PROCEDURE FOR DETERMINING DYNAMICALLY DEFINED REACTION PATH

L. L. STACHÓ ¹ and M. I. BÁN ²

¹JATE Bolyai Institute for Mathematics, Andri Vertanik ter 1, H-6720 Szeged, Hungary
²JATE Institute of Physical Chemistry, P.O. Box 105, H-6701 Szeged, Hungary

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Abstract—A practical computational program and pertinent sections of the code illustrated by flow-charts for a searching procedure to determine dynamically defined reaction paths have been discussed.

1. INTRODUCTION


In the first paper of our series the fundamental theory (Stachó & Bán, 1992a), and in the second paper (Stachó & Bán, 1992b) the mathematical background of a global strategy for determining dynamically defined reaction path (DDRP) has been given. In our third paper (Stachó & Bán, 1993) the algorithm and aspects of numerical applications have been described. In the present paper the characteristic features of a practical/computational program based on the theory laid in the first three papers of this series and pertinent sections of the code illustrated by flow-charts have been discussed. A next paper (Dömödt et al., 1993b) will show the use of the searching procedure of DDRP on examples of simple chemical reactions, by employing quantum chemical methods for calculating the (energy) functional. Here, also experiences gained by the implementations of quantum chemical procedures into the program of DDRP will be discussed.

2. PROCEDURE

Recalling the fundamental theorem and the theoretical considerations described in the first paper (Stachó & Bán, 1992a) we suggest to determine tangent curves of a vector field \( V \) between two given singular points by taking the limit (in the sense of Hausdorff distance) for \( t \to \infty \) of curves of the form

\[
\mathbf{c}(t) = \exp(tV)(\mathbf{c}_0).
\]

Here \( \mathbf{c}_0 \) is any piecewise analytic curve joining the given singularities or simply joining points from the respective catchment regions of these singularities. The exponentsials of the vector field \( V \) are the mappings \( \mathbf{x} \to \mathbf{x}^V \) satisfying the steepest descent path equation

\[
\frac{d}{dt} \mathbf{x}^V = V(\mathbf{x}^V), \quad \mathbf{x}_0 = \mathbf{x} = \exp(tV)(\mathbf{x}_0) = \mathbf{x}^V.
\]

Thus in this manner we approach the reaction path between two singularities of the potential energy function by not trying to move forward in the suspected reaction valley according to some fixed strategy (as most known popular methods do), but—using a well-visibleizable analogy—by "stretching a cord onto the reaction path" from an almost arbitrary starting position joining the given two endpoints. A careful mathematical analysis (Stachó & Bán, 1992b) ensures the convergence of this procedure even in cases with a seemingly very hopeless starting curve or a potential surface with the possibility of a ramifying system of intermediate products. Of course, this high grade of reliability must be paid through a higher amount of calculations. However, as it was pointed out (Stachó & Bán, 1993) our...
Procedure for determination of DDRP

\[ \text{Procedure HOMOGENIZE} \]

\[ d_\phi (Y, Z) = \max \min d_\phi (\mathbf{y}_i, \mathbf{z}_j), \quad \min \max d_\phi (\mathbf{y}_i, \mathbf{z}_j) \]

\[ \text{INPUT: } Y = [y_1, \ldots, y_m], \quad Z = [z_1, \ldots, z_n], \quad d(a, b, c) \text{ distances the point } a \text{ from the line segment joining } b \text{ and } c. \]

\[ \text{OUTPUT: } Z = \{z_1, \ldots, z_n\} \in \mathbb{R}^n \]

Fig. 2. Flow-chart of the program-segment HOMOGENIZE used in the procedure DDRP. (For notations see Section 2.)

between \( Y = [y_1, \ldots, y_m] \) and \( Z = [z_1, \ldots, z_n] \) where \( d(a, b, c) \) denotes the distance

\[ \min \{a - (b + (c - 1))\} \]

of the point \( a \) from the line segment joining \( b \) and \( c \).

The marked boxes in the flow-charts of Figs 1 and 2 show where parallel computation is suggested if parallel facilities are available.

3. FORTRAN REALIZATION

According to the previous section we divide the above described computational program into two subroutines, whose pertinent sections are the following:

NEWCURVE calculating the curve representative \( Z \) from \( Y \) in which a subroutine with name VFIELD generates the values of the vector field \( Y \), HOMOGENIZE determining the a-homogenized fitting \( Y \) of a curve representative \( Z \).
In sections of both subroutines the parameters are interpreted as follows:

N: dimension of the underlying space R^N
T: corresponds to the time step \delta
Y(1, J): the 1st component of the Jth point of Y
Z(1, J): the 1st component of the Jth point of Z
L: the number of points of both Y and Z in NEWCURVE
LX, LY are the cardinalities of Y resp. Z in HOMOGENIZE
EPS, MU, R denote the controlling parameters of L, N.
Inputs of NEWCURVE are N, L, array Y (of type L \times N), T, M, R.
Output of NEWCURVE is array Z (of type L \times N).
Inputs of HOMOGENIZE are N, L, array Z (of type L \times N), EPS.
Outputs of HOMOGENIZE are L, array Y (of type L \times N).

For the sake of completeness we give also the FORTRAN code of the pertinent section of the subroutine HAUSD for determining the approximate Haufdoff distance \delta_{0}(Y, Z) of two curve representatives (consisting of L, resp. Z points in the Euclidean N-space).

Inputs of HAUSD are N, L, LY, array Y (of type L \times N), array Z (of type L \times N).
Output of HAUSD is D.

SUBROUTINE NEWCURVE(N,L,Y,T,M,R)
REAL Y(0:100,30,0:100,30),Z(0:100,30),D(0:100)

SUBROUTINE HOMOGENIZE(N,L,Y,V,L,EP)
REAL Y(0:100,30),V(0:100,30),L(0:100,0:100)

SUBROUTINE HAUSD(N,L,G,H,L,D)
REAL G(0:100,30),H(0:100,30)

REFERENCES