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Quintets

BY H. SCHENK AND N. VAN DER PUTTEN

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

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The phase sum $|q|$ of a quintet, $\phi_H+\phi_K+\phi_L+\phi_M+\phi_{-H-K-L-M}=q$, is controlled by the E's of the main reflexions H, K, L, M and $-H$–K–L–M and those of the 10 cross-reflexions $H+K$, $H+L$, *etc.* It is empirically shown that $|q|$ and the sum S of the 10 cross-E's follow a linear trend, so that $|q|$ can be predicted from S. In this way not only positive ($q\simeq 0$) and negative ($q\simeq\pi$) quintets can be found, but also enantiomorph-sensitive quintets ($q\simeq\pm\frac{1}{2}\pi$). In the primary stages of a phase determination of a non-centrosymmetric structure these $|q|$ values can be used to introduce and maintain the enantiomorph. For polar space groups an enantiomorph-specific refinement procedure can be developed by introducing $|q|$ values in a modified tangent formula.

Introduction

Direct methods are mainly based on the Σ_2 relation: $\phi_H+\phi_K+\phi_{-H-K}\simeq 0$, valid for large values of $E_3=N^{-1/2}|E_HE_KE_{-H-K}|$. With this relation, sets of phases can be set up, extended and refined. The solution with the best Σ_2 consistency is expected to correspond to the correct structure. However, in some cases the Σ_2 relation alone does not contain enough information to carry out a successful phase determination. One of the ways to overcome this is the use of auxiliary phase relations like Harker–Kasper-type relations and quartets. Harker–Kasper-type relations (Schenk & de Jong, 1973; Schenk, 1973*b*) and negative quartets (Hauptman, 1974; Schenk, 1974; De Titta, Edmonds, Langs & Hauptman, 1975) are used to indicate the correct Σ_2 solution in symmorphic space groups. Strengthened quartet relations (Schenk, 1973*a*) can be used successfully for building starting sets of phases.

In polar space groups the Σ_2 relation produces centrosymmetric phases (Schenk, 1972). This can be remedied by a mixed Σ_2-Patterson technique (Schenk, 1972) but, if enantiomorph-sensitive phase relations were available, this problem could be tackled directly. Extrapolating the results of triplets and quartets we expect a quintet relation:

$$\phi_H+\phi_K+\phi_L+\phi_M+\phi_{-H-K-L-M}\simeq\pm\tfrac{1}{2}\pi$$

for special values of the 10 cross-reflexions $H+K$, *etc.* In this paper a first empirical exploration of the quintets is presented and possible applications are suggested. Most of the material was presented at the Xth International Congress of Crystallography (Schenk, 1975).

Σ_2 relations and quartets

For triplets of reflexions H, K and $-H$–K the phase sum can be estimated to be zero

$$\phi_H+\phi_K+\phi_{-H-K}\simeq 0 \qquad (1)$$

on the basis of the three magnitudes $|E_H|$, $|E_K|$ and $|E_{H+K}|$.

The corresponding formula for quartets is

$$\phi_H+\phi_K+\phi_L+\phi_{-H-K-L}=p \qquad (2)$$

with $p\simeq 0$ for large $E_4=N^{-1}|E_HE_KE_LE_{H+K+L}|$. This follows from the generalized Hughes formula (Simerska, 1956) and is also known as the Σ_5 relation (Hauptman & Karle, 1953).

The first attempt to use seven magnitudes to estimate sum (2) of a quartet was empirical (Schenk, 1973*a*,*b*). The quartet relation itself was combined with secondary quartets obtained from two triplets by elimination of one phase, for instance from

$$\left.\begin{aligned}\phi_H+\phi_K+\phi_{-H-K}&\simeq 0\\ \phi_L+\phi_{-H-K-L}+\phi_{H+K}&\simeq 0\end{aligned}\right\}. \qquad (3)$$

In this way the magnitudes of the reflexions $H+K$, $H+L$ and $K+L$ could be used to select the more reliable quartets. It was shown that a good measure for the reliability of $p\simeq 0$ was given by

$$E_4^*=N^{-1}|E_HE_KE_LE_{H+K+L}|\times[1+N^{-1/2}(E_{H+K}+E_{H+L}+E_{K+L})] \qquad (4)$$

[strengthened quartet relation, SQR; Schenk (1973)].

Theoretical work of Hauptman (1974) and practical applications of Schenk (1974) showed that for small E values of the reflexions $H+K$, $H+L$ and $K+L$ the quartet phase sum is $p\simeq\pi$. It was shown also that the Harker–Kasper-type relations

$$\phi_{H+K}+\phi_{H-K}+2\phi_{-H}\simeq\pi$$

for large $|E_{H+K}|$, $|E_{H-K}|$ and $|E_H|$ and small E_K (Schenk, 1973*b*; Schenk & De Jong, 1973) could be considered as a special case of these negative quartets ($p\simeq\pi$).

Quintets

From the general Hughes formula derived by Simerska (1956) the quintet phase relation can be written as

$$\phi_H+\phi_K+\phi_L+\phi_M+\phi_{-H-K-L-M}\simeq q\,. \qquad (6)$$

In a first approximation q is expected to be zero for larger values of $E_5=N^{-3/2}|E_HE_KE_LE_ME_{-H-K-L-M}|$.

Quintets can also be obtained from a triplet (1) and a quartet (2) with one reflexion in common. For instance quintet (6) can be formed by elimination of ϕ_{H+K} from

$$\phi_H+\phi_K+\phi_{-H-K}\simeq 0$$

and

$$\phi_L+\phi_M+\phi_{-H-K-L-M}+\phi_{H+K}=p\,.$$

Altogether this can be done in 10 different ways, so that in a second approximation the value of the quintet phase sum q is controlled by 15 magnitudes, the main reflexions H, K, L, M and $-H-K-L-M$ and the cross-terms $H+K$, $H+L$, *etc.*

From triplet and quartet properties it is possible to predict some values of (6) from the E's of the 10 cross-terms. If all cross-terms are large the elimination quintets are built up from triplets and positive quartets ($p\simeq 0$) resulting in quintet sum estimates $q\simeq 0$. If a quintet can be obtained from a triplet and a negative quartet ($p\simeq\pi$) its q value is estimated to be $q\simeq\pi$. This is the case for four combinations of four strong and six weak cross-terms, for instance the strong reflexions $H+K$, $H+L$, $H+M$, and $-K-L-M$ and the weak $K+L$, $K+M$, $-H-L-M$, $L+M$, $-H-K-M$ and $-H-K-L$ (Table 1).

Table 1. *Four combinations of a* Σ_2 *relation* (*tr*) *and a negative quartet* (*nq*) *leading to the same negative quintet* ($q\simeq 500$ mcycles)

Strong cross-reflexions are indicated with *S*; weak with *W*.

Main reflexions					Cross-reflexions									
H	*K*	*L*	*M*	$-H-K-L-M$	$H+K$	$H+L$	$H+M$	$-K-L-M$	$K+L$	$K+M$	$-H-L-M$	$L+M$	$-H-K-M$	$-H-K-L$
tr	tr	nq	nq	nq	tr+nq *S*							*W*	*W*	*W*
tr	nq	tr	nq	nq		tr+nq *S*				*W*	*W*			*W*
tr	nq	nq	tr	nq			tr+nq *S*		*W*		*W*		*W*	
tr	nq	nq	nq	tr				tr+nq *S*	*W*	*W*		*W*		
Negative quintet					*S*	*S*	*S*	*S*	*W*	*W*	*W*	*W*	*W*	*W*

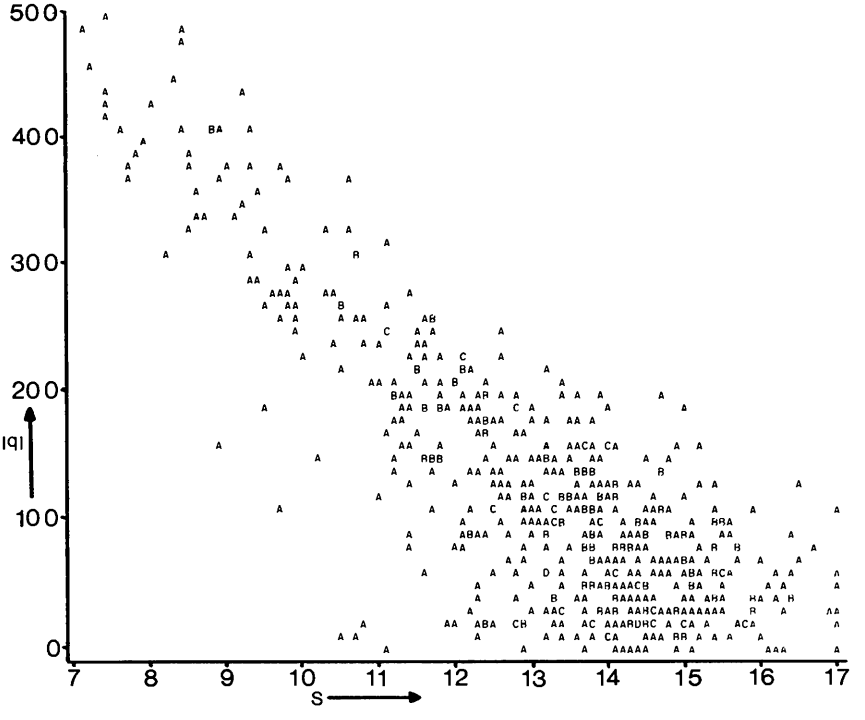

Fig. 1. Quintet phase sum $|q|$ in millicycles for the 10-atom structure as a function of the sum S of the E's of the 10 cross-reflexions. The number of quintets with the same $|q|$ and S are represented by capitals: *A* means 1, *B* 2, *C* 3, *etc.*

Calculations of quintets

For a randomly generated 10-atom $P1$ structure triplets, quartets and quintets have been calculated down to a limiting value of 0·7 for E_3, E_4 and E_5 respectively. The results are given in Table 2 together with the mean values of $|\phi_H+\phi_K+\phi_{-H-K}|$, $|p|$ and $|q|$ for the three relations respectively. Only those quartets and quintets are included for which all cross-terms are present in the group of known reflexions, although it is expected that quintets with less than 10 known cross-terms also contain useful information. From Table 2 a first conclusion may be that, most probably, relations between six phases will have too small E_6 values to be useful.

Table 2. *The number of triplets, quartets and quintets as a function of E_3, E_4 and E_5 respectively*

The total number of relations above a value is given in the columns TNR, the number in an interval $\Delta E_3=\Delta E_4=\Delta E_5=0{\cdot}1$ is given in the columns NR and the average of the absolute values of the phase sum in the intervals is given in columns AAPS.

E_3	Triplets								
E_4				Quartets					
E_5							Quintets		
	TNR	NR	AAPS	TNR	NR	AAPS	TNR	NR	AAPS
2·5	1	1	37·0						
2·4	2	1	59·0						
2·3	5	3	25·0						
2·2	10	5	54·0						
2·1	14	4	27·0						
2·0	18	4	32·0						
1·9	22	4	75·0						
1·8	36	14	47·0						
1·7	55	19	49·0	1	1	26·0			
1·6	79	24	47·0	3	2	27·0			
1·5	114	35	64·0	4	1	42·0			
1·4	153	39	61·0	11	7	50·0			
1·3	198	45	56·0	31	20	67·0			
1·2	264	66	74·0	80	49	86·0			
1·1	363	99	68·0	191	111	82·0			
1·0	524	161	66·0	373	182	90·0	6	6	60·0
0·9	747	223	75·0	736	363	97·0	24	18	92·0
0·8	1083	336	88·0	1515	779	107·0	127	103	116·0
0·7	1509	426	90·0	3173	1658	116·0	577	450	131·0

In the preceding paragraph for positive ($q\simeq 0$) and negative ($q\simeq\pi$) quintets the expected values of the cross-terms were given. With these characteristics less than half the actual number of negative and positive quintets could be indicated, so that this selection procedure is inadequate.

Quintet phase sums and the sum of the cross-terms

A less stringent treatment of the quintets is based on a graph of the phase sum $|q|$ against the sum S of the E's of the cross-reflexions (Fig. 1). A remarkable result is a linear trend for $|q|$ *vs* S, which opens the possibility of predicting $|q|$ on the basis of S.

The quintets can be divided into three groups: the positive ($q\simeq 0$), the negative ($q\simeq\pi$) and the enantiomorph-sensitive quintets ($q=\pm\frac{1}{2}\pi$). Figs. 2, 3 and 4 are produced with S limits at 9·0 and 12·5: the positive quintets have $S>12{\cdot}5$ (Fig. 2), the negative have $S<9{\cdot}0$ (Fig. 3) and the enantiomorph-sensitive have $9{\cdot}0<S<12{\cdot}5$ (Fig. 4). It can be seen that the enantiomorph-sensitive quintets in particular show a distribution which looks promising for practical applications. We have found the distributions of the phases to be rather insensitive to small changes in the limiting values of S.

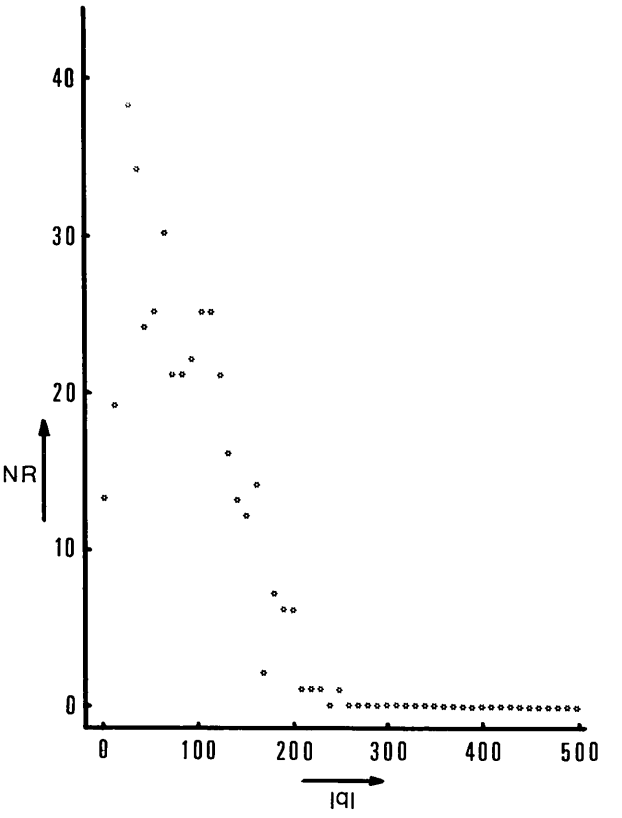

Fig. 2. Number of quintets for the 10-atom structure with $S>12{\cdot}5$ as a function of the phase sum $|q|$.

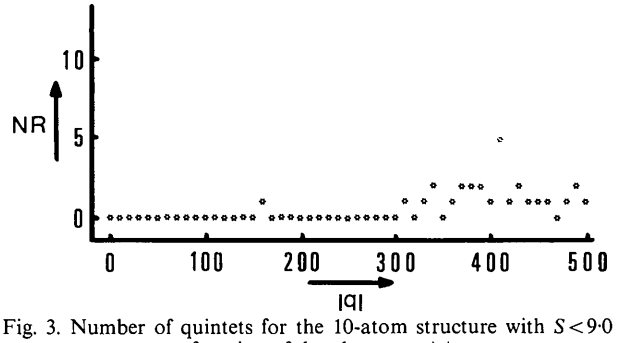

Fig. 3. Number of quintets for the 10-atom structure with $S<9{\cdot}0$ as a function of the phase sum $|q|$.

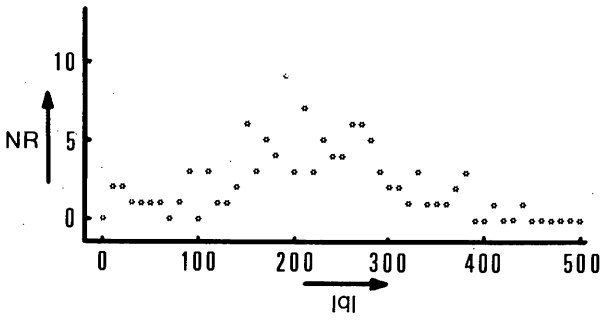

Fig. 4. Number of quintets for the 10-atom structure with $9{\cdot}0 < S < 12{\cdot}5$ as a function of the phase sum $|q|$.

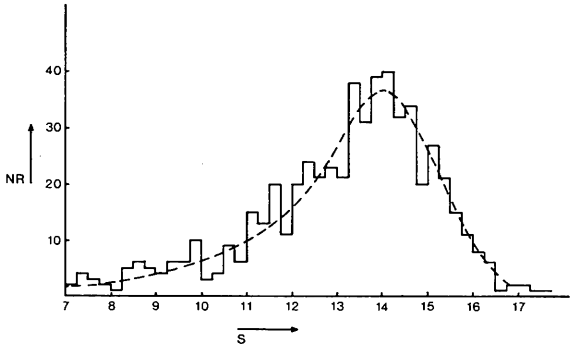

Fig. 5. Number of quintets for the 10-atom structure with $E_5 > 0{\cdot}7$ as a function of the sum S of the E values of the 10 cross-reflexions.

Making use of the linear trend between $|q|$ and S, we can calculate approximate values of $|q|$ by

$$|q_p| = 500 - A(S-B) \qquad (7)$$

with $A=60$ and $B=7$, and $|q_p|$ in millicycles, where if $S-B<0$ then $|q_p|=500$ and if $A(S-B)>500$ then $|q_p|=0$. With (7) $|q|$ values can be predicted such that $\langle||q_{\text{true}}|-|q_p||\rangle = 50$ mcycles for all 577 quintets, which is approximately equal to the average triplet error at an E_3 level of 1·7.

In order to be useful in direct methods, the constants of (7) have to be estimated without knowledge of the phase sums $|q|$. We expect that A and B can be found from the distribution of the quintets as a function of S (Fig. 5) from the following argument: the smallest S-value will correspond to $|q| \simeq 500$ and the larger S values will correspond to $|q| \simeq 0$. In the present structure the smallest S value is 7 and the larger limit is chosen between the top of the distribution at $S=14{\cdot}0$ and the tail at 16·75, resulting in $A=60$ and $B=7{\cdot}0$.

For a $P1$ structure ($N=30$, Kanters & van Veen, 1973) 391 quintets with $E_5 > 0{\cdot}35$ have been calculated. The average E_5 value is approximately 0·40 and the average phase sum $\langle|q|\rangle$ is 158 mcycles. The graph of $|q|$ against S (Fig. 6) tends to be linear just like the graph for the 10-atom structure, but as expected the divergence is greater.

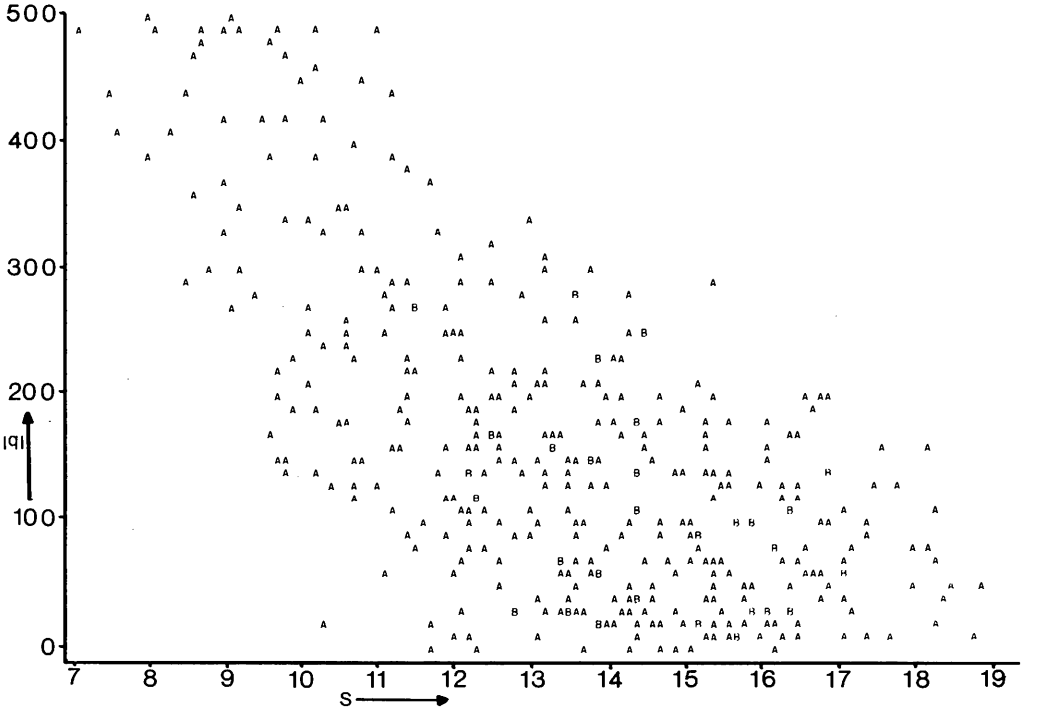

Fig. 6. Quintet phase sum $|q|$ in millicycles for the 30-atom structure as a function of the sum S of the E's of the ten cross-reflexions. The number of quintets with the same $|q|$ and S are represented by capitals: A means 1, B 2, C 3, *etc.*

By the procedure for estimating the A and B values of (7), described in the previous paragraph, in this case values $A=55$ and $B=7{\cdot}0$ are found. In Fig. 7 a graph is given of $|q_{\text{true}}|$ against $|q_{\text{calc}}|$ calculated with (7), from which it can be seen that the empirical procedure of estimating $|q_{\text{calc}}|$ values reproduces the linear trend of Fig. 6. The average $\langle||q_{\text{true}}|-|q_{\text{calc}}||\rangle \simeq 79$ mcycles is approximately equal to the average triplet error at an E_3 level of 1·2. With respect to the initial average phase sum the differences are reduced by a factor of 2, and moreover the systematic errors introduced by taking all $q_{\text{calc}}=0$ are replaced by random errors.

Possible use of quintets

Two applications of quintets in actual phase determinations seem promising: (1) selection of enantiomorph-sensitive quintets in order to introduce and maintain the enantiomorph in the early stages of non-centrosymmetric phase determinations; (2) The use of $|q|$ values in a modified tangent procedure:

$$\tan\phi_{-H}=\frac{\sum_K\sum_L\sum_M E_5\sin(\phi_K+\phi_L+\phi_M+\phi_{-H-K-L-M}+t|q_P|)}{\sum_K\sum_L\sum_M E_5\cos(\phi_K+\phi_L+\phi_M+\phi_{-H-K-L-M}+t|q_P|)} \tag{8}$$

in which $t=\pm 1$. The $|q_p|$ value is calculated with (7) and t is such that all terms of (8) comply with

$$\phi_H+\phi_K+\phi_L+\phi_M+\phi_{-H-K-L-M}+t|q_P|=\text{minumum}.$$

By this modification of the tangent refinement the enantiomorph in polar space groups is maintained, whereas the normal tangent procedure leads to centrosymmetric solutions. In our laboratory we have had encouraging results with the triplet analogue of (8):

$$\tan\phi_{-H}=\frac{\sum E_3\sin(\phi_K+\phi_{-H-K}+t|\delta|)}{\sum E_3\cos(\phi_K+\phi_{-H-K}+t|\delta|)} \tag{9}$$

(Sint & Schenk, 1975), where the values of δ were estimated on the basis of a small number of known phases. This work will be reported more extensively in a forthcoming paper.

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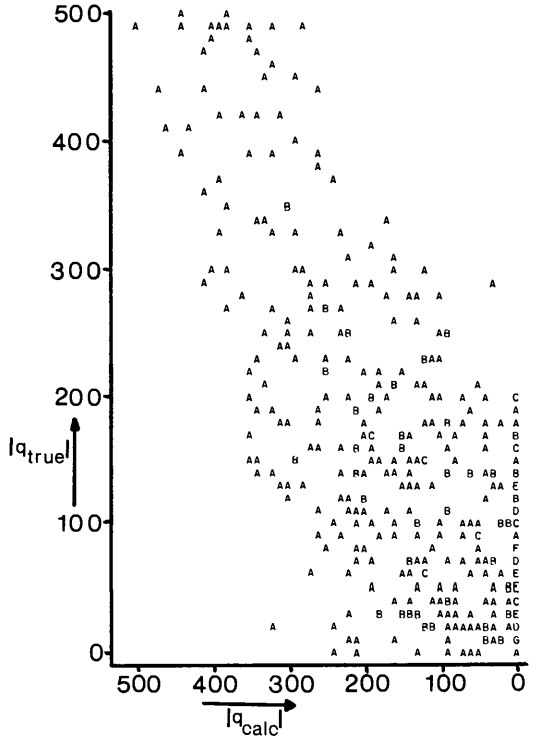

Fig. 7. Graph of $|q_{\text{true}}|$ against $|q_{\text{calc}}|$ calculated with (7) ($A=55$, $B=7{\cdot}0$) for a $P1$ structure ($N=30$).

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