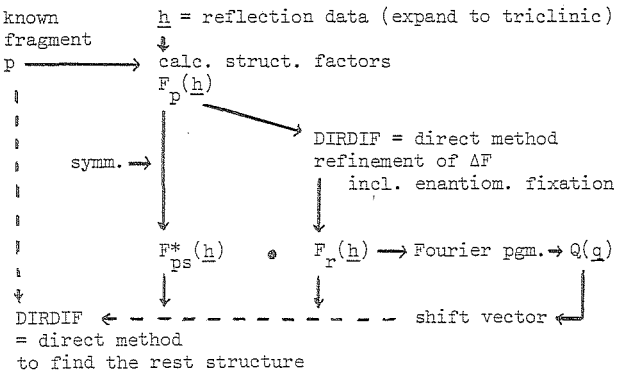
For instance: in space group $P2_1$: the Q function takes the form

$$Q(\underline{q}) = \frac{1}{V} \sum_h \sum_k \sum_l F_p^*(\bar{h}k\bar{l})\, F_r(hkl)\, (-1)^k \exp(-2\pi i \underline{h}.\underline{q})$$

while only one Fourier section ($\underline{q} = x_q, 0, z_q$) has to be calculated. The shift vector is $-\frac{1}{2}\underline{q}_m$ where $\underline{q}_m$ is the position of the highest peak in the Q-function.

The shift can be applied in reciprocal space, to produce Fourier coefficients for a new symmetry - enforced electron density map. Examples in various space groups, simultaneous location of the fragment relative to all symmetry elements, and location of fragments relative to each other, will be shown.
Advantages: automatic, high-speed computer program; no Patterson-overlap; for large structures: multisolution technique and application to small or qualitatively bad fragments is possible.

Flow diagram



17.2-15 BREAKING OF PSEUDOSYMMETRY USING DIRECT METHODS.

By R. Böhme*, Institut für Angewandte Physik, Lehrstuhl für Kristallographie, Universität Erlangen-Nürnberg, Germany (BRD).

Let $\rho(\underline{x})$ describe the electron density distribution of a structure and $F(\underline{h})$ its structure factors. If $\rho(\underline{x})$ satisfies a pseudotranslation $\underline{t}$ of index p it is useful to divide the set of all reflexions into the set of main and the set of superstructure reflexions. The main reflexions $\underline{H}$($\underline{H}.\underline{t}$ integer) determine the structure of the subcell

$$\hat{\rho}(\underline{x}) = \frac{1}{p} \sum_{n=0}^{p-1} \rho(\underline{x}+n\underline{t}) = \frac{1}{V} \sum_{\underline{H}} F(\underline{H}).\exp(2\pi i \underline{H}.\underline{x})$$

and the superstructure reflexions $\underline{U}$ ($\underline{U}.\underline{t}$ not integer) the complement structure

$$\tilde{\rho}(\underline{x}) = \rho(\underline{x}) - \hat{\rho}(\underline{x}) = \frac{1}{V} \sum_{\underline{U}} F(\underline{U}).\exp(2\pi i \underline{U}.\underline{x})$$

(M. Buerger, Vector space 1959). Because $\tilde{\rho}(\underline{x})$ contains equal amounts of positive and negative electron density (J.W. Jeffery (1964), Acta Cryst. 17,776) this concept is not used in direct methods. But there exists a structure $\tilde{\tilde{\rho}}(\underline{x})$ which has positive maxima only and the structure factors $\tilde{\tilde{F}}(U)$ of $\tilde{\tilde{\rho}}(\underline{x})$ coincide with $F(\underline{U})$, whereas the $\tilde{\tilde{F}}(\underline{H})$ remain unknown. If the pseudotranslation has index p=2, the maxima in $\tilde{\tilde{\rho}}(\underline{x})$ cannot be rationally dependent of each other, so that $\langle \tilde{\tilde{F}}^2_{abs}(\underline{H})\rangle = \langle \tilde{\tilde{F}}^2_{abs}(\underline{U})\rangle$. Therefore the E-normalisation is correct also if the $\tilde{\tilde{F}}(\underline{U})$ are known only. Because of $\tilde{E}(U) = \tilde{\tilde{E}}(U)$ phase determination of $\tilde{\tilde{E}}(\underline{U})$ gives phases of $E(\underline{U})$ and $F(\underline{U})$. If the index of $\underline{t}$ is larger than 2, $\tilde{\tilde{\rho}}(\underline{x})$ normally shows less rational dependency among the coordinates of maxima than $\rho(\underline{x})$. So the assumptions for using direct methods are better fulfilled. In these cases ($p \geq 3$) it can be shown that the sums of phases of triplets with high values of κ are more reliably π than 0 under specific conditions. So phase determination is reduced to normalisation of substructure and complement structure. If n atoms having formfactors $f_1,\ldots,f_n$ are expected in the unit cell of $\rho(\underline{x})$, E - values can be calculated if the expected intensity $\langle F^2_{abs}(\underline{U})\rangle$ and $\langle F^2_{abs}(\underline{H})\rangle$ is approximated by

$$\langle F^2_{abs}\rangle = a.\exp(-B.\sin^2\theta/\lambda^2) \sum_{j=1}^{n} f_j^2$$

using different values of a and B for main and superstructure reflexions. This can be done by normalizing $\{F(\underline{H})\}$ and $\{F(\underline{U})\}$ separately using a standard E-normalizing program. If some atoms of the structure satisfy $\underline{t}$ and the others do not this normalisation is equivalent to rescaling the E - values. It can be shown by theory and by example (Eukryptit: Tscherry, Schulz & Laves (1972), Z. Krist. 135, 175-198) that in the case where the pseudotranslation $\underline{t}$ is nearly but not exactly fulfilled,

$\langle F^2_{abs}(\underline{U})\rangle$ versus $\sin\theta/\lambda$ is rather different from the expected intensity of a structure with independent atoms. The proposed procedure can also be applied to pseudocentrosymmetric structures in handling real and imaginary part of structure factors separately. But in this case it is necessary to determine the coordinates of maxima of the centrosymmetric subcell.

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17.2-16 PROBLEMS OF ENANTIOMORPH DISCRIMINATION IN DIRECT METHODS.

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The problem of enantiomorph definition in space groups P1, P2, $P2_1$, C2 and Cc is often wrongly attributed to the presumption that it is not possible, in these space groups, to select a starting reflection with a phase orthogonal to the origin defining set.

In simple structures, that is in structures with a well behaved set of triples (with no unexpectedly large deviation from zero) and no significant character of pseudo-centrosymmetricity, enantiomorph sensitive phases are automatically identified by a convergence type procedure and are left out as part of the basis set of phases. Moreover, inspection of the phases in the basis set, in particular of their interrelationship in terms of accessibility-inaccessibility (linear-rational dependence) often permits one to single out the best candidate for enantiomorph definition.

When the distributions of the normalized structure factors do not suggest any significant degree of pseudo-centrosymmetric character, failure to properly define the enantiomorph is symptomatic of the occurrence of aberrant triples at important links of the phase development. The possible "ways out", i.e. clean-up techniques (editing the triples to weed out the aberrant ones), enantiomorph sensitive invariants and seminvariants and the method of strong enantiomorph discrimination, will be discussed.

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