Experiences and Practical Hints on Using the DDRP Method, Illustrated by the Example of the H₂ + H Reaction

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By using the dynamically defined reaction path (DDRP) method and starting from various ionic polyhedral conformational models, the reaction coordinate (RC) of the H₂ + H → H₃⁺ reaction has been calculated. The H₂ + H → H₃⁺ reaction has been calculated. The numerical stability of the method is illustrated by the evolution phases of the reaction path. Techniques and experiences on the parameter choice and effects of the parameter values on the stability and computer time consumption are discussed. © 1993 by John Wiley & Sons, Inc.

INTRODUCTION

For searching ionizing reaction coordinates (IRCs) and locating critical points (CPs) on potential energy surfaces (PESs) of chemical reactions, a new curve variational [so-called dynamically defined reaction path (DDRP)] method1-12 was recently suggested. The key theoretical foundation of the procedure1 requires an analytic coercive function with Morse-type1 CPs. The first numerical illustrations13 were applied to polynomial functions satisfying this criterion. However, the energy functions of atomic configurations are noncoercive and, to our knowledge, almost nothing is known about their analytic properties and precise behaviors up to the second order around the CPs. It can, nevertheless, be expected that the PESs can be approximated uniformly (up to any order) by analytic functions having finitely many CPs of Morse types located arbitrarily close to the real CPs. In this case, the coercivity plays merely a technical role. Such a function can be modified by adding to it an auxiliary function having small values and derivatives on some given domain containing the CPs and tending rapidly to infinity outside this domain. By structural stability,1 steepest descent paths (SDPs) and CPs can be approximated uniformly in this manner. It readily follows that this adjustment can well be simulated by a numerically much simpler method, namely, given a region with piecewise smooth boundary (e.g., a multidimensional ball or a rectangular polytope) containing the CPs, we may project the overflowing phases of the trial curves to the boundary in each step. In chemical practice, where we always know not too large a priori regions outside of which the energy function changes irreversibly little, the problem of coercivity is settled satisfactorily. On the other hand, it can be expected that the condition of analyticity in the theoretical work2 can drastically be weakened. (The proofs may, of course, become essentially even more complicated.) Therefore, we can hope that any of the frequently applied quantum chemical (semienumerical or ab initio) methods coupled with our procedure can be used without further adjustments if we require polygon approximations of the IRCs with too small edges. Due to the large number of such methods for approximating the energy function provide functions that are piecewise analytic. However, we have no practical information about boundaries of such domains of analyticity and we cannot expect a continuous coincidence of the calculated values of two neighboring domains. If the discontinuities are small with respect to the edges of the IRC approximating polygons, satisfactory results can still be expected. One of the main purposes of this article is to show on perhaps the simplest practical case of the collinear H₂ + H → H₃⁺ reaction that the DDRP procedure,16 works in a stable way even with a theoretically badly behaving semienumerical energy function. In a next step, we are going to apply the same technique16,18 to obtain IRCs of various collinear reactions of three atoms (H atoms and halogen atoms) not yet investigated from this point of view. Searching for IRCs of reactions with configuration spaces of higher dimensions requires effective parallelization. From the experiences gained when working on this subject,4 we may conclude that 100-times vectorization can make reactions practically treatable up to 10 atoms. Of course, it is not yet foreseeable whether some adjustment of the numerical procedure for calculating the energy function will or will not be necessary in such complicated cases.

DISCUSSION

Almost all known methods10-14 work principally in the same way, searching for the reaction path (RP) either by walking SDPs in a "gutter" (or "bubbled track")11 from one into another valley through the col or by finding first the saddle point (SP) and then descending from it into the valleys/minima, again by SDPs. Such methods proved to be satisfactory for conventional computers and searching procedures but for present-day computers, that is, large enough and in most cases, assure convergence. Nevertheless, their disadvantages are that they tend to be unstable when following curved and bifurcating paths and they are parallelizable only in the program segments of computational single geometrical values of the energy function. Therefore, they cannot be run effectively on the most modern vector computers. An obvious alternative to such up/downhill methods is searching for RPs "croswise" (transversely) in the gutters. A drop of rain or a ball on the wall of the eaves trough will always find their way into the draining well or sink hole and their motion will be controlled by the slopes of the walls and the bottom of the gutter. In exactly the same way, the virtual motion of a point selected on a PES will be generated by the actual vector field on it. Due to the numerical methods, such approximations for the energy function provide functions that are piecewise analytic. However, we have no practical information about boundaries of such domains of analyticity and we cannot expect a continuous coincidence of the calculated values of two neighboring domains. If the discontinuities are small with respect to the edges of the IRC approximating polygons, satisfactory results can still be expected. One of the main purposes of this article is to show on perhaps the simplest practical case of the collinear H₂ + H → H₃⁺ reaction that the DDRP procedure,16 works in a stable way even with a theoretically badly behaving semienumerical energy function. In a next step, we are going to apply the same technique16,18 to obtain IRCs of various collinear reactions of three atoms (H atoms and halogen atoms) not yet investigated from this point of view. Searching for IRCs of reactions with configuration spaces of higher dimensions requires effective parallelization. From the experiences gained when working on this subject,4 we may conclude that 100-times vectorization can make reactions practically treatable up to 10 atoms. Of course, it is not yet foreseeable whether some adjustment of the numerical procedure for calculating the energy function will or will not be necessary in such complicated cases.

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accidentally multidimensional) edge $P_i$, $P_{i+1}$ will be divided into $n_i = \lfloor \frac{|P_i - P_{i+1}|}{e} \rfloor$ equal parts, resulting in the points

$$P_{ik} = P_i, P_{k+1}, \ldots, P_{k+n_i+1} = P_{i+1}, \quad k = 0, 1, \ldots, n_i$$

of a new approximating polygon. To avoid too large numbers of points, if $|P_i - P_{i+1}| < \varepsilon$ then the vertices $P_{i+1}, P_{i+2}, \ldots$ will be omitted until we get a value $\geq \varepsilon$ for the sum of their consecutive distances. Hence, we get the new points

$$P_{ik} = P_i, P_{k+1}, \ldots, P_{k+n_i} = P_{i+1}$$

with

$$\sum_{i=1}^{n_i} |P_i - P_{i+1}| < \varepsilon < \sum_{i=1}^{n_i} |P_i - P_{i+1}|$$

Thus, by (4) and (5) we obtain the polygon $P_1 = P_{k0}, P_{k1}, \ldots, P_{kn_c} = P^*_c$, satisfying

$$|P_i - P_{i+1}| < \sup_{\delta \in \mathbb{R}^+} |\delta e| = 2\varepsilon$$

which can be used as initial data for a further step. These steps are continued one after the other until achieving convergence. The criteria of convergence are discussed in ref. 2 and can be formulated in terms of the Hausdorff distance of two consecutive approximating polygons.

If we start from a closed polygon, the convergence of the procedure can easily be verified. In this case, the area of the polygon tends to become zero, i.e., the edges of the polygon represented in a plane shrink to a 1-D line.*

To justify the stability of the algorithm, we started from different initial curves constructed of various polygons. The computations were carried out on an IBM-compatible AT 286 PC, equipped with an arithmetic coprocessor 80287 and were designed to supply comparable results by using a fixed set of the parameters $e$, $\eta$, and $\sigma$. The parameters were kept fixed at values $e = 0.3$, $\eta = 0.002$, and $\sigma = 0.0003$ during the whole procedure although the algorithm would have permitted immediate alterations. The choice of parameters was motivated by results of our former calculations on a number of collinear three-atom systems,† where the above values proved to be advantageous and safe. In the following, we illustrate the working of the algorithm on the development of the final RPs when starting from different initial curves. Eleven cases will be discussed and displayed by sets of distinct curves in Figures 1–6 showing the phases of the evolution of curves. The sequences of approximating polygons in the fig-

*For multidimensional cases, the convergence can be established by examining the Hausdorff distances between the successive trial polygons.†

Figure 1. Evolution of an IRC section from a digon.

Figure 2. Evolution of an IRC section from a II-shaped open polygon.

Figure 3. Evolution of an IRC section from a closed hexagon.

Figure 4. Evolution of an IRC section from a M-shaped open polygon.

Figure 5. Evolution of an IRC section from a + shaped open polygon.

Figure 6. Evolution of an IRC section from an X-shaped open polygon.

Figure 7. Complete IRC of the $\text{H}_2 + \text{H}$ reaction as calculated by the DDRP-modified MNDO method.
first bulges outward, giving a concave curve, then it straightens and is becoming stepwise a deeper convex curve while the left leg of the \( \Pi \)-letter shifts parallel with itself, upward and to the right. Then, the bottom section of the left leg first bends inward, similarly finding concavity while the bottom section of the right leg bending also inward and finally meeting with the top section they give the approximate IRC curve (Fig. 2).

**Case 4**

The initial polygon (first curve) had the same shape as in case 3 except that it had been turned upside down and was determined by the points \((0.66, 2.00; 0.66, 0.66; 2.00, 0.66; 2.00, 2.00)\). The starting position was much more advantageous than that in case 3; therefore, the computation time was much shorter. First, the left bottom vertex became more and more rounded while the vertical line from the right top bent toward left by going from concave to convex curve and finally adhering closely to the baseline formed lastly the approximate IRC.

**Case 5**

The initial curve was a closed tetragon (square) determined by the same points as in case 4. As the bottom left vertex moved inward and got rounded, the top right vertex first bumped outward, then going through the stage of a straight line it became hollow, merging finally into the left bottom section to give the approximate IRC.

**Case 6**

Evolution of the IRC from a closed hexagon (vertices at \(0.35, 2.00; 0.20, 0.50; 1.00, 0.36; 2.00, 0.20; 2.00, 1.50; 2.00, 2.00\) can be seen (Fig. 3). This geometric form can be derived from a square whose diagonal two vertices at \(0.35, 0.50; 2.00, 2.00\) have been cut off by two parallel straight lines. In this mutilation, the evolution of the final curve is accelerated compared to that of the original square. Disregarding this, in the course of evolution, the shapes of the set of curves are similar to that of case 5 while the computation time was shorter.

<table>
<thead>
<tr>
<th>Figure</th>
<th>( \ast )</th>
<th>( \Delta )</th>
<th>( \bigcirc )</th>
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**Table 1.** Consecutive evolution curves indicated by \( \ast \) (first), \( \Delta \) (second), \( \bigcirc \) (third), \( \bullet \) (fourth), \( \bigcirc \) (fifth), and \( \bullet \) (sixth).

**Table 2.** Effects of parameter variations on computing times.

<table>
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<th>( \text{Time (s)} )</th>
<th>( \eta )</th>
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<td>6</td>
<td>16.214</td>
<td>34.981</td>
</tr>
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</table>

Table 1: Consecutive evolution curves indicated by \( \ast \) (first), \( \Delta \) (second), \( \bigcirc \) (third), \( \bullet \) (fourth), \( \bigcirc \) (fifth), and \( \bullet \) (sixth).

The second part of our investigations, the shape and location of the initial curve we kept the same for all cases and the value of \( \sigma = 0.01 \) was fixed while the values of the other two parameters, \( \eta \) between \( 0.002 \) and \( 0.1 \) and \( \sigma \) between \( 0.001 \) and \( 0.03 \), were varied. Starting from the chosen polygon (a concave tetragon with vertices at \(0.50, 2.00; 0.50, 0.50; 0.20, 0.50; 1.00, 1.00\)) advantageous to accelerate convergence and in this case the end of the procedure can easily be checked by observing the fusion of the sides of the tetragon into a solid line. For each pair of values of the varied parameters \( \eta \) and \( \sigma \), the new evolution curve was output in every step. In each case, altogether 20 curves (including the initial one) were computed and recorded. The time \( T_{\text{new}} \) needed to reach convergence was generally less than the total computation time \( T_{\text{sum}} \) necessary to determine all 20 curves. The data reflecting the variations of parameters \( \eta \) and \( \sigma \) and the related computation times are displayed in Table 2. It is obvious from these data how important the right choice of parameters is. By enhancing the value of \( \eta \) at fixed values of \( \sigma \), the total computation time will be higher and the differences in the computation times belonging to the smallest and largest values of \( \eta \) will even be drastic. Similarly, at fixed values of \( \sigma \) one can always find an optimal \( \eta \) value by which the computation time needed to reach convergence is the shortest. Further enhancement of \( \eta \) will increase also the value of \( T_{\text{new}} \). Then, the value of \( \eta \) was fixed while enhancing the value of \( \sigma \) from 0.001 to 3.0. The total computation time first reduced rapidly; then, from around \( \sigma = 0.1 \) the gain in time became negligible. In this case, the change in \( T_{\text{new}} \) was the same as that of \( T_{\text{sum}} \), i.e., it reduced to the end. It is not a surprising although inconvenient experience of ours and still useless information for our simultaneous enhancement of \( \eta \) and \( \sigma \) beyond a certain limit may cause numerical problems. This happened in an investigated case when \( \sigma \geq 0.3 \) and \( \eta = 0.05 \). In this range for \( \sigma = 0.3 \) and \( \eta = 0.05 \), the shape curve became diffuse. For \( \sigma = 1.0 \) or \( 3.0 \) and \( \eta = 0.05 \) \( \pm 0.1 \), the procedure became unstable, the points of the curve did not converge to the RP but deviated from it irregularly, the number of points grew rapidly, and finally, after exceeding the allowed dimension (preset entity 200) the program was exited. It is important to emphasize that this kind of instability is not the usual property of the algorithm and normally does not occur but was due to the extremely bad parameter choice. The most advantageous ranges of parameter values were found to be in \([0.01 - 0.1] \) for \( \eta \) and \([0.005 - 0.05] \) for \( \sigma \). Even the minimum computation times \( T_{\text{new}} \) fell into these ranges. It seems that the values of \( \eta \) and \( \sigma \) should be chosen either equal or near each to other so that each of the curves to reach convergence in the shortest possible times. The best parameter choice proved to be \( \sigma = 0.1 \) and \( \eta = 0.05 \) (see Table 2). Worth mentioning is that it generally not practicable to have the shortest computation time because in this case other problems may occur, e.g., for \( \sigma = 0.3 \) and \( \eta = 0.05 \) diffuse lines appeared.

Our results were also compared to those calculated by other methods. The searching procedure built in the MDNO program of the AMMACC 1.1 version gave an solution after an elapsed time of 28.536. The program is called MDNO program (CQCEP 385) and performing the above location of the SP taken from separate calculation, we determined and obtained the same RP as with the use of the DDDP method by starting from the points \((4.0, 1.0) \) and \((1.0, 4.0) \) using a step length of 0.2 A (Fig. 7). The only differences are in the numbers and locations of the point on the final IRC curves. Figures 8 and 9 show the
**SUMMARY**

We have shown that our DDRP algorithm generally behaves in a stable way. By starting from polygons of arbitrary geometric shapes, the IRC and SP of a simple collinear trivalent system can usually be computed. Our experiences on the $H_2 + H$ reaction and other trivalent systems show that the method could be used with the same effectiveness on more complicated chemical reactions. The run-time demand depends on the choice of the initial polygon and the parameters, and in the present form of the program it is higher than that of other searching procedures. However, because of the high parallelizability of our method, the drastic reduction in computation time can be expected in the near future, especially if a program to exploit this advantage and running it on a computer provided with parallel/vector facilities. This will hopefully make our method useful for the theoretical investigations of fundamental reaction kinetic problems.

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*The polygon can be either open or closed, can have any number of vertices, and can be situated almost anywhere in the space, regardless of whether we start searching from, or from anywhere in the room.*

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**References**