# "*Comment*" on the Reply to the paper "On the Elber–Karplus Reaction Path-Following Method and Related Procedures"

L.L. Stachó [a], Gy. Dömötör [b] and M.I. Bán [b,*]

*[a] Bolyai Institute, 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-6720 Szeged, POB 105, Hungary*
E-mail: {domotor, m.i.ban}@chem.u-szeged.hu

The flaws in the "Reply" [1] to our paper [2] have been pointed out. Elber and Karplus (EK) have not disproved our irrefutable global statement that the energy average cannot be minimized which rebuts the theoretical background of EK-type calculations. Another statement of ours has shown that even a curve for which the average energy is locally minimal for all directional perturbations in the sense of classical variational calculus cannot be identical with the reaction path (RP) defined as a steepest descent path (SDP). EK found an error in the early preprint of our theoretical paper [3] and because of this error they qualified our correct variational statement as false for all the SDPs consisting of a straight line each. Mixing global and variational arguments, EK refuted our criticism in a logically incorrect manner. In this Comment we prove that both of our earlier statements invariably remain in force and the criticism included in those has been as well-established and solid as was before.

**KEY WORDS:** Elber–Karplus procedures, reaction path-following, DDRP method

## 1. Introduction

Based on both theoretical considerations and numerical experiences, we published a paper [2] which pointed out serious conceptual errors in the popular Elber–Karplus (EK) algorithm [5] and in its sequels of path-following procedures [6–9]. In a polemic paper [1] the authors replied to our arguments, insisting on the validity of their strategy. However, as we are going to point out in this "*Comment*", EK do not touch the main issue at all. They absolutely disregard our statement asserting [2,3] that the average functional

$$A = \frac{\int_R^P U(\vec{\ell})|\mathrm{d}\vec{\ell}|}{\int_R^P |\mathrm{d}\vec{\ell}|} \tag{1}$$

* Corresponding author.

## 2. Discussion

We have already proved [2–4,12,13] that the average (1) of the line integral of the energy function serving as a base for the EK method and its sequels has no minimum. In our proof we have presented a procedure by which to any curve $L$ we can construct another curve $L'$ with the same starting and endpoints for which the average of the line integral is strictly smaller than that for $L$ unless the energy function assumes its minimum at every point of $L$. EK did not even try to disprove this our main statement because it was irrefutable and indisputably faultless. Occasional numerical errors in the calculations of our given examples may occur because of the lack of the original authentic algorithms and the use of a general version of the Powell method [14] which does not require the knowledge of the analytic derivative of the function to be minimized. However, it should now be stressed: the gravest insufficiency of the EK method is that based on the minimum of the line integral average *which really does not exist*. Our other objection against the strategy of the EK-type methods is that – though the minimum for the discretized form of the line integral does exist – the concrete calculations based on the discretized line integral are still strongly parameter dependent. EK argue that the penalties that avoid rigid body translations and rotations do not influence the value of the functional and the equidistant constraint does not affect significantly the shape of the RP. Nevertheless, using fixed numbers of points (as they do) this statement is not true as we have already shown by examples [2,4,12,13]. Therefore, the hollow pretext by EK, simply saying that they do not use rigid body constraint in the Müller–Brown curve calculations since it is unnecessary in that case, cannot be accidental. Their true reason for not using the penalty function to avoid rigid body movements is that they would get much worse results if they employed the choice of $\lambda = \lambda' = 4000, 8000$ or $16000$ as they had done in former examples.

Another – even more general – statement has been taken in [3] where we have shown that by using variational analysis (i.e., weaker constraints) even local minima of the line integral average can not be regarded as a steepest descent path (SDP). There we have also acknowledged EK for reminding us to a calculational error. However, after correcting this error our statements [2] are invariably valid. In their "Reply" [1] EK hoped to find a counter-example by constructing the 2D potential energy surface of the energy function (2). They argue that the $y$-axis joining the two minima is an SDP ($x = 0$) and this is also the minimum of the line integral average. Out of this is only true that the $y$-axis is a SDP and may also be true that the curve calculated by the EK procedure is coinciding with it. Nevertheless we can easily demonstrate that line integral averages smaller than those calculated for curves running along the $y$-axis do really exist.

By using MAPLE V calculations [10] ($k = 1$) with the control sequence

```
a:=sqrt(1/2); assume(t>0); assume(u>=-Pi/2,u<=Pi/2);
C:=s+t*sqrt(a^2-s^2); Cu:=simplify(subs(s=a*sin(u),C));
ut:=solve(diff(Cu,u)=0,u);
Lt:=int(diff(Cu,u),u=-Pi/2..ut)-int(diff(Cu,u),u=ut..Pi/2);
U:=k*x^2+y^4-y^2; Fu:=subs(x=0,y=Cu,U)*diff(Cu,u);
```

the exact SDP". The proof of this statement given in [8] is false. OE disregard that by varying the curve its length will also be changed. Assuming two minima and one saddle point (SP) and accepting some chemically not irreal conditions, an absolutely correct proof [11] entirely different from that described in [8] can be given. To verify this we give a simple 2D artificial counterexample the RP of which determined by the OE method [8] is, definitely, not a SDP. Let us take the function

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

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

$$P_k = (\cos k\pi/m, \sin k\pi/m), \quad k = 0, \ldots, 2m - 1. \tag{7}$$

Denote the curve between the points $(-1, 0)$ and $(1, 0)$ by $C_t$ which is composed from the semicircle lying on the upper semiplane and having a radius $t$ and its center in the origin, and from two straight line segments of the section of length $1 - t$. Let $G(C)$ be the functional defined by equation (26) in [8]:

$$G(C) = \int_C \|\nabla U\| \, d\ell. \tag{8}$$

Direct MAPLE calculations [10] show that

$$G(C_{1/2}) < G(C_0), \qquad G(C_{1/2}) < G(C_1). \tag{9}$$

As $G$ is not minimized by $C_0$ and $C_1$ therefore from these two inequalities 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 OE [8] is incorrect. Nevertheless, 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 gained negative experiences by using the authentic Czerminski–Elber (CzE) [6] algorithm implemented in the program package TINKER [7]. These results were presented at the WATOC'99 congress [4,12].

## 3. Conclusions

1. EK have never mentioned in their papers that the minimum of the average of the line integral does not exist, therefore it is unfair that they suppress this fact which we have proved by exact mathematical arguments. In the same time all the RP-following algorithms operating by the EK strategy have been based on the existence of the minimum of the energy functional average.

2. We have also proved that it is not correct to use a new concept introduced by EK which defines the RP as the minimization curve of the energy functional average. We reject the way by which EK are attacking our strictly mathematical proof and its

because the EK paper [5] did not give sufficient basis for the correct reproduction). Nevertheless, we have made several variants [4,12,13] following the principles described in the EK paper [5] (and in papers of other authors [6,8,9,15]) so they may not differ substantially from the authentic versions and, therefore, they should produce the same results with minor deviations. We have already offered and now repeat the possibility to show and give our authentic DDRP algorithm on our homepage asking to exchange it with the authentic other algorithms. In this way the numeric calculation results could be reproduced and checked by the authors working on the same field, immediately. Many misunderstandings could then be cleared up directly and easily.

4. We were ready to admit that we made an error in the derivation of the mathematical proof described at an earlier stage of the preprint form of our paper. This means that equation (6) in the "Reply" [1] is the right expression. For the detection of this error we are very much obliged to EK and this fact has been acknowledged in the published version [3]. However, it must be stressed that this error (made *in the proof* of the arguments in the preprint of [3]) does affect in no way the arguments themselves and their consequences to the EK strategy. Therefore EK have not enough base and right to come to the conclusion that because of the error in the proof our fundamental mathematical arguments are also faulty.

## Acknowledgements

## References

[1] R. Elber and M. Karplus, Chem. Phys. Lett. 311 (1999) 335.

[2] L.L. Stachó, Gy. Dömötör and M.I. Bán, Chem. Phys. Lett. 311 (1999) 328.

[3] L.L. Stachó, Gy. Dömötör and M.I. Bán, J. Math. Chem. 26 (1999) 87.

[4] 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), Book of Abstracts*, London, UK, 1–6 August 1999, p. 335; to be published in J. Comput. Chem. (in preparation).

[5] R. Elber and M. Karplus, Chem. Phys. Lett. 139 (1987) 3755.

[6] R. Czerminski and R. Elber, J. Chem. Phys. 92 (1990) 5580.

[7] S. Huston and J.W. Ponder, TINKER: Software tools for molecular design, Version 3.5 (October 1997) (Copyright Jay William Ponder, 1990–1997).

[8] R. Olender and R. Elber, J. Mol. Struct. (Theochem) 398–399 (1997) 63.

[9] A. Ulitsky and R. Elber, J. Chem. Phys. 96 (1990) 1510.

[10] Maple V Release 4, Version 4.00b (1981–1996).

[11] L.L. Stachó, Gy. Dömötör and M.I. Bán, J. Math. Chem. 28 (2000) 241.

[12] 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), Book of Abstracts*, London, UK, 1–6 August 1999, p. 333; published in [11].

[13] Gy. Dömötör, L.L. Stachó and M.I. Bán, J. Mol. Struct. (Theochem) 501–502 (2000) 509.

[14] W.H. Press, B.P. Flannery, S.A. Teukolsky and W.T. Vetterling, Numerical recipes, in: *The Art of Scientific Computing* (Cambridge University Press, Cambridge, 1986) p. 294.

[15] S.S.L. Chiu, J.J.W. Douall and I.H. Hillier, J. Chem. Soc. Farad. Trans. 90 (1994) 1575.