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THE DEVELOPMENT OF A FULL PROFILE ANALYSIS OF SINGLE-CRYSTAL X-RAY DIFFRACTION DATA

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Résumé - La meilleure façon pour déterminer les vraies intensités des tâches de diffraction est d'utiliser l'analyse des profils. Les diffractomètres à détecteur bi-dimensionnel produisent des profils tri-dimensionnels. Nous proposons que le meilleur moyen de manipuler ces profils est de les développer sous forme de fonctions de Weber-Hermite.

Abstract - The best way to determine the true intensities of diffraction spots is by use of profile analysis. Area-detector diffractometers yield three-dimensional profiles. It is argued that the best way to handle these is by expansion in terms of Weber-Hermite functions.

I - PROFILE FITTING.

It has long been known that the determination of diffraction spot intensities can be improved markedly if use is made of the expected shapes of the spots. The mechanism of this is relatively simple: one effectively multiplies the observed peak pointwise by a curve having the expected shape of the peak and then integrates the result. Where the spot is expected to be weak it is taken that any photons which do arrive have little bearing on the measurement, and being multiplied by a small number, the effects of the bad statistics at that point are minimised. Conversely, where a spot is expected to be strong, any photons which arrive are dominantly indicative of the intensity of the spot, and being multiplied by a large number we take maximum advantage of the expected good statistics at that point. When the statistics of the data are accurately Poissonian, it can be proved that no other strategy can produce a better result. In the language of information theory: tuning the response of the detector to the expectation form of the data is an optimal strategy. In a crystallographer's language, we are profile fitting. The method does require that the expected shape be accurately determined. If it is not, the random errors associated with counting statistics may still be reduced, but a systematic bias in the results will occur, which may well go undetected later.

II - ESTIMATES OF THE STANDARD DEVIATIONS OF MEASUREMENTS

By virtue of having an accurately specified expectation of the shape of any given spot, it is also possible to derive experimentally justifiable estimates of the variances of the data based on the distortions in the observed shape, assuming these to be due to random errors and counting statistics. It is to be hoped that reliably estimated standard deviations, when carried correctly through the entire data analysis will result in more accurate and more easily interpreted electron density maps. This point deserves more attention even in classical data reductions, but assumes paramount importance when using entropy maximisation methods.
III - INCREASED RESOLUTION

There is a further added advantage of profile fitting, which is that the usable resolution of the instrument can be improved slightly. Normally, when spots are taken individually, the interfering effects of their neighbours are reduced simply because little weight is attached to data from the wings of a spot. A more complex strategy, somewhat akin to Rietveld decomposition /1/ (but not assuming Gaussian shapes) can be used in which neighbouring spots are taken into account so that what little influence remaining from their proximity can be minimised. The knowledge of spot shapes must be particularly accurate for this method to work well, and much advantage can be taken of the extra information obtained by moving the crystal in ways very much more complicated than simple rotations, when spots will be swept in several different directions. (The same type of analysis proposed here could also be used to improve the Rietveld decomposition of Debye-Scherrer powder patterns. More accurate results would be expected because the true beam wave-vector distribution could be taken into account.)

In general, and especially when dealing with the three-dimensional profiles obtained from area-detector diffractometers, it would seem to be better to develop a formalism capable of learning and representing to a chosen degree of precision just about any physically reasonable profile, rather than to try to fit a selected parametric curve which may or may not happen to work well. In any case, it must be rather difficult even to define sufficiently flexible parametric curves in three-dimensions. We thus opt for a general learnt-profile formalism rather than a fitted-curve method.

IV - INCOMMENSURATE SAMPLING

With a single-counter diffractometer operating under equatorial geometry, a successful method of learning the one-dimensional profile is to measure neighbouring spots under closely similar conditions, and to prepare an average histogram of their shapes which are assumed to be locally closely similar /2/. It is, of course, a precondition of this method that every spot be measured on a histogram or 1-D pixel grid which is strictly equivalent in size and position relative to the peak.

With an area detector the problem is not so simple; it is not possible to measure every spot on the detecting area in an identical fashion. Firstly, the image will be divided into (two-dimensional) pixels, and even though these may be all the same size and shape with a detector having no spatial distortions, the centroid of a spot will be at some fractional pixel position which is not under our control. With real detectors having spatial distortions, both the shape and size of the pixel grid will also vary from spot to spot. Secondly, for the third dimension of the pixel grid, measurements will also be made at a set of slightly different crystal rotations, and it is again impossible to define these in such a way that they can be said to be strictly equivalent for all spots. Indeed, in some strategies these angular slots may even have irregular sizes. We are thus unable, even locally, to learn the average spot shape by simply adding together three-dimensional images pixel by pixel; the pixel grids are incommensurate, that is, they do not line up. One way to circumvent this problem is by accumulating with interpolation into a single definitive histogram on yet another pixel grid. This method can be used, and indeed has been, but apart from its obvious inelegance, is wasteful of computing resources.

V - LEARNING PROCEDURE BASED ON A FUNCTIONAL EXPANSION

A more promising approach to learning average profiles from data on incommensurate sampling grids is to expand the observations in terms of a judiciously chosen complete set of orthogonal functions. The averaging and all other necessary manipulations of the data can be done in terms of the coefficients of the expansion. The success of data analysis performed by indirect means such as these depends critically on the special properties of the chosen set of functions being ideally matched to the problem. If they are well matched, the analytic derivations will be straightforward, the manipulation of the coefficients will be simple, and the computational implementation will achieve maximal efficiency.
VI - THE VARIATION OF SPOT SHAPE

Even when we consider diffraction from a very small crystal, where the shapes of diffraction spots are only determined by the mosaicity distribution of the crystal, the wave-vector distribution of the beam, and the point-spread distribution of the detector, we find that all of the spots have slightly different shapes. There is, of course, a great deal of local similarity. Any analysis must become very much more complicated if the size of the crystal and the beam become so great that it becomes possible to discern internal structure within them from the fine details of the shapes of the diffraction spots. An example of this would be if, say, the crystal were very long and contained a central fault, so that the diffraction pattern would be more reminiscent of that from two separate crystals mounted at slightly different heights. There are other good experimental reasons for avoiding the use of crystals so large, and thus we shall restrict ourselves at the moment, with little loss of generality to the case of a small homogenous crystal, though we shall make no other assumption about the mosaicity distribution. This means that we shall be able to interpret properly the diffraction pattern from a split or shattered crystal, though obviously not that from a large-angle twin.

VII - POSSIBLE DECOMPOSITIONS OF THE PROFILE

Both theoretical considerations and experimental data taken on an ENRAF-NONIUS FAST system have shown that the perceived three-dimensional shapes of diffraction spots are not accurately represented as fixed shapes on the detector area which wax and wane according to the so-called \( \psi \)-profile as the crystal turns. The spot moves across the detector slightly if the X-ray beam is in any way imperfect (that is not strictly parallel and monochromatic), and its shape also changes. This means that for an analysis of the highest quality, a full three-dimensional description of the shape must be used. This is not, of course, to say that an adequate analysis could not make simplifying assumptions. In some respects, it is somewhat easier to establish the performance of a simpler analysis by reference to a definitive one. Indeed, since it is our ultimate purpose to provide data-reduction programs suitable for all kinds of data from the least demanding to the most, we wish to pursue our analysis in the fullest possible form, at least initially.

VIII - THE INAPPLICABILITY OF A POLYNOMIAL FIT

The simplest analytic method to describe a property which varies smoothly with position is by fitting a polynomial function. In our case, having already expanded the shape of each spot in terms of a set of orthogonal functions we would be fitting a polynomial function of position to the supposedly smoothly varying coefficient of the expansion. The analytic simplicity of this method is, however, not directly useful when the profile is to be determined to high resolution. This is because the number of coefficients in the polynomial expansion would become too large either to be supported by the data or to be computationally manageable.

IX - A MORE FUNDAMENTAL APPROACH

The geometry of the diffraction process is extremely simple, and by exploiting its properties it is possible to avoid fitting polynomials. Given that the shape of every diffraction spot is determined by three distributions describing the mosaicity, the beam and the detector, we choose to work directly with these distributions. These three distributions can be described with a manageable and supportable number of coefficients, even when expressed to high resolution. This choice of working method has some interesting consequences. One is that it is necessary to describe in terms of the coefficients, how the shape of each distribution contributes to the final shape. This turns out to be a rather elegant calculation, expressing itself in terms of projections, sections, rotations and convolutions. Having done this, one must, in essence, do the same thing in reverse to get from the diffraction data to the averaged estimates of the three distributions.
X - THE WEBER-HERMITE FUNCTIONS

The choice of orthogonal functions actually used to perform the calculations is determined by demanding that they permit efficient calculation of the major operations in use; projection, section, rotation and convolution, and also that their form naturally permits an accurate representation of normal diffraction spots with just a few terms. The Cartesian outer products of the Weber-Hermite functions can be shown to be pre-eminently suitable for this analysis. They are well known and much studied, notably in quantum mechanics, where they appear as the wavefunctions of the harmonic oscilator. They are fully competent to perform a wide variety of operations related to image analysis; a paper on this topic is in preparation. Because the Weber-Hermite functions are members of a complete set, any shape can be represented exactly as a linear combination of them. In practice, only a finite number of terms in the expansion will be used, and it is possible to adjust this number to improve or degrade accuracy at will. The Fourier power spectrum of the functions is well controlled, and the overall response of the expansion can be tailored to minimise any artifacts. For these reasons, Weber-Hermite expansions appear more versatile and better behaved than normal parametric curve-fitting methods.

XI - THE COMPLEXITY OF THE GENERAL CASE

Getting all they way from noisy diffraction data back to the three controlling distributions is not an elementary task, even with an optimal form of analysis. The principal reason for this is that the forward path involves convolutions; the reverse path must in some way undo these. If we have a very good prior knowledge of, say, the beam wave-vector distribution and the detector point-spread distribution, then the crystal mosaicity distribution is calculable as a sort of deconvoluted back-projection from the data. This is, of course, about the simplest case we could consider, and experimentally the most important since the beam wave-vector distribution and detector point-spread function can usually be determined to adequate precision by relatively simple calibration procedures, providing that they are not liable to unforseen variation. If, on the other hand, we were to have little or no prior knowledge of two, or worse, three of the distributions, then deconvolution becomes too weak a method; we have to deduce ab initio the distributions which would result in the observed data when convoluted. When expressed in terms of the coefficients of a Weber-Hermite function expansion this problem achieves as simple a form as possible and the necessity of solving, at minimum, simultaneous quadratic equations in many unknowns becomes unmistakeable. It is clear already that the imposition of positivity on the three controlling distributions will become important in this most general case, and it is more than likely that a maximum entropy formalism will be useful. Fortunately, both positivity and entropy have a simple enough description with the Weber-Hermite functions.

XII. CONCURRENT PROCESSING

The number of data arising from high-resolution observations of an entire diffraction pattern is very large. Even when we have sufficient prior knowledge of, say, the beam and detector distributions to make a determination of the mosaicity distribution feasible by linear analysis, we are still talking of a relatively large amount of computer time. In the worse case of inadequate prior knowledge, requiring non-linear and possibly entropic data analysis the amount of computer time required may well rise to the level where it becomes sensible to think in terms of concurrent processing. It is fortunate that the structure of the problem allows this, and it is being borne in mind from the outset.

XIII - RESULTS

The analysis of the three-dimensional profiles of diffraction spots proposed here is still under development, so it is obviously not possible to quote any
practical results of direct relevance. However, full-scale computational tests of various parts of the analysis have already been carried out and the results have been very encouraging. It is clear that the solution to the most general problem is some way off, but it is to be hoped that the simpler, and experimentally more important, case where the beam and detector distributions are known beforehand will be fully implemented in the near future.

REFERENCES