule, it may be seldom satisfied for larger systems. One further advantage of our approach is that it does not require any particular starting curve, especially no previous information is needed concerning the location of SPs of the PHS [36].

The main technical difficulty of determining c^t follows from the fact that (under the hypothesis of the Theorem) for any point $y \in \mathbb{R}^n$ the path $t \mapsto \exp(tV)(y)$ converges to some stationary point y^* of the field V. Thus if we represent the initial curve $\{c^0(s) : 0 \leqslant s \leqslant 1\}$ by a finite subset:

$$\{y_0, \ldots, y_m\} = \{c^0(s_0), \ldots, c^0(s_m)\}$$

of its points then, for sufficiently large values of the parameter t, the set:

$$\{c^t(s_1), \ldots, c^t(s_m)\} = \{\exp(tV)(y_i) : i = 1, \ldots, m\}$$

accumulates around some stationary points of the field V and it does not contain any point from the major part (with respect to arc length) of c^t. One way of avoiding this difficulty is the following.

Let us say that a finite sequence $(y_i : i = 1, \ldots, L)$ of points is ε-homogeneous if the distance in each consecutive couple y_{i-1}, y_i is less than ε. Given any $\varepsilon > 0$ and an ε-homogeneous sequence:

$$(y_i^0 : i = 1, \ldots, L_0)$$

representing the initial curve c^0, let us choose a time unit $T > 0$ such small that the points y and $\exp(TV)(y)$ should lie not too far on the domain D of our primary interest. Then we construct recursively the ε-homogeneous representations:

$$Y^{kT} := (y_i^{kT} : i = 1, \ldots, L_k)$$

of the curves c^{kT} for $k = 1, 2, \ldots$ as follows. Given the system Y^{kT}, first we calculate the points:

$$z_i^{(k+1)T} := \exp(TV)(y_i^{kT})$$

of the system:

$$Z^{(k+1)T} := (z_i^{(k+1)T} := i = 1, \dots, L_k).$$

This step is in general the most time-consuming part of the procedure but it is completely parallelizable. Then we define the representation $Y^{(k+1)T}$ of the next curve as a suitable ε-homogenized approximation of $Z^{(k+1)T}$. Such a system can be constructed e.g. by a spline interpolation of the system $Z^{(k+1)T}$ and then deleting a maximal subset of points such that the remaining system should still be ε-homogeneous. In this manner the cardinality L_{k+1} of the systems Y^{kT} can be controlled from above by a constant multiple of length $(c^{kT})/\varepsilon$. For reasons of stability, it is advisable to keep the most possible members of $Z^{(k+1)T}$ in $Y^{(k+1)T}$.

Next we describe in details the perhaps simplest parallelizable computational method for determining IRC based upon the Theorem.

Since there is no effective global stop-condition for the algorithm described above it is convenient to run a program several times which determines an ε-homogeneous representation Y^{t+T} of c^{t+T} from the inputs Y^t, ε, T.

We compute numerically the points $z_i^{t+T} = \exp(TV)(y_i^t)$ by m affine step approximation of the exponential of V where m is also an input parameter. That is:

$$z_i^{t+T} = F^m(y_i^t)$$

with

$$F(y) := y + \frac{T}{m} V(y) \quad (y \in \mathbb{R}^n).$$

Moreover, if we want to restrict the resulting curves to the sphere $D := \{y \in \mathbb{R}^n : \|y\| \leqslant R\}$ where the radius R is again an input parameter, we may use the transformation $\tilde{F} := P(F)$ instead of F with $P :=$ [projection onto D].

To construct the system Y^{t+T} from Z^{t+T} we apply the following homogenization procedure. First we determine the distances $d_i := \|z_{i+1}^{t+T} - z_i^{t+T}\|$ for $i = 1, \dots, L_t - 1$. Then we choose consecutively the indices:

$$1 = i_1 < i_2 < \cdots < i_m = L_t$$

defined unambiguously by the requirement:

$$\sum_{i_k \leqslant i < i_{k+1}} d_i \leqslant \varepsilon < \sum_{i_k \leqslant i \leqslant i_{k+1}} d_i \quad (k = 1, \dots, m-1).$$

That is, if $i_1, \dots, i_k$ are already constructed and $i_k < L_t$ then $i_{k+1} := \min\{j > i_k : \sum_{i_k \leqslant i \leqslant j} d_i > \varepsilon\}$ whenever $\sum_{i \geqslant i_k} d_i > \varepsilon$ else we finish the construction by setting $m := k + 1$ and $i_m := L_t$. We obtain the sequence Y^{t+T} by deleting all points with indices not belonging to the set $\{i_1, \dots, i_m\}$ and by inserting entier(d_{i_k}/ε) affinely interpolating points between $z_{i_k}^{t+T}$ and $z_{i_{k+1}}^{t+T}$ whenever $i_{k+1} = i_k + 1$. Of course, the latter two steps can not be parallelized but they are carried out very quickly.

3 Application

We illustrate the high stability of the above algorithm for determining IRC by the detailed description of how the curve representations Y^t develop from a quite hopeless starting position.

Let us apply the algorithm to calculate IRC for the hypothetic potential function

$$f(x_1, x_2) := \prod_{j,k=0,1} \|(x_1, x_2) + ((-1)^j, (-1)^k)\|^2 - (x_2^2 - 1)^3 + (x_1^2 - 1)^3$$

used also in [27]. Thus we have to compute IRC for the vector field:

$$V := -\operatorname{grad} f.$$

The singularities of V can be determined elementarily by solving polynomial equations of third degree. They are the minima $(\pm 1, \pm 1)$ and SPs $(\pm 0.37213, 0)$ of f. The family of all IRC of V form the "H"-shaped figure showing bifurcations in Fig. 1 corresponding to valley bottoms and hill ridges between the stationary points of the graph of f in Fig. 2.

Let c^0 be the polygon in Fig. 3 with consecutive vertices:

$$\begin{aligned} Y^0 := (&(-1.4, 1.2), (-1.5, 0.8), (-1.4, 0.7), (-1.3, 0.8), (-1.4, 1.2),\\ &(-1.0, 0.1), (-0.8, -0.1), (-1.0, -0.3), (-1.2, -0.1), (-1.0, 0.1),\\ &(0.0, 0.2), (-0.1, 0.0), (0.0, -0.1), (0.1, 0.0), (0.0, 0.2), (0.7, -0.7),\\ &(0.8, -0.9), (0.7, -1.0), (0.6, -0.9), (0.7, -0.7)).\end{aligned}$$

Notice that c^0 does not pass through any singular point of V. The four deltoid shaped ornaments A, B, C, D serve not only to impose more difficulties but to demonstrate typical features of the algorithm.

Let us apply the algorithm with:

$$\varepsilon := 0.1, \quad T := 0.005, \quad m := 10, \quad R := 1.5$$

to the starting curve representation Y^0 of c^0. It does not make any trouble if Y^0 is not ε-homogeneous (on the figures dots display the computed points in every step). The first homogenization makes $Y^{0.005}$ already ε-homogeneous and cuts

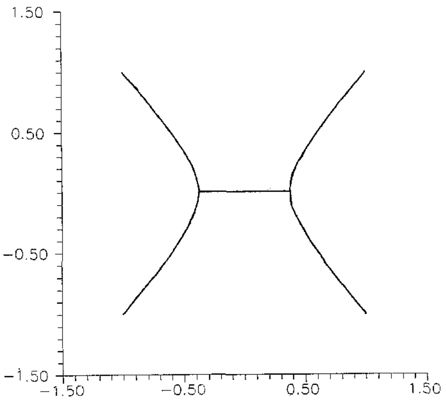

Fig. 1. IRC pieces of $V = -\operatorname{grad} f$

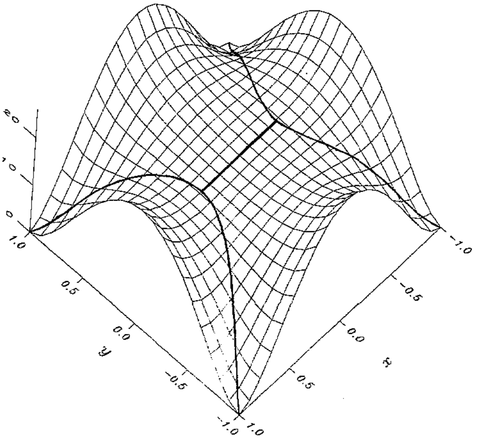

Fig. 2. IRC curves on the potential surface f

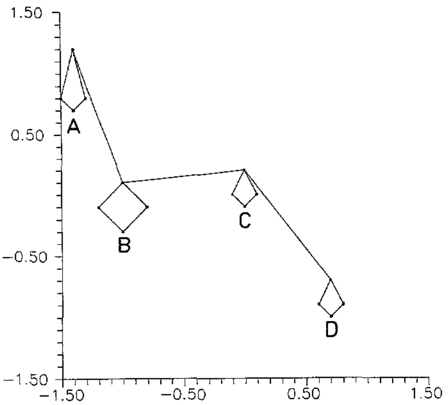

Fig. 3 Y^0

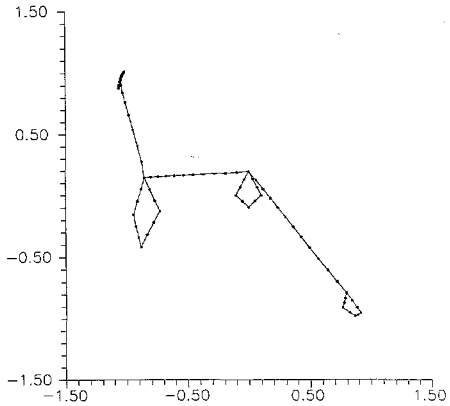

Fig. 4 $Y^{0.005}$

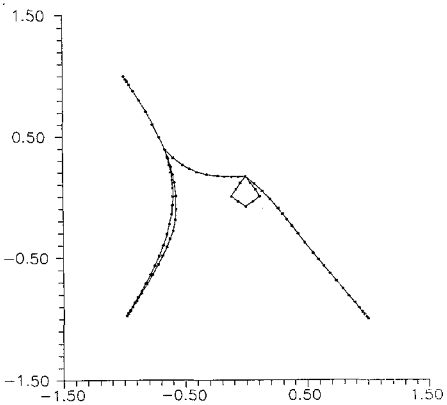

Fig. 5 $Y^{0.03}$

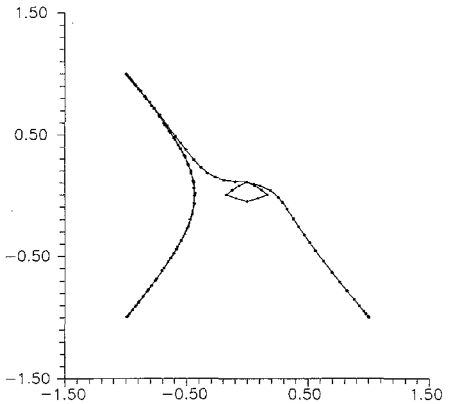

Fig. 6 $Y^{0.01}$

ornament *A* to a small arc (see Fig. 4). Figures lying inside a catchment region near to the attracting point shrink quickly. This can be seen on $Y^{0.03}$ (Fig. 5) where ornament *D* and the rest of ornament *A* vanish.

Where the values of *V* are relatively large (e.g. not far from the left IRC pieces) figures stretch quickly onto the neighbouring IRC segments. This happens to ornament *B* in $Y^{0.1}$ in Fig. 6. It may elapse a long time until figures lying in regions where the values of *V* are small approach the IRC. This is to see on the evolution of ornament *C* in $Y^{0.3}$ and $Y^{0.45}$ (Figs. 7, 8).

Figures lying very near to hyperbolic singularities and intersecting at least two catchment regions develop slowly along IRC segments issued from the singularity. This is shown by the next two selected phases $Y^{0.6}$, $Y^{0.75}$in Figs. 9 and 10 where the top right branch of the "H"-shaped IRC grows from a piece of the segment after ornament *C*.

For similar reason, later the four edges of ornament *C* grow toward the four minima along the left and right IRC segments (very near to them) as we can see on $Y^{0.9}$ and $Y^{1.0}$ (Figs. 11 and 12). When proceeding further, the phase pictures

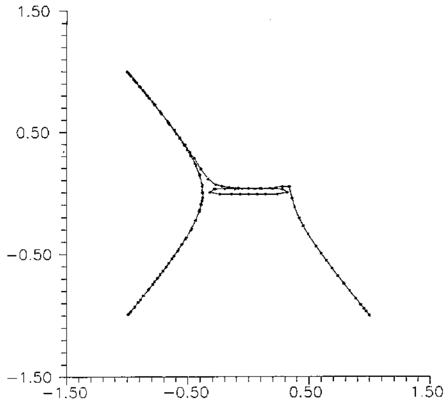

Fig. 7 $Y^{0.3}$

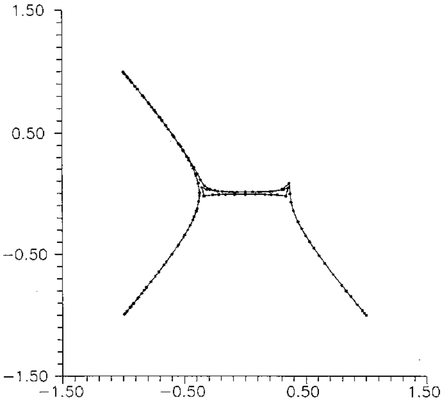

Fig. 8 $Y^{0.45}$

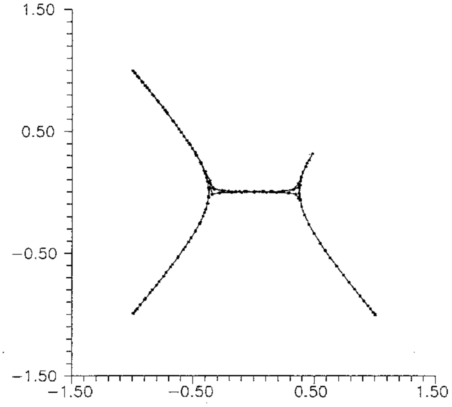

Fig. 9 $Y^{0.6}$

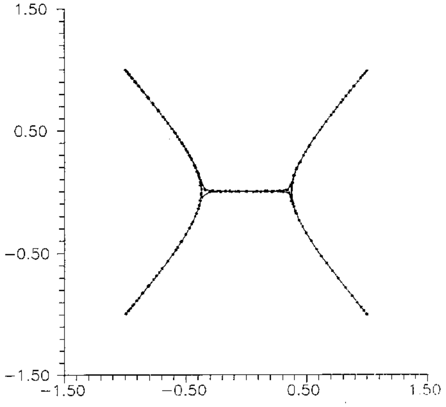

Fig. 10 $Y^{0.75}$

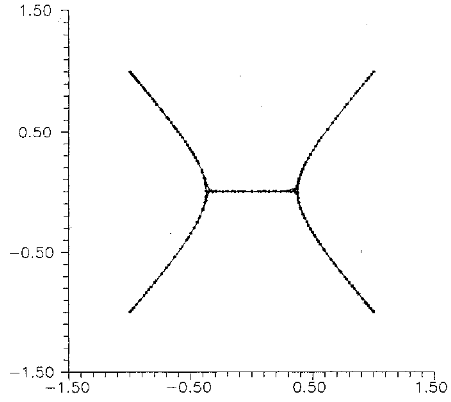

Fig. 11 $Y^{0.9}$

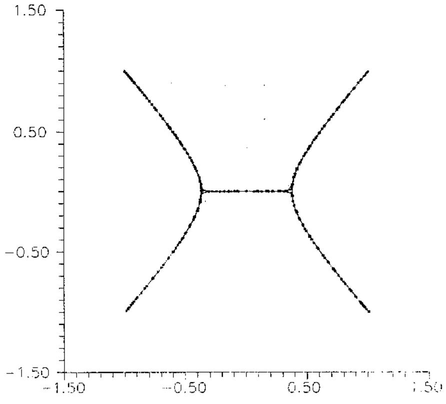

Fig. 12 $Y^{1.0}$

do not change essentially any more. However, a higher accuracy of approximation can only be achieved by decreasing ε because the homogenization may always create points lying apart from the IRC at bendings.

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