02-Methods for Structure Determination and Analysis, Computing and Graphics

Traditionally, crystallographic programs are run from a few standard data files for routine tasks, edited with the values for the current compound and run as batch jobs. For non-routine tasks the user is left searching the manual for elusive information.

An alternative modern strategy provides the user with a menu of procedures. This can be a useful facility for routine tasks, but offers the user little help with obscure or unusual problems.

In CRYSTALS we provide both of these input modes together with an interrogative interface through which the program enters into a dialogue with the user. This dialogue is driven by external 'scripts', and so can be tailored to suit novices (as a teaching aid), to simplify routine tasks, or as an aid for attacking unusual problems.

Since the user can write his own scripts, he can encode in them any special knowledge or experience he has. Since SCRIPTS can read data files, 'call' other SCRIPTS, and can even write new SCRIPTS themselves, the concept has the potential to be developed into an 'Expert System'.

At the meeting we will be showing, as an example, a script written to assist in the anisotropic refinement of large organo metallic compounds containing very many organic ligands and counter ions. Because each script is just a plain language ASCII data file, users can easiy modify them to handle local problems without risk of corrupting the CRYSTALS program itself.

The integration of a wide range of refinement, Fourier, geometry, graphical and analytical functions into a single package which can be used both interactively and in batch, which runs with identical functionality on anything between a PC386 and mainframes like the CONVEX makes CRYSTALS suitable for almost any environment or problem.

For users able to work interactively, there are integrated graphics which can be used both for the production of diagrams for publication, and as a powerful tool when dealing with large structures. The integration of Fourier map contouring with principal axis and TLS analysis of molecules is of great value for understanding disorder and thermal motion.

The ability to switch between the various user modes at will provides the flexibility needed for efficient structure analysis.

Enquiries about obtaining CRYSTALS should be addressed to David Watkin at the address above.

PS-02.08.12 THE ESTIMATION OF PHASE INVARIANTS FOR LARGE DIRECT METHODS STRUCTURE DETERMINATIONS. By D. A. Langs* and D.-Y. Guo, Department of Molecular Biophysics, Medical Foundation of Buffalo, Inc., 73 High Street, Buffalo, NY, U.S.A.

Simple tangent formula phase determination methods usually reach their limit of applicability when the complexity of a light atom structure exceeds 100 to 150 atoms. A new frequency-based triples phase invariant estimation procedure (Langs, Acta Cryst., **A49**, 1993, in press), employing traditional quadrupole relationships, has been shown to be successfully applicable to tangent formula structure determinations of greater than 300 atoms complexity. Efforts to extend the reliability of these frequency-based cosine invariant estimates by exploring higher-order relationships among phase invariants is in progress. Our experience using higher than 4th order Karle-Hauptman determinantal constructions has not been overly encouraging. We have however discovered one particularly interesting high order relationship involving 15 E-magnitudes that is most unusual in that it often embeds an unexpectedly high percentage of aberrant triples which have large A-values. We are currently exploring whether the frequency criterion or derived probability distribution can take advantage of these 15-magnitude constructs to forcefully disclose the identity of the embedded negative triples cosine invariants. If this can be achieved we strongly feel that this information will permit the solution of many more structures of greater than 300 atoms complexity by direct phasing methods.

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PS-02.08.13 COMPARISON OF F AND F^2 STANDARD REFINEMENTS OF SMALL MOLECULE CRYSTAL STRUCTURES. By S. Ianelli, M. Nardelli*, Istituto di Chimica Generale, Università di Parma, Centro di Studio CNR per la Strutturistica Diffrattometrica, Viale delle Scienze 78, I-43100 Parma, Italy.

It has been demonstrated that, in least-squares refinement of crystal structures, exclusion of weak (or "negative") intensities leads to a bias in the remainding experimental data towards too high F^2 values and thus to systematic errors in the refined parameters (F.L. Hirshfeld & D. Rabinovich, *Acta Cryst.* (1973). **A29**, 510-513; L. Arnberg, S. Hovmöller & S. Westman, *Acta Cryst.* (1979). **A35**, 497-499; P. Seiler, W.B. Schweizer & J.D. Dunitz, *Acta Cryst.* (1984). **B40**, 319-327). It seems that, omitting F's smaller than some predetermined size have some effect in the refinement that should be more important for scaling factors and temperature factors than for positional parameters. Moreover, carrying out two refinements with different weighting schemes might reveal the presence of significant but unsuspected defects in the model or systematic errors in the measurements (A.J.C. Wilson, *Acta Cryst.* (1973). **B29**, 1488-1480).

Taking the opportunity of checking the new born SHELXL-92 system for refinement of crystal structures (gamma-test stage) that is based on the use of F^2's, fifteen crystal structures of small organic and metal-organic molecules were refined, using data of standard quality, both on F (by using SHELX-76) and F^2. The results were compared using the half-normal probability plot technique (S.C. Abrahams & E.T. Keve, *Acta Cryst.* (1971). **A27**, 157-165) applied to all the interatomic distances less than 4.65 Å (W.H. De Camp, *Acta Cryst.* (1973). **A29**, 148-150) and to the U_{eq} values. The main results can be summarized as follows:

- The positional parameters obtained through these refinements are in general not significantly different, as only a limited number of long contacts have $\Delta/\sigma > 3$, which means that significant differences may be present only in some values of bonds and mainly torsion angles.
- No indication of systematic errors of some relevance is observed for positional parameters in the major number of cases. For these parameters in six cases the standard deviations are overestimated by factors ranging from 1.06 to 1.7, while in all the other cases the e.s.d.'s are underestimated by factors ranging from 1.07 to 2.25.