
Theoretical and Practical Aspects of the Convergence Properties of the Dynamically Defined Reaction Path Method

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ABSTRACT

In spite of much work on path-following methods, a solid mathematical foundation (especially convergence conditions and their practical measures) are lacking in most cases. In our previous articles the general theory of a new global searching procedure, the dynamically defined reaction path (DDRP) method, its rigorous mathematical formulation, the algorithm, a practical computation program, and some applications to abstract mathematical functions and simple chemical examples have been presented. In this article we give a short theoretical description and some practical criteria and measures for the convergence of the method and illustrate the principles and uses by numerical mathematical and chemical examples. © 1996 by John Wiley & Sons, Inc.

Introduction

For the theoretical investigation of a chemical reaction, it is important to know the potential energy surface (PES) of the given system. Because the determination of even a partial PES requires

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much computer time, one is usually satisfied with the knowledge of the reaction path (RP) and its stationary points. When determining RPs (or intrinsic reaction coordinates, IRCs),¹ the most popular and generally accepted local (or direct) methods²⁻⁶ either follow the steepest descent path in both directions starting from a formerly determined saddle point (SP) toward the minima represented by the reactants and products, or use the

steepest ascent way from the minima toward the SP. In these methods the runtimes are acceptably short and the only problems are the suitable choice of stepsize and the stability of the method. Global (or indirect) methods⁷⁻¹⁰ perform searchings and approach the RP crosswise. A recent and stable global searching procedure is the dynamically defined reaction path (DDRP) method.¹¹ Its rigorous mathematical foundation¹² contains fundamental theoretical information on the convergence properties of the method as well. The algorithm,¹³ a practical computation program,^{14,15} and some applications to abstract mathematical test functions and simple chemical examples¹⁶⁻¹⁸ have been described and a highly efficient acceleration procedure^{17,19} has been suggested. In this article the essence of the theoretical basis and some practical criteria and measures for the convergence of the DDRP method are given and the principles and uses are illustrated by mathematical and chemical examples.

Discussion

Because the exact RP of a chemical reaction is unknown and can only be estimated or guessed by experimental results and/or chemical intuition, the question immediately arises of when the iteration should be terminated (i.e., when the set of successive approximate polygons converges, in a satisfactory way, to the RP). It cannot be told unambiguously whether, in any iteration method, the convergence can surely be accepted under a previously defined limit value. The convergence can be very slow in some phases of the computation, whatever procedure has been applied for the acceleration of convergence. As we have shown in our previous articles,¹⁶⁻¹⁸ the runtimes in the DDRP method depend on the choice of the parameters used: The computation time can be reduced by the strategy of choosing the values of parameters, by selecting a suitable starting polygon, or by taking up points at the start as sparsely as possible. In unfavorable cases, by a suitable transformation of the potential function the computation time can also be reduced drastically.^{17,19} It is obvious that an algorithm is needed by the help of which it can be decided if and when an iteration is to be stopped. In our former calculations this problem did not occur so sharply because both with the

abstract mathematical test functions^{11,13,17,19} and in the chemical systems¹⁶⁻¹⁸ two-variable (two-dimensional, 2D) cases were studied. In these investigations we could start from a closed polygon with an SP inside,[†] and the general applicability and extraordinary stability of the DDRP method have been proved. When progressing in the search, the starting polygon is successively deforming and finely reducing into a curve which fits close to the RP searched for. Consequently, in the 2D case, starting from a closed polygon, the rigorous study of convergence could be avoided. Although this procedure seems to be followable at higher dimensions as well (starting from higher-dimension polygons), the same clearly descriptive representation as in 2D cannot be expected. In the DDRP method we get to the RP searched for through the sequence of the polygons[‡] $C_0, C_1, \dots, C_n, \dots$; therefore, it is suitable to estimate the current distance to the final RP by the reduction rate in the distances between the successive approximate polygons. The first question to answer in relation to this is how this current distance is to be defined. We can choose, for instance, one of the following definitions:

1. Take the distance between the closest points of the polygons C_i and C_{i+1} . This is not the best choice because if, for example, one of the points coincides with either minima then this point will remain invariant in the course of the procedure—that is, the distance chosen in this way will be zero. In this case, if the curve fails to converge to the RP, this fact will not be reflected in the change of this distance. Regarding that the lengths of polygons C_i and C_{i+1} may differ from one another and the numbers of points taken up on them are not necessarily equal, it may be more practical to define the distance, as in the following definition.
2. Determine the maximal bias $d_s(C_i, C_j)$ of the corresponding points with respect to the arc-length proportional parametrization of the polygons C_i, C_j to be compared. This distance concept can well distinguish between the different (consecutive) curves. It follows from the results of ref. 12 that, for analytical

[†]This is not a necessary condition, although it is suitable in the DDRP method.

[‡]Phase or evolution curves.

coercive energy functions,

$$d_s(C_i, C^*) \rightarrow 0 \quad (i \rightarrow \infty) \quad (1)$$

where C^* is some RP between two stationary points whenever the initial curve is piecewise analytic and crosses only finitely many times the boundaries of catchment regions. Since d_s satisfies the triangle inequality, we may examine the convergence of the iterates C_i by studying the distances $d_s(C_i, C_j)$. There is, of course, a naturally arising problem here: Usual numerical representations of curves are given by (finite) sequences of points. Thus some interpolation procedure is necessary to restore complete curves. In most cases simple linear interpolation can be satisfactory. However, in these cases we can only estimate the real d_s distance within some nonvanishing error. A numerical procedure with linear interpolation for determining $d_s(P, Q)$ is described as follows. We are given the representations

$$\begin{aligned} (p_1, p_2, \dots, p_{n+1}) & \quad \text{for } P \\ (q_1, q_2, \dots, q_{m+1}) & \quad \text{for } Q \end{aligned} \quad (2)$$

respectively. First we compute the lengths

$$\begin{aligned} s^* &:= \sum_{i=1}^n \delta_i, & \delta_i &:= \|p_i - p_{i+1}\| \\ t^* &:= \sum_{j=1}^m \varepsilon_j, & \varepsilon_j &:= \|q_j - q_{j+1}\| \end{aligned} \quad (3)$$

of the linearly approximating polygons P' , Q' . For any $\lambda \in [0, 1]$, the respective points of P' and Q' corresponding to the arc-length proportional parameter λ are

$$\begin{aligned} P'(\lambda) &:= p_{N(\lambda)} + \delta_{N(\lambda)}^{-1} \left[s^* \lambda - \sum_{i=0}^{N(\lambda)-1} \delta_i \right] \\ &\quad \times (p_{N(\lambda)+1} - p_{N(\lambda)}), \\ N(\lambda) &:= \min \left\{ k: s^* \lambda < \sum_{i \leq k} \delta_i \right\}, \quad \delta_0 := 0, \\ Q'(\lambda) &:= q_{M(\lambda)} + \varepsilon_{M(\lambda)}^{-1} \left[t^* \lambda - \sum_{j=0}^{M(\lambda)-1} \varepsilon_j \right] \\ &\quad \times (q_{M(\lambda)+1} - q_{M(\lambda)}), \end{aligned} \quad (4)$$

$$M(\lambda) := \min \left\{ l: t^* \lambda < \sum_{j \leq l} \varepsilon_j \right\}, \quad \varepsilon_0 := 0$$

It can be shown by the convexity of the norm that the value $\max_{\lambda} \|P'(\lambda) - Q'(\lambda)\|$ is taken at some vertex of one of the polygons P' or Q' . Thus the linear approximate value of $d_s(P, Q)$ is

$$\begin{aligned} d'_s(P, Q) &:= d_s(P', Q') = \max_{\lambda \in \Lambda} \|P'(\lambda) - Q'(\lambda)\|, \\ \Lambda &:= \left\{ \sum_{i \leq k} \delta_i / s^* : 1 \leq k \leq n \right\} \\ &\quad \cup \left\{ \sum_{j \leq l} \varepsilon_j / t^* : 1 \leq l \leq m \right\} \end{aligned} \quad (5)$$

Alternatively, one can take any L^p distance of the curves. Here

$$\begin{aligned} d^{(L^p)}(P, Q) &:= \left[\int_0^1 \|P(\lambda) - Q(\lambda)\|^p d\lambda \right]^{1/p} \\ &\approx \left[\int_0^1 \|P'(\lambda) - Q'(\lambda)\|^p d\lambda \right]^{1/p} \end{aligned} \quad (6)$$

For practical purposes, linear approximations of the L^1 or L^2 distances come into consideration. They are weaker (more liberal) than the d'_s distance, which is the linear approximation of the L^∞ distance. The calculation of the distances defined in such a manner, by a computational program, is a simple routine task.

3. A less routine task is to take the Hausdorff distance d_H of the curves. Recall¹⁴ that

$$\begin{aligned} d_H(A, B) &:= \max \left\{ \sup_{a \in A} \inf_{b \in B} \|a - b\|, \sup_{b \in B} \inf_{a \in A} \|a - b\| \right\} \end{aligned} \quad (7)$$

This concept gives a faithful description of the family of compact subsets (in particular, rectifiable curves) of the phase space. Recently we have shown²⁰ that, for any continuous initial curve C_0 joining two stationary points of a coercive energy function by continuous gradient, there exists a RP C^H such that

$$d_H(C_i, C^H) \rightarrow 0 \quad (i \rightarrow \infty) \quad (8)$$

Theoretically, it may happen that the curves C_i range more and more in some close neighborhood of C^H ; thus $d_s(C_i, C^H) \rightarrow 0$ if C_0 intersects the boundaries of catchment regions infinitely many times. Following closely the direct definition, we have already published a subroutine calculating linearly approximated Hausdorff distances¹⁴; however, its algorithm works very slowly. Because the DDRP program produces the sequences of RP-approximating polygons from a starting polygon C_0 , it is practical to employ, after each step, the distances between the last polygon and the next to last polygon, whichever distance definition was used. On the basis of the distance value last determined, we can decide to continue or stop the iteration.

Examples

The theory discussed earlier is illustrated on three test functions (i.e., Müller-Brown,⁵ MB; Liotard,²¹ L; and Stachó and Bán,^{11,13} SB) and two simple molecular systems (HHH and HHF). Note that for two of the three mathematical functions (MB and L), open polygons (digon and trigon, vertices at $-2.00, 2.00; 2.00, -2.00$ and $0.00, 7.00; 10.00, 7.00; 10.00, 0.00$, respectively), were used. For the third one (SB), a closed polygon (hexagon,

vertices at $-0.50, 0.50; -0.50, -0.50; 0.00, -1.00; 0.50, -0.50; 0.50, 0.50; 0.00, 1.00$) was used as 0th approximation. For the two chemical species, the procedure was started from the same closed tetragon (see solid curves in Figs. 1 and 2; vertices at $0.50, 2.00; 0.50, 0.50; 2.00, 0.50; 1.00, 1.00$). In addition to the starting polygon and the last approximation to the RP (i.e., the final polygon regarded as the one having been converged; see dotted curves in Figs. 1 and 2), several intermediate evolution/phase curves have been calculated for the cases examined. Nevertheless, for technical reasons, only one intermediate phase curve for each example has been displayed in Figures 1 and 2 (dashed curves). Otherwise the presentations of further phase curves would make the figures confused. However, the phase curves in all iteration steps are available as supplementary materials. The empty and full circles on the curves in Figures 1 and 2 mark pseudo and true SPs, respectively. One can see that the SPs on the approximating (phase) curves (solid and dashed curves) move toward one another as the iterations proceed and close inside the true SPs on the converged curves (dotted curves). The variations in different numerical values characterizing the consecutive phases of evolutions are listed in Table I-V. In Columns 1 and 2, the serial numbers of the polygons to be compared are tabulated. The serial number of the starting polygon (0th approximation) has been chosen zero; therefore, the serial number of the

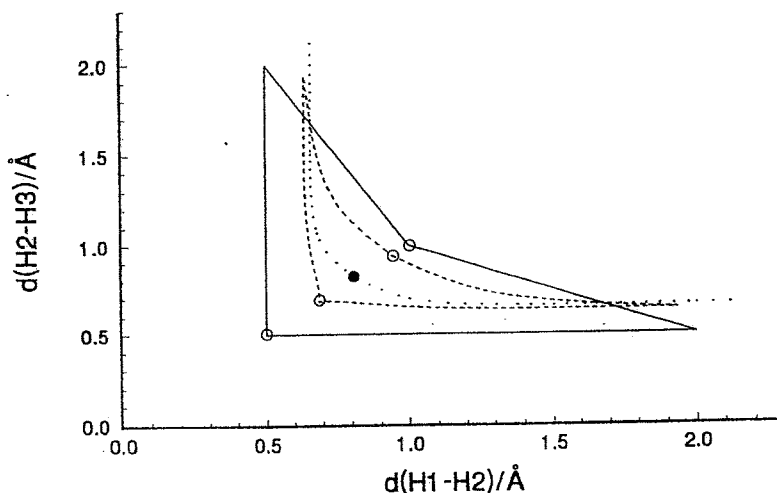


FIGURE 1. Starting polygon (solid lines) and phase curves for the HHH reaction. Intermediate phase curves and the final / converged reaction path are represented by dashed and dotted curves, respectively. Empty / full circle(s) on the curves denote pseudo / true saddle point(s), respectively.

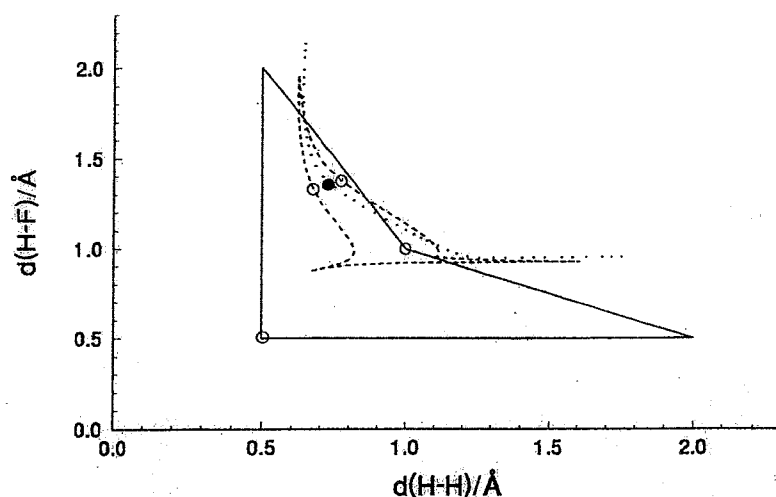


FIGURE 2. Starting polygon (solid lines) and phase curves for the HHH reaction. Intermediate phase curves (dashed curves) and the (final/converged) reaction path (dotted curve) are displayed. Empty/full circle(s) on the curves denote pseudo/true saddle point(s), respectively.

polygon obtained in the i th step can be denoted simply by i . In Column 3 the distances of two consecutive polygons are determined as described in definition 2; in Column 4 the distances of the

same two polygons are expressed in percentages (here the difference between the 0th and first approximations is regarded as 100%). In Column 5 the changes in the number of points reflect turning

TABLE I.
Characteristic Data for the HHH System.

Serial Number of the i th	$(i + 1)$ th	Distances between the i th and $(i + 1)$ th Polygons		Differences between the	
		in Å	in %	in Number of Points	in Total Length
0	1	.320996	100.00	102	-.606140
1	2	.125138	38.98	6	-.049481
2	3	.056828	17.70	6	.023323
3	4	.030772	9.59	7	.032278
4	5	.018537	5.77	0	.032669
5	6	.011829	3.69	0	.029018
6	7	.009078	2.83	4	.026364
7	8	.007538	2.35	0	.024617
8	9	.006659	2.07	0	.023481
9	10	.006148	1.92	4	.022777
10	11	.005819	1.81	2	.022286
11	12	.005622	1.75	2	.021901
12	13	.005474	1.71	4	.021589
13	14	.005350	1.67	0	.021278
14	15	.005275	1.64	0	.021012
15	16	.005201	1.62	-1	.020763
16	17	.005125	1.60	-2	.020489
17	18	.005072	1.58	4	.020256
18	19	.005012	1.56	1	.020040

TABLE II.
Characteristic Data for the HHH System.

Serial Number of the		Distances between the		Differences between the	
<i>i</i> th	(<i>i</i> + 1)th	<i>i</i> th and (<i>i</i> + 1)th Polygons			
Polygons		in Å	in %	in Number of Points	in Total Length
0	1	.605395	100.00		
1	2	.242989	40.14	174	-1.422003
2	3	.175763	29.03	-10	-.094736
3	4	.131618	21.74	2	.013343
4	5	.107222	17.71	4	.009213
5	6	.086548	14.30	0	-.007551
6	7	.085434	14.11	3	.019643
7	8	.070248	11.60	2	.003288
8	9	.061237	10.12	1	.026114
9	10	.055330	9.14	2	.034530
10	11	.050696	8.37	-1	.035547
11	12	.046487	7.68	1	.035884
12	13	.043091	7.12	0	.036518
13	14	.050304	8.31	1	.036392
14	15	.036448	6.02	0	.009787
				5	.036894

from the *i*th polygon to the (*i* + 1)th one (the negative sign means reduction in number of points). In Column 6 the changes in the total lengths of the polygons in the course of the same transition are shown. It can be seen from the tables that the decrease in distances between consecutive approximating polygons will stop or slow down considerably as convergence proceeds. Thus, depending on the choice of parameter values, a turning point can be defined beyond which there is no reason for continuing the iteration. At this point we can either stop the iteration or, by decreasing the values of parameters, we can further improve the last polygon approximating the RP. In the beginning, the changes in numbers of points sitting in the vertices of the polygons depend mainly on the form of the starting polygon. The same is true for the total lengths of the polygons. As convergence proceeds, the monotonous change will be followed by oscillation. In cases of molecular systems (Tables I and II), the minima to be joined by the IRC are in infinity. Therefore, the lengths of the approximating polygons converge slowly to infinity. However, we may cut off the polygon pieces lying outside a given *n*-dimensional ball; thus the remaining pieces converge with respect to the distances determined (no monotonicity can, of course, be expected). However, even in such cases the number of vertices of the polygon may be either

increasing or decreasing. This follows naturally from the homogenization procedure of the DDRP method. Table I gives information on the polygons approximating the IRC of the HHH system. In the first row, the starting polygon (Column 1) and the first polygon obtained in the first iteration step (Column 2) are compared. According to the data in Column 3, the distance between the two polygons is ca. 0.32 Å. This value will be regarded as a basis for comparisons and is denoted by 100% (Column 4). The first (serial number 1) polygon contains 102 vertices more than the 0th one, and in the same time the total length is reduced by 0.61 Å. From the second row on, the numbers of points and the differences in total lengths, respectively, of the *i*th and (*i* + 1)th polygons are decreasing drastically. In the meantime, the distance values between the same polygons are reducing first rapidly and then at a slackening pace. In the ninth iteration step, the starting closed tetragon contracts into a solid line. At this point we can declare that the approximating polygon has been converged to the IRC. The distances between the eighth and ninth, and the ninth and tenth polygons are 2.07 and 1.92%, respectively, of the starting (100%) value (see Column 4). The comparable value for the eighteenth and nineteenth polygons is only 1.56%, so the reduction is not significant. Therefore, the procedure, even by our distance concept, can be re-

TABLE III.
Characteristic Data for the Müller-Brown Function.

Serial Number of the		Distances between the		Differences between the	
<i>i</i> th	(<i>i</i> + 1)th	<i>i</i> th and (<i>i</i> + 1)th Polygons			
Polygons		in Å	in %	in Number of Points	in Total Length
0	1	1.891465	100.00	55	-1.558010
1	2	.472134	24.96	4	-.156841
2	3	.259457	13.72	-5	-.060798
3	4	.121162	6.41	6	.202744
4	5	.038774	2.05	-1	-.019311
5	6	.072093	3.81	-2	.092872
6	7	.065534	3.46	-1	-.096900
7	8	.057400	3.03	6	.068652
8	9	.030350	1.60	-5	-.042607
9	10	.040220	2.13	3	.032262
10	11	.034753	1.84	-3	-.053089
11	12	.032594	1.72	0	.018808
12	13	.048837	2.58	3	-.073236
13	14	.031701	1.68	-2	.021637
14	15	.029215	1.54	-1	-.042597
15	16	.026995	1.43	-1	.013200
16	17	.039535	2.09	0	-.061043
17	18	.020909	1.11	0	-.001636
18	19	.029806	1.58	-2	-.044063
19	20	.026590	1.41	0	.020597
20	21	.033118	1.75	-1	-.047812
21	22	.024482	1.29	2	.014563
22	23	.020394	1.08	0	-.001694
23	24	.021127	1.12	2	-.011490
24	25	.051325	2.71	-3	-.075596
25	26	.026328	1.39	0	.004743
26	27	.059457	3.14	1	-.084240
27	28	.041492	2.19	-4	-.059752
28	29	.053227	2.81	0	-.000360
29	30	.111473	5.89	-1	-.154406
30	31	.366784	19.39	-2	-.317566
31	32	.204493	10.81	-3	-.185505
32	33	.170671	9.02	-5	-.192229
33	34	.088157	4.66	-1	-.048216
34	35	.052104	2.75	1	-.028165
35	36	.073726	3.90	-1	-.075572
36	37	.016306	.86	-2	.016898
37	38	.009693	.51	-1	.009379
38	39	.007349	.39	3	.003055
39	40	.004050	.21	-1	.002542
40	41	.002634	.14	2	.002124
41	42	.003131	.17	-2	.000991

garded as the one converged. The HHF system in the eighth iteration step (Table II), the MB function (Table III) in the forty-second step, the L function (Table IV) in the thirty-first step, and the SB function (Table V) in the twentieth step have been

converged. For technical reasons, we have to disregard printing out complete tables for the test functions. The interpretations of Tables II-V can be carried out as for the HHH system. By using MNDO-level energy calculations, the SPs for the

TABLE IV.
Characteristic Data for the Liotard Function.

Serial Number of the		Distances between the		Differences between the	
<i>i</i> th	(<i>i</i> + 1)th	<i>i</i> th and (<i>i</i> + 1)th Polygons			
Polygons		in Å	in %	in Number of Points	in Total Length
0	1	1.418190	100.00	168	-2.046295
1	2	.458562	32.33	47	-.602822
2	3	.316453	22.31	-7	-.418517
3	4	.231913	16.35	-13	-.278215
4	5	.176638	12.46	-1	-.213972
5	6	.138186	9.74	3	-.200003
6	7	.110293	7.78	-5	-.105056
7	8	.089809	6.33	-8	-.077098
8	9	.074709	5.27	3	-.062543
9	10	.063412	4.47	3	-.052721
10	11	.054008	3.81	-4	-.047370
11	12	.046578	3.28	1	-.036042
12	13	.040130	2.83	-7	-.031441
13	14	.034762	2.45	7	-.025361
14	15	.049208	3.47	-4	-.073492
15	16	.032072	2.26	3	-.050104
16	17	.023680	1.67	-7	-.002172
17	18	.021277	1.50	-6	.003581
18	19	.017603	1.24	12	-.007031
19	20	.041338	2.91	0	-.073736
20	21	.015597	1.10	-5	.013569
21	22	.013907	.98	-4	.014010
22	23	.039167	2.76	-2	-.062309
23	24	.012082	.85	11	.012588
24	25	.010991	.78	0	.010008
25	26	.010386	.73	-6	.018165
26	27	.007447	.53	-8	.009306
27	28	.007329	.52	6	.012604
28	29	.008804	.62	0	.007533
29	30	.005314	.37	9	.008038
30	31	.005764	.41	-8	.001910

HHH and HHF reactions were found to be at 0.82/0.82 Å and 0.731/1.365 Å, respectively (cf. Figs. 1 and 2). We are also planning future path followings by the DDRP method coupled with *ab initio* energy calculations, and comparisons of results with those of local and (other than ours) global methods.

Supplementary Material

Supplementary illustration material (evolution curves, complete tables, etc.) for the examples used

in the text can be obtained on request from the authors. The FORTRAN code for the algorithm used is to be distributed by QCPE.¹⁵

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TABLE V.
Characteristic Data for the Stachó-Bán Function.

Serial Number of the		Distances between the		Differences between the	
<i>i</i> th	(<i>i</i> + 1)th	<i>i</i> th and (<i>i</i> + 1)th Polygons			
Polygons		in Å	in %	in Number of Points	in Total Length
0	1	.719158	100.00	46	4.682285
1	2	.099256	13.80	56	.406288
2	3	.066569	9.26	16	.248203
3	4	.049238	6.85	0	.135945
4	5	.037971	5.28	12	.121412
5	6	.027816	3.87	-4	.090535
6	7	.024393	3.39	4	.062133
7	8	.023000	3.20	-4	.063804
8	9	.020930	2.91	8	.056888
9	10	.015047	2.09	-4	.045011
10	11	.015603	2.17	4	.036818
11	12	.015404	2.14	-4	.027218
12	13	.011841	1.65	0	.029856
13	14	.015365	2.14	0	.022577
14	15	.015539	2.16	-4	.029529
15	16	.011323	1.57	8	.035338
16	17	.010003	1.39	-4	.009172
17	18	.011168	1.55	4	.020604
18	19	.009226	1.28	0	.012350
19	20	.006311	.88	0	.021590

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