About nonrandom character of effective main quantum numbers of hydrogen-like atoms and ions coincidence with common fractions set

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Abstract

Recently opened experimental regularity typical for hydrogen-like atoms and ions (having only one outer shell electron) was presented in several papers, for example [1] and [2].

Chief matter of the opening consists in the fact that effective main quantum numbers of outer electron, i.e. in consideration of quantum defect (Rydberg correction), along with integers can be expressed in common fractions, having substantial constraint on denominator number.

Sensational results of the study caused quite expected alert reaction and even criticism of many readers, because it affects basic foundation of modern physics – atom theory.

Main objection of opponents can be reduced to the assertion that cited facts can be explained with series of random coincidences.

So it was exercised supplementary mathematical treatment of data array of experimental characteristics not only of atoms and ions in ground state, but also of hydrogen-like atoms in excited states.

This statistical treatment completely confirms the nonrandom character of discovered experimental law, and is subject of this paper.

1. Preliminary remarks

Deviations and even exceptions to the rule can be observed in experimental regularities for most different reasons.

In experimental regularity under consideration the deviations are caused not only by measurement errors of atoms and ions characteristics, but also by features of electron interaction with an atomic core having complex structure, including atomic nucleus and interior electron shells. The restriction on denominator number of common fractions should be optimal, as it depends on two opposite factors. On the one hand, the increase of this limiting value results in augmentation of fractions set, therefore should raise precision and quantity of coincidences of common fractions with quantum numbers. And on the other hand, such expansion of set of numbers results in shortening of distance between values of fractions, therefore it becomes comparable with size of error of experimental values of quantum numbers.

Thus, the mathematical (statistical) processing is also important for validation of restriction on denominator number of common fractions set.

Let's remind, that main quantum number *n* is determined immediately from the formula for electron energy in hydrogen atom [3]

$$E = -\frac{me^4}{2\hbar^2} \frac{1}{n^2}.$$
 (1)

The actual (effective) values n^* of hydrogen-like atoms proceeding from (1) are expressed in terms of ionization potentials:

$$n^* = \left(\frac{13,6}{\varphi_i}\right)^{1/2}.$$
 (2)

Here φ_i - ionization potential of atom,

13,6 eV - ionization potential of hydrogen atom.

In general case of a hydrogen-like ion with core charge *ze* formula (2) takes the form:

$$n^* = \left(\frac{13.6z^2}{\varphi_i}\right)^{1/2}.$$
 (3)

At calculation of effective main quantum numbers of electrons in excited states the levels of energy should be count not off the lowermost level corresponding to ionization energy, as it is used in Grotrian diagrams, but off a "zero" energy level (at infinite distance from atom).

Let's also note that at rising of numerator of a common fraction there is a periodic rise of its integer part by unit, and the fractional parts of numbers are circulating. Therefore by comparison of set of common fractions to experimental values of quantum numbers for simplification of the analysis the integer parts of numbers are omitted.

Thus, these two compared to each other sets of numbers locate on a segment between zero and unity.

The purpose of the analysis is to fix the fact of presence (or absence) of interrelation of common fractions set and array of experimental values of effective main quantum numbers of hydrogen-like atoms and ions.

2. Method of statistical analysis

Let's imagine, that on the number axis values (fractional parts) both of common fractions and of experimental quantities of main quantum numbers of energy states of atoms and ions are marked.

In fig. 1 main quantum numbers are shown by round markers, the common fractions are tagged by triangular markers and to simplify record are marked with numerals 1, 2 and 3.



Fig. 1. On the number axis common fractions are tagged by triangular markers (and are marked by numerals 1, 2 and 3), and effective main quantum numbers - by round markers.

Accordingly values of these common fractions are denoted as

$$n_1, n_2, n_3, \qquad \left(n = \frac{N_1}{N_2}\right).$$
 (4)

Here N_1 and N_2 - small integers.

Values of effective main quantum numbers n^* we shall subscript by numerals of the proximate common fraction: n^*_1 , n^*_2 , n^*_3 .

The difference between effective main quantum number and the proximate common fraction can be both positive and negative.

For example, shown in fig. 1 difference Δ with subscripts 2 and 3 are negative, and with subscript 1 - positive

$$\Delta_1 = n_1^* - n_1, \qquad \Delta_2 = n_2^* - n_2, \qquad \Delta_3 = n_3^* - n_3.$$
(5)

Difference between adjacent common fractions is designated as *a*.

Value Δ by definition is less than a/2.

Then, the segment a/2 was divided into two equal parts a/4, so the value of a main quantum number with some probability should hit either one, or other of these segments a/4.

These probabilities detecting is our task.

If to assume, that the array of experimental values of main quantum numbers and common fractions set are unrelated with one another, so the hits of round markers in limits of both segments a/4 will have equal probability.

If experimental values of main quantum number "tend" to appropriate common fractions, then round markers should closer hit the segment a/4, which is nearer to a triangular marker.

Mathematically it can be formulated in following way.

Let's determine the ratio of two segments (sign of δ coincides with the sigh of Δ)

$$\delta = \frac{\Delta}{(a/2)} = \frac{2\Delta}{a}.$$
(6)

If $|\delta| < 0,5$, than the experimental value n^* hits segment a/4, which is closer to a common fraction; if $|\delta| > 0,5$, than quantum number n^* hits segment a/4, which, on the contrary, is closer to middle between adjacent common fractions.

Important is not only ratio of hits numbers of values n^* on this two segments a /4, but also the shape of δ distribution.

3. Results of statistical analysis

At the first stage we shall analyze the experimental data of atoms and ions, which were considered in paper [2]. There were examined characteristics of 37 atoms and ions [4], and the set of common fractions had constraint on denominator number as rather small integer - 13.

The set of common fractions is convenient to represent as the table, where in each column there are values of fractions having only one concrete denominator number (from 2 up to 13).

Table 1

2	3	4	5	6	7	8	9	10	11	12	13
0	0	0	0	0	0	0	0	0	0	0	0
0,5	0,333333	0,25	0,2	0,166667	0,142857	0,125	0,111111	0,1	0,090909	0,083333	0,076923
1	0,666667	0,5	0,4	0,333333	0,285714	0,25	0,222222	0,2	0,181818	0,166667	0,153846
	1	0,75	0,6	0,5	0,428571	0,375	0,333333	0,3	0,272727	0,25	0,230769
		1	0,8	0,666667	0,571429	0,5	0,444444	0,4	0,363636	0,333333	0,307692
			1	0,833333	0,714286	0,625	0,555556	0,5	0,454545	0,416667	0,384615
				1	0,857143	0,75	0,666667	0,6	0,545455	0,5	0,461538
					1	0,875	0,777778	0,7	0,636364	0,583333	0,538462
						1	0,888889	0,8	0,727273	0,666667	0,615385
							1	0,9	0,818182	0,75	0,692308
								1	0,909091	0,833333	0,769231
									1	0,916667	0,846154
										1	0,923077
											1

Values of common fractions $n=N_1/N_2$ in limits $0 \le n \le 1$, when $N_2 \le 13$.

The values of fractions, iterating in different table columns, were omitted in process of analysis.

The experimental data were got from [2] and are represented in the following tables.

In the table 2 are given characteristics of nonexcited states of a sole outer electron of atoms and proximate to n^* common fractions.

Table 2

Atom	Li	Na	K	Cs	Rb	Ag	Pt	Nb	Fr
$arphi_{i}$, eV	5,39	5,138	4,339	3,893	4,176	7,574	8,96	6,88	3,98
n*	1,588	1,627	1,770	1,869	1,805	1,340	1,232	1,406	1,849
$n = N_1/N_2$	19/12	13/8	23/13	15/8	9/5	4/3	16/13	7/5	24/13
	(1,583)	(1,625)	(1,769)	(1,875)	(1,80)	(1,333)	(1,231)	(1,40)	(1,846)

Similar characteristics of hydrogen-like ions with a core charge equal to two and three elementary charges (z=2, z=3), calculated using formula (3), are represented in tables 3 and 4.

Table 3

lon (z=2)	Be⁺	Mg^+	Ca⁺	Sr⁺	Ba⁺	Cd^+	Ra⁺	Fe⁺	La⁺
$oldsymbol{arphi}_{i}$, eV	18,21	15,03	11,87	11,026	10	16,904	10,144	16,18	11,43
n*	1,728	1,902	2,141	2,221	2,332	1,794	2,316	1,834	2,182
$n = N_1/N_2$	19/11	19/10	15/7	20/9	7/3	9/5	30/13	11/6	24/11
	(1,727)	(1,9)	(2,143)	2,222	(2,333)	(1,8)	(2,308)	(1,833)	(2,182)

Table 4

lon (z=3)	B ⁺⁺	Al ⁺⁺	Sc ⁺⁺	Y++	In ⁺⁺
$arphi_{i}$, eV	37,92	28,44	24,75	20,5	28
n*	1,797	2,075	2,224	2,444	2,091
p = N / N	9/5	27/13	20/9	22/9	23/11
$11 - 1N_1/1N_2$	(1,8)	(2,077)	(2,222)	(2,444)	(2,091)

Some other hydrogen-like ions, including ions with high degree of ionization (table 5, 6), were considered too.

Table 5

lon	Si ⁺⁺⁺	P****	S*****	CI+++++++	J ⁺⁺⁺⁺⁺⁺	Ar+++++++
Z	4	5	6	7	7	8
φ_{i} , eV	45,13	65,01	88	114,2	104	143,4
n*	2,196	2,287	2,359	2,416	2,531	2,464
$p = N_{\rm c}/N_{\rm c}$	11/5	16/7	26/11	29/12	33/13	32/13
11 - 101/102	(2,2)	(2,286)	(2,364)	2,417	(2,538)	(2,462)

Table 6

lon	Hg+	Sn ***	Pb ⁺⁺⁺	Sb ****	Bi++++	Te *****	Po*****	Xe *******
Z	2	4	4	5	5	6	6	8
φ_{i} , eV	18,751	46,4	39	63,8	56	83	73	126
n*	1,703	2,166	2,362	2,308	2,464	2,429	2,59	2,628
$n = N_1/N_2$	17/10	13/6	26/11	30/13	32/13	17/7	31/12	21/8
	(1,7)	(2,167)	(2,364)	(2,308)	(2,462)	(2,429)	(2,583)	(2,625)

Represented in these tables characteristics (37 atoms and ions) were used in formulas (5) and (6) evaluations.

As it was already noted, the integer parts of numbers were omitted.

For the convenience of analysis, values of common fractions (triangular markers) and actual effective main quantum numbers (round markers) were sorted in ascending order, as it is shown in fig. 2. Here on the horizontal datum are conditional sequence numbers, and on vertical - increasing values of common fractions and quantum numbers forming curves with markers.

Types of markers used in fig. 2 correspond to those indicated above (pt. 2) while deducing formulas (5) and (6).

It is easy to ascertain that visual detection of concurrences of these sets numbers (markers on curves in fig. 2), and quantitative assessment of these sets coincidence cause certain difficulties.

Naturally therefore statistical analysis specifically was executed.

The formulas evaluation and construction of graphs are quite simple and were made in the usual program Microsoft Office Excel.

In fig. 3 the computing results of δ are shown.

Visually results of the analysis are represented in fig. 4 in the form of distribution diagram δ (with an interval 0,1).

The diagram shows that the number of hits of experimental values n^* on segments a /4 nearest to common fractions ($|\delta| < 0,5$) is 27 and makes 73% of total number of experimental values (37).

Moreover, the shape of distribution has clearly defined maximum in the range $0 < \delta < 0.1$, that is, near the diagram centre.



Fig. 2. The values of common fractions (triangular markers) and effective main quantum numbers (round markers), sorted in ascending order, are represented as two curves. On the horizontal datum are conditional sequence numbers, and on vertical - increasing values of common fractions and quantum numbers forming curves with markers



Fig. 3. The diagram including 37 values of δ ,



Fig. 4. The distribution diagram δ (with an interval 0,1).

Thus, taking into account the results of the first stage of analysis, it is possible with certainty to state that the discovered experimental regularity proves to be true and has nonrandom character.

At the second stage we shall carry out the analysis of characteristics of excited states of hydrogen-like atoms.

The excited states of atoms are characterized by smaller binding energy of outer electron and its greater remoteness from the atomic core.

Energy-level density is accordingly heightened and the energy level spacing diminished.

Therefore it has appeared rational to expand the set of common fractions, correlated with effective main quantum numbers of excited states of hydrogen-like atoms n^* .

The restriction on denominator was augmented double the number (from 13 up to 26), that has increased the set of common fractions almost quadruple.

The increased set of common fractions includes smaller set, as actually formation of increased set of fractions comes to addition of the array of numbers represented in the table 7 to the right side of the table 1 following the same rule.

The experimental data of excited states of atoms with only one outer electron were taken from Grotrian diagrams [5].

In tables 8 - 9 the characteristics of excited states of argentum (ionization potential 7,574 eV), rubidium (ionization potential 4,176 eV), lithium (ionization potential 5,392 eV), cesium (ionization potential 3,893 eV), potassium (ionization potential 4,339 eV), sodium (ionization potential 5,138 eV) are given.

In Grotrian diagrams energy levels W are count off from the lowermost value, that is, from ionization energy. Therefore, for calculations it was necessary to change energy reference point.

Accordingly energy E of excited states in tables 8 - 9 is given relative to defined zero energy at infinite separation from atom.

The energy measure is given in electron-volts.

As it was at the first stage of analysis iterating fractions values in the table 7 hereinafter were omitted.

As we noted before, increasing of common fraction numerator results in periodic rise of the integer part of number by unity, and the fractional part is repetitive. Therefore matching of common fractions set and array of experimental values of effective main quantum numbers should be oriented only to fractional parts of numbers.

Table 7

14	15	16	17	18	19	20	21	22	23	24	25	26
0	0	0	0	0	0	0	0	0	0	0	0	0
0,071429	0,066667	0,0625	0,058824	0,055556	0,052632	0,05	0,047619	0,045455	0,043478	0,041667	0,04	0,038462
0,142857	0,133333	0,125	0,117647	0,111111	0,105263	0,1	0,095238	0,090909	0,086957	0,083333	0,08	0,076923
0,214286	0,2	0,1875	0,176471	0,166667	0,157895	0,15	0,142857	0,136364	0,130435	0,125	0,12	0,115385
0,285714	0,266667	0,25	0,235294	0,222222	0,210526	0,2	0,190476	0,181818	0,173913	0,166667	0,16	0,153846
0,357143	0,333333	0,3125	0,294118	0,277778	0,263158	0,25	0,238095	0,227273	0,217391	0,208333	0,2	0,192308
0,428571	0,4	0,375	0,352941	0,333333	0,315789	0,3	0,285714	0,272727	0,26087	0,25	0,24	0,230769
0,5	0,466667	0,4375	0,411765	0,388889	0,368421	0,35	0,333333	0,318182	0,304348	0,291667	0,28	0,269231
0,571429	0,533333	0,5	0,470588	0,444444	0,421053	0,4	0,380952	0,363636	0,347826	0,333333	0,32	0,307692
0,642857	0,6	0,5625	0,529412	0,5	0,473684	0,45	0,428571	0,409091	0,391304	0,375	0,36	0,346154
0,714286	0,666667	0,625	0,588235	0,555556	0,526316	0,5	0,47619	0,454545	0,434783	0,416667	0,4	0,384615
0,785714	0,733333	0,6875	0,647059	0,611111	0,578947	0,55	0,52381	0,5	0,478261	0,458333	0,44	0,423077
0,857143	0,8	0,75	0,705882	0,666667	0,631579	0,6	0,571429	0,545455	0,521739	0,5	0,48	0,461538
0,928571	0,866667	0,8125	0,764706	0,722222	0,684211	0,65	0,619048	0,590909	0,565217	0,541667	0,52	0,5
1	0,933333	0,875	0,823529	0,777778	0,736842	0,7	0,666667	0,636364	0,608696	0,583333	0,56	0,538462
	1	0,9375	0,882353	0,833333	0,789474	0,75	0,714286	0,681818	0,652174	0,625	0,6	0,576923
		1	0,941176	0,888889	0,842105	0,8	0,761905	0,727273	0,695652	0,666667	0,64	0,615385
			1	0,944444	0,894737	0,85	0,809524	0,772727	0,73913	0,708333	0,68	0,653846
				1	0,947368	0,9	0,857143	0,818182	0,782609	0,75	0,72	0,692308
					1	0,95	0,904762	0,863636	0,826087	0,791667	0,76	0,730769
						1	0,952381	0,909091	0,869565	0,833333	0,8	0,769231
							1	0,954545	0,913043	0,875	0,84	0,807692
								1	0,956522	0,916667	0,88	0,846154
									1	0,958333	0,92	0,884615
										1	0,96	0,923077
											1	0,961538
												1

Thus, the integer parts of specified numbers at comparison are not taken into consideration.

Besides for the analysis were taken only the numbers in an interval 0,45 - 0,93 to eliminate segments adjacent the integers, where density of energy levels is exceedingly high (i.e. segments nearby the integer values n^*). The analysis of these excluded segments should be carried out separately, using even more extended set of common fractions.

So, in the indicated interval there are 55 excited states characteristics of atoms taken for analysis from the tables 8 - 9.

Table 8

Argentum				Rubidium		Lithium			
W, eV	E, <i>eV</i>	n*	W, eV	E, <i>eV</i>	n*	W, eV	E, <i>eV</i>	n*	
3,664	3,91	1,86501	1,56	2,616	2,280083	1,848	3,544	1,958947	
3,75	3,824	1,885865	1,589	2,587	2,292827	3,373	2,019	2,595382	
3,778	3,796	1,892807	2,4	1,776	2,767247	3,834	1,558	2,954512	
4,304	3,27	2,039368	2,496	1,68	2,845213	3,879	1,513	2,998127	
5,276	2,298	2,432733	2,94	1,236	3,317113	4,341	1,051	3,597229	
5,988	1,586	2,928315	2,95	1,226	3,330613	4,522	0,87	3,953756	
6,013	1,561	2,951671	3,186	0,99	3,706396	4,541	0,851	3,997649	
6,044	1,53	2,981424	3,187	0,989	3,70827	4,542	0,85	4	
6,046	1,528	2,983375	3,262	0,914	3,857415	4,749	0,643	4,599006	
6,433	1,141	3,452444	3,322	0,854	3,990621	4,837	0,555	4,950202	
6,7	0,874	3,944698	3,451	0,725	4,331122	4,847	0,545	4,995411	
6,71	0,864	3,96746	3,455	0,721	4,34312	4,848	0,544	5	
6,72	0,854	3,990621	3,557	0,619	4,687315	4,958	0,434	5,597893	
6,721	0,853	3,99296	3,601	0,575	4,86335	5,008	0,384	5,95119	
6,722	0,852	3,995302	3,699	0,477	5,339619	5,014	0,378	5,998236	
6,891	0,683	4,462303	3,701	0,475	5,350848	5,079	0,313	6,591698	
7,02	0,554	4,954668	3,754	0,422	5,676926	5,11	0,282	6,944563	
7,025	0,549	4,977179	3,761	0,415	5,724603	5,114	0,278	6,994345	
7,029	0,545	4,995411	3,797	0,379	5,990318	5,156	0,236	7,591253	
7,03	0,544	5	3,838	0,338	6,343239				
7,031	0,543	5,004602	3,84	0,336	6,36209				
7,12	0,454	5,473203	3,871	0,305	6,677587				
7,154	0,42	5,690426	3,888	0,288	6,871843				
7,197	0,377	6,006186	3,898	0,278	6,994345				
7,198	0,376	6,014168							

The results of calculation δ are represented in fig. 5.

More clearly it is visually illustrated in fig. 6 representing the distribution diagram δ (with an interval 0,1).

The diagram shows that the number of hits of experimental values n^* on segments *a* /4 adjacent to common fractions ($|\delta| < 0,5$) is equal 42 and makes 76,4 % from total amount (55) of experimental values.

Besides the shape of distribution δ , as well as it was at the first analysis stage, has the obviously expressed maximum in limits -0,1 < δ < 0,1, that is, at the centre of diagram.

Therefore, the results of the second analysis stage prove even more precise concurrence of compared number sets.

	Caesium			Potassium		Sodium			
W, eV	E, <i>eV</i>	n*	W, eV	E, <i>eV</i>	n*	W, eV	E, <i>eV</i>	n*	
1,386	2,507	2,329122	1,61	2,729	2,232378	2,102	3,036	2,116501	
1,455	2,438	2,361852	1,617	2,722	2,235246	2,104	3,034	2,117199	
1,798	2,095	2,547871	2,607	1,732	2,802177	3,191	1,947	2,642935	
1,81	2,083	2,5552	2,67	1,669	2,854574	3,617	1,521	2,990232	
2,298	1,595	2,920042	3,063	1,276	3,264706	3,753	1,385	3,133607	
2,699	1,194	3,37495	3,065	1,274	3,267268	4,116	1,022	3,647909	
2,721	1,172	3,406478	3,397	0,942	3,799654	4,284	0,854	3,990621	
2,801	1,092	3,529053	3,403	0,936	3,811812	4,288	0,85	4	
2,806	1,087	3,53716	3,487	0,852	3,995302	4,344	0,794	4,138655	
3,015	0,878	3,935702	3,595	0,744	4,275461	4,345	0,793	4,141263	
3,034	0,859	3,97899	3,597	0,742	4,28122	4,51	0,628	4,653606	
3,188	0,705	4,392127	3,743	0,596	4,776902	4,592	0,546	4,990834	
3,198	0,695	4,423612	3,754	0,585	4,821604	4,595	0,543	5,004602	
3,23	0,663	4,529108	3,795	0,544	5	4,624	0,514	5,143845	
3,232	0,661	4,535955	3,852	0,487	5,284513	4,713	0,425	5,656854	
3,337	0,556	4,945749	3,853	0,486	5,289947	4,759	0,379	5,990318	
3,344	0,549	4,977179	3,93	0,409	5,76644	4,761	0,377	6,006186	
3,427	0,466	5,402273	3,938	0,401	5,823677	4,778	0,36	6,146363	
3,432	0,461	5,43149	3,962	0,377	6,006186	4,779	0,359	6,154917	
3,448	0,445	5,528273	3,996	0,343	6,296836	4,832	0,306	6,666667	
3,45	0,443	5,540738	4,042	0,297	6,766923	4,86	0,278	6,994345	
3,509	0,384	5,95119	4,048	0,291	6,836329	4,861	0,277	7,006959	
3,512	0,381	5,974574	4,062	0,277	7,006959	4,872	0,266	7,150372	
3,562	0,331	6,409962	4,084	0,255	7,302967	4,907	0,231	7,672969	
3,565	0,328	6,439209	4,114	0,225	7,774603	4,926	0,212	8,009428	
3,574	0,319	6,529413	4,128	0,211	8,028386	4,971	0,167	9,024252	
3,575	0,318	6,539671							
3,614	0,279	6,981799							
3,612	0,281	6,956909							
3,646	0,247	7,420292							
3,648	0,245	7,450517							
3,654	0,239	7,543458							
3,68	0,213	7,990605							

Table 9







Fig. 6. The distribution diagram δ (with an interval 0,1).

In particular, there is a singular coincidence of fractional part n^* with common fraction 2/3 (\approx 0,666667). It is about the excited state of sodium W = 4,832 eV, E = 0,306 eV, n^* = 6,666667 given in tab. 9.

In whole, as well as at the first analysis stage, it is possible with complete reliance to state, that the considered experimental regularity proves to be true and has nonrandom character.

At the second analysis stage the compared number sets also were sorted in ascending order (in limits 0,45 - 0,93), just as it was shown in fig. 2. However here these graphs are not represented so that not to overload the paper with the excess information.

Let's also note that there are some collateral bursts on the edge of distribution δ , as at the first analysis stage (fig. 4) and at the second analysis stage (fig. 6). Probably it means that some values n^* correspond to common fractions with denominator number exceeding the restriction.

4. Conclusion

The statistical analysis has shown that the observed coincidences of effective main quantum numbers of atoms and ions, having only one electron on an outer shell, with common fractions are nonrandom.

This experimental regularity takes place both in basic and in excited hydrogen-like states.

The applied method of statistical analysis of compared sets of numbers (common fractions with restriction on denominator number and experimental values of main quantum numbers) proved to be simple enough and effective.

The quantitative assessments (at the first stage - 73 %, at the second stage - 76,4 %), describing coincidence degree of compared sets, enable more argued conclusion about nonrandom character of discovered experimental regularity.

The complementary argument, which is not leaving any doubts about validity of the considered regularity, is properly the shape of distribution diagram δ , which has pronounced maximum in the diagram centre.

The carried out analysis, apparently, is just the beginning of more detailed research, which should be aimed not only on further studying of this experimental regularity, but also on understanding of consequences for atom theory.

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