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Short communication

Acceleration of the DDRP method by potential energy transformations[☆]

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The convergence of the dynamically defined reaction path (DDRP) method [1–4] is very stable; however, it may be slow [3] for potential energy surfaces having extremely steep parts. Here we propose a general procedure for accelerating convergence of the method. This procedure may also be used in other path-following methods. Since the IRC always has an intersection orthogonal to the contours of the potential energy surface, it is invariant under continuously differentiable, strictly monotonically increasing transformations $f(U)$ of the potential energy function U. It is not necessary to have the explicit analytic form for such transformations; it is enough to know the slope of $f(U)$. Thus, the gradient ∇U in any path-following algorithm may be replaced by an expression of the form $\nabla f(U) = g(U)\nabla U$, where g can be any strictly positive continuous function (chosen arbitrarily). For the function $g(U)$ the following general formula is proposed

$$g(U) = a[b + c(U + d)^{2n}]^{-1/k} \qquad (1)$$

The optional parameters should always be adjusted

to the potential energy surface in question, e.g. for

$a = c = k = 1, b = 0$ and $n = 0.5$;

$$f(U) = \log_x(U + d)$$

$a = b = c = 1, d = 0, n = 1$ and $k = 2$;

$$f(U) = \sinh^{-1}(U)$$

$a = b = c = 1, d = 0$ and $k = n = 1$;

$$f(U) = \arctan(U)$$

For testing path-following methods, a celebrated 2-dimensional surface is the graph of the Müller–Brown (MB) function [5]

$$U(x,y) = \sum_i \exp\left[a_i(x - x_{0i})^2 + b_i(x - x_{0i})(y - y_{0i}) + c_i(y - y_{0i})^2\right] \qquad (2)$$

Recall that the MB reaction path has a sharp curvature with three minima and two saddle points, the variations in the function values being very large. The starting polygon for the calculations was a straight line segment joining the points $(-2.0, 2.0)$ and $(2.0, -2.0)$. By using the DDRP method without acceleration, very large run times were required (see Table 1). Here ϵ, η and σ are the controlling parameters described previously [2]. For simplicity, in the present calculations σ was taken to equal η. In order to achieve convergence of the starting digon to the IRC, extremely small

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Table 1
Convergence to the Müller–Brown reaction path without acceleration

ϵ	$\eta = \sigma$	Remark	Run time/s
0.1	0.03	No convergence	
0.1	0.01	No convergence	
0.1	0.003	No convergence	
0.1	0.001	No convergence	
0.1	0.0003	No convergence	
0.1	0.0001		$75673 \approx 21\,h$

Table 2
Acceleration of convergence to the Müller–Brown reaction path using logarithmic transformation

ϵ	$\eta = \sigma$	Remark	Run time/s
0.1	0.1	Diffuse lines	–
0.1	0.03	Diffuse lines	–
0.1	0.01		$2680 \approx 45\,min$
0.1	0.003		$9187 \approx 2.5\,h$

steps had to be chosen, the required run time exceeding 21 h.

When calculating the MB reaction path, the transformations of type $\log_e (U + d)$ and $\sinh^{-1} (U)$ were found to be very effective in accelerating the DDRP procedure. An application of the function $\log_e (U + 160)$ yielded a drastic decrease in run time (see Table 2). The additive constant 160 served to enforce the positivity of the argument of the logarithm. An even better improvement in convergence was achieved by using the function $\sinh^{-1} (U)$ (see Table 3).

The function $\arctan(U)$ could not be applied for the investigated problem because of the difficulty in

Table 3
Acceleration of convergence to the Müller–Brown reaction path using inverse hyperbolic sine transformation

ϵ	$\eta = \sigma$	Remark	Run time/s
0.1	0.3	Dimension overflow	
0.1	0.1	Diffuse lines	
0.1	0.03		$354 \approx 6\,min$
0.1	0.01		$785 \approx 13\,min$
0.1	0.003		$2939 \approx 49\,min$

adjusting correctly the DDRP controlling parameters. Nevertheless, we may have success with this or other functions of the form (1) in accelerating convergences of cases of chemical interest [6].

Supplementary material (tables with further data, evolution curves, etc.) for cases with and without acceleration can be obtained on request from the authors.

Acknowledgement

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