Blocked Matrices

For mesomolecular structures (100-1000) atoms, conventional full matrix least squares becomes increasingly inefficient, but conjugate gradient methods show no advantage.

Dividing up the normal matrix into sub matrices (either within a single cycle, or in successive cycles) is a cost-effective way of handling medium sized problems.

1

Matrix Schemes

For 100 anisotropic atoms in a single block, this means that (900x901)/2 = 405,000 matrix elements must be computed.

Various schemes are available to reduce the size of the computation.

2

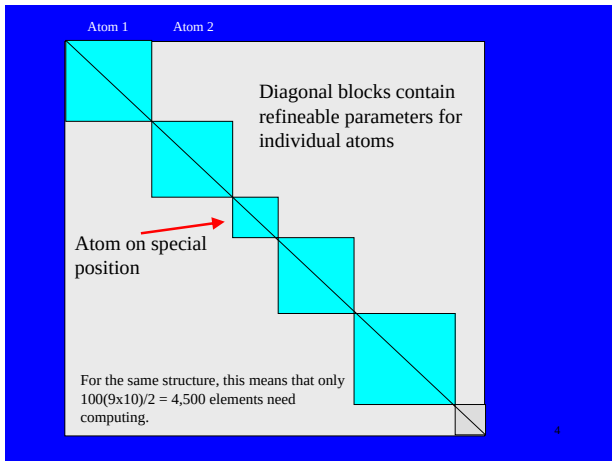
Atom-Block Diagonal

This is the most extreme scheme, and is used in SIR97 etc. It puts all the refinable parameters for each atom into an individual block.

For the same structure, this means that only 100(9x10)/2 = 4,500 elements need computing.

However, the rate of convergence is often poor, (or non-existent). Remember that structure factors and derivatives also have to be computed for each cycle.

3

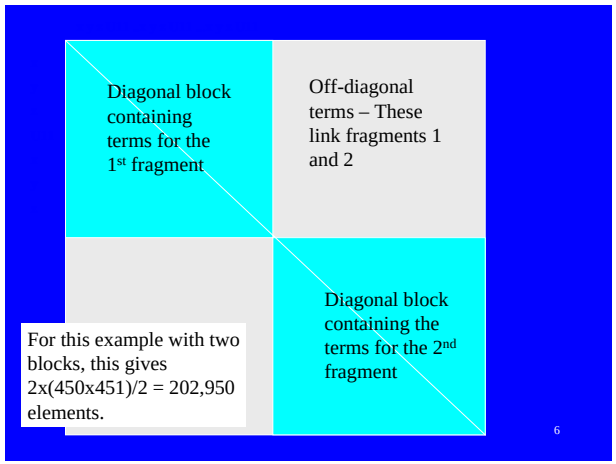


4

Large-Block Approximation

If the structure consists of non-bonded molecular fragments, ***and there is no pseudo-symmetry between them***, then each fragment can be refined in a separate matrix block. For this example with two blocks, this gives 2x(450x451)/2 = 202,950 elements.

5



6

Refining Fragments in Alternate Cycles

This is similar to the large-block approximation.

If the full matrix refinement is unstable because of high correlations, this method will appear to fix it, but in fact only conceals the problem.

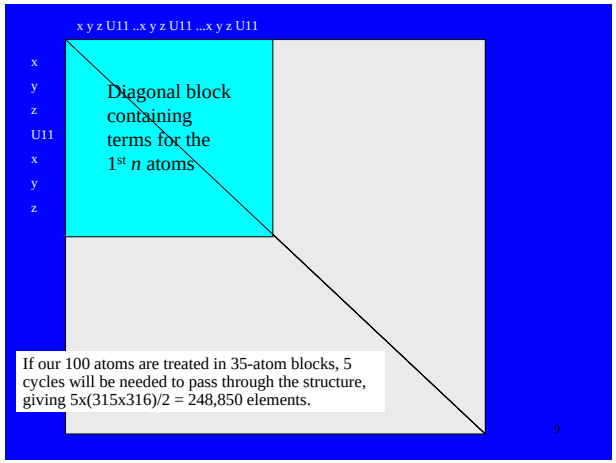
7

Moving Window

In this method, a large number of atoms are refined in a single block. On the next cycle, half the original atoms are not refined, but a similar number of new ones are included. The 'window' passes slowly through the whole structure. If our 100 atoms are treated in 35-atom blocks, 5 cycles will be needed to pass through the structure, giving 5x(315x316)/2 = 248,850 elements.

If the blocks are chosen to contain pairs of correlated atoms, this method is reasonably stable, though tedious to set up.

8



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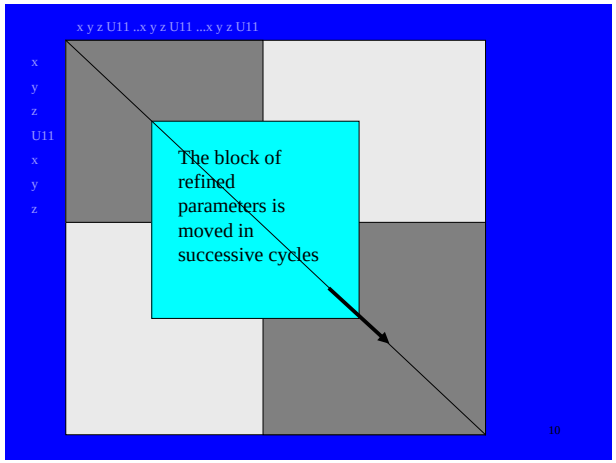
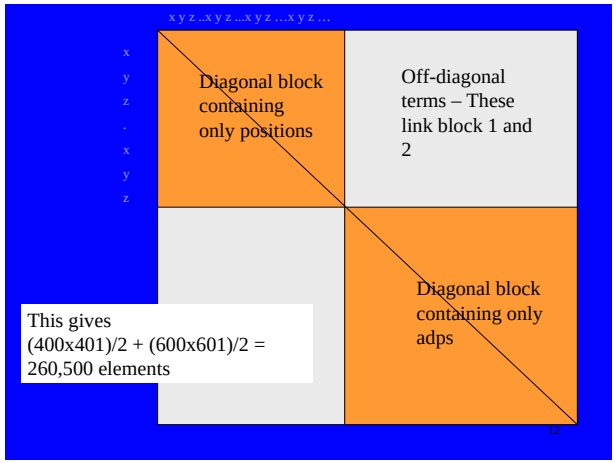


A good data set and a good model

If the data is ‘good’ and the model is ‘good’, an effective scheme is to refine the positions in one block, and the adps in another. In our case, this gives

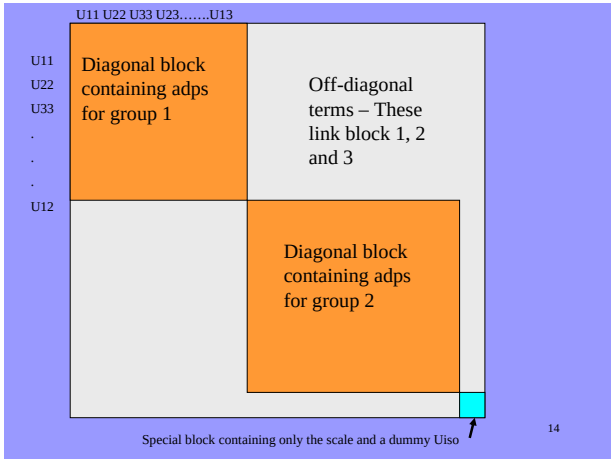
(400x401)/2 + (600x601)/2 = 260,500 elements.



Correlation with the Scale Factor

If the structure is so large that the adps must be divided between smaller blocks, convergence is improved by having an additional block containing the overall scale factor and a ‘dummy’ isotropic adp.

This enables the high correlation between the adps and the over all scale factor to be accounted for.



Some Useful Recipes

Some suggested blocking schemes are:

1. A block for x, y, z separately, plus one for Uiso and scale.
2. A block for x’s, and a block for U’s and scale
3. As in 2, but with adps divided into two, plus dummy and scale.
4. Parameters in directions related by a very oblique angle must be in the same block.

Conclusion

For an unknown material, the safest strategy is almost always to use a full matrix refinement.

Dividing a structure to avoid singularities is **always** dangerous, and may lead to the structure being ‘Marshed’.

However, for very large structures, full matrix is a wasteful strategy (since many off-diagonal elements will sum to zero), and may actually be slow to converge if rounding errors are allowed to accumulate.

More Exercises

Look at questions

12, 18, 10