On the reaction path concept of Olender and Elber [*]

László L. Stachó [a], Gyula Dömötör [b] and Miklós I. Bán [b,**]

[a] *Bolyai Institute for Mathematics, JATE University of Szeged, H-6720 Szeged, Aradi Vértanúk tere 1, Hungary*
E-mail: stacho@math.u-szeged.hu
[b] *Institute of Physical Chemistry, JATE University of Szeged, H-6701 Szeged, P.O. Box 105, Hungary*
E-mail: {domotor,m.i.ban}@chem.u-szeged.hu

The Olender–Elber (OE) reaction path concept [1] is shown to be unrelated in general with a true steepest descent path (SDP) in the mathematical sense yet the solutions of such a variational problem may even replace the old reaction path (RP) concept if the RP passes through several critical points of the potential energy surface. We have found a chemically interesting and sufficient condition for the coincidence of OE's "SDP" and the IRC of Fukui. The OE concept has been discussed here in a rather straightforward manner giving it an exact mathematical description.

KEY WORDS: reaction path, potential energy surface, steepest descent path

1.   Introduction

Attention has been drawn to the reaction path (RP) concept of Olender and El-ber (OE) [1] in our former papers [2,3]. The primary aim of this remarkable work [1] was to propose a numerical algorithm based on the path integral formulation of Brown-ian trajectories for calculating steepest descent paths (SDP). As we have indicated by a counter-example [2] the sketched proof in [1] fails to verify the statement that admissi-ble curves of the path integral of the gradient norm minimizing the OE energy functional lead necessarily to SDPs. Nevertheless, a RP concept – based on variational principles – which is established by physical arguments may still be of important significance. The present paper is to show that a "local" interpretation of the OE concept [1] can be retained (although by entirely different arguments from those in [1]). The theorem in section 2 implies in particular that a minimum energy RP (MERP) in a reaction valley having a single saddle point (SP) does minimize the OE functional. Even if there is no MERP but a sequence of SDPs such that the energy function admits a unique local maximum at a non-degenerate SP (as for the Stachó–Bán function [4,5]), according to our theorem this

sequence of SDPs minimizes locally the OE functional. This fact explains why the OE concept works "locally" but not "globally" in general: if the energy function along the classical RP [6] (consisting of SDPs) increases and decreases several times then there will be a non-negligible chance that an admissible curve minimizing the OE functional should not coincide with the classical RP. We are furnishing a rather simple example in section 2 to illustrate this fact. Since Olender and Elber have given physical arguments (i.e., the Brownian motion) that a true RP is likely to minimize the OE functional, the admissible curves violating the symmetry of the system though minimizing this functional (as in the case of our artificial example) are worth of further investigations using real chemical systems where the classical RP consists of several monotonic SDP pieces.

Therefore, although the OE concept [1] can be regarded [7] as a recent version of algorithms employing the Elber–Karplus (EK) strategy [8], after its proper mathematical reformulation presented here, it may give a useful additional description of the RP. In the present paper, therefore, a strictly exact mathematical discussion of the OE concept has been given.

2.   Discussion

Throughout this work let U denote a continuously differentiable function $\mathbb{R}^N \to \mathbb{R}$. We regard U as the energy function of a molecular system.

Theorem. Assume $p_1, p_2, s \in \mathbb{R}^N$ are points, $C : [a, b] \to \mathbb{R}^N$ is a piecewise continuously differentiable curve, $\tau \in (a, b)$ and $S \subset \mathbb{R}^N$ is a set (e.g., an $(N-1)$-dimensional surface in several cases) such that

(i) we have $s \in S$, $U(s') \geqslant U(s)$ for $s \neq s' \in S$, and the surface S separates the points p_1, p_2, i.e., any continuous curve joining p_1 with p_2 intersects S;

(ii) we have $p_1 = C(a)$, $p_2 = C(b)$, $s = C(\tau)$ and the function $t \mapsto U(C(t))$ is increasing on $[a, \tau]$ and decreasing on $[\tau, b]$;

(iii) C is a meta IRC of U, i.e., the tangent vector $dC(t)/dt$ is parallel to the gradient $\nabla U(C(t))$ almost everywhere on $[a, b]$.

Then the curve C minimizes the OE functional [1]

$$\Omega : G \mapsto \int_G \|\nabla U\| \, d\ell \tag{1}$$

for all piecewise continuously differentiable curves G joining the points p_1, p_2.

The following two examples are not to support the proof of the theorem but just to illustrate the interpretation of the set S appearing in it.

(1) For the RP of the reaction $H_2 + H = H + H_2$ [9,10] the set S can be formed of the points for which the condition $r_1 = r_2$ has been fulfilled (here r_1 and r_2, respectively, are the distances of the two outermost H-atoms to the central H-atom).

(2) For the Stachó–Bán function [4,5] the points of the straight line $x = 0$ can be taken as the set S if the two minima are located on the two different sides of the straight line $x = 0$.

Proof. By assumption (iii),

$$\left\| \nabla U\big(C(t)\big) \right\| \cdot \left\| \frac{\mathrm{d}}{\mathrm{d}t} C(t) \right\| = \left| \left\langle \nabla U\big(C(t)\big), \frac{\mathrm{d}}{\mathrm{d}t} C(t) \right\rangle \right| = \left| \frac{\mathrm{d}}{\mathrm{d}t} U\big(C(t)\big) \right|. \qquad (2)$$

Therefore, by assumption (ii),

$$\begin{aligned}
\Omega(C) &= \int_a^b \left| \frac{\mathrm{d}}{\mathrm{d}t} U\big(C(t)\big) \right| \mathrm{d}t = \int_a^\tau \frac{\mathrm{d}}{\mathrm{d}t} U\big(C(t)\big) \, \mathrm{d}t - \int_\tau^b \frac{\mathrm{d}}{\mathrm{d}t} U\big(C(t)\big) \, \mathrm{d}t \\
&= \big[U\big(C(\tau)\big) - U\big(C(a)\big) \big] + \big[U\big(C(\tau)\big) - U\big(C(b)\big) \big] \\
&= \big[U(s) - U(p_1) \big] + \big[U(s) - U(p_2) \big].
\end{aligned} \qquad (3)$$

Consider any other piecewise continuously differentiable curve $G : [a', b'] \to \mathbb{R}^N$ joining p_1 with p_2 (i.e., $p_1 = G(a')$, $p_2 = G(b')$). By assumption (i), we can find $\tau' \in (a', b')$ with $G(\tau') := s' \in S$ and, hence, necessarily with $U(s') \geqslant U(s)$. Then

$$\begin{aligned}
\Omega(G) &= \int_{a'}^{b'} \left\| \nabla U\big(G(t)\big) \right\| \cdot \left\| \frac{\mathrm{d}}{\mathrm{d}t} G(t) \right\| \mathrm{d}t \\
&\geqslant \int_{a'}^{b'} \left| \left\langle \nabla U\big(G(t)\big), \frac{\mathrm{d}}{\mathrm{d}t} G(t) \right\rangle \right| \mathrm{d}t \\
&= \int_{a'}^{b'} \left| \frac{\mathrm{d}}{\mathrm{d}t} U\big(G(t)\big) \right| \mathrm{d}t \\
&\geqslant \int_{a'}^{\tau'} \frac{\mathrm{d}}{\mathrm{d}t} U\big(G(t)\big) \, \mathrm{d}t - \int_{\tau'}^{b'} \frac{\mathrm{d}}{\mathrm{d}t} U\big(G(t)\big) \, \mathrm{d}t \\
&= \big[U\big(G(\tau')\big) - U\big(G(a')\big) \big] + \big[U\big(G(\tau')\big) - U\big(G(b')\big) \big] \\
&= \big[U(s') - U(p_1) \big] + \big[U(s') - U(p_2) \big].
\end{aligned} \qquad (4)$$

It follows

$$\Omega(G) \geqslant 2U(s') - \big[U(p_1) + U(p_2) \big] \geqslant 2U(s) - \big[U(p_1) + U(p_2) \big] = \Omega(C).$$

The proof is complete. $\qquad \square$

Elber and Karplus state [11] that "other algorithms developed by Elber and coworkers for determining RPs for larger systems, such as that of Ulitsky and Elber [12] and Olender and Elber [1] compute the exact SDP". The proof of this statement given in [1] is false in general. Their original sketched proof is completely wrong as we have already shown in our former comment [13], however, the principle works under some mathematically heavy but chemically not irrealistic conditions if the number of critical points on the potential energy surface is small, but for completely different reasons as are the

arguments in [1]. Olender and Elber disregard that by varying the curve its length will also be changed. Assuming two minima and a single saddle point (SP) and using some chemically acceptable conditions, an absolutely correct proof entirely different from that described in [1] was given in [3]. Elber and Karplus [11] quote another variational principle, due to Olender and Elber [1], stating that RPs minimize the line integral of the gradient norm. We show now that this claim is also false in general.

Example 1. First we give a simple 2D artificial counter-example the RP of which determined by the OE method [1] is definitely not a SDP. Let us take the function

$$U = \left(1 - r^2\right)^8 - r^{14}\left(2 - r^2\right)^7 \cos 6\varphi, \tag{5}$$

where r and φ are polar coordinates. Fukui's RPs [4] are the segments of the unit circle with its centre in the origin and with those radii of the circle which join the centre of the circle with the local minima defined by the relation

$$P_k = \left(\cos \frac{k\pi}{m}, \sin \frac{k\pi}{m}\right), \quad k = 0, \ldots, 2m - 1, \; m = 3. \tag{6}$$

Denote the curve between the points $(-1, 0)$ and $(1, 0)$ by C_ρ which is composed from the semicircle lying on the upper semiplane and having a radius ρ and its center in the origin, and from two straight line segments of the section of length $1 - \rho$. Let $G(C)$ be the functional defined by equation (26) in [1]:

$$G(C) = \int_C \|\nabla U\| \, d\ell. \tag{7}$$

Direct MAPLE calculations [14] show that

$$G(C_{1/2}) < G(C_0), \qquad G(C_{1/2}) < G(C_1). \tag{8}$$

As G is not minimized by C_0 and C_1, therefore, from these two inequalities it follows that the curve which joins the points $(0, 1) = P_0$ and $(0, -1) = P_3$ and minimize G cannot be a SDP. This our counter-example verifies that the proof given in the paper of Olender and Elber [1] is incorrect: *though the curves minimizing G can be used as an optional definition for a new RP concept they cannot be used as a new determination method of SDPs.* In the meantime we also gained negative experiences by using the authentic Czerminski–Elber [15] algorithm implemented in the program package TINKER [16]. These results were presented at the WATOC'99 congress [7,17].

Example 2. Now we are going to show another function

$$f(x, y) = \frac{y^2 \sin^2 x + y^4}{\delta^2 \sin^2 x + \delta^4}(2 - \cos x) + \cos x \tag{9}$$

by which the RP of Olender and Elber is also no SDP. One can easily realize that for the function $f(x, y)$ no IRC-segment deviating from the x-axis can exist. Indeed, we have $\partial f/\partial y > 0$ if $y > 0$ and $\partial f/\partial y < 0$ if $y < 0$. Thus, by fixing the parameters x and δ

the minimum of $f(x, y)$ are surely along the x-axis. On the other hand, for any fixed $-\delta < y < \delta$ the minima of the function $f(x, y)$ are in the points with $x = (2k + 1)\pi$. Furthermore, $f \equiv 2$ is constant along the straight lines $y = \pm\delta$.

Let us define the sections as follows:

$$
\begin{aligned}
C_0 &= \left[\left(-(2k + 1)\pi, 0 \right), \left(0, (2k + 1)\pi \right) \right], \\
C_1 &= \left[\left(-(2k + 1)\pi, 0 \right), \left(-(2k + 1)\pi, \delta \right) \right], \\
C_2 &= \left[\left(-(2k + 1)\pi, \delta \right), \left((2k + 1)\pi, \delta \right) \right], \\
C_3 &= \left[\left((2k + 1)\pi, \delta \right), \left((2k + 1)\pi, 0 \right) \right].
\end{aligned}
\tag{10}
$$

For these, the natural number k will be selected later. Then we can see that the value of the OE functional

$$
\int \| \nabla f(x, y) \| \, d\ell
\tag{11}
$$

calculated along the curve $C_1 + C_2 + C_3$ is smaller than that along C_0, therefore, C_0 cannot be an RP (SDP) in the sense of the OE concept. From the derivative df/dx issues $df/dx = 0$ for the section C_1, C_2 and C_3, therefore, $\| \nabla f(x, y) \| = |df/dy|$. For the sections C_1 and C_3 the OE functional can be written – by the Newton–Leibniz theorem – as the simple expression $f(\pm(2k + 1)\pi, \delta) - f(\pm(2k + 1)\pi, 0) = 3$ and for the curve C_2

$$
\int_{C_2} \| \nabla f(x, y) \| \, d\ell = \int_{-(2k+1)\pi}^{(2k+1)\pi} \left| \frac{\partial f}{\partial y} \right| dx = \int_{-(2k+1)\pi}^{(2k+1)\pi} \frac{2\delta \sin^2 x + 4\delta^3}{\delta^2 \sin^2 x + \delta^4} (2 - \cos x) \, dx
\tag{12}
$$

will be valid in which assuming $\delta > 1$ for the last integrand we get

$$
\int_{-(2k+1)\pi}^{(2k+1)\pi} \left| \frac{\partial f}{\partial y} \right| dx \leqslant \frac{18}{\delta} 2(2k + 1)\pi.
\tag{13}
$$

Therefore, along the whole path $C_1 + C_2 + C_3$:

$$
\int_{C_1+C_2+C_3} \| \nabla f(x, y) \| \, d\ell \leqslant 6 + \frac{36}{\delta}(2k + 1)\pi.
\tag{14}
$$

On the other hand,

$$
\int_{C_1+C_2+C_3} \| \nabla f(x, y) \| \, d\ell = 4(2k + 1)
\tag{15}
$$

also holds. It can easily be seen that for $k = 1$ and $\delta \geqslant 72$:

$$
\int_{C_1+C_2+C_3} \| \nabla f(x, y) \| \, d\ell < \int_{C_0} \| \nabla f(x, y) \| \, d\ell.
\tag{16}
$$

It is worth mentioning that for all natural numbers $k \geqslant 1$ there exists such a $\delta > 0$ for which C_0 cannot be an RP (SDP) in the sense of the OE concept.

Acknowledgement

References

[1] R. Olender and R. Elber, J. Mol. Struct. (Theochem) 398–399 (1997) 63.
[2] L.L. Stachó, Gy. Dömötör and M.I. Bán, Chem. Phys. Lett. 311 (1999) 328.
[3] Gy. Dömötör, L.L. Stachó and M.I. Bán, J. Mol. Struct. (Theochem) 501–502 (2000) 509.
[4] L.L. Stachó and M.I. Bán, Theor. Chim. Acta 83 (1992) 433.
[5] L.L. Stachó and M.I. Bán, Theor. Chim. Acta 84 (1993) 535.
[6] K. Fukui, J. Phys. Chem. 74 (1970) 4161.
[7] L.L. Stachó, M.I. Bán and Gy. Dömötör, Reaction paths defined by global variational principles, in: *WATOC'99 (5th World Congress of Theoretically Oriented Chemists)*, London, UK (1–6 August 1999) p. 333.
[8] R. Elber and M. Karplus, Chem. Phys. Lett. 139 (1987) 375.
[9] Gy. Dömötör, M.I. Bán and L.L. Stachó, J. Comput. Chem. 14 (1993) 1491.
[10] M.I. Bán, Gy. Dömötör and L.L. Stachó, J. Mol. Struct. (Theochem) 311 (1994) 29.
[11] R. Elber and M. Karplus, Chem. Phys. Lett. 311 (1999) 335.
[12] A. Ulitsky and R. Elber, J. Chem. Phys. 96 (1990) 1510.
[13] L.L. Stachó, Gy. Dömötör and M.I. Bán, J. Math. Chem. (2001) (to be published).
[14] MAPLE V Release 4, Version 4.00b, Waterloo Maple Inc. (1981–1996).
[15] R. Czerminski and R. Elber, J. Chem. Phys. 92 (1990) 5580.
[16] S. Huston and J.W. Ponder, TINKER: Software tools for molecular design, Version 3.5 (October 1997).
[17] Gy. Dömötör, L.L. Stachó and M.I. Bán, Comparative study of global path-following methods, in: *WATOC'99 (5th World Congress of Theoretically Oriented Chemists)*, London, UK (1–6 August 1999) p. 335.