

17.2-2 MULTAN87. By T Debaerdemaeker¹, C Tate² and M.M. Woolfson².

¹Universität Ulm, D-7900 Ulm, Oberer Eiseisberg, W Germany

²Department of Physics, University of York, Heslington, York YO1 5DD, UK

The latest version of MULTAN incorporates a number of structure solving algorithms, eg

1. SAYTAN - based on a tangent formula derived from Sayre's equation (Debaerdemaeker, T., Tate, C. and Woolfson, M.M., Acta Cryst., 1985, A41, 286-90).

2. X-Y - based on a parameter-shift approach which maximises a function of phases.

$$\Psi_D = \sum_{hk} |E(h)E(k)E(h-k)| \{ \cos\phi_3(h,k) - \sin\phi_3(h,k) \}$$

$$\text{where } \phi_3(h,k) = \phi(h) - \phi(k) - \phi(h,k).$$

It has been noted (Debaerdemaeker, T. & Woolfson, M.M., Acta Cryst., 1983, A39, 193-196) that this function is illogical but very effective.

3. YZARC (Declercq, J.P., Germain, G., Woolfson, M.M. and Wright, H., Acta Cryst., 1981, A37, C237).

4. MAGEX (Zhang Shao-hui and Woolfson, M.M., 1982, A38, 683-85).

In the basic SAYTAN mode phase refinement begins with a complete set of random phases and only the 'strongest' path is followed throughout. This is enabled by an efficient algorithm which minimises the computational work at each step.

Examples of the application of MULTAN87 will be given.

17.2-3 PHASE DETERMINATION OF STRUCTURE-FACTOR TRIPLETS AND QUARTETS USING HIGH-ORDER MULTIPLE DIFFRACTION OF X-RAYS. By S.-L. Chang, H.-H. Huang, S.-W. Luh, H.-P. Pan and M.T. Tang Department of Physics, National Tsing Hua University, Taiwan, Rep. of China and J.M. Sasaki, Instituto de Física, Universidade Estadual de Campinas, Campinas, S.P. Brazil

The sign relation $S_p = S_L \cdot S_R$ (Chang, Phys. Rev. Lett. 1982, 48, 163-166) is applied to the determination of the signs of structure-factor triplets and quartets involved in high-order multiple diffractions, such as 4-, 5-, 6- and 8-beam cases. S_p is the sign of the cosine of a triplet or quartet phase. S_L and S_R are the signs determined from the diffracted intensity asymmetry and from the relative motion of the reciprocal lattice points to the Ewald sphere, respectively. Experimentally determined S_p 's show a good agreement with the theoretical ones.

The applicability of this sign relation for phase determination in high-order multiple diffraction is discussed, based on the Bethe approximation and the dispersion relation of the dynamical theory.

17.2-4 A PSEUDO-RANDOM STARTING SET TENDENCIALLY MAXIMALLY ENTROPICAL. By M.C. Burla⁺, G. Cascarano⁻, C. Giacovazzo⁻, A. Munzi⁺, G. Polidori⁺.

⁺) Dipartimento di Scienze della Terra, Università di Perugia, Italy.

⁻) Dipartimento Geomineralogico, Università di Bari, Italy.

In the multisolution procedures several phase sets are developed by applying the tangent formula or similar techniques to starting sets usually provided by a magic integer sequence or by random generation. The magic integer approach may be considered as an optimized generator of pseudo-random phase values, evenly distributed into the n-dimensional phase space.

Both magic integers (for long sequences) and random starting sets are in general inconsistent with positivity and atomicity of the electron density. This information is normally introduced by tangent formula which may be considered as a procedure for maximizing the entropy under these physical constraints.

It seems therefore of some interest a procedure which generates sets of pseudo random phases tendentially maximally entropical. The starting idea is the following:

let $\phi_h - \phi_k - \phi_{h-k}$ be a triplet invariant and ϕ_k, ϕ_{h-k} known quantities, then ϕ_h is distributed around θ_h ($= \phi_k + \phi_{h-k}$) according to a Von Mises distribution $M(\phi_h, \theta_h, G)$ where G is the measure of the triplet reliability. If a phase shift Δ is generated according to the Von Mises distribution $M(\phi_h, 0, G)$, the variable $\theta_h + \Delta$ may be used as a starting estimate of ϕ_h . In practice each trial of a multisolution process may be started by randomly generating N Von Mises phase shifts each one associated to a triplet invariant.

The generated sets of pseudo-random phases, tendentially compatible with positivity and atomicity, can be expanded more easily into the correct solution.

The procedure has proved to be very successful and its results will be shown.

17.2-5 A RECONSIDERATION OF THE ROLE OF TWO-PHASE SEMINVARIANTS. By M.C. Burla⁺, G. Cascarano⁻, C. Giacovazzo⁻, A. Munzi⁺, G. Polidori⁺.

⁺) Dipartimento di Scienze della Terra, Università di Perugia, Italy.

⁻) Dipartimento Geomineralogico, Università di Bari, Italy.

According to the representation theory (Giacovazzo, Acta Cryst. A33, 1977) a procedure has been already devised (Giacovazzo et al., Acta Cryst. A35, 1979), which is able to recognize in an automatic way two-phase structure seminvariants of first rank among all pairs of structure factors chosen between the largest reflexions. According to the algebraic results $\phi = \phi_{u_1} + \phi_{u_2}$ is a two-phase structure seminvariant of first rank if at least two vectors h_1 and h_2 and two rotation matrices R_α and R_β exist such that the following system:

$$\phi_{u_1} = \phi_{h_1} - \phi_{h_2} R_\beta$$

$$\phi_{u_2} = \phi_{h_1} - \phi_{h_2} R_\alpha$$

is satisfied. When $\{h_1\}$ and $\{h_2\}$ are obtained, the special quartets:

$$\phi_{u_1} + \phi_{u_2} R_\beta - \phi_{h_1} + \phi_{h_2} R_\alpha R_\beta$$

$$\phi_{u_1} R_\alpha + \phi_{u_2} - \phi_{h_1} + \phi_{h_2} R_\alpha R_\beta$$

can be constructed and the probabilistic estimation of ϕ via the first representation can be obtained.

The above procedure is quite general and may be applied to any space group, however it is rather time consuming, in fact for each pair of reflexions (u_1, u_2) all the possible pairs of matrices (R_α, R_β) have to be introduced to search the sets $\{h_1\}$ and $\{h_2\}$. In order to reduce computing cost, usually a small number of two-phase seminvariants were estimated; furthermore, since two-phase seminvariants are phase relationships of order N^2 , the average reliability level of the probabilistic estimates is low.

The present communication deals with a new algorithm which is able to estimate two-phase seminvariants in all the space groups and drastically reduces computing time. The new procedure identifies all the one-phase structure seminvariants of first rank and calculates the three-phase structure invariants involving at least one-phase seminvariant; therefore the list of triplet invariants directly provides all the pairs (U_1, U_2) which are two-phase seminvariants of first rank. The probabilistic formula used is an effective modification of older formulas. The result is that a large number of reliable two-phase seminvariants is usually available for active use with a reliability often comparable with triplet invariants estimates.

17.2-6 INVESTIGATION OF PHASE INVARIANTS FROM A POWER SERIES EXPANSION OF THE ENTROPY FUNCTIONAL. By I.R. Castleden, Department of Physics, University of Western Australia, Nedlands 6009, Australia.

The entropy functional for N atoms

$$S = -N \int_V p(x) \log\{ \Psi_p(x) \} d^3x$$

where $p(x)$ is single atom probability density can be expanded as a power series about a 'point' $p_0(x)$. This expansion is equivalent to an asymptotic expansion of the probability density of N independently distributed atoms. Expressed in terms of the Fourier components of $p(x)$ and $p_0(x)$ S is represented as a sum of invariants. The ability of these invariants to predict correct phases can be tested in a similar manner to the invariants encountered in direct method calculations. The phase indications from the invariants of a second order expansion of the entropy are tested using a routine that compares them to actual phases values. The program is similar to the XTAL program REVIEW (Hall, S.R., 1986, Tech. Rep. TR-1364.2, University of Maryland). A number of known structures are tested. For each structure a selection of expansion points $p_0(x)$ are used ranging from the uniform distribution to the true structure. For each point data such as the number of correct phase indications can be plotted. R-factors and figure-of-merits can also be calculated giving an indication of the likelihood that structure solution methods using second order entropy expansions (Wilkins, S.W. et al. 1983, *Acta Cryst.*, A39, 47-60; Bricogne, G. 1984, *Acta Cryst.*, A40, 410-445; & Navaza, J. 1985, *Acta Cryst.*, A41, 232-244) will be applicable as routine and robust procedures.

17.2-7 DIRECT METHODS SOLUTIONS FROM VERY WEAK DATA. By M.J. Begley, Department of Chemistry, University of Nottingham, Nottingham, England.

The diffraction data obtainable from very small crystals, using conventional X-ray sources, is usually very weak and limited by the sample size. If a heavy atom is present this data is sometimes sufficient to solve the structure by the Patterson method. With no heavy atom, attempts to solve the structure by direct methods using, for example, the MULTAN80 program are usually unsuccessful because of the severe limitations of the data set. It has been suggested by Sheldrick (BCA Meeting York, 1986) that at least 50% of the theoretically measurable reflections in the resolution range 1.1 to 1.2 Å should be observed for the data to be of adequate quality for direct methods solution of noncentrosymmetric structures. It is the lack of sufficient intensity data in this and higher angle ranges that causes the direct methods procedure to fail. If most of the reflections in this range are unobserved then the few weakly observed reflections have calculated E values that are too low to allow them to play their proper major role in the phase determination process. A method has been developed that attempts to overcome this problem. In this, E values are calculated by a conventional normalisation process for low angle reflections only. The high angle observed reflections are then inspected and estimated E values are manually added to the data set for phase determination using the MULTAN80 program. Several examples of structures (both centrosymmetric and noncentric) that have been successfully solved from very weak data, using this procedure, will be described.

17.2-8 THE USE OF E-MAGNITUDE WEIGHTING SCHEMES IN CONVERGENCE MAPPING AND TANGENT REFINEMENT IN DIRECT METHODS. By S.R. Brown and C.J. Gilmore, Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland.

Traditionally, direct methods do not exploit the standard deviations of the E-magnitudes. However, it is possible to simulate the use of $\sigma(|E_h|)$ via a simple weighting scheme applied to the triplets and quartets at convergence mapping and carried through the subsequent tangent refinement procedure.

Examination of $\sigma(|E_h|)$ as a function of Bragg angle shows the expected increase at high angle, so that a suitable weighting scheme should downweight (or even remove) phase relationships involving one or more high angle E-magnitudes. A simple weighting scheme has been incorporated into the MITHRIL direct methods program:

$$\omega = 1 \text{ if } \sin^2\theta/\lambda^2 < t$$

$$\omega = f(\sin^2\theta/\lambda^2) \text{ if } \sin^2\theta/\lambda^2 > t$$

where t is a selected cut-off point (usually 0.95).

Alternatively a filtering system can be used in which certain invariants are removed.

This simple method is extraordinarily successful. Over half the structures are routinely solved by this technique. A 138 atom polypeptide structure has also been solved with minimal difficulty.