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Abstract

Neutron powder diffraction has, over the past two decades, developed into a powerful technique for the refinement of moderately complex crystal structures. The advent of a new generation of ultra-high resolution X-ray and neutron powder diffractometers, however, not only permits the refinement of more complex materials but also opens up new areas of research. Perhaps the most exciting development in powder diffraction techniques associated with high resolution is the ab initio determination of crystal structures. This has until recently been possible, in a routine way, only by single crystal studies. The compression of three dimensions of diffraction data to the one dimension of a powder diffraction pattern leads to an unavoidable loss of information. For many, but not all, crystal symmetries high resolution minimises this loss thus allowing the intensities of a sufficient number of resolved Bragg reflections from moderately complex materials to be extracted for use in structure solution by direct methods of phase determination and by Patterson methods. Recent structure determination using the high resolution powder diffractometer, HRPD, at ISIS will be presented. The inherent limitations resulting from crystal and instrumental resolution are discussed along with maximum entropy techniques that seek to optimise the information content of a powder diffraction pattern.

Introduction

Powder diffraction has developed into an important crystallographic tool over the past thirty years largely because of the success of the Rietveld profile method in structure refinement. The improvements in instrumentation in this period have led to the successful refinement of increasingly complex materials and, more recently, have opened up new areas of research, in particular ab initio structure determination, that have previously been the domain of single crystal studies. In this paper, both the potential and limitations of structure determination by high resolution powder diffraction are discussed.

The principal limitation of the powder diffraction method arises from the reduction of three dimensions of crystallographic information to the one dimension of a powder diffraction pattern. Bragg reflections with crystallographically distinct Miller indices overlap and lead to an irretrievable loss of information. Although very high instrumental resolution may separate closely spaced peaks, for a large number of crystal symmetries there is complete overlap of such a large fraction of reflections that truly ab initio structure determination is essentially untenable. These may be summarised in the following three categories:

(1) Polar groups (applies to all symmetries except cubic).
(e.g. with c axis unique, $d(hkl) = d(hk\bar{l})$: $F(hkl) \neq F(hk\bar{l})$)

(2) Structures with Laue classes that are not lattice point groups (holohedries).

(e.g. Pm3	$d(hkl) = d(khl)$	: $F(hkl) \neq F(khl)$
$P\bar{3}m1$	$d(hkl) = d(hk\bar{l})$	: $F(hkl) \neq F(hk\bar{l})$
P4/m	$d(hkl) = d(khl)$	: $F(hkl) \neq F(khl)$)

(3) Higher symmetry systems (above orthorhombic and particularly cubic symmetry).

(e.g. Pm3m	$d(511) = d(333)$	: $F(511) \neq F(333)$
P4/m	$d(714) = d(554)$	: $F(714) \neq F(554)$
P6/mmm	$d(700) = d(530)$	: $F(700) \neq F(530)$)

Such completely overlapped reflections cannot be separated by any amount of improved resolution, and to date equal intensities have been assigned to the components of such a degenerate set. As is discussed below this may lead to problems (in direct methods for example) if a very weak reflection is given a high intensity and hence a large structure factor due to being degenerate with a strong reflection. Techniques for improving the separation of such overlapped reflections are discussed later.

Partial Structure Determination

In many crystallographic problems, although a substantial fraction of the structure is known, the position of a crucial fragment may be undetermined. A good example of this, that is particularly applicable to neutron powder diffraction, is the location of hydrogens in organic materials where only the non-hydrogen atoms (e.g. carbon, nitrogen and oxygen) have been accurately determined from X-ray structural studies. In the following sections, two techniques are discussed:
(i) difference Fouriers
(ii) bond length & bond angle slack constraints in conjunction with profile refinement.

Location of Hydrogen by Difference Fourier Techniques

The procedure for obtaining unknown hydrogen positions using difference Fourier techniques may be summarised in the flow diagram below (Figure 1).

Squaric Acid (3,4-dihydroxy-butene-1,2-dione)
A difference Fourier map was calculated using the refined C_4O_4 fragment as input model and the result is shown in Figure. As can be seen the positions of the hydrogen atoms are indicated clearly as troughs in the map. The positions of the hydrogens as determined by this neutron study differ substantially from those indicated in an earlier X-ray experiment and are considerably better-determined. The refinement including the hydrogen atoms was very satisfactory.

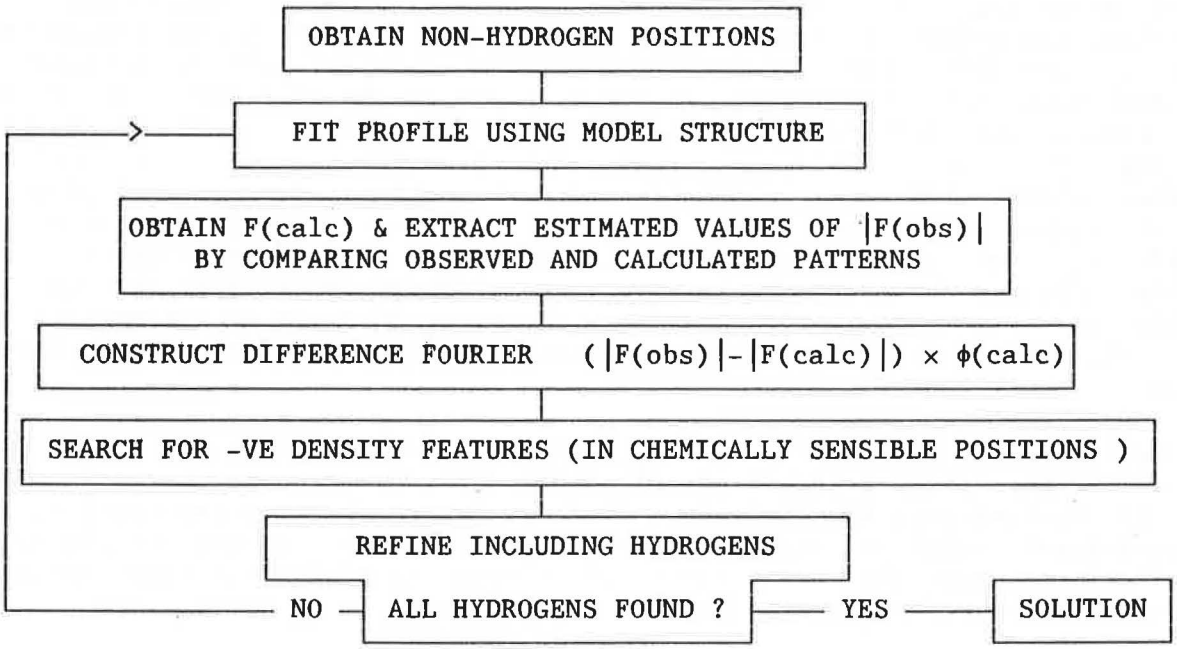

Figure 1. Flow diagram indicating the procedure for determining H positions in a crystal structure.

Location of Hydrogen by Restrained Profile Refinement Techniques

Dimethyl-ammonium tin chloride

In this example all non-hydrogen positions were again refined satisfactorily but there are potential problems with the stability of the refinements when the hydrogen atoms are included due to possible rotational disorder of the methyl group about the N-C bond. To counter some of these problems the hydrogen atoms are constrained to have sensible bond lengths and to lie on a circle at a sensible angle from the N-C bond. The H positions, site occupancies and temperature factors can then be refined subject to these constraints and the shape of the potential in which the methyl hydrogen atoms sit can be inferred. As can be seen in Figure the result of this constrained least-squares refinement of the hydrogen atoms indicates a twofold rotational degeneracy of each methyl hydrogen atom, thus defining the disposition of these atoms with far more reliability than could an X-ray experiment.

Completely Unknown Structures

The determination of completely unknown crystal structures from powder diffraction data has now been established as a reasonable technique performed on several materials in both true ab initio and "as ab initio" cases (Rudolf and Clearfield, 1985; Christensen, Lehmann and Nielsen, 1985; Cheetham et al, 1986; Attfield, Sleight and Cheetham, 1986; Lehmann et al, 1987; Lightfoot, Cheetham and Sleight, 1987)

The experimental requirements for producing a set of $|F_{hkl}|$ values that are of sufficient quality to lead to a structural solution are straightforward though relatively demanding. First and foremost, an accurate unit cell must be determined before Miller indices can be assigned to the reflections. Most

auto-indexing programs require the accurate location of around 20 of the highest d-spacing reflections to produce a reliable solution. Having obtained a lattice, the pattern is then checked for systematic absences that enable the number of possible space groups to be reduced substantially. This requires good peak/background statistics. In order to obtain the most extensive set of Bragg intensities the pattern should be profile-fitted using the method developed by Pawley (1981), in which the peak intensities are refined as variables along with cell constants and peak-shape parameters. As a general rule of thumb, experience shows that for a structural determination to succeed, the set of reflections obtained should extend as close to 1Å as possible. Clearly, however, the largest range of Bragg intensities that can be reliably extracted should be obtained. Methods do exist for attempting to extend the Bragg intensity data set and are discussed further in a later section.

Assuming that one has a list of $|F_{hkl}|$ values extracted from the pattern the problem is no longer uniquely one of powder diffraction until the refinement stage is reached when the Rietveld method is used on the measured profile. At the structural solution stage, however, the problem is one of standard crystallography and the full range of single crystal structure solving techniques are in principle available to be exploited.

The Solution of Crystal Structures

The general strategy of structural solution is summarised below :

1. If the structure can be solved by comparison with an expected similar structure or by trial-and-error, then do so. This intuitive approach is perfectly valid and of especial use when a series of similar and possibly isomorphous materials are under study.

2. If a heavy atom is present use heavy-atom Patterson methods. This technique is more applicable to X-ray structures where there are more likely to be genuine "heavy" atoms because of the Z^2 dependence of the Patterson peaks.

3. If there is expected to be a group of known stereochemistry in the structure information can be obtained about the orientation and positioning of this group again in Patterson methods. This can be especially useful if there is a significant planar moiety in the structure. For inorganic compounds this technique should be more widely applicable in the neutron than in the X-ray case since location of orientation of a group can be difficult if a heavy atom is present to swamp out the contributions of the remaining atoms.

4. In the case where no information can be garnered from any of the above, or when such information is insufficient in itself to solve the structure, the most powerful structure solving technique remains to be exploited - direct methods. Many codes are available for direct methods calculations, offering a wide range of options for the solution of structures.

5. There are other less well established techniques which have shown some promise in this field. Strategies based on maximum entropy methods using algebraic recombination techniques have produced hopeful results in fairly simple cases as described below. Also under consideration with the advent of super-fast computers are methods based on statistical mechanics using a Monte-Carlo random-walk simulation technique (Semenovskaya, Khatchaturyan and Khatchaturyan, 1985), using the crystallographic R-factor as the criterion for

acceptance or otherwise of any individual incremental motion of an atom in the cell.

6. Development of a structure - Once a fragment is located by any of the above methods some type of recycling procedure is often required to locate the remaining atoms in the structure. In the most favourable case straightforward Fourier recycling using $|F^{obs}_{hkl}|$ along with ϕ_{hkl} calculated from the fragment can be sufficiently accurate to reveal the remainder of the structure. Providing the fragment produced in the structural solution is of large enough size structural solution should follow routinely by Fourier recycling.

7. If this is not the case then some other form of recycling can be adopted to try to exploit the correct fragment already located, rather than throw this information away and begin again. Karle recycling (Karle, 1968) where the phases calculated from the known fragment are refined using the tangent formula and used to calculate a new E-map can often modify the phases sufficiently to lead to structural solution in an E-map.

8. If all possible recycling schemes fail, then one can still exploit the located fragment by using this as a known group in direct methods calculations (Main, 1976). Provision of a group of known stereochemistry and known or unknown orientation and position can alter the normalisation of the data (extraction of $|E_{hkl}|$ from $|F_{hkl}|$) and also can alter the probabilities calculated for particular phase relations and hence change the phasing path, hopefully to a more successful route.

9. Refinement - Once all (or most) of the atoms are found, least squares and profile refinement together with further Fourier and difference Fourier calculations are used to complete definition of the structure.

Adaptation of Crystallographic Programs for Neutron Data

The adaptation of the direct methods program MITHRIL (Gilmore, 1984) and the Patterson methods program PATMET (Wilson and Tollin, 1986) and the implementation of these in structural solution from neutron data has been discussed recently (Wilson, 1987).

For direct methods the main adaptations are in normalisation and Fourier map calculation, where scattering lengths rather than scattering factors are used and in Patterson methods they are in calculation of the model molecular transform where scattering lengths are used and in sharpening where either analytical or non-analytical (maximum entropy smoothing) techniques can be employed.

Possible Problems

Many of the possible problems inflict themselves evenhandedly on both single crystal and powder workers but some are certainly more pronounced in the case of powder experiments, primarily due to the lack of resolved data. In addition until fully optimised codes for neutron diffraction data are available (Wilson, 1987) structure solving methods will not be as reliable as for the X-ray case even given sufficiently good data.

Patterson methods

The main problem with these methods is that the sharpening of $|F|^2$ data must be optimised to improve the quality of the Patterson functions calculated. The techniques for doing so with X-rays are fairly well-established but remain

undetermined for neutron data. Either an analytical approach akin to that of Lipson and Cochran (1953) or an ME smoothing approach to generate the best set of $|F^{s}_{hkl}|$ values in a non-systematic way could be used.

In addition the PATMET methods tend to break down for very high symmetry structures.

Direct Methods

Where there are a fairly small number of |E| magnitudes large enough to be of use in phase determination, generating enough reliable phase relationships can be a problem. Usually higher invariants will be needed in addition to triplets but the close relation of positive quartets to triplets can lead to problems of close correlation of the two sets of invariants. In terms of computing time invoking further options on quartet generation such as the third neighbourhood, 13 |E|-magnitude formulae (Hauptmann, 1977a; 1977b) are not as serious due to the low number of |E| values available to be used. If there is a serious paucity of triplets and one has invoked quartets and possibly quintets then the proportion of higher invariants can be somewhat larger than ideal which can lead to problems with the phasing path (Gilmore, 1984).

In addition to the above, problems can arise in the calculation of |E|-(Fourier) maps. These are calculated after the direct method procedures have produced a set of phases to be used, but are calculated using just those |E| magnitudes which have been used in the phasing process. If there are a very limited number of reflections with |E|>1.0 in the data set then a Fourier calculation based on this can very easily miss details. There is a possibility of lowering the acceptable |E| value for inclusion in the phasing and the safest way of exploiting this may be to use these low |E| reflections in a passive way. This would involve using the low |E| magnitudes more than just to calculate probabilities for negative quartet relations (Schenk, 1982) but instead allowing these to be allocated phases in the phasing procedure but not to be used in further expansion. These reflections could then be used to improve the resolution of the Fourier calculations.

A different type of problem can arise due to the paucity of good, reliable invariants which can render less useful the more complicated procedures for phase determination such as YZARC (Baggio, Woolfson, Declercq and Germain, 1978), MAGEX (Hull, Viterbo, Woolfson and Shao-Hui, 1981), RANTAN (Yao Jia-Xing, 1981) etc., thus removing some powerful weapons from the armoury of the crystallographer trying to solve stubborn structures.

The importance of the data in the 1-1.2Å range cannot be overstressed. While many structures will solve in direct methods at 1.2Å resolution, many which would solve easily at 1Å may in fact fail at 1.2Å due to a combination of a paucity of phase relationships and a small number of |E| magnitudes used in E-map calculations.

One interesting point which has arisen in studies of direct methods solutions from HRPD data is that occasionally a higher resolution data set can fail to solve a structure as easily as a lower resolution set. This can be caused by even a single reflection being included at an early stage of the phasing procedure which leads to some incorrect phases at a later stage. If there are very few invariants available, even a few incorrect relations can dramatically alter the phasing path and lead to problems. If unresolved reflections have been split by some method then invariants involving these which occur early in the phasing path should be regarded with some suspicion, since an overestimate in |E| can give undue prominence to an individual reflection in the phasing

procedure.

The problem of the effect of negative scatterers (such as hydrogen) in a neutron experiment could be severe if these form a substantial part of the structure. Merely searching for negative peaks in a Fourier map is trivial, but the existence of such "holes" in the scattering density map raises serious questions about the applicability of the basic tenets of direct methods philosophy. There have been some suggestions of how to modify the direct methods procedures if this problem proves to be serious, and these are discussed elsewhere (Wilson, 1987).

Fourier Recycling

Most packages need adaptation for neutron data, although some such as CCSL (Brown and Matthewman, 1987) already have fully integrated neutron diffraction calculations. Fourier calculations can often give poor results if only a small fragment is obtained, especially in high symmetry cases where the located atoms may lie on special positions. For interpretation of Fourier maps the use of chemical and crystallographic intuition can be very important and occasionally crucial.

Karle Recycling

This procedure can suffer as ever from the paucity of large $|E|$ magnitudes, leading to a restricted phase expansion and again poor E-maps.

Examples

Patterson Methods - Squaric acid

Data were collected on HRPD from a sample of 3,4-dihydroxy-cyclobutene-1,2-dione (squaric acid) (Nelmes, Tun, David and Harrison, unpublished) and intensities of 193 reflections were extracted from the profile. Overlapping reflections were given equal proportions of the total intensity of the peak.

Many attempts were made to solve the structure of squaric acid in MITHRIL, using various numbers of triplets, quartets, various weighting schemes, the procedures YZARC (random phasing - steepest descents), MAGEX (magic integers) and RANTAN (random phase tangent recycling) and various types of input groups. Since squaric acid was attempted "as ab initio" the published model of Semmingsen, Hollander and Koetzle (1977) was used in a Karle (phase) recycling procedure, but even this did not produce the correct answer.

In addition to the above attempts, exhaustive attempts were made to solve the structure using 1Å resolution **simulated** data, but again these failed to produce even a fragment of the correct structure.

A rationale can be given for the failure of MITHRIL to solve this structure since the molecule is strictly planar with all atoms at y=0.25. Traditionally direct methods have been at their weakest in such cases, i.e. where a planar moiety is a significant fraction of the scattering power of the cell. In this case the planar group is the whole molecule and hence the direct methods assumption of "equal atoms, randomly distributed" is grossly invalid, thus putting the methods under severe pressure. This severe problem is evidenced by the failure of the phasing procedure even when Karle recycling is employed using the full published coordinates as model. These problems suggest recourse to the Patterson methods program PATMET which is designed with precisely this type of problem in mind.

A model of just a C_4 square of atoms, with all bond lengths 1.4Å and all bond angles 90° was used as input to the PATMET program. The $I(\theta,\phi)$ function revealed the plane of the molecule, a 1D rotation function calculation completed the orientation of the fragment and the Q- (translation) functions were used to position the oriented fragment with respect to the symmetry elements in the cell. The coordinates produced by PATMET were then used as input to a Fourier map calculation in MITHRIL and there appeared in this map all 4 carbon and all 4 oxygen atoms in the structure. The hydrogen atoms were not located since the program was not configured to search for troughs. However extraction of the 8 non-hydrogen positions can be said to have "solved" the structure by any reasonable criterion since standard recycling and refinement would lead to final atomic parameters for all atoms. Similar results were obtained using an 8 atom fragment [C-C, 1.4Å, C-O, 1.3Å, C-C-C, 90°, C-C-O, 135°], again all 8 non-hydrogen atoms were revealed easily in PATMET followed by Fourier calculations.

Hence PATMET has easily solved the structure of squaric acid from HRPD data assuming just a perfect square C_4 group or a C_4O_4 group as input model.

Direct Methods - Copper Phosphate

A total of 768 intensities were extracted for reflections collected from a sample of $Cu_3(PO_4)_2$ on HRPD (Forsyth, David, Harrison, Ibberson and Moze, unpublished). Again overlapping reflections were given equal proportions of the total intensity.

The MITHRIL program was run with default values for input parameters for data cut off at 1Å resolution (289 reflections). TRIPLETS and QUARTETS were calculated for the top 98 $|E_{hkl}|$ values and the top 8 peaks in the first E-map were as follows :

Peak	Height	X	Y	Z
1	3019	1.0000	0.0000	1.0000
2	2979	0.2718	0.2312	0.3051
3	2501	0.3907	0.1361	0.6390
4	2218	0.8541	0.3446	0.3538
5	2129	0.2249	0.2313	0.9951
6	1948	0.3501	0.3621	0.7669
7	1791	0.6875	0.3296	0.8390
8	759	1.0043	0.2390	0.1536

By comparing with the refined coordinates from the profile fit :

Atom	b	X	Y	Z	Peak
Cu(1)	0.7718	0.0000	0.0000	0.0000	1
Cu(2)	0.7718	0.2776	0.2258	0.3157	2
P	0.5130	0.3586	0.3534	0.7785	6
O(1)	0.5805	-0.1536	0.3443	0.3389	4
O(2)	0.5805	0.3324	0.6515	0.1695	7
O(3)	0.5805	0.2303	0.2274	0.0049	5
O(4)	0.5805	0.3786	0.1498	0.6334	3

it can be seen that the top 7 peaks in the E-map correspond to the 7 atoms in the asymmetric unit of the structure. The noise level in the map is shown by peak number 8 which is at less than half the height of peak 7. Thus MITHRIL has solved the structure of $Cu_3(PO_4)_2$ from HRPD data.

To investigate the effect of resolution on the structural solution, attempts were made to solve the structure using the same input parameters with different sections of the data. These attempts are summarised in Table 1, along with the number of degenerate (overlapping) reflections in the data set.

As can be seen from this the structure seems to solve with data down to a resolution of ~1.25Å but fails thereafter. However the failure of the attempt at 0.9Å resolution warrants some comment.

There is no doubt that with 397 reflections available and judging from the other successful attempts at structural solution, the solution for this data should be straightforward. However with a relative paucity of invariants any error early in the phasing path can be fatal, especially if the erroneous phase is then used extensively in the further development of phases. If such a reflection is introduced with high |E| when the resolution is increased from 1Å to 0.9Å then the first attempt at phasing might fail. This occurrence brings out a general point for direct methods solution from powder data (Wilson, 1987). If a reflection which is given an "arbitrary" intensity in the splitting of overlapping reflections is used early and often in the phasing process because it has a high |E| value derived from this intensity, then the phasing path should be regarded with some caution - if this reflection is in fact weak some of the invariants derived will be invalid and the phasing incorrect. In such cases it may be best to disregard such reflections totally and omit them from the observed data set.

Table 1 - Direct methods solution of $Cu_3(PO_4)_2$.

d_{min}(Å)	singles	doubles	triples	quads	quints	total	solution ?
0.70	629	50	10	1	1	768	✓
0.75	586	42	5	1	1	694	✓
0.78	542	32	3	-	-	615	✓
0.79	527	28	3	-	-	592	✓
0.80	506	28	3	-	-	571	✓
0.90	363	17	-	-	-	397	×
1.00	269	10	-	-	-	289	✓
1.25	140	2	-	-	-	144	✓
1.33	115	-	-	-	-	115	×
1.43	98	-	-	-	-	98	×
						(some atoms indicated)	

The Probabilistic Determination of Intensities of Completely Overlapping Reflections in Powder Diffraction Patterns

Two techniques have been developed for the extraction of the individual intensities of completely overlapping reflections in a powder diffraction pattern (David, 1986). The first is analogous to Sayre's (1952) squaring method while the second is based upon maximising the entropy of the Patterson function subject to the constraints imposed by the observed intensities of single and overlapping groups of reflections. The agreement between true $|F|^2$ values of overlapping reflections and the values obtained by maximum entropy is, in most simulated cases, excellent.

The Squaring Method

Sayre (1952) developed an elegant argument, which he called the squaring method, that was useful as a new method of phase determination. An analogous argument may be used for the extraction of the relative contributions of degenerate reflections. Consider a Patterson function P(r) and its square $P^2(r)$. Their Fourier transforms are respectively

$$g_{\vec{h}} = \int_V (P(\vec{r}) \cos (2\pi \vec{h}.\vec{r})\, dV = |F_{\vec{h}}|^2 \qquad (1)$$

and

$$G_{\vec{h}} = \int_V P^2(\vec{r}) \cos (2\pi \vec{h}.\vec{r})\, dV = \Sigma\, g_{\vec{k}}\, g_{\vec{h}-\vec{k}} \qquad (2)$$

where $|F_h|$ is the modulus of the structure factor of reflection h, V is the unit cell volume and the latter equation is obtained by the convolution theorem. Consider a simple Patterson with N identical non-overlapping Gaussian inter-atomic vector loci. The square of that Patterson looks similar to the Patterson itself. Indeed, if the Gaussians are situated at $r_o(n)$, n = 1,...,N with standard deviation $s/\sqrt{(2\pi)}$ then

$$P(\vec{r}) = \sum_{n=1}^{N} \exp\left(-\pi\, (\vec{r} - \vec{r}_o^{\,n})^2/s^2\right) \qquad (3a)$$

and

$$P^2(\vec{r}) = \sum_{n=1}^{N} \exp\left(-2\pi\, (\vec{r} - \vec{r}_o^{\,n})^2/s^2\right) \qquad (3b)$$

Manipulation of equations 1 and 2 yields

$$|F_{\vec{h}}|^2 = (\sqrt{2}/V) \exp\left(-\tfrac{1}{2}\pi s^2/d_{\vec{h}}^{\,2}\right) \sum_{\vec{k}} |F_{\vec{k}}|^2\, |F_{\vec{h}-\vec{k}}|^2 \qquad (4)$$

where d_h is the d spacing of the reflection, h. The scale factor linking $|F_h|^2$ with its self-convolution depends only on the magnitude of the d spacing and is thus identical for overlapping reflections. The fractional intensity contribution of the nth of N overlapping reflections may then be estimated by the following equation :

$$\frac{j_n\, |F_{\vec{h}_n}|^2}{\sum_{i=1}^{N} j_i\, |F_{\vec{h}_i}|^2} = \frac{j_n \sum_{\vec{k}} |F_{\vec{k}}|^2\, |F_{\vec{h}_n-\vec{k}}|^2}{\sum_{i=1}^{N} j_i \left(\sum_{\vec{k}} |F_{\vec{k}}|^2\, |F_{\vec{h}_i-\vec{k}}|^2\right)} \qquad (5)$$

Experience indicates that the squaring method shifts the relative intensities in the correct sense away from equipartitioning but, in the majority of cases, to a degree often substantially less than the true amount.

Maximum Entropy Patterson Methods

The principle of maximum entropy (ME), originally developed by Jaynes (1957, 1968), is a powerful technique that has been applied to many areas of research and, in particular, more recently in crystallography to direct phase determination (Britten and Collins 1982, Narayan and Nityanda 1982, Piro 1983, Wilkins, Varghese and Lehmann 1983, Bricogne 1984, Livesey and Skilling 1985, Wei 1985). The power of the maximum entropy principle is that it yields as a

solution the mean of the maximum information probability density (i.e. the most probable solution) consistent with experimental observation (i.e. the constraints imposed on the solution) (Shore and Johnson 1980, Bricogne 1984).

In the probabilistic determination of overlapping integrated intensities the function maximised is the "Patterson entropy"

$$E_p = \int_V P(\vec{r}) \ln (P(\vec{r})/P_o(\vec{r})) \, dV \qquad (6)$$

where the integral is taken over the unit cell volume, V. P(r) is the Patterson function and $P_o(r)$ the initial estimate of the Patterson function. $P_o(r)$ is taken to be uniform throughout the cell and equal to $|F_{000}|^2 /V$, where $|F_{000}|^2$ is the square of the modulus of the structure factor of the 0 0 0 reflection. Given that the Patterson function, P(r), is normalised (i.e. $\int P(r) \, dV = |F_{000}|^2$) then the unconstrained maximum entropy Patterson function must be $P(r) = P_o(r)$. This is clearly physically unreasonable as it implied that $|F_{hkl}|^2 = 0$ for all (h k l) $\neq$ (0 0 0). Thus the observed integrated intensities impose constraints upon the maximisation of the Patterson entropy. Consider a non-overlapping reflection characterised by h_i with multiplicity j_i (i.e. there are j_i symmetry equivalent reflections, $\{h_i(1), \ldots, h_i(j_i)\}$. The constraint imposed upon the Patterson entropy is clearly

$$\int_{cell} P(\vec{r}) \left[\sum_{k_i=1}^{j_i} \cos (2\pi \vec{h}_i(k_i).\vec{r}) \right] dV = j_i |F_{h_i}|^2 \qquad (7)$$

For N overlapping crystallographically distinct sets of reflections ($n_1 \leq i \leq n_2$; $N = n_2 - n_1 + 1$) the constraint becomes

$$\int_{cell} P(\vec{r}) \left[\sum_{i=n_1}^{n_2} \sum_{k_i=1}^{j_i} \cos(2\pi \vec{h}_i(k_i).\vec{r}) \right] dV = \sum_{i=n_1}^{n_2} j_i |F_{h_i}|^2 \qquad (8)$$

According to the maximum entropy principle, the resulting ME Patterson map yields the maximum amount of information from the available observations. Overlapping reflections are neither left unconsidered nor arbitrarily partitioned into equal contributions as in traditional ab-initio powder diffraction Patterson techniques. The ME Patterson is thus optimal for structure determination from powder diffraction patterns.

Although Patterson methods play an important role in structure determination in their own right, the relative intensities of overlapping reflections may be extracted in an unbiased manner to provide an extended list of structure factor amplitudes ,for use in direct methods procedures of phase determination using the following approach. Let $P_{ME}(r)$ be the ME Patterson function and h_i be one of a set of overlapping functions. $|F(h_i)|^2$ may be estimated by evaluating the Fourier component of $P_{ME}(r)$ corresponding to h_i;

$$|F_{\vec{h}_i}|^2 = \int_{cell} P_{ME}(\vec{r}) \cos(2\pi \vec{h}_i.\vec{r}) \, dV \qquad (9)$$

The results presented by David (1986) indicate that excellent agreement may be achieved in (simulated) examples. In particular, it was found that the partitioning of reflections with large $|F|^2$ values ($|F|^2 \geq 1$) wass over 90% correct both in sense and magnitude. Moreover, perhaps surprisingly, the $|F|^2$ partitioning is reliable even for reflections with highest Miller indices.

Ab Initio Structure Determination using an Image Reconstruction Technique

A new algorithm, MEDIC (Maximum Entropy Direct Inversion of Crystallographic Data), has been developed (Johnson & David, 1987) that provides a direct method of inverting the observed integrated intensities in a diffraction experiment to yield the scattering density within a unit cell. The method, based upon the METRIC algorithm (Johnson 1987), uses an image reconstruction technique employing the maximum entropy principle. It has been successfully tested on model systems with both centrosymmetric and non-centrosymmetric structures and on experimental neutron powder diffraction data from two small inorganic structures, $Cu_3(PO_4)_2$ and $FeAsO_4$.

One of the more interesting developments over the past few years has been the application of maximum entropy (ME) techniques. These techniques, originally derived for underdetermined problems in information theory (Jaynes 1957), and discussed extensively by Bricogne (1984), show much promise in tackling the lack of knowledge associated with the absence of a-priori phase information. The recent work of Gull, Livesey and Sivia (1987) exemplifies this approach that focuses on the need to determine the phases using combinations of the information provided by n-tuple phase relationships and the ME principle of maximising the objective function

$$S = - \Sigma \rho(r) \ln\{\rho(r)/\rho_o(r)\} \qquad (10)$$

subject to the constraint ($\chi^2 \simeq m$) imposed by the observed structure factors $|F^o_{hkl}|$:

$$\chi^2 = \sum_{k=1}^{m} \frac{(|F^o_{hkl}| - |F^c_{hkl}|)^2}{\sigma_{hkl}^2} \qquad (11)$$

The summation in equation 10 is taken over the unit cell and $\rho_o(r)$ is an 'a priori' value for $\rho(r)$.

The maximum entropy approach proposed by the MEDIC method differs from previous ME techniques in that it does not operate in Fourier space in the determination of phases but instead operates using the Patterson function in real space. The process thus proceeds in two stages:

$$\{|F_{hkl}|\} \xrightarrow[i]{} \{P(r)\} \xrightarrow[ii]{} \{\rho(r)\} \qquad (12)$$

(i) The Patterson map is generated either by standard Fourier transformation of $|F_{hkl}|^2$ or by ME methods [6].

(ii) The Patterson map is inverted (decorrelated) to provide the real space structure.

The MEDIC algorithm consists of treating the Patterson map decorrelation as an image reconstruction problem in which the real space structure (the scattering density, $\rho(r)$, within a unit cell) represents the image to be reconstructed.

The method has been tested on two Patterson maps derived from experimentally recorded $\{|F_{hkl}|\}$ lists determined from neutron powder diffraction patterns of $Cu_3(PO_4)_2$ and $FeAsO_4$. The use of a powder diffraction $\{|F_{hkl}|\}$ set means that structure factors of overlapping reflections were averaged - a process likely to hinder rather than aid the inversion.

$Cu_3(PO_4)_2$

Neutron diffraction data were recorded up to a maximum $\sin\theta/\lambda$ of 0.7Å^{-1} on the HRPD powder diffractometer at the ISIS facility. Although a total of 672 reflections lie within this range only 610 reflections were non-overlapping. In the present analysis the structure factors for reflections in overlapping groups were obtained by simply assigning the same, average value to each reflection within the group. To minimise Fourier truncation errors the Patterson map was averaged over a cube of 0.7Å. All negative Patterson density was set to zero prior to the Patterson decorrelation.

The MEDIC program produced a separation of the true 13 atomic positions from noise in the ρ map after 16000 cycles. Further cycles of the program led to dramatically improved signal-to- noise such that after 60000 cycles the ratio of the height of the lowest 'genuine' peak to the highest noise peak in the ρ map was 8000/1. This may be compared with the ratio of 'lowest signal/highest noise' of 2.4 obtained from the same set of structure factor magnitudes using the direct methods package, MITHRIL (Gilmore 1984).

$FeAsO_4$

Neutron diffraction data were similarly recorded up to a maximum $\sin\theta/\lambda$ of 0.7Å^{-1} on the HRPD powder diffractometer. In this case a total of 901 reflections lie within the range although only 550 reflections were non-overlapping. Hence a total of 351 reflections lay in overlapping groups and were assigned average structure values.

The MEDIC program produced a separation of the true 24 atomic positions from the noise in the ρ map after 50,000 cycles. In all subsequent cycles up to 300,000 the ρ map produced a correct separation of 23 atomic positions (40% of maps) or 24 positions (60%). The 'lost' position in the maps which only separated 23 of the 24 positions varied from one map to another, and even using only these 'incomplete' maps the correct structure would be revealed by a simple correlation technique.

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