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MATHEMATICAL FOUNDATION OF A GLOBAL STRATEGY FOR SEARCHING REACTION PATHS

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Abstract

For the determination of reaction paths and critical points on the potential energy hypersurface of chemical reactions, a rigorous mathematical background for the theory of a global searching procedure based on the catchment regions of the gradient field is given.

1. Introduction

In order to obtain a faithful approximative picture of the course of a chemical reaction, instead of struggling with a Schrödinger many-body problem it is sufficient to determine the curve of the so-called intrinsic reaction coordinate (IRC) [1]. The IRC is a reaction path (RP) which connects two minima and is tangent to the gradient field of the energy function of the manifold of all mass weighted space configurations. For simple reactions, the IRC is composed of two steepest descent paths leading from a saddle point of index one (transition structure/state) to two minima belonging to stable configurations of reactants and products. There exist several algorithms (see, for example, refs. [2–19]) for calculating RPs in various special cases; however, their global convergence properties have not yet been investigated thoroughly. The most popular procedures try to find meta-IRCs [20–22] starting from the col and leading towards valleys or, inversely, they try to hit the col by meta-IRCs from the minima. Such algorithms are very likely unstable, and parallelizable only with low efficiency. We propose here another approach to the problem. Our basic idea lies in the concept of the exponential of analytical vector fields. Having a curve c and a potential function f on $\mathbb{R}^n$, a sufficient condition is that $\exp(t \operatorname{grad} f)c$ converges uniformly to an IRC if $t \to \infty$. Our main theorem contains interesting information on the attractor behaviour [23,24] of IRCs and the convergence properties of the exponentials of gradient fields and opens many possibilities of generalization.

In our first paper [25], based on Mezey's theory [26–30] on catchment regions, the general theory of a procedure for searching IRCs was described and illustrated by some artificial model functions. Our main idea has been the utilization of the observation that starting from an almost arbitrary path connecting two minima, the (nonlinear) shifts of this curve along the negative gradient of the potential function constitute a path homotopy which converges uniformly to some IRC under not too restrictive conditions. It is an interesting problem to elucidate the relationship of our method to variational principles concerning the concept of IRC [31,32]. In the second paper of this series [33], the algorithm of the numerical realization of the procedure and a detailed demonstration, on the model function of ref. [25], of the most important features of the algorithm were presented. In the third paper [34], the flow-charts and FORTRAN codes of a highly parallelizable simple computer program showing the main characteristics of the procedure were published.

The aim of the present paper is to give a firm and rigorous mathematical basis to the general theory of a well-parallelizable curve variational method [25] for searching RPs and locating saddle points (SP) or other stationary points on potential energy hypersurfaces (PHS) of chemical reactions. This paper contains indispensible information for those who are interested in the numerical application of the idealized algorithm for larger chemical systems on the convergence properties of the method. We present here a mathematical discussion of the gradient field of the potential function, representing the simplest situation of chemical interest. Using the mathematical formulation described in this paper and the techniques presented in refs. [25,33,34], the method and procedure will be illustrated using chemical examples in a future paper [35].

2. Main results

Throughout this section, let $f: \mathbb{R}^n \to \mathbb{R}$ be an analytic function such that

(a) the set $S := \{x : \mathrm{D}f(x) = 0\}$ of singularities is finite;

(b) every singularity of f is of Siegel type (i.e. if $y \in S$, then $\det \mathrm{D}^2 f(y) \neq 0$ and the vector field $-\mathrm{D}f(x)\partial/\partial x$ is analytically linearizable in some neighbourhood of the point y);

(c) $f(x), \|\mathrm{D}f(x)\| \to \infty$ for $\|x\| \to \infty$.

Let S_k ($k = 0, 1, \ldots, n$) denote the set of those singularities $x \in S$ of f where the second derivative $\mathrm{D}^2 f(x)$ admits k negative (and hence $n-k$ positive) eigenvalues. Note that S_0 is the set of local minima of f and necessarily $S_0 = \emptyset$.

For fixed $z \in \mathbb{R}^n$, we shall denote by $\Psi(z, .)$ the maximal solution of the initial value problem

$$\frac{\mathrm{d}}{\mathrm{d}t} y(t) = -\mathrm{D}f(\Psi(z,t)) \qquad y(0) = z. \tag{1}$$

Since

$$\frac{\mathrm{d}}{\mathrm{d}t} f(\Psi(z,t) = -\|\mathrm{D}f(y(t))\|^2 \leq 0 \tag{2}$$

for any $t \in \operatorname{dom} \Psi(z, .)$ and the set $\{x : f(x) \leq f(x)\}$ is compact, the function $t \mapsto \Psi(z,t)$ is strictly decreasing or constant and it is well-defined for every $t \geq 0$.

Given a singular point $y \in S$, according to assumption (b), by writing

$$\lambda_1^y \leq \lambda_2^y \leq \ldots \leq \lambda_n^y \tag{3}$$

for the eigenvalues of $\mathrm{D}^2 f(y)$, we can fix $\varepsilon_y > 0$ and a neighbourhood $\tilde{U}_y$ of the point y with an analytic diffeomorphism onto some neighbourhood of the closure of $\tilde{U}_y$ in such a way that

$$\tilde{T}_y(\tilde{U}_y) = \{x : \|x\| < \varepsilon_y\} \tag{4}$$

and for any $z \in U_y$

$$\tilde{T}_y(\Psi(z,t)) = \Lambda_y^t(\tilde{T}_y(z)) \qquad (\Psi(z,[0,t]) \subset \tilde{U}_y), \tag{5}$$

where

$$\Lambda_y^t : \upsilon \mapsto (\exp(-\lambda_k^y t)\upsilon_k : k = 1, \ldots, n). \tag{6}$$

We assume, without loss of generality, that the domains U_y are pairwise disjoint and that they are so small that the steepest descent paths of f starting from $\tilde{U}$ do not return to $\tilde{U}$. (This is possible because f decreases strictly along its steepest descent paths outside S.)

Finally, for $y \in S$ we shall denote by Δ_y the catchment region of the singular point y. Thus,

$$\Delta_y := \{z \in \mathbb{R}^n : \Psi(z,t) \to y \ \ (t \to \infty)\} \quad (y \in S). \tag{7}$$

2.1. PROPOSITION

We have $\mathbb{R}^n = \cup_{y \in S} \Delta_y$ and, for any $y \in S_k$, the region Δ_y is an $(n-k)$-dimensional analytic submanifold of $\mathbb{R}^n$. Moreover, each coordination $\tilde{T}_y$ admits a bianalytic extension T_y to the domain U_y consisting of all maximal steepest descent paths of f touching $\tilde{U}_y$ and

$$\Delta_y = T_y^{-1}\{x \in U_y : x_1 = \ldots = x_k = 0\} \quad (y \in S_k). \tag{8}$$

Proof

Consider any $z \in \mathbb{R}^n$ and define $\varphi(t) := f(\Psi(z, t))$ $(t \geq 0)$. Regarding (2), the function φ is decreasing and analytic. Since the level set $\{x : f(x) \leq f(y)\}$ is compact by assumption (b), the functions φ, φ', φ'' are bounded. Since $\varphi(t) \downarrow \inf \varphi$ $(t \to \infty)$, the boundedness of φ'' implies that necessarily $\varphi' \to 0$ $(t \to \infty)$. Hence, by (2), $\| Df(\Psi(z, t)) \| \to 0$ $(t \to \infty)$. Since $\nu : u \mapsto \| D f(u) \|$ is a continuous function and $S = \{x : \nu(x) = 0\}$ is a discrete set, it follows that $\Psi(z, t) \to y$ $(t \to \infty)$ for some $y \in S$. By the arbitrariness of z, this proves that $\mathbb{R}^n = \cup_{y \in S} \Delta_y$.

Assume $y \in S_k$. Define

$$W_{y,\tau} := \{z : \Psi(z,t) \in \tilde{U}_y\} \qquad (\tau \in \mathbb{R}) . \tag{9}$$

By the analyticity of Ψ, the figures $W_{y,\tau}$ are open and connected. The mapping

$$T_{y,\tau}(z) := \Lambda_y^{-\tau} \tilde{T}_y(\Psi(z,\tau)) \qquad (z \in W_{y,\tau}) \tag{10}$$

satisfies (5) with $T_{y,\tau}$ and $W_{y,\tau}$ in place of $\tilde{T}$ and $\tilde{U}$, respectively. We show that $T_{y,\tau}$ and $T_{y,\vartheta}$ coincide on $W_{y,\tau} \cap W_{y,\vartheta}$. Let $\tau < \vartheta$. Since, by assumption, steepest descent paths of f issued from $\tilde{U}_y$ do not return in $\tilde{U}_y$, we must have

$$\Psi(z,t) \in \tilde{U}_y \qquad (\tau \leq t \leq \vartheta,\ z \in W_{y,\tau} \cap W_{y,\vartheta}) . \tag{11}$$

Thus, if $W_{y,\tau} \cap W_{y,\vartheta}$, then by (8) and (5) we have $\Lambda_y^{\vartheta-\tau} \tilde{T}_y \Psi(z,\tau) = \tilde{T}_y \Psi(z, \tau + (\vartheta - \tau))$. Hence,

$$\begin{aligned} T_{y,\vartheta}(z) &= \Lambda_y^{-\vartheta} \tilde{T}_y(\Psi(z,\vartheta)) \\ &= \Lambda_y^{-\vartheta} \Lambda_y^{\vartheta-\tau} \tilde{T}_y(\Psi(z,\tau)) = T_{y,\tau}(z) \quad (z \in W_{y,\tau} \cap W_{y,\vartheta}) . \end{aligned} \tag{12}$$

Therefore, $T_y := \cup_{\tau \in \mathbb{R}} T_{y,\tau}$ is well-defined.

We complete the proof by observing that $\Delta_y \subset U_y$ and

$$T_y(\Delta_y) = \left\{ \upsilon \in \bigcup_{\tau \in \mathbb{R}} W_{y,\tau} : \lim_{t \to \infty} \Lambda_y^t \upsilon = 0 \right\} \subset \{\upsilon : \upsilon_1, \ldots, \upsilon_k = 0\} . \tag{13}$$

Our fundamental result is the following theorem (to be proved in section 3 in a sharper form):

2.2. THEOREM

Let $f : \mathbb{R}^n \to \mathbb{R}$ be an analytic function satisfying (a), (b), (c). Then the catchment regions of the points of S cover the whole $\mathbb{R}^n$. Assume $\{c(p) : p \in [0, 1]\}$ is a piecewise analytic curve joining two local minima of f which changes catchment regions finitely many times. Then, by writing $\bar{c}^t$ for the curve $\exp(-t Df(x) \partial/\partial x) c$ with parameterization proportional to the arc length on $[0, 1]$, the curves $\{\bar{c}^t(s) : s \in [0, 1]\}$ converge uniformly to some IRC joining $c(0)$ and $c(1)$ for $t \to \infty$.

2.3. REMARK

A careful examination of the boundaries of catchment regions (see proposition 2.1) shows that the hypothesis of the theorem is very probably satisfied for an arbitrary admissible initial curve. For example, if we restrict our attention to polygons with a fixed number of vertices joining the two minima, then such a polygon changes catchment regions finitely many times with respect to a homogeneous distribution with probability 1.

Concerning the local linearizability of vector fields around stationary points, we refer to the famous Hartman–Grobman theorem [36,37] and its analytic extension by Siegel [38].

3. The proof and a generalization of the fundamental theorem

3.1. DEFINITION

To prove theorem 2.2, we need the following concept. We call a function $\varphi : [0, \rho) \to \mathbb{R}$ *root-analytic* if $\varphi \equiv 0$ or if φ is analytic on $(0, \rho)$ and we can write

$$\varphi(u) = \sum_{\omega \in \Omega} a_\omega u^\omega \quad (0 \leq u \leq r), \qquad \sum_{\omega \in \Omega} |a_\omega| r^\omega < \infty \tag{14}$$

for some $r > 0$ and a strictly increasing sequence $0 \leq \Omega \uparrow \infty$ with suitable non-zero reals a_ω $(\omega \in \Omega)$.

It is not difficult to see that root-analytic functions are continuous also at 0. Hence,

$$\min \Omega = \max \left\{ \mu \geq 0 : \lim_{u \downarrow 0} |\varphi(u)| u^{-\mu} < \infty \right\} \tag{15}$$

holds in (14). The uniqueness of decomposition (14) follows immediately. We call the value $\min \Omega$ the *order* of φ.

Given a root-analytic function φ with decomposition (14), it follows from the discreteness of Ω that

$$\varphi'(u) = \sum_{0 < \omega \in \Omega} \omega a_\omega u^{\omega - 1} \quad (0 < u < r), \tag{16}$$

where the series is absolutely convergent. Thus, if μ is the order of the function $\varphi - \varphi(0)$, then $u^{1-\mu} d\varphi(u)/du$ is also root-analytic.

Note that if F is an anlytic function of n variables and $\varphi_1, \ldots, \varphi_n$ are root-analytic, then $F(\varphi_1, \ldots, \varphi_n)$ is root-analytic when defined in some right neighbourhood of 0.

3.2. NOTATIONS FOR 3.3–3.8

Let $\delta \in [-\infty, 0)$ and $\lambda_1, \ldots, \lambda_n \neq 0$ be real and $\upsilon : [0, \rho] \to \mathbb{R}^n$ a root-analytic curve (i.e. υ extends root-analytically to some right neighbourhood of $[0, \rho]$).

For any $t \in \mathbb{R}$, we introduce the transformation

$$\Lambda^t : (x_1, \ldots, x_n) \mapsto (e^{-\lambda_k t} x_k : k = 1, \ldots, n). \tag{17}$$

Concerning the component functions of the curve υ, we assume

$$\upsilon_k(0) = 0 \quad \text{whenever} \quad \lambda_k < 0. \tag{18}$$

We write μ_k for the order of υ_k and decompose

$$\upsilon_k(u) = u^{\mu_k} w_k(u) \qquad (k = 1, \ldots, n) \tag{19}$$

using suitable root-analytic functions w_k of order 0 (in the trivial case $\upsilon_k \equiv 0$, we set formally $\mu_k = \infty$, $w_k \equiv 1$). Define

$$\upsilon^t : u \mapsto \Lambda^{t-(1/\delta)\log u} \upsilon(u), \quad V^t(p) := \upsilon^t(p e^{\delta t}). \tag{20}$$

Next, we define the value $\overline{\delta} < 0$ by

$$\frac{1}{\overline{\delta}} - \frac{1}{\delta} = \max_{\lambda_k < 0,\, \upsilon_k \not\equiv 0} \frac{\mu_k}{\lambda_k} \tag{21}$$

(if $\lambda_k > 0$ for all k or $\upsilon_k \equiv 0$ whenever $\lambda_k < 0$, then set $\overline{\delta} := \delta$). Finally, we introduce the conjugate functions and orders

$$\overline{V}^t(p) := \upsilon^t(p e^{\overline{\delta} t}), \quad \overline{\mu}_k := -\lambda_k / \overline{\delta} + \mu_k + \lambda_k / \delta. \tag{22}$$

Immediate calculations yield

$$V_k^t(p) = e^{\mu_k \delta t} p^{\mu_k + \lambda_k/\delta} w_k(p e^{\delta t}), \quad \overline{V}_k^t(p) = e^{\overline{\mu}_k \overline{\delta} t} p^{\mu_k + \lambda_k/\delta} w_k(p e^{\overline{\delta} t}). \tag{23}$$

Hence:

3.3. LEMMA

We have $\upsilon(u) = V^{(1/\delta)\log u}(1)$ and $\mu_k > 0$ if $\lambda_k < 0$. The components $u \mapsto \overline{V}_k^{(1/\overline{\delta})\log u}(u)(1)$ are root-analytic functions of order $\overline{\mu}_k \geq 0$ for every index k. We have $\overline{\mu}_k = 0$ if and only if $\lambda_k < 0$ and $\mu_k / \lambda_k = \overline{\delta}^{-1} - \delta^{-1}$.

Next, we establish the pointwise convergence of V^t, $\overline{V}^t$ for $t \to \infty$.

3.4. LEMMA

The curves $V := \lim_{t\to\infty} V^t$, $\overline{V} := \lim_{t\to\infty} \overline{V}^t$ are well-defined on $(0, \infty)$ and they are Λ^t-invariant for every $t \in \mathbb{R}$. For any fixed $p > 0$, we have $\lim_{t\to\infty} \Lambda^t V(p) = \lim_{t\to\infty} \Lambda^{-t} \overline{V}(p) = 0$.

Proof

We know $\mu_k \delta, \overline{\mu}_k \overline{\delta} \leq 0$ for any k. Hence, by (23)

$$V_k^t(p) \to 1_{\{0\}}(\mu_k) p^{\lambda_k/\delta} w_k(0), \quad \overline{V}_k^t(p) \to 1_{\{0\}}(\overline{\mu}_k) p^{\lambda_k/\overline{\delta}} w_k(0) \tag{24}$$

as $t \to \infty$.* Thus, $V_k(p) \neq 0$ implies $\mu_k = 0$ and hence $\lambda < 0$ because if $\lambda > 0$, then $\upsilon_k(0) = 0$ and so $\mu_k > 0$. Therefore, $\Lambda^t V(p) \to 0$ $(t \to \infty)$. Similarly, $\overline{V}_k(p) \neq 0$ implies $\overline{\mu}_k = 0$, which means $\lambda_k > 0$ by lemma 3.3. Hence, $\Lambda^{-t} \overline{V}(p) \to 0$ $(t \to \infty)$. Finally observe that, disregarding the trivial case $\delta = -\infty$ (where $V \equiv 0$), for any k,

$$[\Lambda^t \upsilon(p)]_k = 1_{\{0\}}(\mu_k) e^{-\lambda_k t} p^{\lambda_k/\delta} w_k(0) = V_k(p e^{-\delta t}). \tag{25}$$

The argument can be repeated with $\overline{V}$ in place of V. Thus,

$$\Lambda^t V(p) = V(p e^{-\delta t}), \ \Lambda^t \overline{V}(p) = \overline{V}(p e^{-\overline{\delta} t}) \qquad (t \in \mathbb{R}). \tag{26}$$

For purposes of proving theorem 2.2, we investigate the convergence of the derivatives of V^t and $\overline{V}^t$, respectively. To do this, it is convenient to introduce, for any $N = 0, 1, \ldots,$ the decompositions

$$\frac{d^N}{du^N} [u^{\mu_k + \lambda_k/\delta} w_k(u)] = u^{\mu_k + \lambda_k/\delta - N} w_{k,N}(u). \tag{27}$$

Since any w_k is a root-analytic function of order 0, it follows that the functions $w_{k,N}$ are also root-analytic. Note that the order of $w_{k,N}$ is >0 if $\mu_k = 0$. From (23) we obtain

$$\begin{aligned} \frac{d^N}{dp^N} V_k^t(p) &= e^{(\mu_k + N)\delta t} p^{\mu_k + \lambda_k/\delta - N} w_{k,N}(p e^{\delta t}), \\ \frac{d^N}{dp^N} \overline{V}_k^t(p) &= e^{(\overline{\mu}_k + N)\overline{\delta} t} p^{\mu_k + \lambda_k/\delta - N} w_{k,N}(p e^{\overline{\delta} t}). \end{aligned} \tag{28}$$

*For a set S, 1_S denotes the Kronecker function $1_S(x) := [1, (x \in S), 0 (x \notin S)]$.

3.5. LEMMA

For any $\nu \in (0, \bar{\delta} - \delta)$ and N, k there exists $\omega > 0$ with

$$e^{\omega t} \sup_{p \in [1, e^{\nu t}]} p^N \left| \frac{d^N}{dp^N} V_k^t(p) - \frac{d^N}{dp^N} V_k(p) \right| \to 0 \quad (t \to \infty). \tag{29}$$

Proof

Since $\mu_k \geq 0$ and $\delta < 0$, for fixed p,

$$\frac{d^N}{dp^N} V_k^t(p) \to 1_{\{0\}}(\mu_k) p^{\mu_k + \lambda_k/\delta - N} w_{k,N}(0) \quad (t \to \infty). \tag{30}$$

Case 1. $\mu_k = 0$. Then we have, by assumption, $\lambda_k > 0$ and hence $\lambda_k/\delta < 0$. Thus, we can estimate

$$p^N \left| \frac{d^N}{dp^N} V_k^t(p) - p^{\lambda_k/\delta - N} w_{k,N}(0) \right| \leq p^{\lambda_k/\delta} |w_{k,N}(pe^{\delta t}) - w_{k,N}(0)|$$

$$\leq \sup_{u \leq e^{(\nu+\delta)t}} |w_{k,N}(u) - w_{k,N}(0)| \quad (p \leq e^{\nu t}). \tag{31}$$

Case 2. $\mu_k > 0, \lambda_k > 0$. Then we have $\mu_k\delta + \nu(\mu_k + \lambda_k/\delta) < \mu_k(\delta + \nu) < \mu_k\bar{\delta} < 0$. Hence,

$$p^N \left| \frac{d^N}{dp^N} V_k^t(p) \right| \leq e^{\mu_k t} \max |w_{k,N}| \quad (p \geq 1). \tag{32}$$

Case 3. $\mu_k > 0$, $\lambda_k < 0$. Again from the definition of $\bar{\delta}$, we have $\mu_k\delta + \nu(\mu_k + \lambda_k/\delta) < \mu_k\delta + (\bar{\delta} - \delta)(\mu_k + \lambda_k/\delta) = (\bar{\delta}/\lambda_k)(\mu_k\lambda_k^{-1} + \delta^{-1} - \bar{\delta}^{-1}) \leq 0$. Hence,

$$p^N \left| \frac{d^N}{dp^N} V_k^t(p) \right| \leq e^{\mu_k \delta t} e^{\nu(\mu_k + \lambda_k/\delta)t} \max |w_{k,N}| \quad (p \leq e^{\nu t}). \tag{33}$$

Thus, the three estimates and the root-analyticity of $w_{k,N}$ establish that

$$\sup_{p \in [1, e^{\nu t}]} p^N \left| \frac{d^N}{dp^N} V_k^t(p) - 1_{\{0\}}(\mu_k) p^{\mu_k + \lambda_k/\delta - N} w_{k,N}(0) \right| = o(e^{-\omega t}) \tag{34}$$

for some $\omega > 0$ as $t \to \infty$. In particular, the derivatives $d^N V_k^t(p)/dp^N$ are locally uniformly convergent, whence the statement is immediate.

3.6. LEMMA

Given k, N there exists $\varepsilon > 0$ such that for any $\bar{\nu} \in (0, \varepsilon)$

$$\sup_{p \in [e^{-\bar{\nu} t}, 1]} \left| \frac{d^N}{dp^N} \bar{V}_k^t(p) - \frac{d^N}{dp^N} \bar{V}_k(p) \right| \to 0 \quad (t \to \infty). \tag{35}$$

Proof

Case 1. $\bar{\mu}_k = 0$. According to lemma 3.3, in this case we have $\lambda_k < 0$ and $\mu_k + \lambda_k/\delta = \lambda_k/\bar{\delta} (> 0)$. Therefore,

$$\left| \frac{d^N}{dp^N} \bar{V}_k^t(p) - p^{\lambda_k/\bar{\delta} - N} w_{k,N}(0) \right| = p^{\lambda_k/\bar{\delta} - N} |w_{k,N}(pe^{\bar{\delta} t}) - w_{k,N}(0)|$$

$$\leq e^{\bar{\nu} |\lambda_k/\bar{\delta} - N| t} \max_{u \leq e^{\bar{\delta} t}} |w_{k,N}(u) - w_{k,N}(0)| \quad (e^{-\bar{\nu} t} \leq p \leq 1). \tag{36}$$

Since the function $w_{k,N}$ is root-analytic,

$$|w_{k,N}(u) - w_{k,N}(0)| \leq u^{\omega} \quad (0 \leq u \leq \rho) \tag{37}$$

for some $\omega > 0$. Thus, if $e^{-\bar{\nu} t} \leq p \leq 1$, we can estimate

$$\left| \frac{d^N}{dp^N} \bar{V}_k^t(p) - p^{\lambda_k/\bar{\delta} - N} w_{k,N}(0) \right| \leq \exp[(\bar{\nu} |\lambda_k/\delta - N| + \bar{\delta}\omega)t]. \tag{38}$$

Here, the right-hand side $\to 0$ for $t \to \infty$ if $\bar{\nu} < \omega|\bar{\delta}|/|\lambda_k/\delta - N|$.

Case 2. $\bar{\mu} > 0$. If $e^{-\bar{\nu} t} \leq p \leq 1$, then from (28) we infer directly

$$\left| \frac{d^N}{dp^N} \bar{V}_k^t(p) \right| \leq \exp[(\bar{\mu}_k \bar{\delta} + \bar{\nu} |\mu_k + \lambda_k/\delta - N|)t] \max |w_{k,N}|. \tag{39}$$

Here, the right-hand side $\to 0$ for $t \to \infty$ if $\bar{\nu} < \bar{\mu}_k |\bar{\delta}|/|\mu_k + \lambda_k/\delta - N|$.

3.7. LEMMA

If $\upsilon_k \equiv 0$ whenever $\lambda_k < 0$, then

$$\sup_{e^{\delta t} \leq u \leq p} \|\upsilon^t(u)\| \to 0, \quad \text{length}\{\upsilon^t(u) : e^{\delta t} \leq u \leq \rho\} \to 0 \quad (t \to \infty). \tag{40}$$

Proof

It follows from (27) that

$$\frac{d^N}{du^N} v_k^t(u) = \frac{\partial^N}{\partial u^N} V_k^t(ue^{-\delta t}) = e^{-\lambda_k t} u^{\mu_k + \lambda_k/\delta - N} w_{k,N}(u). \tag{41}$$

Since $v_k \not\equiv 0$ implies $\lambda_k > 0$, we have $d^N v_k^t(u)/du^N \to 0$ for any fixed $u \in (0, \rho)$ if $t \to \infty$. Therefore, it suffices to show that

$$\int_{e^{\delta t}}^{\rho} \left| \frac{d}{du} v_k^t(u) \right| du \to 0 \qquad (\lambda_k > 0,\ t \to \infty). \tag{42}$$

Fix k with $\lambda_k > 0$. Since the root-analytic function $w_{k,1}$ has non-zero order if $\mu_k = 0$,

$$u^{\mu_k} |w_{k,1}(u)| \le \gamma_k u^{\mu_k + \omega_k} \qquad (0 \le u \le \rho) \tag{43}$$

for some γ_k, $\omega_k \ge 0$ such that $\mu_k + \omega_k > 0$. However,

$$e^{-\lambda_k t} \int_{e^{\delta t}}^{\rho} u^{\mu_k + \lambda_k/\delta - 1 + \omega_k}\, du = a_k e^{(\mu_k + \omega_k)\delta t} + b_k e^{-\lambda_k t} \tag{44}$$

for suitable constants a_k, b_k. Since $\mu_k \ge 0$ and $\delta < 0$, hence (42) is immediate.

3.8. LEMMA

In the case $\delta = -\infty$ for every $\overline{\nu} > 0$, we have

$$\mathrm{length}\{ v^t(u) : 0 \le u \le e^{(\overline{\delta} - \overline{\nu})t} \} \to 0 \qquad (t \to \infty). \tag{45}$$

Proof

As we have noted in the course of the proof of lemma 3.7, for any k there exists γ_k, $\omega_k \ge 0$ such that

$$\left| \frac{d}{du} v_k^t(u) \right| du \le \gamma_k u^{\mu_k + \omega_k + \lambda_k/\delta - 1} = \gamma_k u^{\mu + \omega_k - 1} \qquad (0 \le u \le \rho) \tag{46}$$

and $\mu_k + \omega_k > 0$. Since $-\lambda_k + (\mu_k + \omega_k)(\overline{\delta} - \overline{\nu}) < -\lambda_k + \mu_k \overline{\delta} \le 0$ by the definition of $\overline{\delta}$, we can estimate for $t \to \infty$

$$\int_0^{e^{(\overline{\delta} - \overline{\nu})t}} \left| \frac{d}{du} v_k^t(u) \right| du \le \frac{\gamma_k}{\mu_k + \omega_k} \exp[(-\lambda_k + (\mu_k + \omega_k)(\overline{\delta} - \overline{\nu}))t] \to 0. \tag{47}$$

This completes the proof.

3.9 PROOF OF THEOREM 2.2

Let $\tilde{c} : [0, 1] \to \mathbb{R}^n$ be a piecewise analytic curve changing catchment regions finitely many times. Thus, there is a partition of [0, 1] into consecutive pairwise disjoint intervals $I_1, \ldots, I_K$ and there is a sequence $\tilde{y}_1, \ldots, \tilde{y}_K \in S$ such that for every i we have $\tilde{c}(I_i) \subset \Delta_{\tilde{y}_i}$ and the restriction of $\tilde{c}$ to I_i extends analytically to some neighbourhood of the closure of the interval I_i. Let $0 = \rho_1 < \ldots < \rho_{2K+1} = 1$ be the enumeration of the end points and middle points of the intervals I_i. Write $\tilde{c}^t := \exp(-Df(x)\partial/\partial x)\tilde{c}$. Fix any index i and for $u \in [0, 1]$ define

$$c^t(u) := \begin{cases} \tilde{c}^t(\rho_i + (\rho_{i+1} - \rho_i)u) & \text{for odd } i, \\ \tilde{c}^t(\rho_{i+1} - (\rho_{i+1} - \rho_i)u) & \text{for even } i. \end{cases} \tag{48}$$

Observe that $c^t = \exp(-Df(x)\partial/\partial x)c$ and

$$c^t(0) \in \Delta_{y'}, \quad c^t((0,1]) \subset \Delta_{y''} \qquad (t \ge 0) \tag{49}$$

for some $y', y'' \in S$.

Thus, it suffices to see that, in arc length parameterization, c^t converges uniformly to some IRC joining the singularities y' and y''. This follows immediately from the deeper statement below.

3.10 PROPOSITION

Let $c : [0, 1] \to \mathbb{R}^n$ be a root-analytic curve, $y', y'' \in S$ satisfying (49) with $c^t := \exp(-Df(x)\partial/\partial x)c$.

Then, in the case of $y' = y''$, we have $\lim_{t\to\infty} \mathrm{length}\ c^t = 0$.

If $y' \ne y''$, then there exists a sequence $y' = y_0, y_1, \ldots, y_L = y'' \in S$ with $-\infty = \delta_0 < \eta_1 < \delta_1 < \eta_2 < \delta_2 < \ldots < \eta_L < \delta_L < 0$ and there are steepest descent paths $C_1, \ldots, C_L : (0, \infty) \to \mathbb{R}^n$ with the following properties:

$\lim_{t\to\infty} c^t(e^{\eta_m t}) = y_{m-1}$ $(m = 1, \ldots, L)$. For every index $m > 0$, the points y_{m-1} and y_m are joined by C_m and

(i) $\mathrm{length}\ c^t([0, e^{\eta_1 t}]) \to 0 \qquad (t \to \infty),$

(ii) $\sup_{p \in [e^{(\eta_m - \delta_m)t}, 1]} \left\| \frac{d^N}{dp^N} [c^t(pe^{\delta_m t}) - C_m(p)] \right\| \to 0 \quad (t \to \infty,\ N = 0, 1,\ m > 0),$

(iii) $\sup_{p \in [e^{(\delta_m - \eta_{m+1})t}, 1]} \left\| \frac{d^N}{dq^N} [c^t(e^{\eta_{m+1} - \delta_m)tq} e^{\delta_m t}) - C_m(e^{(\eta_{m+1} - \delta_m)tq})] \right\| \to 0$

$(t \to \infty,\ N = 0, 1,\ m < L),$

(iv) $\mathrm{length}\ c^t([e^{\eta_L t}, 1]) \to 0. \qquad (t \to \infty).$

Proof

It is convenient to use the extended coordinatizations T_y $(y \in S)$ introduced in proposition 2.1. First, let us consider any $\gamma \in [0, 1]$ such that $c([\gamma, 1]) \subset \Delta_{y''}$. Then, $c([\gamma, 1]) \subset U_{y''}$ and, by 2.1, the component functions of the curve $W : u \mapsto T_{y''}(c(u-\gamma))$ satisfy $W_k \equiv 0$ $(\lambda_k^{y''} < 0)$. Applying 3.7 with $\upsilon = W$ and $\delta = -\infty$, we obtain

$$\text{length } T_{y''}(c^t([\gamma,1])) \to 0 \quad (t \to \infty). \tag{50}$$

Since the mapping $T_{y''}$ is bianalytic, its inverse $T_{y''}^{-1}$ is locally Lipschitzian. Therefore,

$$c^t(\gamma) \to y'', \text{ length } c^t([\gamma,1]) \to 0 \quad (t \to \infty,\ c(\gamma) \in \Delta_{y''}). \tag{51}$$

In particular, if $y' = y''$, then the first statement is contained in (51) for $\gamma = 0$.

Henceforth, assume that $y' \neq y''$. Define

$$Y := \{y \in S : \exists \rho > 0 \ c((0,\rho]) \subset U_y\}. \tag{52}$$

Note that $y', y'' \in Y$. Fix $\rho > 0$ such that $c((0,\rho]) \subset \cap_{y \in Y} U_y$.

We carry out the following finite recursion. Set

$$\begin{aligned} &\delta_0 := -\infty, \qquad y_0 := y', \\ &{}^0c(u) := c(u) \quad (0 \le u \le \rho), \\ &C_0(p) := y_0 \quad (p \ge 0). \end{aligned} \tag{53}$$

Suppose that $\delta_m, y_m, {}^mc, C_m$ are already constructed and fulfill

$$\begin{aligned} &\delta_m < 0, \\ &C_m(p) = \lim_{t\to\infty} c^t(pe^{\delta_m t}) \quad (p > 0), \\ &C_m(p) \to y_m \qquad (p \to \infty), \\ &C_m(p) \to y_{m-1} \qquad (p \to 0,\ m > 0), \end{aligned} \tag{54}$$

where C_m is a steepest descent path and the curve ${}^mc : [0, \rho] \to \mathbb{R}^n$ is root-analytic so that

$$\begin{aligned} &{}^mc(0) = C_m(1), \\ &{}^mc(u) = c^{(1/\delta_m)\log u}(u) \quad (0 < u < \rho). \end{aligned} \tag{55}$$

We finish the recursion by setting $L := m$ if $y_m = y''$.

In the case $y_m \neq y''$, we define $\delta_{m+1}, y_{m+1}, {}^{m+1}c, C_{m+1}$ to satisfy (54) and (55) for $m + 1$ in place of m as follows. Consider the curve

$$\upsilon(u) := T_{y_m}({}^mc(u)) \qquad (0 \le u \le \rho). \tag{56}$$

Since the mapping T_{y_m} is analytic, the curce υ is root-analytic. Furthermore, we have

$$\upsilon(0) = T_{y_m}(C_m(1)) \in T_{y_m}(\Delta_{y_m}),\ \upsilon((0,\rho]) \subset \Delta_{y''},\ \Delta_{y''} \cap \Delta_{y_m} = \emptyset \tag{57}$$

By setting $\lambda_k = \lambda_k^{y_m}$ $(k = 1, \ldots, n)$, in view of (8) we then have

$$\upsilon_k(0) = 0 \quad (\lambda_k < 0), \quad \{k : \lambda_k < 0,\ \upsilon_k \not\equiv 0\} \neq \emptyset. \tag{58}$$

Now we define δ_{m+1} in terms of the notation 3.2 as $\delta_{m+1} := \bar{\delta}$ for $\delta = \delta_m$. That is, by writing $\mu_k = {}^m\mu_k$ for the order of the root-analytic component function $\upsilon_k = (T_{y_m})_k$,

$$\frac{1}{\delta_{m+1}} - \frac{1}{\delta_m} = \max\left\{ \frac{{}^m\mu_k}{\lambda_k^{y_m}} : \lambda_k^{y_m} < 0,\ (T_{y_m})_k \not\equiv 0 \right\}. \tag{59}$$

Remark that $\delta_m < \delta_{m+1} < 0$.

Having defined δ_{m+1} with a value in $(0, \infty)$, we can set formally

$$\begin{aligned} &C_{m+1}(p) := \lim_{t\to\infty} c^t(pe^{\delta_{m+1}t}) \qquad (p > 0), \\ &{}^{m+1}c(u) := c^{(1/\delta_{m+1})\log u}(u) \qquad (0 < u \le \rho). \end{aligned} \tag{60}$$

Observe that the meaning of the notations 3.2 for $\upsilon = T_{y_m}({}^mc)$, $\delta = \delta_m$, $\bar{\delta} = \delta_{m+1}$ and $\Lambda^t = \Lambda^t_{y_m}$ is the following:

$$\begin{aligned} \upsilon^t(u) &= \Lambda^{t-(1/\delta)\log u}\upsilon(u) = \Lambda_{y_m}^{t-(1/\delta_m)\log u} T_{y_m}(c^{t-(1/\delta_m)\log u}(u)) \\ &= T_{y_m}(\exp[-(t-(1/\delta_m)\log u)\mathrm{D}f(x)\partial/\partial x]c^{t-(1/\delta_m)\log u}(u)) \\ &= T_{y_m}(c^{(1/\delta_m)\log u + [t-(1/\delta_m)\log u]}(u)) = T_{y_m}(c^t(u)) \qquad (0 < u < \rho), \end{aligned} \tag{61}$$

$$V^t(p) = \upsilon^t(pe^{\delta t}) = T_{y_m}(c^t(pe^{\delta_m t})) \qquad (p, t \ge 0)$$

and

$$\bar{V}^t(p) = T_{y_m}(c^t(pe^{\delta_{m+1}t})) \qquad (p, t \ge 0). \tag{62}$$

Hence,

$${}^{m+1}c(u) = T_{y_m}^{-1}(\bar{V}^{(1/\delta_{m+1})\log u}(1)) \qquad (0 < u \le \rho). \tag{63}$$

From lemma 3.3 it follows that the curve $T_{y_m}({}^{m+1}c)$ admits a root-analytic extension to $[0, \rho]$ and consequently ${}^{m+1}c$ is also a root-analytic curve on $[0, 1]$ with the extension ${}^{m+1}c(0) := \lim_{u\to 0}{}^{m+1}c(u)$. Again, by writing $\overline{V} := \lim_{t\to\infty}\overline{V}^t$, from lemma 3.4 we see that

$$\{\overline{V}(p) : p > 0\} \subset \{x : \lim_{t\to\infty}\Lambda^{-t}x = 0\}$$

$$\subset \{x : \exists t\ \Lambda^t x \in \tilde{T}_{y_m}(\tilde{U}_{y_m})\} = T_{y_m}(U_{y_m}). \tag{64}$$

Thus, the curve $T_{y_m}^{-1}(\overline{V}):(0,\infty)\to\mathbb{R}^n$ is well defined and

$$T_{y_m}^{-1}(\overline{V}(p)) = T_{y_m}^{-1}\Big(\lim_{t\to\infty}\overline{V}^t(p)\Big) = T_{y_m}^{-1}\Big(\lim_{t\to\infty}T_{y_m}(c^t(pe^{\delta_{m+1}t}))\Big)$$

$$= \lim_{t\to\infty}c^t(pe^{\delta_{m+1}t}) = C_{m+1}(p) \qquad (p>0). \tag{65}$$

This shows that C_{m+1} is also well defined on the whole $(0,\infty)$. Moreover, (26) ensures that C_{m+1} is a steepest descent path issued and, by lemma 3.4,

$$\lim_{p\to-\infty}C_{m+1}(p) = T_{y_m}^{-1}(0) = y_m. \tag{66}$$

We also see that

$${}^{m+1}c(0) = T_{y_m}^{-1}\Big(\lim_{u\to 0}\overline{V}^{(1/\delta_{m+1})\log u}(1)\Big) = T_{y_m}^{-1}\Big(\lim_{t\to\infty}\overline{V}^t(1)\Big) = C_{m+1}(1). \tag{67}$$

From proposition 2.1, we know the steepest descent paths converge to points from S. Define

$$y_{m+1} := \lim_{p\to\infty}C_{m+1}(p). \tag{68}$$

Choose $p_0 > 0$ such that $C_{m+1}(p_0)\in\tilde{U}_{y_{m+1}}$. By the definition of C_{m+1}, we have $\mathrm{dist}(y_{m+1}, c^t([0,\rho]))\to 0$ $(t\to\infty)$. Thus, for some $\tau>0$, $c^t(p_0e^{\delta_{m+1}t}) = T_{y_m}^{-1}(\overline{V}^t(p_0))\in\tilde{U}_{y_{m+1}}$ $(t\geq\tau)$, that is,

$$c^{(1/\delta_{m+1})\log(u/p_0)}(u)\in\tilde{U}_{y_{m+1}} \qquad (0<u<p_0e^{\delta_{m+1}\tau}). \tag{69}$$

Hence, from the definition of Y we can see directly that $y_{m+1}\in Y$. This completes the proof of (54) and (55) with $m+1$ in place of m.

Since the function f decreases strictly along non-constant steepest descent paths,

$$f(y_0) < f(y_1) < \ldots < f(y_{m+1}). \tag{70}$$

Since the family Y is finite, this means that the recursion stops in finitely many steps.

We define the logarithmic speeds $\eta_1,\ldots,\eta_L$ in the following manner. Lemma 3.6 applied with $\delta=\delta_m$ to the curve υ defined in (56) ensures in view of (35) that for any $m<L$ we may choose $\overline{\nu}_{m+1}\in(0,\delta_{m+1}-\delta_m)$ such that

$$\sup_{p\in(e^{-\overline{\nu}_{m+1}t},1]}\Big\|\frac{d^N}{dp^N}[T_{y_m}(c^t(pe^{\delta_{m+1}t})) - T_{y_m}(C_{m+1}(p))]\Big\|\to 0 \tag{71}$$

for $t\to\infty$ and $N=0,1$. Choose $\overline{\nu}_{m+1}$ in this way and define

$$\eta_{m+1} := \delta_{m+1} - \overline{\nu}_{m+1} \qquad (m=0,\ldots,L-1). \tag{72}$$

Observe that since the steepest descent path C_{m+1} starts from y_m and ends in y_{m+1}, the curve

$$\tilde{C}_m := \{C_m(p) : p\geq 1\}\cup\{y_m\}\cup\{C_{m+1}(p) : p\leq 1\} \tag{73}$$

is a compact subset of the domain U_{y_m}. Therefore, for any $0\leq m<L$, there exists a precompact neighbourhood $G_m\subset U_{y_m}$ of $\tilde{C}_m$ such that all the derivatives of the mapping T_{y_m} are bounded on G_m and all the derivatives of $T_{y_m}^{-1}$ are bounded on $H_m := T_{y_m}(G_m)$. Note that H_m is also a precompact neighbourhood of $T_{y_m}(\tilde{C}_m)$.

On the basis of the previous observation and lemmas 3.5–3.8, the statements 3.10 (i)–(iv) can easily be verified.

Proof of (i): For $\upsilon = T_{y_0}(c)$, $\delta=-\infty$, we have $\overline{\delta}=\delta_1$ and $\upsilon^t = T_{y_0}(c^t)$ with the notations 3.2 by the previous considerations. Apply lemma 3.8 with $\overline{\nu}=\delta_1-\eta_1$. Hence, we find that

$$\text{length }T_{y_0}(c^t([0,e^{\eta_1 t}]))\to 0 \qquad (t\to\infty). \tag{74}$$

Thus, for sufficiently large t, we have $T_{y_0}(c^t([0,e^{\eta_1 t}]))\subset H_0$ and hence (i) is immediate by the boundedness of the derivatives of $T_{y_0}^{-1}|H_0$.

Proof of (ii), (iii): For $\upsilon = T_{y_m}({}^mc)$, $\delta=\delta_m$, we have $\overline{\delta}=\delta_{m+1}$ and

$$\begin{aligned} V^t(p) &= T_{y_m}(c^t(pe^{\delta_m t})), & \overline{V}^t(p) &= T_{y_m}(c^t(pe^{\delta_{m+1}t})),\\ V(p) &= T_{y_m}(C_m(p)), & \overline{V}(p) &= T_{y_m}(C_{m+1}(p)) \end{aligned} \tag{75}$$

with the notations 3.2. By setting $\nu := \eta_{m+1}-\delta_m$ and $\overline{\nu} := \delta_{m+1}-\eta_{m+1}$, by the definition of η_{m+1} we obtain

$$\sup_{p\in[e^{(\eta_{m+1}-\delta_{m+1})t},1]}\Big\|\frac{d^N}{dp^N}[T_{y_m}(c^t(pe^{\delta_{m+1}t})) - T_{y_m}(C_{m+1}(p))]\Big\|$$

$$= \sup_{p\in[e^{-\overline{\nu}_{m+1}t},1]}\Big\|\frac{d^N}{dp^N}[\overline{V}^t(p)-\overline{V}(p)]\Big\|\to 0 \qquad (t\to\infty,\ N=0,1). \tag{76}$$

Notice that for $N = 0, 1$ we have

$$\frac{\mathrm{d}^N}{\mathrm{d}p^N}\,[T_{y_m}(c^t(\mathrm{e}^{(\eta_{m+1}-\delta_m)tq}\mathrm{e}^{\delta_m t})) - T_{y_m}(C_{m+1}(\mathrm{e}^{(\eta_{m+1}-\delta_m)tq}))]$$
$$= \frac{\mathrm{d}^N}{\mathrm{d}p^N}\,[V^t(\mathrm{e}^{\nu tq}) - V(\mathrm{e}^{\nu tq}) = (\nu t)^N [p^N \frac{\mathrm{d}^N}{\mathrm{d}p^N}\,(V^t(p) - V(p))]_{p=\mathrm{e}^{\nu tq}}\,. \tag{77}$$

Hence, lemma 3.5 entails

$$\sup_{q\in[1,\mathrm{e}^{(\eta_{m+1}-\delta_m)t}]} \| \frac{\mathrm{d}^N}{\mathrm{d}p^N}\,[T_{y_m}(c^t(\mathrm{e}^{(\eta_{m+1}-\delta_m)tq}\mathrm{e}^{\delta_m t}))$$
$$- T_{y_m}(C_{m+1}(\mathrm{e}^{(\eta_{m+1}-\delta_m)tq}))] \| \to \infty \qquad (t \to \infty). \tag{78}$$

Thus, for sufficiently large t,

$$H_m \subset T_{y_m}(c^t(\{p\mathrm{e}^{\delta_{m+1}t} : \mathrm{e}^{(\eta_m-\delta_{m+1})t} \le p \le 1\}$$
$$\cup \{\mathrm{e}^{(\eta_{m+1}-\delta_m)tq+\delta_m t} : 1 \le q \le \mathrm{e}^{(\eta_{m+1}-\delta_m)t}\})$$
$$= T_{y_m}(c^t([\mathrm{e}^{\eta_m t}, \mathrm{e}^{\eta_{m+1}t}])). \tag{79}$$

Now the boundedness of the derivatives of $T_{y_0}^{-1}|H_0$ establishes (ii), (iii).

Proof of (iv): For $\upsilon = T_{y_L}(c)$, $\delta = \delta_L$, we have $\upsilon^t = T_{y_L}(c^t)$ with the notations 3.2. In this case, $\upsilon^t(0) = {}^{L-1}c(0) = C_L(1) \in \Delta_{y_L} = \Delta_{y^*}$. However, $c^t(u) \in \Delta_{y^*}$ for every t and u. Therefore, $u([0, \rho]) \subset \Delta_{y_L}$, whence $\upsilon_k \equiv 0$ $(\lambda_k^{y_L} < 0)$. Thus, applying lemma 3.7 we see that

$$T_{y_L}(c^t([\mathrm{e}^{\delta_L t}, \rho])) \to 0, \qquad \text{length } c^t([\mathrm{e}^{\delta_L t}, \rho]) \to 0 \quad (t \to \infty). \tag{80}$$

The boundedness of the derivatives of $T_{y_0}^{-1}|H_0$ provides the result immediately.

The relations $c^t(\mathrm{e}^{\eta_m t}) \to y_{m-1}$ $(m = 1, \ldots, L)$ follow directly from (iii) with the substitution $p = \mathrm{e}^{(\eta_m - \delta_m)t}$.

The proof of proposition 3.10 is now complete.

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