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

The extensive use of Fourier transform methods and the large sizes of unit cell and data sets in macromolecular crystallography make it highly desirable to use efficient methods of computation. Fast Fourier transform (FFT) methods are very useful for solution of these problems. With a few exceptions, the libraries of FFT subroutines that have been available in the past have been restricted to sample sizes (numbers of grid points per period) that were products of small, prime numbers, which results in rather large gaps between numbers that may be used for large unit cells and moderately high resolution. Efficient FFT routines for different types of numbers -- prime numbers, powers of prime numbers, or products of distinct prime numbers and their powers - follow many different procedures, so it is not possible to write general routines that can handle all cases. Also, when many transforms are required for sample sequences all of the same size, a routine that is optimized for that particular size is desirable.

The crystallographic problem allows exploitation of certain special conditions to make computation still more efficient. Electron density is a real function, so its Fourier transform has Hermitian symmetry. Three dimensional transforms may be performed as sequences of one dimensional transforms, and the data in the intermediate steps may have a symmetric structure. For example, a 2_1 screw axis gives a data structure in which values separated by half of a lattice translation are complex conjugates, and centered lattices produce rows that are alternately symmetric and antisymmetric. Techniques for exploiting space group symmetry for space groups that have no rotation axes of order higher than two have been described by Ten Eyck (*Acta Cryst.*, 1973, A29, 183-191), but space group symmetry with three-, four- and six-fold axes may also be used to reduce the computational load.

We have developed a package of FORTRAN routines for one-dimensional FFTs for all odd number sample sizes from 11 to 99 and all even number sample sizes from 20 to 200 that have no prime factors larger than 17. The package also includes transforms from real sequences to Hermitian sequences and from Hermitian sequences to real sequences, as well as between sequences that have translational conjugate symmetry and sequences that have alternating Hermitian symmetry and Hermitian antisymmetry. These routines are utilized by transform routines for a set of space groups that contain more than 80% of reported protein crystals.

PS–02.08.09 STATISTICAL ANALYSIS AND REACTION PATHWAYS OF MOLECULES. By K.Huml* , F.Soldán and W.Hummel. Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovského nám.2, 162 06 Praha 6, Czech Republic

A hypothesis concerning possible minimum energy conformations and conformational interconversions can be supported by statistical analysis of similar molecular fragments, potential energy, calculation, topology and other methods (Bürgi H.-B. and Dunitz J.D., Acc.Chem.Res., 1983, 16, 153–161; Mezey P.G. Potential Energy Hypersurfaces, Amsterdam: Elsevier, 1987). Molecular symmetry of a fragment under study gives additional limiting conditions (Frei H., Bauder A. and Günthard H.H., Top.Curr.Chem., 1979, 81, 1–97). It is believed that properly chosen model of a static and/or dynamic behaviour of the molecular fragment leads to a good mutual agreement among results reached by the methods mentioned above. Potential energy minima correspond to chemical entities which represent the most frequently occurring conformations (molecular templates). On the other hand, sporadically scattered conformations bridging stable conformations map the probable reaction pathways during the conformational interconversions.

1,2-dihydroxybenzene (catechol) and 1,2-dimethoxybenzene molecules were exploited to elucidate the procedure. Structural information was retrieved from the Cambridge Structural Databank and two-dimensional potential energy maps were calculated using the molecular mechanics method.

PS–02.08.10 SHELXL-92 A NEW LEAST-SQUARES REFINEMENT PROGRAM FOR USE WITH SINGLE CRYSTAL DIFFRACTION DATA

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SHELXL-92 is a FORTRAN-77 program for the refinement of crystal structures from X-ray or neutron diffraction data, and is primarily designed for single crystal data from small structures (1-1000 unique atoms) at atomic resolution. It is intended to be easy to install and use on a wide variety of computers, and replaces the structure-refining part of SHELX-76.

SHELXL-92 is general and efficient for all space groups in all settings and there are no arbitrary limits to the size of problems which can be handled, except for the total memory available to the program. All instructions are in machine independent free format, with extensive use of default settings to minimize the amount of input required from the user. Instructions and data are taken from two standard (ASCII) text files, so that input files can easily be transferred between different computers. SHELXL-92 is a PUBLIC DOMAIN progam; it is provided in source form, also as a precompiled version which has been optimized for Pc's. There are no restrictions on its use or distribution anywhere in the world for non-commercial purposes.

The program produces all the information required for efficient development of a complete structural model from a partially correct one derived using separate direct or vector methods programs such as SHELXS86. It contains many options for fully automatic handling of constraints on positional and thermal parameters and for placement of hydrogen atoms. Structural models can also be restrained to conform with chemically reasonable expectations for interatomic distances and thermal displacement parameters. These similarity restraints can be particularly useful in refinements of macromolecular structure. The atom designation rules, which accommodate standard practices, help minimize the instructions required to invoke constraints and restraints. All tables necessary for electronic mail submission to both Acta Cryst. (C) and the CSD are provided in CIF format and a companion program CIFTAB can produce hard copy in formats suitable for other journals.

PS–02.08.11   'CRYSTALS' in control

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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.

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.