

XD2006 Primer

A Computer Program Package for Multipole Refinement, Topological Analysis of Charge Densities and Evaluation of Intermolecular Energies from Experimental or Theoretical Structure Factors

**Document Version September 2006
Program Version 5.00 September 2006**

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1. Introduction

This primer is intended to address some of the more common misconceptions and mistakes made by beginners to charge density studies and the XD2006 program suite. There is no substitute for a comprehensive reading of the XD2006 manual, which contains full details of how to run all the programs. However, unlike the most commonly used programs for standard spherical atom refinement of crystal structure, XD2006 does not have many "user friendly" features. Many of the commonly required crystallographic constraints, which are automatically applied by programs like SHELX and CRYSTALS, are not done by XDLSM (the refinement program of XD2006). They need to be explicitly entered by the user. The failure to do so correctly is a common source of error.

1.1 Data issues

1.1.1 Data collection procedures

For a meaningful multipole refinement, the quality of the experimental data is paramount. Two essential features are necessary in the reflection data :

1. the data must be collected such that *the kinematical theory of diffraction is closely adhered to, and errors due to dynamical scattering are eliminated as far as possible*. Error due to sample absorption and extinction should be minimised by using small crystal sizes and thermal diffuse scattering and anharmonicity reduced by measuring at the lowest feasible temperature. Crystal quality in terms of morphology and optical criteria should be the best available for the sample under study. Needless to say, defects like twinning or disorder are likely to render the data useless. Experience suggests that problems will start to be significant using laboratory sources such as Mo- K_{α} radiation when the sample contains elements with $Z > 35$. In these cases, it will probably be essential to obtain data measured with very short wavelengths, for instance at synchrotron sources.
2. great care must be taken to *measure accurately both the low angle data and the high angle data*. The latter should be measured to the highest resolution that is practicable, taken cognisance of the instrumental limitations and the intensity of diffraction by the sample at these high Bragg angles. Consideration should also be given as to the accuracy of integration (with laboratory sources, the α_1 - α_2 splitting becomes a serious problem for many commercial area-detector integration packages). With area-detector instruments, it will be necessary to collect data with a high mean redundancy, and the data collection strategy should ensure that this is obtained. Experience suggests that the mean redundancy should be at least 10 fold. The low angle data are those most affected by charge density effects, but unfortunately also by many other sources of error like extinction. Reflections affected by obvious problems, like obstruction by the beamstop, should be removed. In area detector

data, reflections close to the rotation axis have small Lp corrections and are generally suspect. Many integration packages ignore such reflections.

1.1.2 The reflection file XD.HKL

The reflection file used in XD2006 is called XD.HKL and the format is given in the XD2006 manual in Table 2-2. Unless anisotropic extinction is being refined, this file should contain ONLY unique reflections and should NOT contain any of the systematically absent reflections. It is a common mistake to use the same set of unmerged reflections which is acceptable for programs like SHELXL. SORTAV is an excellent program to perform data merging.

1.1.3 What to look for in the spherical atom refinement

Before attempting a multipole refinement, the spherical atom refinement using programs like SHELXL, CRYSTALS or JANA2000 should be examined carefully for potential problems. In particular, the difference maps should be scrutinised, preferably by examination of contour maps (here the concise summary given by programs like SHELXL is not helpful). The highest remaining peaks/troughs should be clearly attributable to charge density effects (i.e. peaks in the middle of covalent bonds, ligand field charge redistributions around transition metal atoms). Artifacts like absorption ripples around heavy atoms should cause considerable worry. While it is true that a multipole refinement may reduce these artifacts, the results are likely to be meaningless. If such ripples are observed, serious consideration should be given to abandoning that data set.

Programs like SHELXL print out an analysis of variance, which should be carefully scrutinised. The scale factor across resolution ranges should be reasonably constant - if not, it is possible that there are systematic problems with the data which will require further consideration (e.g. integration difficulties?). Also check whether there are any reflections which are wildly discrepant, for instance low angle reflections which are measured weak, but calculated as strong - these may be obscured by the beam stop. Remove such reflections from the file.

1.2. Refinement problems

1.2.1 Required constraints

As stated above, the program XDLSM does NOT have automatic implementation of constraints. These need to be explicitly entered by the user, see Section 4.6.10 in the XD2006 manual. The failure to do so correctly is a common source of error.

In general, if an atom lies on a special position (i.e. its occupation parameter is less than 1.0) then some constraints will need to be applied, to the positional, thermal or multipole parameters using the CON instruction. Some thought should be given to definition of the local axial system. The default definitions written by XDINI to XD.MAS are most likely to be inadequate in these cases. Often a practical definition will require the use of dummy atoms. Think carefully about the choice of these. For instance, if the particular site symmetry requires the local z axis to be perpendicular to the

crystallographic mirror plane, it may be more convenient to define the local x and y axes as lying *in the mirror plane*, rather than trying to use dummy atoms to define the z axis *perpendicular to the plane*. It is certainly better that the positions of dummy atoms are clearly related to the space group operations (*e.g.* 0.0, 0.0, 0.0 or 0.25, 0.0, 1.0), rather than lying in completely general positions.

In particular, remember :

- always read the output file XD_LSM.OUT after each refinement job. If there are warnings about difficulties in inverting the matrix, this is usually an indicator that constraints have not been applied correctly. You should always use the Gauss-Jordan inversion method for refinement (the default) as the first choice, unless there are good reasons to do otherwise.
- in polar space groups like $P2_1$ the polar axes need to be defined by fixing (*i.e.* not refining) the corresponding coordinate of ONE atom (best the heaviest one). For the $P2_1$ example, the z coordinate of one atom must be fixed.
- in non-centrosymmetric space groups, the correct absolute configuration should be used.

1.2.2 Which parameters should be refined ?

It is neither practicable nor useful to refine all possible parameters for every atom. Some general advice

- for H atoms, wherever possible their positional parameters should be fixed at neutron defined distances, in the absence of neutron data. The RESET BOND command, see section 4.6.5 of XD2006 manual is very useful for this purpose. The only multipoles which are normally refined are P_v and a bond-directed dipole. There may be high correlation coefficients between these and the isotopic thermal parameter.
- the kappa parameters (κ) and especially the kappa-prime (κ') parameters are the most difficult to refine. Only with exceptional data is it possible to refine individual values for κ' - usually the KEEP KAPPA directive needs to be used to constrain them to be equal. In general the κ and κ' parameters for H atoms should NEVER be refined (common reason for XDLSM blowing up). Take great care when refining κ and κ' parameters. Their values should not differ greatly from 1.0 ; this is especially true for κ . The further the magnitudes of the κ' parameters deviate from 1.0, the more suspicious they are. The program will print a warning - take heed ! If these parameters do not refine sensibly, then fix them at 1.0. Negative values are physically meaningless !
- avoid refining the anharmonic Gram-Charlier coefficients. These are usually strongly correlated with the multipole parameters, and are only needed in special cases (NOTE - these are also subject to site symmetry restrictions).
- there are two monopole functions P_v and P_{00} in the XD model It is inadvisable to attempt to refine both, unless you are trying to model densities with very different radial properties (*e.g.* 3d and 4s orbitals of first row transition metals). Normally only P_v is refined.

1.2.3 How do I know if my multipole refinement is OK ?

There a number of criteria which indicate a good analysis :

- the R values are significantly better than for the spherical atom refinement. This will almost always be the case anyway, since more parameters are being refined.
- there are no significant residuals in the difference maps. XDFFT gives a summary of maximum and minimum residuals. These should be less than $0.3 \text{ e}\text{\AA}^{-3}$ if heavy atoms are present, or even less for light atom structures. The lower the better. If they are much larger than this, you may have problems. Look at Fourier maps with XDFOUR to see what the high/low regions look like. Structured features around atoms are not good news. This criterion is probably the most sensitive test for the data quality and/or the adequacy of the model.
- the MSDA for all anisotropic bonded atoms is < 10 in the table at the end of XD_LSM.OUT (the DMSDA directive must be active - it should always be used !)
- the GOF is small, hopefully less than 2.0
- the multipole populations for chemically similar atoms should not be wildly different (NOTE that if you are to comparing multipole populations, it is VITAL that commensurate local axial schemes on the relevant atoms are used).
- the number of large correlation coefficients (> 0.75) is not high. If it is, consider blocking the refinement.
- the topological properties of the density defined by the multipole parameters is sensible (XDPROP & TOPXD). Chemically related atoms should have similar topological properties, and the variation should not be large. Properties like the Bader integrated atomic charges can be sensitive to the exact model used, but chemically similar atoms should have similar charges.