On reaction paths in quantum chemistry

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1. Introduction

Throughout this note let $U : (\mathbb{R}^3)^N \to \mathbb{R}$ denote a continuosly differentiable function. Here $\mathbb{R}$ is the standard notation for the field of reals and we regard $\mathbb{R}^3$ as the Euclidean 3-space with the classical distance $d_3(p,q) := \big[(x(p)-x(q))^2+(y(p)-y(q))^2+(z(p)-z(q))^2\big]^{1/2}$ in terms the usual coordinate functions $x, y, z : \mathbb{R}^3 \to \mathbb{R}$. We shall assume

$$U(Tx_1, \dots, Tx_N) = U(x_1, \dots, x_N) \tag{1.1}$$

for all even d_3-isometries $T : \mathbb{R}^3 \to \mathbb{R}^3$ (tranlations composed with rotations) and configurations $(x_1, \dots, x_N) \in (\mathbb{R}^3)^N$. From a pure mathematical view point, U can play the role of the potential energy function of chemist as follows. The value $U(x_1, \dots, x_N)$ is the Bohr-Oppenheimer energy associated with the configuration of a system of N atoms $(A_1, \dots, A_N)$ (e.g. $(C, H, H, H, H, C, O, O, O, O)$ for reactions of metan with oxygen) situated at the points with mass-weighted coordinates $x_1, \dots, x_N \in \mathbb{R}^3$. Indeeed rigid motions, translations and rotations do not change the potential energy of a system. The geometrical arragements of stable chemicals ($CH_4 + 2O_2$ or $CO_2 + 2H_2O$ in the example) correspond to local minima of U. Moreover, in most known cases, a small non-isometric change of the geometrical shape of a stable molecule causes a strict incase in the potential energy. This latter property can precisely be formulated in terms of the factor semidistance

$$d(x,y) := \min\Big\{\Big[\sum_{k=1}^{N} d_3(x', y')^2\Big]^{1/2} : \ x' \approx x, \ y' \approx y\Big\}$$

on $(\mathbb{R}^3)^N$ with respect to the isometric equivalence

$$(x_1, \dots, x_N) \approx (y_1, \dots, y_N) \quad \text{ if } y_1 = Tx_1, \dots, y_N = Tx_N$$

for some d_3-isometry $T : \mathbb{R}^3 \to \mathbb{R}^3$. Namely the function U can be factored with respect to $\approx$ (i.e. U is constant on the equivalence classes by $\approx$) and the the local minima of the factored function $U^{\approx} : x^{\approx} \to U(x)$ are isolated in the factor topology given by the factor semidistance d.

By a *Fukui type reaction path* of the potential energy function U we mean a continuous curve $t \mapsto x(t)$ from the standard parameter interval $[0,1]$ into the configuration space $(\mathbb{R}^3)^N$ such that

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- the endpoints $x(0), x(1)$ are local minima of U,
  the tangent vector $\frac{d}{dt}x(t)$ exists and does not vanish
  for all but finitely many parameters $0 < t < 1$,
- the gradient $\nabla U(x(t))$ of U at the point $x(t)$ is parallel to $\frac{d}{dt}x(t)$
  whenever the latter exists.

This concept was introduced in a less rigorous mathematical formulation by Fukui [4] in the 1970-eth with the aim of describing the set of most possible geometrical configurations of the involved atoms during a chemical reaction transforming the stable molecular formation corresponding to the local minimum place $x(0)$ into another one corresponding to $x(1)$. Its theoretical background is a heuristical quasi static consideration, and the parameter t in the mapping $t \mapsto x(t)$ does not correspont to real time. Actually piecewise smooth reparametrizations (i.e. by passing to $t \mapsto x(s(t))$ with an increasing piecewise smooth function $s : [0,1] \leftrightarrow [0,1]$) may provide reaction paths again which are continuously differentiable everywhere with vanishing derivative at the singular point of the original path. It seems, as far only heuristical numerical algorithms were developped in large numbers by chemists to calculate approximate reaction paths (typical examples [2],[3],[9],[13],[21]). Even the author's and other theoretical mathematician's works written together with chemists (e.g. [12],[16]) fall into this category, because the technical assumptions in mathematically nice and precise theorems were either unrealistic (e.g. the assumption in [15] of finitely many extreme points for U along with analyticity) or regarded only small submaifolds of $(\mathbb{R}^3)^N$ corresponding to forced conformal changes [1]. Other more exigent works dealt with essentially different alternative concepts (e.g. [10],[11]) or very strong implicit assumptions [8]. On the other hand, it is obvious that any two given local minima cannot be connected with a Fukui type reaction path – it is just enough to tranlate one of the endpoints of a given reaction paths. Actually, one of the most popular computer programs, the algorithm PATH [2] within the molecular dynamical package TINKER replaces first the given endpoint $x(1)$ with the closest equivalent point $\widetilde{x}(1)$ to $x(1)$ and then tries to transform the straight line $t \mapsto (1-t)x(0) + t\widetilde{x}(1)$ into an approximate reaction path which, however, cannot be the the proper one except for very simple cases). This remark supports the use of a weakened version of Fukui's concept.

By a *Fukui type weak reaction path* of the potential function $U : (\mathbb{R}^3)^N \to \mathbb{R}$ we mean a continuous curve $y : [0,1] \to (\mathbb{R}^3)^N$ such that there are finitely many parameters $0 = t_0 < t_1 < \cdots < t_K = 1$ satisfying that

- each of the points $y(t_k)$ is a stationary point of U
  i.e. $\nabla U(y(t_k)) = 0, \;\; k = 0, \ldots, K$,
- for every segment (t_{k-1}, t_k) there exists a continuously differentiable curve
  $x_k : (t_{k-1}, t_k) \to (\mathbb{R}^3)^N$ with the properties
  $\nabla U(x_k(t)) \parallel \frac{d}{dt}x_k(t), \quad x_k(t) \approx y(t), \quad t_{k-1} < t < t_k$.

The aim of this note is to show that, under realistic hypothesis, any couple of stationary points of a potential function U can be joined by a Fukui type weak reaction path. Namely such paths can be constructed by means of the exponential flow of the vector field $x \mapsto -\nabla U(x)$. We give some hints concerning the numerical realizations and outline some related open mathematical problems.

2. Theoretical results

2.1 Theorem. *Let Ω be a connected set in $(\mathbb{R}^3)^N$ which is open with respect to the factor semidistance d of the isometric equivalence relation $\approx$. Assume $U : (\mathbb{R}^3)^N \to \mathbb{R}$ is a twice continuously differentiable function with the property* (1.1) *and*

(2.1a) *up to isometric equivalence, there are only finitely many stationary points of U,*

(2.1b) *all the level sets $\{x : U(x) < \lambda\}$, $\lambda \in \mathbb{R}$ are compact in the topology of d,*

(2.1c) *around each stationary point of U, the projection of the gradient of U along the fibres of $\approx$-equivalence classes onto some transversial submanifold is linearizable (details see* 2.2d *below).*

Then given any two stationary points $p^*, q^* \in \Omega$, there exists a Fukui type weak reaction path $y : [0,1] \to (\mathbb{R}^3)^N$ of U such that $y(0) = p^*$ and $y(1) = q^*$.

2.2 Remarks.

a) Condition (2.1a) implies that given any point $p \in \Omega$ with $\nabla U(p) = 0$ there exists $\delta > 0$ such that $\nabla U(q) \neq 0$ whenever $q \not\approx q$ and $d(p,q) < \delta$. As we have noted, such an assumption is rather natural for local minima of U. Wast computer experiences suggest that (2.1a) is no strong restriction even for other type of stationary points. Experimental results are very scarse concerning unstable stationary points.

b) Condition (2.1b) is not fulfilled automatically for real chemical systems. Namely [8] "almost the contrary" happens: if $\widetilde{U} : (\mathbb{R}^3)^N \to \mathbb{R}$ is the Born-Oppenheimer energy function of a chemical system then its restrictions to the sets

$$\Omega_\varepsilon := \{(x_1, \dots, x_N) : \ d_3(x_i, x_j) \geq \varepsilon, \ 1 \leq i < j \leq N\}, \quad \varepsilon > 0$$

are bounded. However, $\lim_n \widetilde{U}(x^{(n)}) \to \infty$ whenever the sequence $x^{(1)}, x^{(2)}, \dots \in (\mathbb{R}^3)^N$ satisfies $x^{(n)} \in (\mathbb{R}^3)^N \setminus \Omega_{\varepsilon_n}$ with $\lim_n \varepsilon_n = 0$. On the other hand, we have $\lim_n \widetilde{U}(x^{(n)}) \to 0$ whenever $x^{(n)} \in \Omega_{\varrho_n}$ and $\lim_n \varrho_n = \infty$. Therefore, in practice one passes to a *modified potential energy function* $U := \widetilde{U} + \phi : \Omega \to \mathbb{R}$ where, for some large $\lambda > 0$, $\Omega := \{x : \ 1/\lambda < \min_{i<j} d_3(x_i, x_j) < \lambda\}$ and ϕ is a smooth non-negative function vanishing on $\Omega_{2/\lambda} \setminus \Omega_{\lambda/2}$ and converging to ∞ toward the boundary of Ω. The chemically relevant actions are expected to happen in the region where the penalizing function ϕ vanishes.

c) It is straightforward to verify that a subset S of $(\mathbb{R}^3)^N$ consisting of equivalence classes of $\approx$ is compact with respect to the factor distance d if and only if $S = \bigcup_{x\in C} x^{\approx}$ for some compact subset of $(\mathbb{R}^3)^N$ (in the usual sense i.e. bounded and closed), or equivalently, if the set $\{(x_1+\cdots+x_N)/N :\ x \in S\}$ of the masscenters of the elements of S is compact. Hence the modified potential energy function described in b) above satisfies hypothesis (2.1b).

d) Given a stationary point a of U, let W denote the subspace of the vectors $w \in (\mathbb{R}^3)^N$ being orthogonal to the tangent space of the equivalence class $a^{\approx}$ at the point a. Then there exists a neighborhood A of the point a in $(\mathbb{R}^3)^N$ such that the intersection $x^{\approx} \cap [a+W]$ consists of a unique element for any $x \in A$. By writing $P : A \ni x \mapsto [a+w \in x^{\approx} :\ w \in W]$ for the projection onto the tranversial manifold $a+W$ along the $\approx$-equivalence classes, condition (2.1c) means the following. We can find a linear mapping $L : W \to W$ along with a diffeomorphism $T : B \leftrightarrow A \cap [a+W]$ where B is a neighborhood of 0 in W such that $T(0) = a$ and $Lw = \frac{d}{dt}|_{t=0} P\big(T(w) - t\nabla U(T(w))\big)$ for all $w \in B$.

Though (2.1c) seems to be rather technical, by the Hartman-Grobman theorem [5], this is not a heavy restriction from the view point of applications. Namely we have the above linearizability if the matrix of the differential DF of the mapping $F := (DP)(-\nabla U)$ has no eigenvectors with eigenvalue 0 from W at the point a. In terms of differential matrices this means that $\nabla F(a)w \neq 0$ for $0 \neq w \in W$ where
$\nabla F := \big[-\sum_{k=1}^{3N} \big(\partial^2 P_i/\partial\xi_i\partial\xi_k\big)\big(\partial U/\partial\xi_k\big) - \sum_{k=1}^{3N} \big(\partial P_i/\partial\xi_k\big)\big(\partial^2 U/\partial\xi_k\partial\xi_j\big)\big]_{i,j=1}^{3N}$
with the coordinates $\xi_{3k-2} := x_k$ $\xi_{3k-1} := y_k$, $\xi_{3k} := z_k$.

In course of the proof of the theorem we shall use only the following well-known topological consequence of condition (3.1c).

Let a be a stationary point of U. If $x_1, x_2, \ldots : \mathbb{R} \to (\mathbb{R}^3)^N$ is a sequence of integral curves of $-\nabla U$ (i.e, $\frac{d}{dt}x_n(t) = -\nabla U(x_n(t))$) with $\liminf_{t\to\pm\infty} d(x_n(t), a) > \varepsilon$, $n = 1, 2\ldots$ for some $\varepsilon > 0$ and $x_n(t_n) \to a$ for some sequence $t_1, t_2, \ldots \in \mathbb{R}$ then there is an integral curve $x : \mathbb{R} \to (\mathbb{R}^3)^N$ of $-\nabla U$ such that $\lim_{t\to-\infty} d(x(t), a) = 0$.

3. Proof of Theorem 2.1

Throughout this section $U : \Omega \to \mathbb{R}$ denotes a twice continuously differentiable function fulfilling the hypthesis (1.4),(2.1a),(2.1b) of Theorem 2.1 and $p_1^*, \ldots, p_{n^*}^* \in \Omega$ are pairwise isometrically non-equivalent stationary points of U such that $S^* := \{x \in \Omega :\ \nabla U(x) = 0\} = \bigcup_{i=1}^{n^*} (p_i^*)^{\approx}$.

Before stating the proof, we recall the concept of the *flow* (or *exponential* in another terminology) of a continuously differentiable vector valued mapping $X : \Omega \to (\mathbb{R}^3)^N$. By

definition, if $p \in \Omega$ and $t \in \mathbb{R}$,

$$\exp tX(p) := \big[q \in \Omega : \ \exists\ t_1, t_2 > 0 \quad t \in (-t_1, t_2) \ \text{ and } \ \exists\ x : (-t_1, t_2) \to \Omega \\ x(0) = p,\ \tfrac{d}{d\tau}x(\tau) = V(x(\tau)) \ \ (-t_1 < \tau < t_2), \ \ q = x(t)\big].$$

By the Piccard-Lindelöf theorem, the vector q in the above formula is unique if it exists. It is also well-known that the mapping $(t, p) \mapsto \exp tX(p)$ is defined on an open subset of Ω and it is continuous there. Moreover if $t_i \to t \in \mathbb{R}$, $p_i \to p \in \Omega$ and $\exp t_i X(p_n) \to q \in \Omega$ for $i \to \infty$ then $\exp tX(p)$ is necessarily well-defined and $= q$.

In the sequel, by a *complete U-path* we mean a curve $x : \mathbb{R} \to \Omega$ fulfilling the differential equation $\frac{d}{dt}x(t) = -\nabla U(x(t))$.

3.1 Proposition. *Given any $\lambda \in \mathbb{R}$, the flow $F^t := \exp(-t\nabla U)$ $(t \geq 0)$ is well-defined for all points of the level set $C := \{x \in (\mathbb{R}^3)^N : \ U(x) \leq \lambda\}$. The sets $F^t(C)$ are unions of $\approx$-equivalence classes and decrease for $t \to \infty$. The limit set $\bigcap_{t\geq 0} F^t(C)$ consists of complete U-paths $x : \mathbb{R} \to C$ such that $\lim_{t\to-\infty} d(x(t), p) = \lim_{t\to\infty} d(x(t), q) = 0$ for some stationary points p, q of the function U.*

Proof. By assumption the level set C is compact in the topology of the factor semidistance d. Since the function U assumes the same values for points with zero d-semidistance, it gradient is also continuous with respect to the topology of d. In particular ∇U is bounded on C. Given any solution of the ordinary differential equation $\frac{d}{dt}x(t) = -\nabla U(x(t)$, we have

$$\frac{d}{dt}U(x(t)) = \nabla U(x(t))\frac{d}{dt}x(t) = -\nabla U(x(t))\nabla U(x(t)) \geq 0 \tag{3.2}$$

along the whole interval where $x(.)$ is defined. Therefore the maximal solutions of the initial problems $\frac{d}{dt}x(t) = -\nabla U(x(t)$, $x(0) = c$ with $c \in C = \{z : \ U(z) \leq \lambda\}$ are defined on the whole $[0, \infty)$ and satisfy $U(x(t) \leq U(x(0)) = \lambda$ that is $x(t) \in C$ for all $t \geq 0$. This means that $F^s(C) \subset C$ for all $s \geq 0$. Since U assumes the same value on $\approx$-equivalence classes, we have $F^s(x) \approx F^s(y)$ for $x \approx y \in C$ and $s \geq 0$. Thus the sets $F^s(C)$ are the unions of $\approx$-equivalence classes. In general $F^{t+s}(z) = F^t(F^s(z))$ whenever the maximal solution of the initial value problem $\frac{d}{dt}x(t) = -\nabla U(x(t)$, $x(0) = z$ is defined on some open interval containing $s, t, s+t$ and 0. Hence $F^{t+s}(C) = F^t(F^s(C)) \subset F^t(C)$ whenever $s, t \geq 0$. It also follows that the set $F^t(C)$ consists of those points $z \in C$ for which the maximal solution of $\frac{d}{dt}x(t) = -\nabla U(x(t)$, $x(0) = z$ is defined on some open interval containing $[-t, \infty)$ and satisfies $x(s) \in C$ for $s \in [-t, \infty)$. Consequently $\bigcap_{t\geq 0} F^t(C)$ consists of those points $z \in C$ for which the maximal solution of $\frac{d}{dt}x(t) = -\nabla U(x(t)$, $x(0) = z$ is defined on the whole $\mathbb{R}$ and ranges in C. To finish the proof, consider any of these U-paths $x : \mathbb{R} \to C$. Since the

level sets $\{y:\ U(y)\le\mu\}$ are compact wrt. the topology of the semidistance d and since U is assumed to be d-continuous, we have $\lambda_*:=\inf U>-\infty$. Thus, by (3.2),

$$0\le\int_{t_1}^{t_2}\big\|\nabla U\big(x(t)\big)\big\|^2\,dt=U(x(t_1))-U(x(t_2))\le\lambda-\lambda_*<\infty,\quad t_1<t_2. \tag{3.3}$$

Due to the assumption that U is continuously differentialble, necessarily

$$\lim_{t\to\pm\infty}\|\nabla U(x(t))\|=0.$$

Indeed, both ∇U and $\nabla U\|^2$ are bounded and uniformly continuous on the d-compact set C. Hence, given any $\varepsilon>0$, there exists $\delta(\varepsilon)>0$ with $\|\nabla U(y)\|^2-\|\nabla U(z)\|^2<\varepsilon$ for $y,z\in C$ such that $\|y-z\|<\delta(\varepsilon)$ and $\|x(s)-x(t)\|<<\varepsilon$ for any couple $s,t\in\mathbb{R}$ with $|s-t|<\delta(\varepsilon)$. Then we have $\|\nabla U(x(t+h))\|^2>\varepsilon/2$ whenever $\|\nabla U(x(t))\|^2>\varepsilon$ and $|h|<\delta\big(\delta(\varepsilon/2)\big)$. Therefore (3.3) ensures that the set $\{t\in\mathbb{R}:\ \|\nabla U(x(t))\|^2>\varepsilon$ must be bounded for all $\varepsilon>0$ and this latter fact is equivalent to (3.4). It is a well-known fact from elementary topology that the accumulation points for $t\to\infty$ of a continuous curve mapping $\mathbb{R}$ into a compact space form a connected set. In particular, the accumulation points of $t\mapsto x(t)^{\approx}$ form a connected set A in the factor topology of the semidistance d. By the previous consideration, these accumulation points are stationary points of U. Hence $A\subset\{(p_1)^{\approx},\dots,(p_n)^{\approx}\}$ and we conclude that $\lim_{t\to\infty}d\big(x(t),p_j^*\big)=\lim_{t\to\infty}d\big(x(t)^{\approx},(p_j^*)^{\approx}\big)=0$ for a unique index j. Similarly $\lim_{t\to-\infty}d\big(x(t),p_\ell^*\big)=\lim_{t\to-\infty}d\big(x(t)^{\approx},(p_\ell^*)^{\approx}\big)=0$ for some ℓ. $\square$

From the above proof we see that any for any complete U-path $x(.)$ with bounded energy range $\{U(x(t):\ t\in\mathbb{R}\}$ there exists a unique pair p_j^*,p_ℓ^* of U-stationary points such that $\lim_{t\to\infty}d\big(x(t),p_j^*\big)=\lim_{t\to-\infty}d\big(x(t),p_\ell^*\big)=0$ Conveniently we shall write $x(\infty),x(-\infty)$ for them. That is

$$x(\varepsilon\infty):=\big[p^*\in S^*:\ \lim_{t\to\varepsilon\infty}d\big(x(t),p^*\big)=0\big],\quad\varepsilon=\pm1.$$

Notice that, in the factor space, the extended curve $[-\infty,\infty]\ni t\mapsto x(t)^{\approx}$ is continuous and hence has compact range wrt. the topology of d.

3.5 Lemma. *If there exists a finite sequence $q_0,q_1,\dots,q_{m-1},q_m$ in S^* along with a sequence $z_1(.),\dots,z_m(.)$ of complete U-paths such that*

$$p^*\approx q_0=z_1(-\infty),\ z_1(\infty)=q_1=z_2(-\infty),\dots,z_{m-1}(\infty)=q_{m-1}=z_m(-\infty),\ z_m(\infty)=q_m\approx q^*$$

then the statement of Theorerem 2.1 *holds.*

Proof. Choose any partition $0 = \alpha_0 < \alpha_1 < \cdots < \alpha_{m+1} = 1$ of the interval $[0,1]$ and, for each index k, let $\psi_k : [\alpha_k, \alpha_{k+1}] \leftrightarrow [-\infty, \infty]$ be a smooth function with strictly positive derivative inside. (E.g. let $\alpha_k := k/(m+2)$ and $\psi_k(t) := \tan\big[(m+2)\pi(t-(k+\frac{1}{2})\big]$). Define

$$x_k(t) := z_k\big(\psi(t)\big), \quad t \in [\alpha_k, \alpha_{k+1},\ k = 1, \ldots, m.$$

Then $x_k'(t) = \psi_k'(t) z_k\big(\psi_k(t)\big) = -\psi_k'(t)\nabla U\big(z_k\big(\psi_k(t)\big)\big) \parallel U\big(x_k(t)\big)$ for all $t \in [\alpha_1, \alpha_m] \setminus \{\alpha_1, \ldots, \alpha_m\}$. Therefore it only suffices to construct a sequence $y_1, \ldots, y_{m+1}$ of continuous functions $y_k : [\alpha_k, \alpha_{k+1}] \to (\mathbb{R}^3)^N$ (where $(\mathbb{R}^3)^N$ is regarded with its standard Hausdorff topology) such that

$$y_k(t) \approx x_k(t) \ \text{ for } t \in [\alpha_k, \alpha_{k+1}] \ \text{ and } \ \widetilde{y}_k(\alpha_{k+1}) = \widetilde{y}_{k+1}(\alpha_{k+1})$$

for all $k = 1, \ldots, m$. Indeed, we can choose a couple of continuos functions $y_0 : [0, \alpha_1] \to (p^*)^{\approx}$ resp. $y_{m+1} : [\alpha_{m+1}, 1] \to (q^*)^{\approx}$ with $y_0(0) = p^*$, $y_0(\alpha_1) = y_1(\alpha_1)$, $y_{m+1}(\alpha_m) = y_m(\alpha_m)$, $y_{m+1}(1) = q^*$ because $p^* \approx y_1(\alpha_1)$, $q^* \approx y_m(\alpha_{m+1})$ and since the equivalence classes of $\approx$ are connected. Then the concatenated curve $y : [0,1] \to (\mathbb{R}^3)^N$ given by $y(t) := \widetilde{y}_k(t)$, $\alpha_k \le t \le \alpha_{k+1}$ suits the requirements of being a Fukui type weak reaction path joining p^* with q^*.

To complete the proof, fix any index $1 \le k \le m$ and construct the curve $y_k : [\alpha_k, \alpha_{k+1}] \to (\mathbb{R}^3)^N$ as follows. Since the equivalence classes of $\approx$ form a fibration over $(\mathbb{R}^3)^N$ and since fibre bundles are trivial locally, for every point $q \in (\mathbb{R}^3)^N$ there exists $\varepsilon_q > 0$ along with an affine submanifold M_q of $(\mathbb{R}^3)^N$ passing through q and a non-linear projection $P_q : \{x \in (\mathbb{R}^3)^N : \ d(x,q) < \varepsilon_q\} \to M_q$ such that $P_q(x)$ is the unique point of $M_q \cap x^{\approx}$ whenever $d(x,q) < \varepsilon_q$. Using the projection $P_{k-1} := P_{q_{k-1}}$ and $P_k := P_{q_k}$, first we modify the curve x_k into a curve $\widetilde{y}_k : [\alpha_k, \alpha_{k+1}]$ which is continuous (wrt. the standard topology of $(\mathbb{R}^3)^N$) also at the endpoints α_k, α_{k+1} and satisfies $\widetilde{y}_k(t) \approx x_k(t)$ for $\alpha_k < t < \alpha_{k+1}$. This can be done by fixing a suitable subinterval $\emptyset \ne [\beta_k, \gamma_k] \subset (\alpha_k, \alpha_{k+1})$ such that we have $d(x_k(t), q_{k-1}) < \varepsilon_{q_{k-1}}$ for $\alpha_k < t \le \beta_k$ and $d(x_k(t), q_k) < \varepsilon_{q_k}$ for $\gamma_k \le t < \alpha_{k+1}$. Then we fix two d_3-isometries $L_k, R_k : \mathbb{R}^3 \leftrightarrow \mathbb{R}^3$ with the effect

$$\big(L_k[P_k x(\beta_k)]_1, \ldots, L_k[P_k x(\beta_k)]_N\big) = x(\beta_k), \ \big(R_k[P_k x(\gamma_k)]_1, \ldots, R_k[P_k x(\gamma_k)]_N\big) = x(\gamma_k).$$

Observe that the curve $\widetilde{y}_k(t) := \big[x_k(t)$ for $\beta_k \le t \le \gamma_k$, $L_k P_k x_k(t)$ for $t \le \beta_k$, $R_k P_k x_k(t)$ for $t \ge \gamma_k\big]$ is continuous and satisfies $\widetilde{y}_k(t) \approx x_k(t)$, $\alpha_k \le t \le \alpha_{k+1}$. By applying suitable d_3-isometries $T_1, \ldots, T_m : \mathbb{R}^3 \leftrightarrow \mathbb{R}^3$, we can achieve that the curves $y_k(t) := \big(T_k[\widetilde{y}(t)]_1, \ldots, T_k[\widetilde{y}_k(t)]_N\big)$, $\alpha_k \le t \le \alpha_{k+1}$ have concatenable endpoints in the sense that $y_{k-1}(\alpha_k) = y_k(\alpha_k)$, $k = 2, \ldots, m$. $\square$

3.6. Lemma. *Suppose $x(.), x_1(.), x_2(.), \ldots$ are complete U-paths with bounded energy range and $t, t_1, t_2, \ldots \in \mathbb{R}$ is a sequence such that $x_n(t_n) \to x(t)$ in the standard topology of $(\mathbb{R}^3)^N$. Then there exists a sequence $s_1, s_2, \ldots > 0$ along with a subsequence $x_{n_1}(.), x_{n_2}(.), \ldots$ such that $x_{n_k}(t_{n_k} + s_k) \to x(\infty)$ in the topology of d.*

Proof. Given any $\varepsilon > 0$, there exist $s_\varepsilon > 0$ with $d(x(t+s), x(\infty)) < \varepsilon$, $s \geq s_\varepsilon$. In terms of the flow $F^s := \exp(-s\nabla U)$, $s \in \mathbb{R}$ we have

$$x_n(t_n + s) = F^s\big(x_n(t_n)\big) \to F^s\big(x(t)\big) = x(t+s), \quad s \in \mathbb{R}.$$

Thus, given any integer $k > 0$, we can choose an index n_k such that $d\big(x_{n_k}(t_{n_k} + s_{1/k}), x(t + s_{1/k})\big) < 1/k$ and hence $d\big(x_{n_k}(t_{n_k} + s_{1/k}), x(\infty) < 2/k$. $\square$

3.7. Finishing the proof of Theorem 2.1

Let Γ be the graph whose vertices are the representative stationary points $p_1^*, \ldots, p_{n^*}^*$ and we have an edge between p_i^* and p_j^* if there is a complete U-path $x(.)$ such that $\{x(-\infty), x(\infty)\} = \{p_i^*, p_j^*\}$. We have to show that Γ is connected. Since the domain Ω is connected, we can find a continuous curve $z : [0,1] \to \Omega$ whose range contains the points $p_1, \ldots, p_{n^*}$. Let $\lambda := \max_{0 \leq t \leq 1} U(z(t))$ and $C := \{x \in \Omega : \ U(x) \leq \lambda\}$. According to 3.1, the mappings $F^t := \exp(-t\nabla U)$, $t \geq 0$ are continuous, the transformed sets $F^t(C)$ decrease when the parameter t increases and they shrink to a d-compact set C^* which is the union of the complete U-paths $x(.)$ with bounded energy range connecting the points of $S^* = \{p_1^*, \ldots, p_{n^*}^*\}$ in the sense that $x(-\infty), x(\infty) \in S^*$. Observe that C^* is connected in the topology of the semidistance d (d-*connected* for short). To prove this fact, consider the d-accumulation set

$$Z^* := \big\{q \in C : \ \exists\, t_1, t_2, \ldots \to \infty \ \ \exists\, s_1, s_2, \ldots \in [0,1] \quad \lim_{n\to\infty} d\big(q, F^{t_n}\big(z(s_n)\big)\big) = 0\big\}.$$

Observe that $Z^* \subset C^*$ because $\{F^t(z(s)) : \ s \in [0,1]\} \subset F^t(C) \searrow C^*$. Since the curves $s \mapsto \big[F^t\big(z(s)\big)\big]^{\approx}$ are continuous in the factor topology by the equivalence relation $\approx$ and since $\{q^{\approx} : \ q \in C^*\}$ is compact in the same topology, Z^* must be d-connected. We have

$$C^* = Z^* \cup \bigcup_{j=1}^{n^*} Z_j^* \quad \text{where} \ \ Z_j^* := \bigcup \big\{\text{complete } U \text{ paths } x(.) \text{ with } p_j^* \in \{x(\pm\infty)\}\big\}.$$

Thus since the range $\{x(t) : \ t \in [-\infty, \infty]\}$ of each complete U-path is d-connected and since Z^* contains the points $p_1^*, \ldots, p_{n^*}^*$, the set C^* is indeed d-connected.

Suppose indirectly, that the graph Γ is disconnected that is the set $I = \{1, \ldots, n^*\}$ of its vertices can be split into a disjoint union $J = J_1 \cup J_2$ with $J_1, J_2 \neq \emptyset$ such that no edges pass between their points. This means that C^* is the disjoint union of the non-empty sets $C_k^* := \bigcup_{i \in J_k} Z_j^*$, $k = 1, 2$. To finish the proof, it suffices to show that both C_1^*, C_2^* are d-closed. Since, for the d-closures, we have $\overline{C_k^*}^d = \bigcup_{j \in J_k} \overline{Z_j^*}^d$, $k = 1, 2$, There exist $j_1 \in J_1$ and $j_2 \in J_2$ with $\overline{Z_{j_1}^*}^d \cap \overline{Z_{j_2}^*}^d \neq \emptyset$. Since also $C^* = \bigcup_{j \in J} Z_j^*$, we have even $(*)$ $\overline{Z_{j_1}^*}^d \cap Z_{j_2}^* \neq \emptyset$ or $(**)$ $Z_{j_1}^* \cap \overline{Z_{j_2}^*}^d \neq \emptyset$. We may assume without loss

of generality the firs case $(*)$. Furhermore we may assume that value $U(p^*_{j_2})$ is *minimal* among the possibilities satisfying $(*)$. Then we get a contradiction as follows. Condition $(*)$ means that there exists a sequence $z_1(.), z_2(.), \dots$ of complete U-paths ranging in $Z^*_{j_1}$ along with a sequence $t_1, t_2, \dots \in \mathbb{R}$ such that $d\big(z_n(t_n), q\big) \to 0$ for some point $q \in Z^*_{j_2}$. For the $\approx$-equivalent sequence $x_1(.), x_2(.), \dots$ of complete U-paths defined as $x_n(t) := z_n(t) - \big(m([z_n(t)], \dots, m([z_n(t)]\big)$, $t \in \mathbb{R}$ where $m(p) := (p_1, \dots p_N)/N$ denotes the mass center of the points $p \in (\mathbb{R}^3)^N$, the sequence $x_1(t_1), x_2(t_2), \dots$ is bounded in $(\mathbb{R}^3)^N$. Hence we can find a subsequence $x_{n_1}(t_1), x_{n_2}(t_2), \dots$ converging to some point $p \approx q$ in the standard topology of $(\mathbb{R}^3)^N$. Since Z_{j_2} is the union of a family of $\approx$-equvalence classes, also $p = x(t)$ for some $t \in \mathbb{R}$ and a complete U-path $x(.)$ with $x(\infty) = p^*_{j_2}$. By Lemma 3.6, there exists a sequence $s_1, s_2, \dots > 0$ along with a sequence $k_1, k_2, \dots \to \infty$ of indices such that $\lim_{i\to\infty} d\big(x_{k_i}(t_{k_i} + s_i), p^*_{j_2}\big) = 0$. However, then Remark (2.2e) implies the existence of a complete U-path $y(.)$ with $y(-\infty) = p^*_{j_2}$. By the disconnectedness of Γ, for the index of the other endpoint $p^*_\ell = y(\infty)$ we must have $\ell \in J_2$. Necessarily $U(p^*_{j_2}) = U(y(-\infty)) > U(y(\infty)) = U(p^*_\ell)$ which contradicts the minimality of $U(p^*_{j_2})$. $\square$

4. Remarks on numerical applications, problems

4.1. Since the beginnig of the 1990's, several computer programs appeared for determining approximate reaction paths [2],[3],[9],[13],[21]. Partly they had no mathematical background at all, worked with a small number of coordinates and heavy constrains on the molecular system. The first ad hoc programs were local type and operated special situations. They tried to find a "saddle point" that is a stationary point U with indefinite second derivative matrix $\nabla^2 U$ and then tried to find integral curves of $\pm\nabla U$ "starting toward the directions of the eigenvectors of $\nabla^2 U$ with the belief that these integral curves would end in local minima of U corresponding to familiar stable chemicals. Spectacular failures of such methods increased the demand for global algorithms transforming a given curve which connects two given local minima of U into a reaction path. Unfortunately, except perhaps for the works [10],[11],[12],[14],[15],[18],[19] and some reference therein, almost no rigorous mathematical attention was paid for such procedures. Later on several of them proved to be false from a pure mathematical view point despite their "practical" achievements (see [18],[19],[20]).

4.2. The message for numerical applications of our main result is that modifying the energy fuction (see 2.2b) in a region only far from the stationary points, the exponential flow of the vector field $-\nabla U$ makes to shrink sufficiently large d-compact lower level sets C of U to the union C^* of the weak Fukui type reaction paths. By the d-compactness of the sets C^* and $C^t := \exp(-t\nabla U)C$, $t \geq 0$, necessarily we have $\max\{d(p, C^*) : \ p \in C^t\} \to 0$ for $t \to \infty$ where $d(p, C^*) := \min\{d(p, q) : \ q \in C^*\}$. In particular,

if $z : [0,1] \to (\mathbb{R}^3)^N$ *is a continuous curve with* $z(0) = p_0$, $z(1) = p_1$ *where* p_0, p_1 *are local minima of* U, *then the ranges* $Z^t := \{z^t(s) : \ s \in [0,1]\}$ *of the curves* $z^t(s) := \exp(-\nabla U)z(s)$ *approach the set of the possible points of the weak Fukui reaction paths in d-semidistance.*

Thus for any $\varepsilon > 0$ there exists t_ε such that given any $t \geq t_\varepsilon$ each point $z^t(s)$ in the geometrical curve is closer than ε in the Euclidean distance of $(\mathbb{R}^3)^N$ to some point $q \in C^*$ which is regarded as the coordinate tuple of a possible molecular configuration during the chemical reactions described with the energy function U.

4.3. One of the main difficulies concerning the numerical computation of the curves Z^t is the following fact (an immediate consequence from 3.1). Given any point $p \in (\mathbb{R}^3)^N$, we have $\lim_{t\to\infty} d\big(\exp(-t\nabla U)p, p^*\big) = 0$ for some stationary point p^*. Thus if one tries to represent Z^t with the polygon $Z_n^t := \{z^t(k/n) : \ k = 1, \dots, n\}$ where n is a fixed number (independently of t) then, for large values of t, the shape of Z_n^t has no practical relationship with the real shape of the curve Z^t because it consists only of nearly stationary points. To fill in the gaps, in the works [1],[6],[7],[14],[16] *polygon homogenization procedures* were used. For instance [16], for given $\varepsilon > 0$ and $T > 0$ we started from a polygon $\Pi^0 = \{z(s_k^{(0)}) : k = 0, \dots, n^{(0)}\}$ representing $Z = Z^{(0)}$ such that the partition $0 = s_0^{(0)} < \dots < s_{n^{(0)}}^{(0)} = 1$ such that the distance $d(s_{k-1}^{(0)}, d(s_k^{(0)})$ between consecutive points should be $< \varepsilon$. Then successively we represented the curve $Z^{t+T} = \exp(-T\nabla U)Z^t$ with a polygon Π^{t+T} whose consecutive points were closer than ε which was constructed from the shifted polygon $\Pi_T^t := \exp(-T\nabla U)\Pi^t$ by adding new points from the line segment between two consecutive points of Π_T^t or by droppin points from Π_T^t in a suitable manner.

4.4. The polygon homogenization procedures raise the following challanging problem.

Under which (not too restrictive) conditions on U *or with which (not too sophisticated) modififcation of the homogenization procedure can we ensure the convergence*

$$\max\left[\left\{d(x(s), \Pi^t) : \ s \in [0,1]\right\} \cup \left\{d(p, \{x(s) : \ s \in [0,1]\}) : \ p \in \Pi^t\right\}\right] \to 0, \quad t \to \infty$$

of Hausdorff semidistances for some Fukui reaction path $x : [0,1] \to (\mathbb{R}^3)^N$ *?*

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