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Probability Distribution Connected with Structure Amplitudes of two Related Crystals. III. Probability Distribution of the Quotient

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This part deals with the theory of the probability distribution of the quotient of the structure amplitudes of a pair of crystals, and forms a continuation of the earlier two parts wherein the distribution of the difference and the product were considered. The distribution of the quotient is found to be markedly different for related and unrelated crystals and this property enables one to use the function for testing isomorphism or relatedness in practice. Explicit expressions for the quantity P_+ defined in part I are derived from the distribution of the quotient. Certain other interesting properties exhibited by the quotient distribution, such as the equivalence of the distribution of the normalized quotient and its reciprocal, are also considered.

1. Introduction

In parts I and II of this series (Ramachandran, Srinivasan & Raghupathy Sarma, 1963; Srinivasan, Raghupathy Sarma & Ramachandran, 1963*a*) the theory of the probability distribution of the X-ray intensities belonging to a pair of crystals was developed. The distribution of the difference of the structure amplitudes was considered in part I while part II was chiefly concerned with the distribution of the product. The possible application of the results for testing 'isomorphism' or 'relatedness' in actual practice was pointed out earlier (part I) and further quantitative criteria were developed for this purpose (part II). A more detailed account of these appeared in a later publication (Srinivasan, Raghupathy Sarma & Ramachandran, 1963*b*, hereafter referred to as SRR) wherein some results of practical tests of the various results were also reported.

During the course of the above investigations it occurred to the authors that it would be of interest to work out the distribution of the quotient of the structure amplitudes under conditions and assumptions identical with those in parts I and II. The present paper is mainly concerned with this problem. As in the earlier parts, the theory is worked out both for centrosymmetric and for non-centrosymmetric cases, corresponding to the two situations, namely when the two crystals are unrelated and related respectively.

It is found that the curves of the distribution of the quotient exhibit a marked difference in their nature for the related and unrelated cases and in this respect they are similar to the $P(w)$ function considered in part I. This enables us to use these curves also for testing isomorphism or relatedness in practice. The other interesting aspect of the quotient distribution arises purely from a theoretical viewpoint. For instance, it is found that the quotient and its reciprocal (properly normalized) have identical distributions. These will be discussed in detail in § 3. Explicit expressions are also given for the quantity P_+ defined in part I, for the related and unrelated cases. These have been derived by means of the expressions for the quotient distribution.

The various formulae are derived in the next section, while § 3 will be devoted to a discussion of the results.

The notation used in this paper follows closely that of the earlier parts.

2. Derivation of the formulae

To obtain the distribution of the quotient we use the general theorem that if x and y are random variables, the distribution of the quotient $z=y/x$ is given by

$$P(z) = \int P_1(x)P_2(zx;\ x)\times dx \tag{1}$$

where $P_1(x)$ is the probability density function for x and $P_2(y; x)$ is the conditional probability density function for y, for a given value of x.

2·1. *The case of related structure amplitudes*

(*a*) *Non-centrosymmetric case*

Let us define $q=|F_N|/|F_P|$. The distribution of q is given by

$$P(q) = \int_0^\infty P_1(|F_P|)P_2(q|F_P|;\ |F_P|)|F_P|d|F_P| \tag{2}$$

where $P_1(|F_P|)$ and $P_2(|F_N|; |F_P|)$ are given by (see part I)

$$P_1(|F_P|) = \frac{2|F_P|}{\sigma_P^2}\exp\left\{-\frac{|F_P|^2}{\sigma_P^2}\right\} \tag{3}$$

$$P_2(|F_N|;|F_P|) = \frac{2|F_N|}{\sigma_Q^2}\exp\left\{-\frac{|F_N|^2+|F_P|^2}{\sigma_Q^2}\right\}I_0\left(\frac{2|F_N||F_P|}{\sigma_Q^2}\right). \quad (4)$$

Here σ_N, σ_P and σ_Q represent the root mean square values of the structure amplitudes $|F_N|$, $|F_P|$ and $|F_Q|$ respectively. Substituting these in (2) we obtain

$$P(q) = \int_0^\infty \frac{4q|F_P|^3}{\sigma_P^2\sigma_Q^2}\exp\left\{-\left(\frac{|F_P|^2}{\sigma_P^2}+\frac{(q^2|F_P|^2+|F_P|^2)}{\sigma_Q^2}\right)\right\} \times I_0\left(\frac{2q|F_P|^2}{\sigma_Q^2}\right)d|F_P|. \quad (5)$$

The above integral can be evaluated (see Appendix I) and it reduces to

$$P(q) = \frac{2q\sigma_P^2\sigma_Q^2(\sigma_N^2+\sigma_P^2q^2)}{[(\sigma_N^2+\sigma_P^2q^2)^2-4\sigma_P^4q^2]^{3/2}}. \quad (6)$$

It is convenient at this stage to change the variable to its normalized form, namely,

$$v = \frac{y_N}{y_P} = \frac{|F_N|}{\sigma_N}\frac{\sigma_P}{|F_P|} = q\frac{\sigma_P}{\sigma_N}. \quad (7)$$

Thus v is the ratio of the normalized structure amplitude (y_N) of one crystal to that (y_P) of the other. Making the appropriate transformation, using (5), we obtain the distribution $P(v)$ from (6) to be

$$P(v) = \frac{2v\sigma_2^2(1+v^2)}{[(1+v^2)^2-4\sigma_1^2v]^{3/2}} \quad (8)$$

where $\sigma_1^2=\sigma_P^2/\sigma_N^2$, $\sigma_2^2=\sigma_Q^2/\sigma_N^2$ so that $\sigma_1^2+\sigma_2^2=1$.

(b) Centrosymmetric case

For the centrosymmetric case the expressions $P_1(|F_P|)$ and $P_2(|F_N|;|F_P|)$ are given by (see part I):

$$P_1(|F_P|) = \sqrt{\frac{2}{\pi\sigma_P^2}}\exp\left\{-\frac{|F_P|^2}{2\sigma_P^2}\right\}. \quad (9)$$

$$P_2(|F_N|;|F_P|) = \frac{1}{\sqrt{(2\pi\sigma_Q^2)}}\left[\exp\left\{-\frac{(|F_N|-|F_P|)^2}{2\sigma_Q^2}\right\} + \exp\left\{-\frac{(|F_N|+|F_P|)^2}{2\sigma_Q^2}\right\}\right]. \quad (10)$$

Substituting these in (2) we get

$$P(q) = \frac{1}{\pi\sigma_P\sigma_Q}\int_0^\infty \exp\left\{-\frac{|F_P|^2}{2\sigma_P^2}\right\}\left[\exp\left\{-\frac{|F_P|^2(q-1)^2}{2\sigma_Q^2}\right\} + \exp\left\{-\frac{|F_P|^2(q+1)^2}{2\sigma_Q^2}\right\}\right]|F_P|d|F_P \quad (11)$$

which simplifies to

$$P(q) = \frac{2}{\pi\sigma_P\sigma_Q}\int_0^\infty \exp\left\{-\frac{|F_P|^2(\sigma_N^2+\sigma_P^2q^2)}{2\sigma_P^2\sigma_Q^2}\right\} \times \cosh\left(\frac{|F_P|^2q}{\sigma_Q^2}\right)|F_P|d|F_P|. \quad (12)$$

The above integral can be evaluated (see Appendix II) and we obtain

$$P(q) = \frac{2\sigma_P^2\sigma_Q^2(\sigma_N^2+\sigma_P^2q^2)}{\pi[(\sigma_N^2+\sigma_P^2q^2)^2-4\sigma_P^4q^2]}. \quad (13)$$

Corresponding to expression (8) for the non-centrosymmetric case, the distribution of the normalized quotient v takes the form

$$P(v) = \frac{2}{\pi}\frac{\sigma_2(1+v^2)}{[(1+v^2)^2-4\sigma_1^2v]}. \quad (14)$$

2·2. *The case of unrelated structure amplitudes*

We might expect, guided by the result obtained in the case of the distribution of the product (part II), that the distribution for the case of unrelated structure amplitudes should be obtainable from that of the related case by substituting $\sigma_1^2=0$ in the corresponding expression. This, in fact, turns out to be true. Thus, putting $\sigma_1^2=0$ ($\sigma_2^2=1$) in expressions (6) and (10) we obtain the following expressions.

Non-centrosymmetric case:

$$P(v) = \frac{2v}{(1+v^2)^2}. \quad (15)$$

Centrosymmetric case:

$$P(v) = \frac{2}{\pi(1+v^2)}. \quad (16)$$

That the expressions (15) and (16) are correct may be verified by a detailed derivation from first principles which, in fact, yields the above expressions. However, we outline here quite an independent derivation of equations (15) and (16), which brings out certain interesting relations to some well-known distributions in probability theory, the so called 'gamma distributions' (Weatherburn, 1961).

Thus if x and y are two independent gamma variables with parameters l and m then the quotient $u=x/y$ has the distribution

$$\varphi(u) = \frac{u^{l-1}}{B(l,m)(1+u)^{l+m}} \quad 0 \le u < \infty \quad (17)$$

denoted symbolically by $\beta_2(l,m)$, the beta distribution of the second kind with parameters l and m (Weatherburn, 1961). In this expression, $B(l,m)$ stands for the well-known beta function.

The possibility of using this result in our present case arises from the fact that the two basic distributions of the normalized intensity for the centrosymmetric and non-centrosymmetric cases can be described as gamma distributions with parameters $\frac{1}{2}$ and 1 respectively (Srinivasan & Subramanian, 1964). From this it follows at once that the quotient of the normalized intensities, $(|F_N|^2/\sigma_N^2)/(|F_P|^2/\sigma_P^2)=t$ (say) is a $\beta_2(1,1)$ distribution for the non-centrosymmetric case, given by

$$\varphi(t)=1/(1+t)^2 \quad (18)$$

and a $\beta_2(\frac{1}{2}, \frac{1}{2})$ distribution for the centrosymmetric case, given by

$$\varphi(t) = \frac{1}{\pi\sqrt{(t)}(1+t)}. \tag{19}$$

Since we are finally interested in the quotient of the normalized structure amplitudes, the simple transformation $v^2=t$ in (18) and (19) yields two expressions which are identical with (15) and (16) respectively.

2·3. *Distribution of the reciprocal of the quotient*

In this section we show a rather interesting relation that exists between the distributions of the quotient and its reciprocal. Suppose we consider the reciprocal (u say) of the normalized quotient variable v, *i.e.* take $u=1/v=y_P/y_N$. The distribution of u can be worked out from that of v by making the appropriate transformations in the expression for $P(v)$.

We obtain the following expressions for the related case.

Non-centrosymmetric:

$$P(u) = \frac{2\sigma_2^2 u(u^2+1)}{[(u^2+1)^2-4u^2\sigma_1^2]^{3/2}}. \tag{20}$$

Centrosymmetric:

$$P(u) = \frac{2\sigma_2(u^2+1)}{\pi[(u^2+1)^2-4\sigma_1^2u^2]}. \tag{21}$$

These are identical with the corresponding expressions (13) and (14) for $P(v)$. This relation holds good for the unrelated case also, as may be verified independently.

In contrast to the above, the distribution of the direct ratio of the two structure amplitudes does not possess this property. Thus, if $q=|F_N|/|F_P|$, $q'=1/q=|F_P|/|F_N|$, it is easy to show that, for the non-centrosymmetric case,

$$P(q) = \frac{2\sigma_1^2\sigma_2^2 q(1+\sigma_1^2q^2)}{[\sigma_1^4q^4+2\sigma_1^2(\sigma_2^2-\sigma_1^2)q^2+1]^{3/2}} \tag{22}$$

whereas

$$P(q') = \frac{2\sigma_1^2\sigma_2^2 q'(\sigma_1^2+q'^2)}{[q'^4+2\sigma_1^2q'^2(\sigma_2^2-\sigma_1^2)+\sigma_1^4]^{3/2}}. \tag{23}$$

The corresponding expressions for the centrosymmetric case are

$$P(q) = \frac{2\sigma_1\sigma_2(1+\sigma_1^2q^2)}{\pi[\sigma_1^4q^4+2\sigma_1^2q^2(\sigma_2^2-\sigma_1^2)+1]} \tag{24}$$

$$P(q') = \frac{2\sigma_1\sigma_2(\sigma_1^2+q'^2)}{\pi[q'^4+2\sigma_1^2q'^2(\sigma_2^2-\sigma_1^2)+\sigma_1^4]}. \tag{25}$$

This aspect of the relation between the quotient and its reciprocal will be discussed in detail in § 3.

2·4. *Explicit expressions for* P_+

The parameter P_+ defined as the fraction of the total number of reflexions for which $w=(|F_N|-|F_P|)/\sigma_N$ is positive was obtained earlier numerically by measuring the area of the $P(w)$ curve lying on the positive side and these were tabulated in SRR. It is now possible to give an explicit expression for this quantity by making use of the quotient distribution. Since P_+ measures the fraction of the total number of reflexions for which $|F_N|>|F_P|$ we can write

$$P_+ = \int_1^\infty P(q)dq = \int_{\sigma_1}^\infty P(v)dv. \tag{26}$$

The definite integral can be evaluated and we give below the final expressions for the different cases.

When the crystals are related, the expressions are:

Non-centrosymmetric case:

$$P_+ = \frac{1}{2}\left[1+\frac{\sigma_2}{\sqrt{(1+3\sigma_1^2)}}\right]. \tag{27}$$

Centrosymmetric case:

$$P_+ = \left[1-\frac{1}{\pi}\tan^{-1}\frac{2\sigma_1}{\sigma_2}\right]. \tag{28}$$

When they are unrelated the results take very simple forms:

Non-centrosymmetric case:

$$P_+ = \frac{1}{1+\sigma_1^2}. \tag{29}$$

Centrosymmetric case:

$$P_+=1-\frac{2}{\pi}\tan^{-1}\sigma_1. \tag{30}$$

The values of P_+ obtained from the above expressions agree with the values given earlier (SRR). For convenience they are given in the form of curves in Fig. 3. If we take the lower limit of integration in (26) as 0 we see that all the expressions (27)–(30) reduce to unity. This only checks incidentally that the expressions for the quotient distribution for the different cases are all correct and represent real density functions.

There is an interesting result connected with the integral of the quotient distribution, when this is represented in its normalized form. That is, when we take the integral $\int_1^\infty P(v)dv$ (which is not the same as P_+ given by expression (26)) it is found that it always has the value $\frac{1}{2}$ whatever be the value of σ_1^2 and this holds good whether the crystals are related or not.

3. Discussion

The most prominent feature of the distribution of the quotient is the marked difference in the nature of the curves for the related and unrelated cases (Fig. 1). In this respect it has close similarity to the $P(w)$ curves (part I). One contrasting feature that emerges when we compare the two functions is that while in the $P(w)$ curves the maxima are clustered

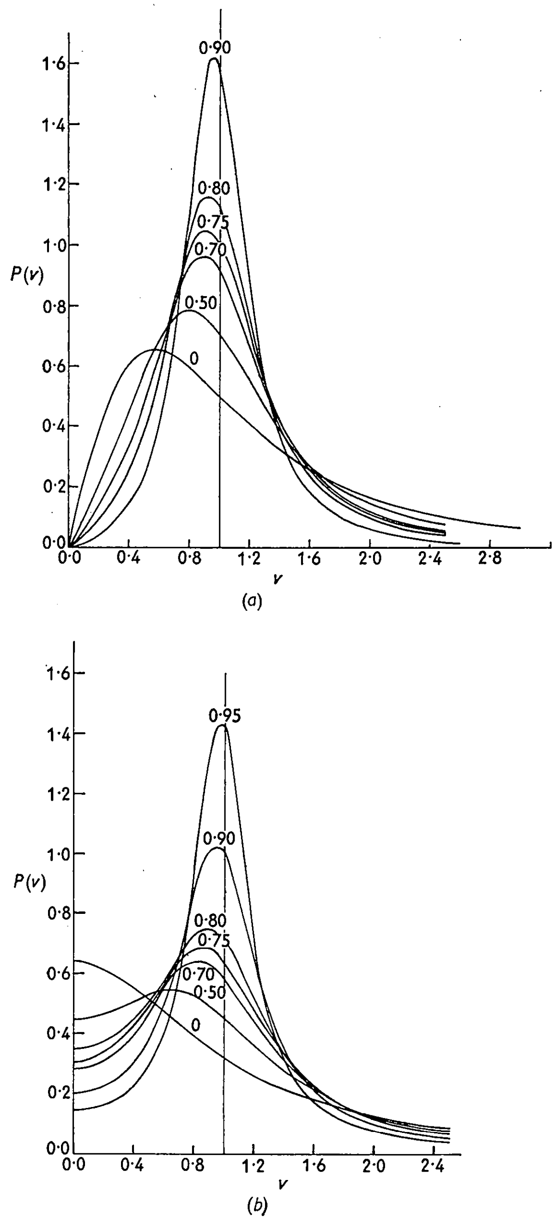

Fig. 1. Probability distribution of the normalized quotient for (*a*) non-centrosymmetric and (*b*) centrosymmetric case. Value of $\sigma_1{}^2$ is marked near each curve. Unrelated case corresponds to $\sigma_1{}^2 = 0$. For $\sigma_1{}^2 = 1$, $P(v)$ is a delta function at $v = 1$.

around the origin, in the $P(v)$ curves they tend to be around $v=1$. Thus, in the limiting case when $\sigma_1^2=1$, the function $P(w)$ is a delta function at the origin while $P(v)$ is a delta function at $v=1$. This is also physically obvious since this limiting case corresponds to all the $|F_N|$'s being equal to the $|F_P|$'s. In view of the above property it is clear that the function $P(v)$ should also prove useful as a test for 'isomorphism' or 'relatedness' in practice. It looks as if it might even prove to be slightly better than the function $P(w)$ since the possible fluctuations in the experimental curves arising out of errors in observed intensities may not affect the quotient as much as they do the difference.

While using the quotient distribution in practice one may choose any one of the curves $P(v)$, $P(q)$ and $P(q')$. Although theoretical curves have been given only for the function $P(v)$ it is not difficult to obtain the curves $P(q)$ and $P(q')$. It involves only a simple transformation, namely $q=v/\sigma_1$ and $q'=\sigma_1/v$, and since v and $1/v$ have identical distributions, the distribution of q and q' would correspond to a compression or expansion of the $P(v)$ curve along the abscissa for any given value of σ_1^2. This is illustrated in Fig. 2 for $\sigma_1^2=0{\cdot}8$. The curves $P(q)$ and $P(q')$ have the advantage that they are easily computed in practice since they involve the direct ratio of the two structure amplitudes.

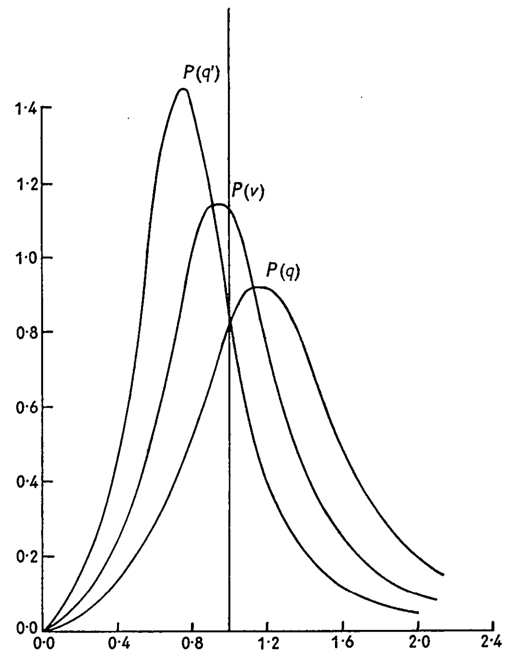

Fig. 2. Comparison of the probability distribution of the normalized quotient v with that of the direct ratios $q = |F_N|/|F_P|$ and $q' = |F_P|/|F_N|$ for the non-centrosymmetric case; $\sigma_1{}^2 = 0{\cdot}8$.

The rather interesting property exhibited by the quotient distribution, namely that v and its reciprocal u have identical distributions (§ 2·3), needs some discussion here. This result seems rather surprising at first since one would expect, purely from a physical consideration, that the distribution of $v=y_N/y_P$ and $u=y_P/y_N$ should show some asymmetry in view of the fact that $N>P$. Although for the unrelated case an explanation may be found in the fact that the expressions for $P(v)$ are independent of σ_1^2 this is not true for the related case for which σ_1^2 directly enters

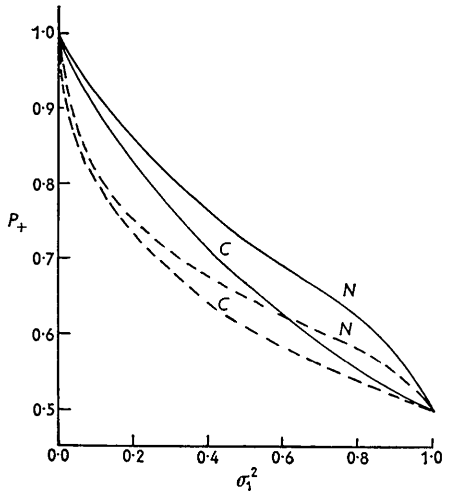

Fig. 3. P_+ as a function of $\sigma_1{}^2$ for the related (continuous line) and the unrelated (broken line) cases. N and C denote non-centrosymmetric and centrosymmetric cases respectively.

the expression and yet the two distributions are the same.

It should, however, be pointed out that the chief requirement for the quotient distribution to exhibit this symmetry property is that the variables involved should be in their normalized form. This becomes clear from the fact that the expected asymmetry is present in the distribution of q and its reciprocal q', as may be seen by comparing, for instance, expressions (22) and (23) (see also Fig. 2).

The other property mentioned in the last section, namely that the integral $\int_1^\infty P(v)dv$ has a constant value of $\frac{1}{2}$ for all values of σ_1^2 is also, it appears, a reflexion of this basic symmetry property of the normalized quotient.

APPENDIX I

The integral on the right hand side of equation (3) can be written

$$\frac{2q}{\sigma_P^2\sigma_Q^2}\int_0^\infty |F_P|^2 \exp\,(\alpha|F_P|^2)I_0(\beta|F_P|^2)d(|F_P|^2) \quad \text{(A1)}$$

where

$$\alpha = \frac{\sigma_N^2+\sigma_P^2q^2}{\sigma_P^2\sigma_Q^2} \quad \text{and} \quad \beta = \frac{2q}{\sigma_Q^2}.$$

We may use the result (Watson, 1944, p. 386)

$$\int_0^\infty e^{-at}J_\nu(bt)t^{\nu+1}dt = \frac{2a(2b)^\nu\Gamma(\nu+\frac{3}{2})}{(a^2+b^2)^{\nu+(3/2)}\sqrt{\pi}} \quad \text{(A2)}$$

which, when we put $b=ib'$, $\nu=0$ gives

$$\int_0^\infty e^{-at}I_0(bt)\,t\,dt = \frac{2a\Gamma(\frac{3}{2})}{(a^2-b^2)^{3/2}\sqrt{\pi}}. \quad \text{(A3)}$$

Expression (A1) then reduces to

$$\frac{2q}{\sigma_P^2\sigma_Q^2}\left[\frac{\alpha}{(\alpha^2-\beta^2)^{3/2}}\right] = \frac{2q\sigma_P^2\sigma_Q^2(\sigma_N^2+\sigma_P^2q^2)}{[(\sigma_N^2+\sigma_P^2q^2)^2-4\sigma_P^4q^2]^{3/2}}. \quad \text{(A4)}$$

APPENDIX II

The integral on the right hand side of equation (8) can be written

$$\frac{1}{\pi\sigma_P\sigma_Q}\int_0^\infty \exp\,\{-(k_1|F_P|^2)\}\cosh k_2(|F_P|^2)\,d(|F_P|^2) \quad \text{(A5)}$$

where

$$k_1=(\sigma_N^2+\sigma_P^2q^2)/2\sigma_P^2\sigma_Q^2 \quad \text{and} \quad k_2=q/\sigma_Q^2\,.$$

This is simple to evaluate since

$$\int_0^\infty e^{-k_1x}\cosh\,(k_2x)dx = \tfrac{1}{2}\int_0^\infty [e^{x(k_2-k_1)}+e^{-x(k_2-k_1)}]dx$$
$$=k_1/(k_1+k_2)(k_1-k_2)\,.$$

Therefore our integral reduces to

$$\frac{2}{\pi}\frac{\sigma_P^2\sigma_Q^2(\sigma_N^2+\sigma_P^2q^2)}{[(\sigma_N^2+\sigma_P^2q^2)^2-4\sigma_P^4q^2]}. \quad \text{(A6)}$$

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