Faster Least-Squares Refinement of Larger Molecules using the Program CRYSTALS

Stefan D. Pantos[a], D. J. Watkin[a], R. I. Cooper[b], [a]*Chemical Crystallography, University of Oxford, Oxford, UK.* [b]*Oxford Diffraction Ltd, Abingdon, Oxfordshire. UK.* E-mail: stefan.pantos@chem.ox.ac.uk

Least-squares is both powerful and the most widely used method of structure refinement for small molecules. However normal matrix accumulation is very time-consuming when using full matrix least-square for larger problems.

The sparsity of the normal matrix has long been recognized, and Jelsch[1] has explained the origin of the sparsity in macro-molecular structure refinement where the resolution reaches atomic and subatomic levels. This analysis of the normal matrix revealed a rapid diminution of the cross terms between "distant atoms".

Jelsch's findings can be used to post-rationalize a development in CRYSTALS, where anticipated sparsity was used to optimize the accumulation of a true sparse full matrix. This matrix has almost the full rate of convergence of a traditional full matrix, but for a trial structure with 1,700 parameters the time per cycle was cut by a factor of 12.

The poster describes the implementation of this strategy for building the sparse full normal matrix in CRYSTALS. This has been achieved without compromising any of the existing features, and has the potential to be extended and automated for situations involving pseudo-symmetry.

[1] Jelsch C., *Acta Cryst.,* 2001, **A57**, 558.

Keywords: least-squares refinement, algorithms, optimization