Integration of Single-Crystal Reflections Using Area Multidetectors

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Abstract

The development of multidetectors for use in X-ray and neutron scattering experiments has created an interest in methods for integrating Bragg peaks in three-dimensional data arrays representing intensity scattered from single crystals. A method of using a priori information, extracted from the strongest peaks, to obtain statistically optimum results has been developed at the Institut Laue-Langevin (ILL), Grenoble. The method is outlined in this paper and results of its application to neutron diffraction are discussed.

Introduction

Large-area detectors for X-ray crystallography (Xuong, Freer, Hamlin, Nielson & Vernon, 1978) and for neutron diffraction (Schoenborn, 1983; Schultz, Srinivasan, Teller, Williams & Lukehart, 1984; Roth & Lewit-Bentley, 1982) are now in routine use. Larger detectors are under development and will be particularly important in data collection at the synchrotron X-ray and pulsed neutron sources which are now coming into use. Whatever the physical mechanism of detection, the data from area detectors can be presented in 'detector space' as a three-dimensional array of integers representing the intensity diffracted by the crystal. This array is built from frames of data on which the events over a given time at each spatial element of the detector are registered. Successive frames represent crystal-rotation steps in the case of monochromatic beam or units of energy discrimination for a static crystal and a white beam. Bragg reflections occur in this distorted reciprocal space as high regions and the process of data analysis is therefore to identify these regions, index the reflections and evaluate their integrated intensities.

The method described by Xuong et al. for the integration of peaks with an X-ray area detector used a rectangular box of fixed volume surrounding the reflection. A software window of 3 x 3 elements is placed at the predicted reflection position and can be adjusted by ±1 element so that its centre corresponds more closely with this window over nine successive frames. Although it has the virtue of being simple, this technique does not attempt to take advantage of the ability to optimize statistically the peak intensity relative to the background in a three-dimensional data set. The adjustment of the centre can also give a strong positive bias in the case of weak reflections.

Dynamic-mask techniques have been described (Spencer & Kossiakoff, 1980; Sjölin & Wlodawer, 1981) which rely on the fact that the Bragg peaks are almost ellipsoidal in the detector space. They define an elliptical boundary for a peak by consideration of the ratio of the signal in contiguous elements within the ellipse to the variance of the background outside the ellipse. These methods reduce the estimated standard deviation of the integrated peak intensities as they exclude the measurement of unnecessary background points. A somewhat similar technique has been described by Filhol, Thomas, Greenwood & Barthelemy (1983).

The one-dimensional profile-analysis technique which was first described by Diamond (1969) has been developed by Ford (1974) for analysis of precession photographic data. It takes advantage of the fact that the estimated uncertainty in the intensity of the reflection is lower when a fitted function incorporating a priori information is integrated than when the raw intensity measured in each position is used for integration, as it allows an improved separation of peak and background. The drawback of using such a technique in three dimensions is that the profile changes more rapidly than its projection into one or two dimensions and the processing time increases rapidly with the number of data points used.

The method described by Roth & Lewit-Bentley (1982) for the analysis of data from the D17 small-angle scattering diffractometer at ILL is based on an a priori calculation of the intensity distribution for each reflection from a knowledge of the primary-beam parameters and the crystal mosaic spread. A scheme,
similar in principle, has been described by Schoenborn (1983) for the analysis of neutron diffraction data collected with an area detector at Brookhaven National Laboratory.

The work which is described here uses a priori information in the form of a learned profile to minimize the standard deviation of weak reflections. It is based on the $\sigma(I)/I$ minimum method for one-dimensional data (Lehmann & Larsen, 1974) and uses an acquired knowledge of the peak profile of strong reflections to optimize the integration of weak reflections. It has been used with data collected on the D17 and D19 diffractometers at ILL. A preliminary description of the method has been given by Wilkinson & Khamis (1983).

The Lehmann and Larsen $\sigma(I)/I$ method

As originally described by Lehmann & Larsen (1974) for one-dimensional data scans, the ratio $\sigma(I)/I$ of the standard deviation of the integrated intensity (taking into account background subtraction) to the intensity $I$ is calculated for points which are successively more distant from the peak of a reflection. The boundary of the peak is defined to occur when $\sigma(I)/I$ reaches a minimum, with one or two further points added for safety. In this form the technique is not, however, suitable for the analysis of two- or three-dimensional data.

Firstly, and particularly in the case of weak reflections, it is not immediately obvious which points should be tested for the $\sigma(I)/I$ minimum criterion, as there are three directions to sample. Secondly, in the case of weak peaks, the method often fails to find a clear minimum in $\sigma(I)/I$ owing to statistical fluctuations, which are more acute when the intensity is distributed in three dimensions as this results in a lower mean count per element. Since one of the major advantages of using a multidetector is to be able to tailor a suitable software window for weak reflections this is a problem. Thirdly, it is very time consuming to have to compute $\sigma(I)/I$ for a three-dimensional data set on a point-by-point basis. Speed is an important factor in processing area detector data which often arrives in such volume that not all of it can reasonably be saved. Fourthly, although the minimization of $\sigma(I)/I$ gives the correct statistical decision for the point at which integration should stop, it underestimates the intensities of the reflections as it occurs before the peak boundary. This is more serious in three dimensions than in one and although the fraction of intensity missed in the case of strong reflections is quite small, an underestimate of 30% or more in the intensity of weak reflections is quite common.

$\sigma(I)/I$ with a priori knowledge of the peak shape

The difficulties mentioned above can be overcome if the peak shape is known. Suppose that this is measured on a statistically well observed (strong) peak in terms of $p$, the number of peak points within a certain contour level of intensity. (Equal-intensity contours in the three-dimensional intensity distribution about each reflection normally approximate to concentric ellipsoids centred at the Bragg position.) Let the integrated intensity within those $p$ points be $I(p)$ (the diagonally shaded area in Fig. 1), a fraction $x(p)$ of the ‘total’ integrated intensity of the peak $I_0(p_0)$. It is shown in the Appendix that when the peak sits on a well known background level $B$ which is determined from points outside the peak, the minimum value of $\sigma(I)/I$ occurs when the equation

$$\frac{d(p/p_0)/dx - 2(p/p_0)/x}{I_0/p_0B}$$

is satisfied. In the case of a strong peak ($I_0/p_0B \gg 1$) this minimum point will be close to $p_0$.

Consider now the application of this to a weak peak which has exactly the same shape as the strong peak and sits on a flat background $B$, but is only a fraction $f$ as strong. We may attempt to evaluate the terms in the equation from the weak-peak data in order to determine the minimum $\sigma(I)/I$ position, but this will usually be difficult owing to statistical fluctuations. Better still, we may use the parameters which we have derived from the strong peak (these are the same if the peaks are of the same shape) on the left side of the equation and the signal-to-noise ratio for the weak peak on the right to predict the position of the minimum $\sigma(I)/I$ for that peak. The signal-to-noise ratio for the weak peak needs only to be known approximately and can be adequately estimated for the purpose by a preliminary background/peak/background reduction of the weak-reflection data.

In fact what we really wish to do is minimize the quantity $\sigma[I(x)] = \sigma[I(x)]$ for the weak reflection. In the Appendix it is shown that the minimum value of $\sigma[I(x)]$ occurs at the same point as the minimum in.

\[\text{Fig. 1. Peak of total integrated intensity } I_0 \text{ containing } p_0 \text{ elements sitting on a level background } B. \text{ The signal contained within } p \text{ elements (shaded by diagonal lines) is } I(p). \text{ The background } B \text{ is determined from } q \text{ points outside the peak.}\]
\( \sigma(I)/I \) when \( f \) is a small fraction. The value of \( p/p_0 \) at which the integration should be terminated can therefore be predicted from the equation above, with the terms on the left side determined from the strong peak and the signal-to-noise ratio on the right side being that of the weak peak.

Curves of \( d(p/p_0)/dx \) and \( (2/x)(p/p_0) \) are shown in Fig. 2 for a strong reflection observed from a crystal of lysozyme* with the D19 diffractometer at ILL (Thomas, Stansfield, Berneron, Filhol, Greenwood, Jacob, Feltin & Mason, 1983). They are typical of Bragg peaks which are adequately sampled on a three-dimensional grid. The arrow in the diagram shows where the equation is satisfied for a weak reflection which has a signal-to-noise ratio of 1.0.

As the reflection becomes weaker and the signal-to-noise ratio tends to zero, the statistically optimum point at which the integration should stop approaches the crossover point of the two curves, which can be seen in the expanded portion of the diagram. In practical cases, this point is normally well below the minimum volume which would be considered.

**Improvement in precision**

The improvement in precision of \( I/x \) by stopping the integration at the \( \sigma(I)/I \) minimum point can be judged from the curves of Fig. 3, which illustrate the variation of \( \sigma(I_0) \) at several signal-to-noise ratios for different values of \( f \). The improvement is shown numerically in Table 1 as a function of signal-to-noise ratio for the case where \( f \to 0 \), when the contribution from the correction factor is negligible. Comparison of the

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*Unpublished data kindly made available by M. S. Lehmann.

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\( \sigma(I_0) = \sigma(I/x) \) in units of \( I_0/2 \) plotted as a function of \( p/p_0 \) for peaks integrated with a model of strength \( I_0/f \). \( x \) is the fraction of \( I_0 \) included within \( p \) points. The value of \( p/p_0 \) for which equation (11) of the Appendix is satisfied for a signal-to-noise ratio of 1 is arrowed. The region near the origin has been expanded in the centre of the diagram.
Table 1. $\sigma_{\min}(I/x)$ and $\sigma[I_0(p_0)]$ in units of $I_0$ for strong, intermediate, weak and very weak peaks modelled on a very strong peak ($f \rightarrow 0$) of the same shape.

<table>
<thead>
<tr>
<th>Peak intensity</th>
<th>$p$, $p_0$ at</th>
<th>$\sigma(I/x)_{\min}$</th>
<th>$\sigma(I/x)_{\min}$</th>
<th>$\sigma[I_0(p_0)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong</td>
<td>$I_0, p_0 B &gt; 10$</td>
<td>0.025</td>
<td>1.02</td>
<td>1.05</td>
</tr>
<tr>
<td>Intermediate</td>
<td>$2.5 &gt; I_0, p_0 B &gt; 1$</td>
<td>0.116</td>
<td>1.10</td>
<td>1.41</td>
</tr>
<tr>
<td>Weak</td>
<td>$0.5 &gt; I_0, p_0 B &gt; 0.5$</td>
<td>0.081</td>
<td>1.51</td>
<td>3.32</td>
</tr>
<tr>
<td>Very weak</td>
<td>$0.1 &gt; I_0, p_0 B &gt; 0.01$</td>
<td>0.081</td>
<td>3.50</td>
<td>10.05</td>
</tr>
</tbody>
</table>

Table 1. $\sigma_{\min}(I/x)$ and $\sigma[I_0(p_0)]$ in units of $I_0$ for strong, intermediate, weak and very weak peaks modelled on a very strong peak ($f \rightarrow 0$) of the same shape.

The standard deviation of the intensity calculated by integration to the optimum precision point with that to the full volume of the peak shows that when the signal-to-noise ratio is high the standard deviation is governed by the peak intensity and there is little to be gained from optimizing $\sigma(I)/I$, but that when the signal-to-noise ratio is low the precision is governed by the background and there is a potential gain of several hundred percent.

The analytic technique for optimizing the precision of measurement of the integrated intensity of a reflection overcomes the drawbacks mentioned in the previous section. The statistically optimum point at which to stop integrating a reflection can be simply identified and the factor to apply to the intensity to correct for the truncation of the integration is known from neighbouring strong reflections. The technique is quicker to apply than a numerical evaluation of $\sigma(I)/I$ for weak peaks and means that the data can be analysed on line.

Comparison with least-squares profile fitting

For reasons of space, a full comparison of the analytic $\sigma(I)/I$ method with a least-squares profile fit to a model function will not be attempted here, but will be the subject of a future publication. However, some insight into the similarities and differences of the two methods (which both use a priori information) and the precision obtained in each case under identical boundary conditions can be gained by examining a particular one-dimensional case. Consider a perfectly known normalized peak profile $dx/dp$ which has a Gaussian form described by

$$dx/dp = \left[1/2\pi^{1/2}(p_0/6)\right] \exp[-\frac{3}{4}(p/p_0)^2]$$

so that $x(p)$, the fraction of the total intensity included within $p$ points is $\text{erf}(3 \times 2^{1/2} p/p_0)$. Suppose that this peak (which has a standard deviation of $p_0/6$) sits upon a level background of $B$ per element (Fig. 1). The first $p_0$ points about the peak centre (which contain 0.997$I_0$) will be taken as the effective limit of the peak for the $\sigma(I)/I$ analysis, with the background determined from an additional $q$ points lying immediately outside the peak region. Let $q$ be equal to $p_0$, a common one-dimensional experimental strategy. [There will be a slight negative bias of $(1/x)$

\begin{equation}
\times (0.003 I_0 p/p_0)
\end{equation}

when the intensity of the peak is calculated from $p$ points, as $0.3\%$ of the peak will be included in the background. This is negligible in comparison with $\sigma(I_0)$ if $I_0$ is small. In the present example, if $I_0$ is 100 counts, the bias is $\sim 0.15$ counts at the $\sigma(I_0)$ minimum point, while $\sigma(I_0)$ is $\sim 33$ counts.]

The statistical uncertainty in $I(p)$ [equation (5), Appendix] shows that

$$\sigma(I) = \left[I + pB(1 + p/q)\right]^{1/2}$$

as $q = p_0$. Since $1/x$ is perfectly known, we may write

$$\sigma(I_0) = (1/x)\sigma(I)$$

$$= (1/x)\left[I + pB(1 + p/p_0)\right]^{1/2}$$

$$= I_0^{1/2}\{(1/x)[1 + pB/xI_0(1 + p/p_0)]\}^{1/2}$$

$$= I_0^{1/2}\{(1/x)[1 + (1/x)(p_0 B/I_0)(p/p_0)]\}^{1/2}$$

$\sigma(I_0)$ is therefore a function only of the signal-to-noise ratio $I_0/p_0 B$ for a peak of known profile. It is shown (in units of $I_0^{1/2}$) in Fig. 4 for a weak reflection with the Gaussian profile described above and a signal-to-noise ratio of 0.1. The curve has a minimum value of $p \sim 0.4 p_0$. As the number of points in the integration is increased, although more peak intensity is included, the statistical uncertainty contribution from the additional background counts more than outweighs this and the value of $\sigma(I_0)$ rises. This arises because the background has been calculated from points outside the defined peak region. Thus in the $\sigma(I)/I$ analysis the inner $p$ points of the peak and (in this case) the $p_0$ points which lie immediately outside the defined peak boundary are the ones used in estimating $\sigma(I_0)$.

In the least-squares fitting method, on the other hand, each data point contributes to the estimate of

![Fig. 4. $\sigma(I_0)$ [$= 1 \times \sigma(1)$] in $I_0^{1/2}$ units calculated for a Gaussian peak with signal-to-noise ratio $I_0, p_0 B = 0.1$ by the $\sigma(I)/I$ method and by a least-squares fit (LS fit). The least-squares minimum value is indicated by the horizontal dashed line. Also shown is the result for $B = 0$, when the signal-to-noise ratio is $x$.](image-url)
both $I_0$ and $B$. With the known profile $dx/dp$, a set of $p$
linear equations of the form

$$(dI/dp)_{obs} = I_0 x(p) + B$$

is available for a least-squares fit of $I_0$ and $B$ and an
estimate of the uncertainties $\sigma(I_0)$ and $\sigma(B)$. With
weights of $1/(dI/dp)_{est}$ for the normal equations of the
least-squares fit (which assumes Poissonian counting
statistics apply to each observation) the expectation
value of $\sigma(I_0)$ has been calculated for the Gaussian
profile and is shown as a function of the number of
peak points in Fig. 4. An average has been taken over
all possible samplings of the experimental profile, as is
the case in a multidetector experiment when the
observations are equally spaced, but arbitrarily
located relative to the peak centre. It can be seen that
the estimate of $\sigma(I_0)$ falls monotonically as the number
of points in the fit is increased, as expected, since every
additional observation should improve the estimate of
$I_0$ and $B$. The minimum value of $\sigma(I_0)$ is reached at
$p = 2\rho_0$, where $\rho_0(I_0)$ is only slightly lower than that
obtained by the $(I)/I$ method. The case correspond-
ing to a very strong reflection $(I_0/\rho_0 B \rightarrow \infty)$ is also
illustrated in Fig. 4. This has been calculated by setting
$B = 0$, when both the least-squares fit and $(I)/I$
methods predict that $\sigma(I_0)$ is $I_0^{1/2} x^{-1/2}$. Curves for
signal-to-noise ratios lying between these limits are
intermediate between those shown in Fig. 4, with the
minimum point in the $(I)/I$ curve moving to larger $p$
as the signal-to-noise ratio increases, tending to $2\rho_0$ as
$I_0/\rho_0 B \rightarrow \infty$. The difference between the minimum
value for $\sigma(I_0)$ for the two methods is greatest at low
signal-to-noise ratios, and therefore never very large.

**Integration of strong peaks and construction of a model library**

A Fortran computer program (PEAKINT) has been
written to carry out the $(I)/I$ integration procedures
and to construct a library of peak profiles for the D19
diffractometer at ILL. A peak is defined to be strong
and added to a library built for the purpose of
integrating weak peaks if there is no substantial
increase in the value of $\sigma(I/x)$ as the volume of
integration is increased to a large number of elements.
From Fig. 3 it is clear that this is the case when the
signal-to-noise ratio is greater than about ten and
such peaks are defined to be 'strong'. When the signal
is less than the noise there is an appreciable increase in
$\sigma(I/x)$ and these peaks are 'weak'. (In the program, the
user may choose the signal-to-noise ratios which
define the strong and weak peaks.) Reflections with
signal-to-noise ratios between the weak and the strong
peaks are defined to be 'intermediate' and are
integrated in the same way as strong peaks but are not
added to the library as models.

Since the observed intensity contours of peaks are
approximately ellipsoidal, the peak profile $x(p)$ is
found for strong peaks by dividing the reflection into
concentric ellipsoidal shells. [Other methods of divid-
ing the reflection are possible and do not introduce
any bias in the integrated intensity, except in so far
that the shapes chosen may not permit the truly
minimum $\sigma(I)/I$ point to be found.]

The smooth ellipsoid which most closely resembles
a constant-intensity contour is found by calculating
the components of the three-dimensional moment-
of-inertia tensor for unit-weight elements which lie
inside the contour, in a similar way to that described
for ellipses by Sjölin & Wlodawer (1981). Typically,
the one-twentieth peak-height contour is chosen and
the smooth ellipsoid which has those tensor compo-
nents is used as the modelling volume. The shape is
expanded and contracted in suitable steps about the
observed centre of gravity of the modelling contour to
give the integrated intensity $I(p)$, the profile $dI/dp$ and
$\sigma(I)/I$ as a function of $p$, the number of points in the
ellipsoidal volume. For a strong peak the position of
the minimum of $\sigma(I)/I$ is not critically dependent on
the precise level chosen for the background.

The value of the background to be used in estimating
the integrated intensity of the reflection is obtained
from an ellipsoidal shell of constant volume lying
immediately outside the peak boundary. The peak
boundary is defined to be the ellipsoidal shell enclos-
ing a volume which is a user-determined multiple
(typically $\sim 4$) of the volume at which $\sigma(I)/I$ is
a minimum. The integrated intensity of the peak is then
taken to be the sum of the counts in the elements
within the peak boundary, minus a constant back-
ground count per element.

The ellipsoidal volume containing the peak varies
slowly in size and shape throughout detector space
owing to the effects of the incident-beam divergence
and wavelength spread and the mosaic spread of the
crystal. Figs. 5(a) and (b) show sections through the
peak ellipsoids for a crystal of lysozyme obtained with
the D19 multidetector in normal-beam geometry on
the H11 beamline at ILL. It is apparent that, for
the instrumental arrangement of the experiment, the
major variation in the size and orientation of the
integration ellipsoid is the rocking-curve width.

The spatial extent on the detector was nearly constant
over the whole range of detector angles in this experi-
ment. New peaks are added to the library as they are
measured. The library is divided into bins of given
angular range in the detector coordinates (usually 3°
on each) and a model replaces an old one in a
particular bin if it has been more recently measured.

**Integration of weak peaks**

When a peak is classified as weak, the surface of
minimum $\sigma(I/x)$ which envelops the optimum in-
tegration volume is found by solving equation (11)
from the Appendix, using information interpolated from nearby strong peaks. When a weak peak occurs in the same library bin as a model, that model is used. If there is no model peak in that bin a linear interpolation is made from nearby models. The background, which is particularly important in the calculation of the intensity of a weak peak, is calculated within a shell identical to that which would have been used to calculate the background for a strong reflection in that position. The peak intensity within the calculated optimum integration volume centred on the predicted position of the peak is summed and the background subtraction made. A minimum volume for integration is set in the program and this is used when it is larger than the predicted optimum volume. The effects of mis-centring of the integration volume and the discrete nature of the detector elements become important at very small integration volumes. The minimum volume is therefore chosen sufficiently large in a particular experiment to ensure that the intensities derived from the weak reflection data are stable against poor predictions of the peak-centroid positions. The volume is normally chosen on the shoulder of the \( x(p) \) curve of Fig. 2, where the fraction of the integrated intensity varies only slowly with \( p \). The correction factor \( 1/x \) obtained from the model is used to scale the intensity within the optimum integration volume, placing it in the same scale as the strong peaks. The final uncertainty in the intensity of the reflection is calculated from the statistical uncertainty of the peak counts within the optimum integration volume and the statistical uncertainty in the factor \( 1/x \).

**Results obtained with the **\textsc{peakint}** program**

The \textsc{peakint} program has been used on-line to the D19 diffractometer at ILL to reduce multidetector diffraction data from single crystals since 1984. Data from a variety of samples from proteins to ionic structures with small unit cells have been successfully treated. In general, the internal consistency among symmetrically equivalent reflections has been comparable to the statistical uncertainties of the intensities predicted by the program.

For example, a total of some 15 000 reflections (of which 5000 were Friedel opposites) were measured out to 1.8 Å in twelve days from a triclinic crystal of hen egg white lysozyme which had been previously soaked in dimethyl sulfoxide.* Of the 10 000 independent reflections, 9420 were measured with an accuracy greater than 3σ and gave an agreement of 13.2% on structure factors in a restrained least-squares refinement.

A second example is the determination of the structure of the nonsuperconducting phase of \( \text{Ba}_2\text{YCu}_3\text{O}_{7-x} \) (Renault, McIntyre, Collin, Pouget & Comes, 1987). In the room-temperature study of the exceptionally small single crystal (0.08 mm³), 369 reflections were scanned out to 0.68 Å\(^{-1}\). The vertical focusing monochromator used gave a double peak in the vertical direction in the intensity distribution of each reflection. The distribution was not truly ellipsoidal but was the same for all reflections observed at the same detector position. The analysis of the \( \sigma(I)/I \) function with elliptical contours is still valid, although the true minimum would not be found exactly. This reduces slightly the precision of the final intensity but does not affect its accuracy. The internal consistency amongst equivalent reflections was 5.3% on intensity, compared to 4.5% predicted from the uncertainties given by the program.

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\* Unpublished data kindly made available by M. S. Lehmann.
Discussion
The analytic $\sigma(I)/I$ algorithm which has been developed has been demonstrated to integrate successfully Bragg peaks in three-dimensional data arrays from steady-state reactor neutron diffraction experiments. The technique has also been applied to single-crystal integrated intensity data measured on pulsed neutron sources (Wilkinson, 1986). It meets the challenge of how to deal quickly and on-line with the large amounts of data generated by large area detectors. Using a priori knowledge from strong reflections, the algorithm significantly improves the precision with which the intensities of weak reflections can be measured and compares favourably with the precision which can be achieved by a least-squares profile fit.

The knowledge of the peak profile can also be used to extend the method to deal with other problems which occur when treating data, such as reflections which lie partly beyond the edge of the detector and the separation of the intensities of partially overlapping reflections. In these cases, a small integration volume is used for all strengths of reflection.

In common with other a priori methods, however, the derived intensity is subject to systematic error if the a priori information is incorrect. In the case of the $\sigma(I)/I$ method, most errors bias the weak intensities negatively. One obvious source of error is a significant difference between the predicted centre of a weak reflection (where the integration volume is centred) and its actual centre. This emphasizes the need for a good $UB$ matrix for the description of the peak positions. Care must be taken to set the minimum acceptable integration volume sufficiently large to allow for errors of this type. The loss of intensity due to this effect has been investigated in the case of pulsed neutron sources (Wilkinson, 1986), where it can be important due to the short rise time of the neutron pulse.

A second problem common to all integration algorithms is how to define the background. This is especially difficult in the presence of strong thermal diffuse scattering when the peaks have long tails which can give rise to a high background estimate and a negative bias to the derived intensities. The definition adopted with this algorithm is that a local background is measured in an ellipsoidal shell immediately around the peak. This appears to give internally consistent results; the merging $R$ factors on the intensities of symmetry-related reflections do compare favourably with the uncertainties predicted by the program.

APPENDIX
$I(p)$ is the integrated intensity in $p$ points of a peak which sits upon a level background $B$ (Fig. 1).

If the fraction of the total peak intensity contained within these $p$ points is $x(p)$ we can estimate the total intensity $I_0(p_0)$ of the peak as $I_0 = I/x$ with standard deviation $\sigma(I/x)$. Let $x(p)$ be measured from a second peak of the same shape as the first. We may then write

$$\sigma^2(I/x) = \sigma^2(I/x^2) + \sigma^2(I/I^2),$$

since the errors in $I$ and $1/x$ are statistically independent.

Thus

$$\frac{\sigma^2(I/x)}{(I/x)^2} = \frac{\sigma^2(I/x)}{(1/x)^2} + \frac{\sigma^2(I)}{I^2}$$

and

$$\sigma(I/x) = I_0 \left[ \frac{\sigma^2(I/x)}{(1/x)^2} + \frac{\sigma^2(I)}{I^2} \right]^{1/2}.$$ (3)

When $\sigma^2(I/x)$ is very small (the reference peak is strong and well measured) minimizing $\sigma(I/x)$ amounts to minimizing $\sigma(I)/I$, which corresponds to the Lehmann–Larsen criterion. If we assume that Poissonian counting statistics apply, the variance of $I$ is given by

$$\sigma^2(I) = I + pB + p^2B/q$$

$$= I + pB(1 + p/q)$$

when the value of $B$ is estimated from $q$ background points.

Thus

$$\sigma^2(I)/I^2 = [I + pB(1 + p/q)]/I^2.$$ (6)

Differentiating this expression with respect to $p$, we get

$$\frac{d}{dp} \left[ \frac{\sigma^2(I)}{I^2} \right] = \left\{ \left( \frac{dI}{dp} + B + \frac{2pB}{q} \right) \right. I^2$$

$$\left. - 2I \frac{dI}{dp} [I + pB(1 + p/q)] \right\} / I^4$$

and setting this to zero to find the minimum, we have

$$\frac{dI}{dp} = I B(1 + 2p/q)$$

$$\frac{dI}{dp} = I + 2pB(1 + p/q)$$

at the minimum $\sigma(I)/I$ point.

This may be more usefully written

$$\frac{dp}{dl} - \frac{2p(p + q)}{l(2p + q)} = \frac{1}{B(2p + q)}.$$ (9)

Taking the limit $p \ll q$, which is normally the case near the minimum $\sigma(I)/I$ point for a weak reflection, we have

$$\frac{dp}{dl} - \frac{2p/q}{l} = 1/B$$

$$\frac{dp}{dl} - 2p/l = 1/B$$

and normalizing by $p_0/I_0$ we get

$$\frac{d(p/p_0)}{dx} - 2(p/p_0)x = I_0/p_0 B.$$ (11)

If $\sigma^2(1/x)$ is not negligible, it is necessary to make a slightly more complicated analysis of the statistically optimum limit for the integration. When $\sigma^2(1/x)$ is
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determined from a strong peak of the same shape and
sitting on a flat background $B'$ we may derive

$$\frac{\sigma^2(1/x)}{(1/x)^2} = \frac{1}{(I_0')^2} \left[ (I_0'x + pB') \left(1 - \frac{x}{x'} \right)^2 + (1 - x)I_0' \right. $$

$$\left. + (p_0 - p)B' + \left( \frac{p}{x} - p_0 \right)^2 \frac{B'}{q} \right] $$

$$= \frac{1}{(I_0')^2} \left[ (I_0'x + pB') \left(1 - \frac{2x}{x^2} \right) + (I_0' + p_0B') \right. $$

$$\left. + \left( \frac{p}{x} - p_0 \right)^2 \frac{B'}{q} \right], \quad (12)$$

where $I_0'$ is the total intensity of the strong peak. If the
ratio of the intensity of the weak to the strong peak is $f$
we may write $I_0' = I_0/f$ and from (3) and (12)

$$\sigma(I/x) = I_0^{1/2} \left\{ f \left( x + \frac{fpB'}{I_0} \right) \left(1 - 2x \frac{1}{x^2} \right) + f \left( 1 + \frac{fp_0B'}{I_0} \right) \right. $$

$$\left. + \left[ x + \frac{pB}{I_0} (1 + p/q) \right] \frac{1}{x^2} \left. \right\}^{1/2} + f^{2} \B \left( \frac{p}{x} - p_0 \right)^2 \frac{1}{I_0q} \right\}^{1/2}. \quad (13)$$

Again taking the limit $p \ll q$ and setting $B' = B$, since
the strong peak is normally a near neighbour of the
weak peak, we find that the expression reduces to

$$\sigma(I/x) \approx I_0^{1/2} \left\{ f \left( x + \frac{fpB}{I_0} \right) \left(1 - 2x \frac{1}{x^2} \right) + f \left( 1 + \frac{fp_0B}{I_0} \right) \right. $$

$$\left. + \left( x + \frac{pB}{I_0} \right) \frac{1}{x^2} \right\}^{1/2}. \quad (14)$$

It is not possible to derive a relationship as simple as
(11) to locate the minimum value of this expression,
but it can be plotted as a function of the reduced
variable $p/p_0$ and the minimum point observed. This
has been done in Fig. 3, where graphs are plotted for
different signal-to-noise ratios. The units of $\sigma(I_0)$ are
$I_0^{1/2}$, which is the standard deviation of the peak in the
absence of any background.

The limiting curves for which $f \to 0$ correspond to
the case where $\sigma^2(1/x)$ is negligible. The arrows indicate where equation (11) is satisfied, which as
expected occurs at the minimum point of the function.
It can also be seen that for values of $f < 0.5$ the minima
on the curve, although higher, occur at virtually the
same $p/p_0$ value as for $f = 0$. Equation (11) can
therefore be used when $f$ is small to find the value of
$p/p_0$ at which the minimum occurs.

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