

17.4-4 THE ROLE OF BACK FOURIER TRANSFORMS IN LEAST SQUARES REFINEMENT. A.D.Rae and A.T.Baker, School of Chemistry, University of New South Wales, Kensington, N.S.W. 2033, Australia.

If the sampling of a difference map is confined to grid points  $n_1/N_1, n_2/N_2, n_3/N_3$  and if  $h_{\max} - h_{\min} < N_1$ ,  $k_{\max} - k_{\min} < N_2$ ,  $l_{\max} - l_{\min} < N_3$ , then the values of residuals  $F_o - F_c$  used to create this map can be reobtained exactly by a Back Fourier Transform (BFT) of the map, accurate to the limits of round off through digitisation of the map. Reflections omitted from the map will have  $F_o - F_c$  values calculated as zero. If the map is altered so that values at certain grid points are reset to zero, then residuals calculated from such a map can be used to recreate the altered map. Consequently, it is possible to undertake least squares refinement of part of a structure under the assumption that an appropriate model exists so that the residual scattering density at certain grid points is zero. A parameterised model is not needed to impose this condition. It is simply necessary to BFT the appropriate region of the map. This BFT is included in the structure factor calculation as an "atom" at the origin with scattering factor  $A+iB$  for the equivalent position  $x, y, z$ , but scattering factor zero for other equivalent positions. The contribution is put on scale by choice of occupancy factor. Maps are put on scale using  $F_o = (I_o/I_c)^{1/2} F_c$  where  $F_c$  is on an absolute scale and  $I_c$  is obtained from  $F_c$  by incorporating corrections for scale, extinction, twinning, etc.

For many structures an inability to correctly model certain structural features imposes an accuracy limit on other structural features, i.e. error is not evenly distributed over a difference map. For example, the difference map for  $Rh_2(C_{12}H_9N_3)_3(PF_6)_2 \cdot CH_3CN$  shows peaks of about  $2e^{-3}$  about the two  $PF_6$  anions. These peaks could not be removed from maps using models involving ordered anions and Gaussian thermal displacement distributions. Refinement using disordered anions is awkward and not necessarily very informative or effective. There is little interest in the anion and there is no necessity for parameterisation to remove a source of systematic error from the refinement. Refinement before the use of BFTs converged at  $R_1 = 0.044$  using RAELS, a comprehensive constrained least squares refinement program. The  $PF_6$  ions were constrained to have local mmm symmetry for refinable positional parameters and to have refinable TLX thermal motion. The use of BFTs evaluated using all grid points within  $2.5\text{\AA}$  of P atoms enabled  $R_1$  to be reduced to 0.027 upon further refinement. Parameter shifts of up to twice standard deviation occurred and standard deviations halved. Differences in bond lengths associated with coordinated and uncoordinated N atoms in the same position on different ligands changed from 3 to 6 times standard deviation. The major peaks on the difference map were now near the Rh atoms and of approximately  $0.8e^{-3}$  in magnitude.

A program was written to handle map editing and to calculate the BFT. All editing is done in an asymmetric unit which is found automatically from the equivalent positions. All spacegroups can be processed but for cubic groups it is necessary to use the tetragonal or orthorhombic subgroup implied by the direct product  $C_3^*g$ . Maps are in layers about  $z$ .  $F_o$  is phased from a "complete" model and the desired BFT is evaluated each cycle of least squares refinement. Definition in the BFT region of a map improves. The procedure has robust refinement properties and may be used to estimate the effect per reflection of noise and omitted model parameters. The procedure offers a valid alternative to sparse and blocked matrix methods of least squares refinement since it offers a means by which to use full matrix methods without excessive time penalties since not all atoms are included. These aspects are being further studied.

17.4-5 THE USE OF EXTERNAL DIRECTIVES TO COUPLE PARAMETER CHANGES IN LEAST SQUARES REFINEMENT. A.David Rae, School of Chemistry, University of New South Wales, Kensington, N.S.W. 2033, Australia.

If  $[u]$  denotes a set of standard parameters and  $[v]$  denotes an alternative set of parameters spanning the same space, then it is often desirable to refine a structure using only a subset of  $[v]$  (strict constraints). Least squares refinement minimises  $\sum w\Delta^2$  where, for X-ray diffraction data,  $\Delta$  can be either  $|F_o - F_c|$ , or a parameter change  $\Delta v_j$  (damping), or a discrepancy in geometry (slack constraint). It is necessary to select  $[v]$  and evaluate differentials  $\partial\Delta/\partial v_j = \sum^T (\partial\Delta/\partial u_i) (\partial u_i/\partial v_j)$ . Busing (Acta Cryst. (1971) A27,683) showed how numeric differentiation can be used to evaluate the  $\partial u_i/\partial v_j$  but his method requires job specific subroutines since "extra" parameters are used. The program RAELS was written so that wherever possible the need for user written subroutines is avoided. Rae (Acta Cryst. (1975) A31,560) showed that parameters described relative to local orthonormal axial systems can be refined by simply making appropriate transformations of hkl. Since this implicitly describes  $\partial u_i/\partial v_j$ , RAELS can apply slack constraints to geometry involving atoms defined relative to differing axial systems and evaluate all geometry together with standard deviations each refinement cycle. Axial systems are found by the program from the overlay of idealised objects in 1:1 correlation with existing atoms. Inserted atoms are given zero weight in this least squares fitting, then replace original dummy atoms. Multiple axial transformations (allowing imposition of local symmetry) are permitted and a recipe is used to describe how local coordinates transform to orthonormal crystal coordinates. Identical objects can reference the same local coordinates, which can be generated from crystal coordinates using the local axial systems. Thermal parameter description is independent of positional parameter models. Segmented body thermal motion may be invoked since atoms have their thermal motion described as the sum of independent contributions which may be described relative to local axes. Parameters are symmetrised so that local symmetry constraints can be imposed as zero values. Axes for rigid body thermal motion are updated each cycle to be in the principal axis directions of the L matrix and at the centre of action which can be tied to an atom position. Parameters of the T and S matrices are symmetrised to relate to physical interpretation (Rae, 1975 *ibid*). The elements of the L matrix are individually refined, however, since certain objects are best described using a TLX model with a single reorientable, relocatable libration axis. Initial parameters can be zero and model choice invoked by simple YES/NO indicators. Any parameter can be coupled to any other by the use of identical change, equal percentage change and equal but opposite sign change instructions. Multiple referencing of parameters is allowed in this process. The desired instructions can be worked out by simply writing down the desired parameter update sequence starting from the changes in the independent variables. The reverse sequence is then the desired sequence for the evaluation of derivatives for the independent variables. These instructions allow, for example, imposition of local symmetry, maintenance of chemical composition in disordered structures, coupling of changes in H atom parameters to those of other atoms. The tying together of parameter changes is essential for the rapid, meaningful refinement of structures showing disorder, pseudosymmetry or twinning. Structure independent variables (scale, overall thermal motion, extinction, twinning, absorption) can be refined with or without simultaneous structure factor calculation.

The use of "extra" parameters is still an option but their use has only proved necessary when (i, atomic scattering factors are refined to allow for bonding, (ii, stacking faults occur that translate all or part of a structure, (iii, allowance is made for imperfect overlap of twin components of observed data, (iv, attempts are made to parameterise anisotropic decomposition.