PS02.05.10 A NEW MONTE CARLO APPROACH TO STRUCTURE SOLUTION FROM POWDER DATA.

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Unlike Monte Carlo procedures for structure solution reported thus far we report a new approach which not only allows random movements of individual atoms and rigid-body fragments comprising an asymmetric unit but offers a means of changing internal configuration of stereochemically constrained constituent groups. The last option can be crucial when flexible atomic assemblies like chains, sheets and other moieties are considered.

A way of describing the flexible groups mentioned above is proposed which uses stereochemical descriptors such as bond lengths, bond and torsion angles along with positional and orientational parameters of the group as a whole. An appropriate Monte Carlo algorithm combined with simulated annealing for the solution of this type of structure is discussed in detail. Similar to the previuosly reported algorithm[1], the Pearson-distribution χ^2 criterion of powder-profile fit is used as an analogue of the 'energy' function.

The new technique is illustrated by solving the previously unknown structure of poly(ethylene oxide)$_3$:$LiN(CF_3SO_2)_2$ comprising 25 non-hydrogen atoms in the asymmetric unit partitioned into an imide moiety, poly(ethylene oxide) chain and individual Li atom.

[1] Newsam, J. M., Deem, M. W. and Freeman, C. M. NIST Spec. Publ 846., Proc. Int. Conf. Accuracy in Powder Diffraction II, held at NIST, Gaithersburg, MD. May 26-29, 1992.

PS02.05.11 SOLVING CRYSTAL STRUCTURES FROM POWDER DATA: EXTRA AND SIRPOW PACKAGES.

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The principal limitation of the diffraction methods for crystal structure analysis from powder data is originated by the collapse of the three-dimensional reciprocal space into the one dimension of the powder diffraction pattern.

Current decomposition methods disregard a large amount of information which can become available during the process for crystal structure solution and analysis. The use of such an information is essential for making direct methods procedures more robust and for improving the accuracy of the least-squares techniques. EXTRA [Altomare A., Burla M.C., Cascarano G., Giacovazzo C., Guagliardi A., Moliterni A.G.G. & Polidori G., (1995), J. Appl. Cryst. 28, 842-846], a program for full pattern decomposition based on the Le Bail algorithm, is able to exploit the following types of prior information:
1) the positivity of the electron density through the Patterson function.
2) the pseudo-translational symmetry, which becomes available as soon as normalized structure factors are calculated.
3) the preferred orientation. Also this information can be obtained by a suitable analysis of the normalized structure factors.
4) the partial structure. This information becomes available as soon as a reliable structure fragment is provided in the first E-map.

PS02.05.12 AB-INITIO STRUCTURE DETERMINATION BY THE MAXIMUM ENTROPY AND LIKELIHOOD METHOD USING POWDER DIFFRACTION DATA AND THE CONCEPT OF HYPEROCTANT PHASE ANGLES.

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The problem of reflection overlap in powder diffraction is the factor which most limits our ability to solve crystal structures ab initio from such data. The conventional multiplicity weighted eqipartition of the intensity among the overlapped reflections is often much too crude to make structure solution possible with conventional methods. In the maximum entropy - likelihood approach (Bricogne, Acta Cryst. (1991), A47, 803-829) as programmed in the MICE program (Gilmore, Henderson & Bricogne (1991). Acta Cryst. A47, 830-841; Shankland, Gilmore, Bricogne & Hashizume (1993). Acta Cryst. A49, 493-501) partitioning the intensity of overlapped reflections is carried out by the concept of a hyperoctant phase permutation. Each overlap has associated with it the phase angles of the reflections comprising it plus one or more angles which define the intensity partitioning. These hyperoctant angles are permuted as normal phases and used to build the nodes of a phasing tree, which are then subjected to entropy maximisation. Following this, each node has a likelihood measure associated with it. We have now established a statistical method of analysing such likelihoods to determine both the phase angles and the intensities for strong overlaps, and have applied the technique successfully to organic molecules and zeolites with a mixture of laboratory and synchrotron data. It is a significant step forward in our goal to make the MICE program totally automatic.

PS02.05.13 STRUCTURE DETERMINATION FROM POWDER DATA USING SYMMETRY ADAPTED FUNCTIONS: SIMREF22.

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The novel method presented here determines and refines an unknown structure (S^R), which is the result of a commensurate or incommensurate perturbation of a known idealized structure (S^I). In such cases, the difference vectors between the atomic positions of S^R and S^I are the sum of a few symmetry adapted shift vectors $\vec{e}_v$ of S^I. The latter are irreducible representations of S^I, their magnitude may be understood as order parameter η_v in the sense of the Landau theory for a phase transition leading from S^I to S^R. When the appropriate representations are found, the full profile refinement program SIMREF22 applied to the diffraction pattern of the unknown structure refines, besides the coordinates of S^I, the order parameter η_v for each active representation. The symmetry of $\vec{e}_v$ determines the symmetry of S^R, therefore, the careful analysis of line splitting in highly resolved powder patterns is the first step to select an order parameter of proper symmetry. Further restrictions for its selection arise from the assumption, that certain molecules or parts of the lattice remain rigid. The program package consists of the following parts:
1. Visual choice of the atomic setting for S^I
2. Computation of all irreducible representations of S^I
3. Visualisation of the atomic shift vectors with display of its symmetry S^R for each irreducible representation of S^I
4. Full profile refinement of S^I and, η_v with SIMREF22.

An example for the application of the method is the structure determination for the four phases of $Pb_5Al_3F_{19}$.