The results show that:-

(i) The P_{13} formula gives a more reliable estimate for both positive and negative quartets, although an underestimation still exists.

(ii) There is a considerable increase in the availability of quartets ($^nP_7$:$^nP_{13}$) having a high associated probability. This increase is most dramatic in the range $1.0 > P^+ > 0.99$.

(iii) There is also a pronounced increase in the availability of negative quartets.

(iv) In cases of limited data, the multiplicity of third neighbourhoods can generate strong indications in situations where P_7 alone is of limited use.

(v) Multiplicity of individual estimates also enhances the phase estimation procedure.

Practical experience indicates that as few as 50 negative quartets with good estimated probabilities is enough to solve difficult structures.

17.2–10 PHASE RELATIONSHIPS FOR SUPERSTRUCTURES

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Statistical relationships between phases of structure factors are usually derived for structures with rationally independent atom coordinates. Prominent deviations of the mean squared normalized structure factors from unity for certain index parity classes (in general a 'strong' subset of 'main' reflections and 'weak' cosets) are a characteristic feature of systematic rational dependence.

A formula for phase determination has been derived in which the different mean coset intensities are explicitly taken into account:

$$P\{\varphi(\underline{h}_n)\} = \{1/(2\pi I_o[\alpha_n])\}\exp\{\alpha_n \cos[\varphi(\underline{h}_n) - \beta]\}$$

with

$$\alpha_n \exp(i\beta) = \sum_{h'}^{(s)} K(\underline{h}_n\underline{h}')\exp\{i[\varphi(\underline{h}') + \varphi(\underline{h}_n - \underline{h}')]\}$$

and

$$K(\underline{h}_n\underline{h}') = \{2p/(\sqrt{N}\sum_{m=0}^{p-1} v_{\underline{m}} v_{\underline{n}-\underline{m}})\} E(\underline{h}_n)E(\underline{h}')E(\underline{h}_n - \underline{h}') .$$

$P\{\varphi(\underline{h}_n)\}$ is the von Mises distribution of the phase of the structure factor $E(\underline{h}_n)$

n is an appropriate numbering of the cosets (or possibly parity classes), n=0,1,...p-1

I_o is a modified Bessel function

s is the number of contributors

N is the number of atoms in the unit cell

$v_{\underline{m}}$ are the means of the squared normalized structure factors of coset $\underline{m}$

$\underline{n}$ is an appropriate vector numbering $\underline{n}$(n) of the cosets; e.g. the index of a given coset reflection reduced modulo G* with G* the reciprocal lattice of the 'main' reflections

No unique probability distribution for triplet phase relationships could be obtained. However, the following conclusions support recent proposals for superstructure determination:

- Phases of reflections of the 'weak' cosets can be developed from 'weak-strong-weak' triplets (cf. Fan, Yao, Main & Woolfson, 1983, Acta Cryst. A39, 566-569).
- You should not determine a phase of the 'strong' subset using 'weak' reflections.
- You should not determine a 'weak' reflection exclusively from other 'weak' ones. But the 'weak-weak-weak' relationships may be essential in the final stages of tangent refinement.

The peculiar connectivity of the phases in superstructures with the inherent weak link between different cosets requires considerable care for the selection of the starting set. If partially occupied positions are involved in a superstructure, homometric solutions can become indiscernible by the conventional figures of merit.

17.2–11 ON THE ESTIMATION OF SEMINVARIANTS BY THE AID OF HARKER RELATIONS.

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As the direct inspection of seminvariant phases leads to a remarkable increase of computation time if higher symmetry is present and "upper representations" are included another approach is proposed:

(i) A Patterson function is computed on the base of E^2 - values

(ii) Space-group symmetry is applied to construct a "Harker" space.

(iii) The Fourier transform of the Harker space gives information on the phases of seminvariant reflexions.

The procedure is tested on the base of some difficult structures, the result will be reported.