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On the Use of Negative Quartets*

BY H. SCHENK

Laboratory for Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, *Amsterdam, The Netherlands*

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The number of negative quartets (NQ) $\varphi_h+\varphi_k+\varphi_l+\varphi_{-h-k-l}=\pi$ is small compared with the number of $\sum_2$-triplets. Also the associated weights $B=2N^{-1}|E_hE_kE_lE_{-h-k-l}|$ are small relative to the weights of the triplets. Therefore negative quartets cannot be used to find phases of reflexions. However, in symmorphic space groups they are very useful for selecting the correct phase set from all sets produced by a multisolution procedure. Negative quartets can also be employed to remove most of the errors in a normal quartet list, so that for quartets a reliability can be obtained better than for triplets. This error-cleaning procedure can be used to improve the reliability of the strengthened quartet relation.

Introduction

In the preceding paper Hauptman (1974) has derived the negative cosine invariant expression

$$\cos(\varphi_h+\varphi_k+\varphi_l+\varphi_{-h-k-l})\simeq -\frac{I_1(B)}{I_0(B)} \qquad (1)$$

with $B=2N^{-1}|E_hE_kE_lE_{-h-k-l}|$. This formula holds only if $|E_{h+k}|$, $|E_{h+l}|$ and $|E_{k+l}|$ are sufficiently small. For large B (1) can be approximated by

$$\varphi_h+\varphi_k+\varphi_l+\varphi_{-h-k-l}=\pi. \qquad (2)$$

Throughout the paper this relation is referred to as the negative quartet relation (NQ).

The special case of (1) with $h=k$ has been found to be valuable in symmorphic space groups, *e.g.* space groups without screw axes and glide planes, for the selection of the correct phase set from the $\sum_2$ solutions (Schenk & De Jong, 1973; Schenk, 1973*a*).

The object of this paper is to explore the strength of the NQ's relative to that of the $\sum_2$ relation. Moreover the use of NQ's in symmorphic space groups is discussed and the possibility is pointed out that part of the errors of the strengthened quartet relations (Schenk, 1973*b*) can be removed by making use of NQ's. In this paper only centrosymmetric structures will be discussed but the methods can also be applied to non-centrosymmetric space groups.

NQ's with $h=k$

For the special case $h=k$ (2) reduces to

$$2\varphi_h+\varphi_l+\varphi_{-2h-l}=\pi$$

or after re-indexing

$$2\varphi_h+\varphi_{-h+k}+\varphi_{-h-k}=\pi. \qquad (3)$$

This relation has already been tested in space group $P1$ (Schenk, 1973*a*). It appeared that the number of relations (3) with sufficiently large B values is small. Nevertheless, in resolving the ambiguities of direct solutions in non-centrosymmetric symmorphic space groups a criterion based on relation (3)

$$\mathrm{P1C}=\sum_h\sum_k \frac{(|U_h|-|U_k|)^2}{(1-|U_{-h+k}|)\,(1-|U_{-h-k}|)} \times|\pi-(2\varphi_h+\varphi_{-h+k}+\varphi_{-h-k})| \qquad (4)$$

proved to be valuable. In P1C the weights are in conformity with one of the Harker–Kasper inequalities for $\bar{1}$ rather than with $B=2N^{-1}|E_h^2E_{-h+k}E_{-h-k}|$ as suggested by (1).

In $P\bar{1}$ an analogous method was described (Schenk & De Jong, 1973) in which the criterion based on (3) has the form

$$\mathrm{HKC}=\sum_h\sum_k \frac{(|U_h|-|U_k)^2}{(1-|U_{-h+k}|)\,(1-|U_{-h-k}|)} \times s(-h+k)s(-h-k). \qquad (5)$$

This criterion, which has to be small for the correct solution, can be applied successfully, as was illustrated by the sign determinations of four structures.

Strengthened quartet relation

The Strengthened Quartet Relation, SQR, (Schenk, 1973*b*) states that the reliability of the relation between four structure factors

$$\varphi_h+\varphi_k+\varphi_l+\varphi_{-h-k-l}=0 \qquad (6)$$

depends on

$$E_4^*=N^{-1}|E_hE_kE_lE_{-h-k-l}|\left\{1+\frac{|E_{h+k}|+|E_{h+l}|+|E_{k+l}|}{E_{000}}\right\} \qquad (7)$$

in the same way as that of the $\sum_2$ relation depends on

$$E_3=N^{-1/2}|E_hE_kE_{-h-k}|.$$

* Part of the work described here was presented at the 'Workshop on the Use of Structure Invariants in Phase Determination', Medical Foundation of Buffalo and SUNY/Buffalo, August 1973.

By applying the strengthening procedure it appears that the quartets which contradict (6) and hence agree with (2) are found among the non-strengthened quartets, *i.e.* the quartets with small $|E_{h+k}|$, $|E_{h+l}|$ and $|E_{k+l}|$ (compare Tables 1 and 4 in Schenk, 1973*b*).

Selection of reliable NQ's

In order to be able to use (1) in structure determinations the condition that $|E_{h+k}|$, $|E_{h+l}|$ and $|E_{k+l}|$ are sufficiently small has to be expressed numerically.

For triplets an expression similar to (1) is

$$\cos(\varphi_h+\varphi_k+\varphi_{-h-k}) \simeq \frac{I_1(A)}{I_0(A)} \qquad (8)$$

with $A=2E_3=2N^{-1/2}|E_hE_kE_{-h-k}|$ (see, *e.g.*, page 156 of Hauptman, 1972). From the similarity of (1) and (8) it is possible to obtain a limit value for $|E_{h+k}|$ $|E_{h+l}|$ and $|E_{k+l}|$ for which the reliability of the NQ's is equal to that of the triplet relations. By analogy in centrosymmetric structures this value can be found by collecting the complete triplet list and the percentage of correct sign products as a function of A and compare these numbers with the percentages of correct NQ's as function of B for different limit values of

$$m=(|E_{h+k}|+|E_{h+l}|+|E_{k+l}|)/3. \qquad (9)$$

It may be noted that this m limit is less strict than the condition that each of the reflexions $h+k$, $h+l$ and $k+l$ has to be smaller than a limit value.

Table 1. *Total number* (nr) *of triplets above a variable A/2 value with the percentage* (%) *of correct sign relations for a* 20 *atom model structure*

For NQ's the numbers and percentages are given above variable $B/2$ values for different values of $m=(|E_{h+k}|+|E_{h+l}|+|E_{k+l}|)/3$.

	1		2		3		4	
$A/2$			NQ's		NQ's		NQ's	
$B/2$	Triplets		$m=0{\cdot}6$		$m=0{\cdot}7$		$m=0{\cdot}8$	
	nr	%	nr	%	nr	%	nr	%
3·0	8	100						
2·5	28	100						
2·0	94	100						
1·8	162	100						
1·6	272	100						
1·4	454	100	1	100	1	100	1	100
1·2	764	99·5	2	100	2	100	2	100
1·0	1370	98·6	13	100	17	100	19	100
0·9	1844	97·6	25	100	32	93·8	40	95·0
0·8	2531	95·8	51	100	67	94·0	83	91·6
0·7	3485	93·8	113	97·3	144	93·8	190	90·0

NQ's in a model structure

As the theory behind (1) assumes that no overlap is present in the Patterson function, for a first examination of the NQ's a structure was generated fulfilling this condition. By means of a procedure based on the method of Lehmer (*e.g.*, Greenberger, 1961) the coordinates of ten atoms were randomly generated in space group $P\bar{1}$ ($N=20$). 1000 reflexions, approximately the number of reflexions usually measured for an organic structure of this size, were calculated. Then all triplets down to an $A/2$ value of 0·7 were collected and the NQ's for different limit values of m. The results are summarized in Table 1.

From this Table it follows that NQ's are as reliable as triplets for $m \leq 0{\cdot}7$. By choosing smaller values for m it is even possible to get better percentages for the NQ's than expected. However, the number of useful NQ's is small compared with that of the triplets: in the group of 800 relations with highest A or B there are only two NQ's. The number of reliable NQ's is so small that in a sign determination procedure like symbolic addition they cannot be expected to be important

Table 2. *Number of relations* (nr) *and percentage of correct relations* (%) *of triplets and NQ's above variable A and B values for the structure of an aza-steroid*

The NQ's are given for different values of $m=(|E_{h+k}|+|E_{h+l}|+|E_{k+l}|)/j$ and for three ($j=3$) or two ($j=2$) of the reflexions $h+k$, $h+l$, $k+l$ within the set of measurements.

			2		3		4		5		6		7		8		9		10		11		12	
			NQ		NQ		NQ		NQ		NQ		NQ		NQ		NQ		NQ		NQ		NQ	
$A/2$	1		$j=3$		$j=3$		$j=3$		$j=3$		$j=3$		$j=2$		$j=2$		$j=2$		$j=2$		$j=2$		$j=1$	
$B/2$	Triplets		$m=0{\cdot}1$		$m=0{\cdot}2$		$m=0{\cdot}5$		$m=0{\cdot}6$		$m=0{\cdot}7$		$m=0{\cdot}1$		$m=0{\cdot}2$		$m=0{\cdot}3$		$m=0{\cdot}4$		$m=0{\cdot}5$		$m=0{\cdot}1$	
	nr	%	nr	%	nr	%	nr	%	nr	%	nr	%	nr	%	nr	%	nr	%	nr	%	nr	%	nr	%
8·0																								
7·0	8	100																						
6·0	21	100																						
5·0	61	100																						
4·0	143	100																						
3·0	353	100													1	100	1	100	1	100	2	100		
2·5	583	99·8													2	100	2	100	2	100	3	100		
2·0	980	99·7									1	100	1	100	3	100	4	100	5	100	6	100		
1·5	1823	99·2	1	100	1	100	2	100	2	100	5	80	5	100	18	100	23	96	32	94	38	92	18	28
1·4	2101	98·9	1	100	1	100	6	100	8	100	11	91	8	100	29	100	37	97	53	94	61	92	30	27
1·3	2438	98·4	1	100	2	100	11	100	13	100	18	89	18	94	42	98	54	94	79	92	92	89	40	30
1·2	2888	97·8	2	100	4	100	17	100	20	100	28	89	33	97	62	98	82	92	119	87	148	84	70	33
1·1	3395	96·9	4	100	10	100	30	100	39	90	52	83	48	94	91	93	120	87	169	85	220	80	112	38

enough to force the total consistency towards the correct solution.

NQ's in a real structure

The NQ's have been calculated for an aza-steroid ($P\bar{1}$, $Z=2$, $N=40$) recently solved by means of the criterion (5) (De Jong, Dik-Edixhoven & Schenk, 1973). They are summarized in the columns 2, 3, 4, 5 and 6 of Table 2 for different values of m. From a comparison of these columns and the triplets (column 1) it can be seen that for a value $m \simeq 0{\cdot}55$ triplets and NQ's are equally reliable. This limit is slightly smaller than the limit value in the random structure. Comparing the number of relations (triplets and NQ's) available it is striking that among the 1000 relations of largest A (or B) there is no NQ; in the group of 3400 relations only approximately 1 % are of the type NQ.

For the formulation of the Harker–Kasper-type relations (3) only two secondary reflexions were taken into account, so that it was expected that also those quartets for which only two of the three reflexions $h+k$, $h+l$, $k+l$ are present in the set of measured reflexions ($j=2$) may contain useful information. These NQ's have also been collected for different values of m and are given in Table 2, columns 7 to 11. From the figures it follows that here an m value of 0·2 gives approximately the same percentage of correct relations as the triplets. The total number of useful NQ's ($j=3,2$) is 120 or about 3 % of the number of triplets.

In column 12 those NQ's are given for which only one secondary reflexion is present ($j=1$). Although the percentage of correct NQ's (38 %) deviates significantly from the percentage of incorrect triplets (3 %), the negative information is not good enough for a successful use in sign determinations.

The above figures suggest another application of the NQ's; they can be used effectively to minimize the number of errors in the normal quartet relationships. In column 1 of Table 3 a survey of all quartets above $B/2=1{\cdot}1$ is given in column 2 a survey of all NQ's with $j=1,2,3$ and $m \leq 1{\cdot}0$, together with the percentages of correct relations.

Of course the quartets contain the NQ's, so that the correct NQ's are part of the errors of the quartets. For $B/2=1{\cdot}1$ this implies that 511 of the 729 quartet errors can be removed losing only 1193 of the 14544 quartets. The last column of Table 3 gives the reduced quartet list, and from a comparison with Table 1 it follows that the percentage of correct relations is far better than the same percentage of the triplets.

In Table 4 all sign relationships are summarized, including the SQR's which were calculated from the reduced quartet list using (7). With $A/2$ and $B/2$ values above 3·0, a total number of 3649 relations are available with no error at all. By means of this set it should

Table 4. *Numbers* (nr) *of triplets, SQR's and NQ's of an aza-steroid which can be used simultaneously in a sign determination procedure, because their percentages of correct relations are approximately equal*

$A/2$	1		2		3		4	
$B/2$	Triplets		SQR's–NQ's		NQ's $j=3$ $m=0{\cdot}5$		NQ's $j=2$ $m=0{\cdot}2$	
	nr	%	nr	%	nr	%	nr	%
9·0			5	100				
8·0			28	100				
7·0	8	100	73	100				
6·0	21	100	185	100				
5·0	61	100	454	100				
4·0	143	100	1213	100				
3·0	353	100	3295	100			1	100
2·5	583	99·8	5813	99·8			2	100
2·0	980	99·7	10006	99·4			3	100
1·5	1823	99·2	13114	98·6	2	100	18	100
1·4	2101	98·9	13240	98·5	6	100	29	100
1·3	2438	98·4	13324	98·4	11	100	42	98
1·2	2888	97·8	13339	98·4	17	100	62	98
1·1	3395	96·9	13351	98·4	30	100	91	93

Table 3. *Number* (nr) *of different types of quartets with percentage of correct sign products above variable values of B/2 for an aza-steroid*

Because the quartets contain the NQ's, the correct NQ's are part of the errors of the quartets. Therefore the quartets–NQ's have a much better percentage of correct relations than the quartets.

	1 Quartets			2 NQ's $j=1,2,3$; $m \leq 1{\cdot}0$ Number of correct relations			3 Quartets – NQ's		
$B/2$	nr	Errors	%	nr		%	nr	Errors	%
5·0	1	0	100				1	0	100
4·0	30	0	100				30	0	100
3·0	240	2	99·2	2	2	100	238	0	100
2·5	623	3	99·5	7	3	43	616	0	100
2·0	1726	12	99·3	24	10	42	1702	2	99·9
1·5	5254	108	97·9	210	82	39	5044	26	99·5
1·4	6729	171	97·5	322	128	40	6407	43	99·3
1·3	8630	275	96·8	503	207	41	8127	68	99·2
1·2	11244	451	96·0	793	334	42	10451	117	98·9
1·1	14544	729	95·0	1193	511	43	13351	218	98·4

be possible to sign the strong reflexions in terms of one or more symbols. However there is only one NQ in the group which will not be sufficient to indicate the true values of the symbolic phases.

From this structure, the model structure and other cases investigated it follows that NQ's are useful if employed separately from triplets and SQR's at a stage where the set of symbolically phased reflexions has already been built up. Only in very rare cases can the NQ's be successfully used in an earlier stage of the phase determination.

Practical procedure for structure determinations in symmorphic space groups

Using the results of the preceding paragraphs, for structure determinations in symmorphic space groups essentially the same procedure has been adopted as already described for the Harker–Kasper type relations (Schenk & De Jong, 1973):

(1) Calculation of $\sum_2$ list, SQR's and NQ's.

(2) Construction by means of triplets and SQR's of a set of symbolically phased reflexions, which contains a large percentage of the strong structure factors.

(3) Calculation for each solution of a Negative Quartet Criterion (NQC)

$$\mathrm{NQC}=\sum_h \sum_k \sum_l j\times(C_j-m_j)\times B_{hkl} \times|\pi-(\varphi_h+\varphi_k+\varphi_l+\varphi_{-h-k-l})| \quad (10)$$

in which j is the number of secondary reflexions $h+k$, $h+l$, $k+l$ present in the measured set,

C_j are constants to be chosen in the interval $0<C_j<1$,

$m_1=|E_{h+k}|$,

$m_2=(|E_{h+k}|+|E_{h+l}|)/2$,

$m_3=(|E_{h+k}|+|E_{h+l}|+|E_{k+l}|)/3$,

$C_j-m_j\geq 0$, thus negative values are ruled out,

$B_{hkl}=2N^{-1}|E_hE_kE_lE_{-h-k-l}|$

and $0\leq\varphi_h+\varphi_k+\varphi_l+\varphi_{-h-k-l}<2\pi$.

The justification of the weights can be inferred from Table 2: the larger j the larger the reliability of the NQ's; the larger m_{hkl} the smaller the reliability of the NQ's.

From this Table and Table 1 an estimate of the three C_j constants can be made: $C_1=0$, $C_2=0{\cdot}5$ and $C_3=0{\cdot}9$, implying that NQ's with $j=1$ are not used at all NQ's with $j=2$ only if $m\leq 0{\cdot}5$ and NQ's with $j=3$ only if $m\leq 0{\cdot}9$.

(4) Extension of the group of signed reflexions for the $\sum_2$ solutions with smallest NQC. Back to step (3).

(5) Finally E map's are computed for the solutions in order of NQC.

One very important point has to be made: the quality of the NQ's is critically dependent on the weak reflexions. For instance if for some reason a strong reflexion is measured as weak, then the NQ's can be influenced dramatically, whilst the $\sum_2$ and quartet listings are only a little bit shorter and the Patterson function shows only a minor change.

Applications

For the aza-steroid ($P\bar{1}$, $Z=2$, $N=40$), one of the structures solved by means of the HKC method (Schenk & De Jong, 1973), two sets of NQC values have been calculated, one with $C_1=C_2=0$ and $C_3=0{\cdot}7$ (only the most reliable $j=3$ relations are used) and one with $C_1=0$, $C_2=0{\cdot}5$ and $C_3=0{\cdot}9$. The results are given in Table 5, together with the last cycle of the HKC values. Whereas solution number 1 in order of HKC proved to be correct, both NQC columns give also a sequence with the correct solution as number 1. The order of the other solutions is different for HKC and NQC, but of course this is of less importance.

During the 1973 Workshop on the use of Structure

Table 5. *$\sum_2$ consistency criteria, HKC values and NQC values for 14 out of 32 $\sum_2$ solutions of an aza-steroid* ($P\bar{1}$, $Z=2$, $N=40$)

The numbers for $\sum_2$ consistency and HKC are taken from Schenk & De Jong (1973). The NQC values are calculated with the same set of signed reflexions used for the HKC calculation.

Number of the $\sum_2$ solution	$\sum_2$ consistency (CC)	Order of solutions after CC	HKC	Order of solutions after HKC	NQC $C_3=0{\cdot}7$ $C_2=0$	Order of solutions after NQC	NQC $C_3=0{\cdot}9$ $C_2=0{\cdot}5$	Order of solutions after NQC
2	1267	12	−40·17	1	−49·84	1	−166·95	1
5	4335	27	−29·41	2	8·06	9	35·71	9
9	1525	15	−26·01	5	−37·80	4	−106·98	3
12	1158	8	−9·64	11	13·52	10	95·98	11
15	4601	31	9·97	10	−36·98	5	−86·46	7
16	4154	20	−1·90	14	37·12	14	130·74	14
18	1212	10	−9·07	12	−27·82	7	−92·62	6
20	1525	16	−18·25	7	−44·84	2	−146·83	2
21	4203	23	−2·56	13	30·08	13	104·00	12
23	4614	32	−28·47	3	3·06	8	30·03	8
26	878	7	−13·92	9	18·52	12	105·16	13
27	1506	14	−16·92	8	−32·80	6	−97·13	5
29	4344	28	−19·19	6	−41·98	3	−101·95	4
32	4240	25	−26·12	4	15·10	11	83·01	10

Invariants in Phase Determination (Medical Foundation of Buffalo and SUNY/Buffalo) an unknown structure has been solved with the help of a more primitive version of NQC, which will be described elsewhere (Schenk, Gartland, Einspahr & Freeman, 1974).

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The Joint Probability Distribution Applied to a Weak Sign Relationship

By C. Giacovazzo

Università di Bari, Istituto di Mineralogia e Petrografia, 70121 *Bari, Italy*

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The probability of the sign of the product $E_{\mathbf{h}-\mathbf{k}}E_{\mathbf{h}+\mathbf{k}}$ is derived by the mathematical device of the joint probability distribution. Some previous formulae, in contrast with Harker–Kasper inequalities, are criticized. Some experimental tests fit quite well the theory developed here.

Introduction

In a short communication, Gillis (1956) suggested the conditional sign relationship

$$S(\mathbf{h}+\mathbf{k}) \simeq -S(\mathbf{h}-\mathbf{k}) \tag{1}$$

if

$$|U_{\mathbf{h}}|^2+|U_{\mathbf{k}}|^2 \leq |U_{\mathbf{h}+\mathbf{k}}U_{\mathbf{h}-\mathbf{k}}| \; ; \tag{2}$$

$S(\mathbf{h})$ represents the sign of $U_{\mathbf{h}}$.

Woolfson (1957) criticized this result and suggested that the most favourable condition for sign relationship (1) is that one of $U_{\mathbf{h}}$ and $U_{\mathbf{k}}$ should be large and the other small. Furthermore, by a application of the central-limit theorem, Woolfson (1957) obtained a mathematical expression of the ratio P_+/P_-, where P_+ represents the probability that $S(\mathbf{h}-\mathbf{k})S(\mathbf{h}+\mathbf{k})$ is positive while P_- is the probability that $S(\mathbf{h}-\mathbf{k})S(\mathbf{h}+\mathbf{k})$ is negative. According to Woolfson, this ratio depends on a knowledge of the signs of $U_{2\mathbf{h}}$ and $U_{2\mathbf{k}}$.

Later Woolfson (1961) derived the validity conditions for relation (1) by a suitable use of the Harker–Kasper inequalities.

From these inequalities we have

$$(U_{\mathbf{h}}+U_{\mathbf{k}})^2 \leq (1+U_{\mathbf{h}+\mathbf{k}})\,(1+U_{\mathbf{h}-\mathbf{k}}) \, , \tag{3}$$

and

$$(U_{\mathbf{h}}-U_{\mathbf{k}})^2 \leq (1-U_{\mathbf{h}+\mathbf{k}})\,(1-U_{\mathbf{h}-\mathbf{k}}) \, . \tag{4}$$

When $|U_{\mathbf{h}}|$, $|U_{\mathbf{h}+\mathbf{k}}|$, $|U_{\mathbf{h}-\mathbf{k}}|$ are large, $|U_{\mathbf{k}}|=0$, and

$$U_{\mathbf{h}}^2 > (1-|U_{\mathbf{h}+\mathbf{k}}|)\,(1-|U_{\mathbf{h}-\mathbf{k}}|) \, , \tag{5}$$

then it follows from (3) and (4) that the sign relationship (1) must hold. No use of $U_{2\mathbf{h}}$ and $U_{2\mathbf{k}}$ is made in equations (3), (4) and (5).

In a recent paper, Schenk & de Jong (1973) showed that in centrosymmetric symmorphic space groups the correct $\sum_2$ solution can be found using a new criterion (the HKC criterion), related to the sign relation (1) through the Harker–Kasper inequalities. Since the application field of the Harker–Kasper inequalities is limited, it is of some interest to draw a probability law for the sign relation (1). In this paper the mathematical device of the joint probability distribution will be used.

The joint probability distribution $P(E_{\mathbf{h}}, E_{\mathbf{k}}, E_{\mathbf{h}-\mathbf{k}}, E_{\mathbf{h}+\mathbf{k}})$

We introduce the abbreviation

$$E_1=E_{\mathbf{h}}; \; E_2=E_{\mathbf{k}}; \; E_3=E_{\mathbf{h}-\mathbf{k}}; \; E_4=E_{\mathbf{h}+\mathbf{k}} \, .$$

By following Klug (1958), we derive the characteristic function $C(u_1,u_2,u_3,u_4)$ of the multivariate distribution $P(E_1,E_2,E_3,E_4)$:

$$C(u_1,u_2,u_3,u_4) = \exp\left\{-\tfrac{1}{2}[u_1^2+u_2^2+u_3^2+u_4^2]\right\}\left\{1+\frac{S_3}{t^{3/2}}+\frac{S_4}{t^2}+\frac{S_3^2}{2t^3}+\ldots\right\}, \tag{6}$$