$k(U/V)\mathbf{F}_h(000)$ when $|\mathbf{p}|=0$. Here $re^{i\varphi}$ represents the sum over n in equation (1). The constant quantity $[k(U/V)\mathbf{F}_h(000)-U\varrho_s]$ will appear in every equation except when $|\mathbf{p}|=0$, and may therefore be estimated by averaging the lack of closure of each equation. Also $k(1-U/V)\mathbf{F}_h(000)$ may be found from the $\mathbf{F}_p(000)$ equation. Hence k and ϱ_s can be determined, given reasonable initial estimates of these quantities. Since the size of the interaction $re^{i\varphi}$ decreases as $|\mathbf{p}|$ increases, the effect of salt concentration or an inaccurate knowledge of the absolute scale becomes rapidly less significant as we go out in reciprocal space.

The author is indebted to Dr M.G. Rossmann for his help and inspiration in this work, to Mr John Steele at Purdue University's Computer Sciences Center for giving valuable advice, and to Mrs Margaret Wonacott for aid in the preparation of the manuscript. This work was supported by N.I.H. grant GM 10704-03 and by N.S.F. grant GB 02905.

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Least-Squares Weighting Schemes for Diffractometer – Collected Data

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(*Received* 7 *October* 1966 *and in revised form* 2 *March* 1967)

An analysis is made of various diffractometer techniques for obtaining data, and expressions are obtained for the weighting functions that may be used in subsequent least-squares refinement. It is shown that for a constant-time diffractometer experiment the weighting function is independent of the magnitude of the counts obtained and dependent on the diffractometer geometry. The results for the constant-count diffractometer experiment are compared.

Introduction

The most accurate set of parameters that can be obtained by the least-squares technique of minimizing the function

$$R=\sum_{\mathbf{h}} w(\mathbf{h})|\Delta(\mathbf{h})|^2$$

is when $w(\mathbf{h})$ is the reciprocal of the variance of $|\Delta(\mathbf{h})|$. The two forms of $|\Delta(\mathbf{h})|$ which have been most used in refining crystal structures are

$$|\Delta_1(\mathbf{h})|=\big||F_o(\mathbf{h})|-|F_c(\mathbf{h})|\big|$$

and

$$|\Delta_2(\mathbf{h})|=\big||F_o(\mathbf{h})|^2-|F_c(\mathbf{h})|^2\big|\,.$$

If the standard deviation of each $\big||F_o(\mathbf{h})|-|F_c(\mathbf{h})|\big|$ is small in comparison with $|F_o(\mathbf{h})|$ then

$$4|F_o(\mathbf{h})|^2w_2(\mathbf{h})=w_1(\mathbf{h})$$

where

$$R_1=\sum_{\mathbf{h}} w_1(\mathbf{h})|\Delta_1(\mathbf{h})|^2$$

and

$$R_2=\sum_{\mathbf{h}} w_2(\mathbf{h})|\Delta_2(\mathbf{h})|^2\,.$$

It is often assumed that the value of $w(\mathbf{h})$ is dependent only on the statistical errors in the experimentally observed structure factor, the non-random errors such as those associated with inaccurate instrument setting or the scattering factors making an unknown, and assumed negligible contribution to the standard deviation of $|\Delta(\mathbf{h})|$. This assumption can be shown to be valid provided

$$\sum w(\mathbf{h})|\Delta(\mathbf{h})|^2=m-n\,,$$

where m is the number of structure factors included in the summation, n is the number of variables and $w(\mathbf{h})$ are the weights on the absolute scale for the equation being minimized (*Computing Methods in Crystallography*, 1965).

It is possible to perform at least two different types of diffractometer experiment. An experiment may be performed in which an integrated count is obtained for each reflexion over a constant time and in some instruments such as the linear diffractometer of Arndt and Philips there is, owing to the present construction of the instrument, no option but to use this technique. Alternatively, with more versatile instruments, either this technique or a constant count technique in which the intensity is proportional to the inverse of the time taken to achieve this constant count may be used (Lonsdale, 1948).

A more novel way of collecting data would be to count at each reflexion for a time inversely proportional to the Lorentz–polarization factor. This technique yields $|F_o(\mathbf{h})|^2$ directly, apart from a scaling constant, and gives constant weight, w_1, to each reflexion.

Constant-time, variable-count experiments

The standard deviation of a specific $|\Delta_2(\mathbf{h})|$ for this type of experiment is, assuming a negligible background count,

$$\sigma\{|F_o(\mathbf{h})|^2\} \simeq \frac{K}{\mathrm{Lp}} \sqrt{N(\mathbf{h})} = \left(\frac{K}{\mathrm{Lp}}\right)^{\frac{1}{2}} |F_o(\mathbf{h})| \, ,$$

where $N(\mathbf{h})$ is the number of counts obtained for the integrated intensity of $F_o(\mathbf{h})$, Lp is the Lorentz–polarization factor for the experiment and K is a scaling constant. Consequently

$$R_2 = \sum_{\mathbf{h}} \frac{\mathrm{Lp}|\Delta_2(\mathbf{h})|^2}{K|F_o(\mathbf{h})|^2}$$

and

$$R_1 = \sum_{\mathbf{h}} \frac{4\mathrm{Lp}}{K} |\Delta_1(\mathbf{h})|^2 \, .$$

Neither of these expressions can be used on many existing least-squares programs written mainly for use with photographic data, but a simple rearrangement of terms gives a usable expression. Consider R_1:

$$R_1 = \sum_{\mathbf{h}} \frac{4\mathrm{Lp}}{K} \{|F_o(\mathbf{h})| - |F_c(\mathbf{h})|\}^2 \, .$$

It is doubtful whether it is desirable to have a weighting function which varies as Lp. However, rearrangement of this function gives

$$R_1 = \sum_{\mathbf{h}} 4\{N(\mathbf{h})^{\frac{1}{2}} - (1/K^{\frac{1}{2}})|\sum_{\mathbf{i}} (f_i(\mathrm{Lp})^{\frac{1}{2}}) \exp 2\pi j \mathbf{h} \, . \, \mathbf{x}_i|\}^2 \, .$$

This is now in the form where a standard 'visual' least-squares program can be used with $w_1(\mathbf{h}) = 1$ for all data, $N(\mathbf{h})^{\frac{1}{2}}$ possibly scaled by a constant for all data used instead of $|F(\mathbf{h})|$, and $f_i(\mathrm{Lp})^{\frac{1}{2}}$ used instead of f_i. Note that $f_i(\mathrm{Lp})^{\frac{1}{2}}$ increases over a certain range of $\sin\theta$. A similar expression can be obtained for R_2.

It should be noted that the reliability index output by the least-squares program will not correspond to the usual reliability index, but with this exception all other values will be the same. If three- or four-circle geometry is used then tables of $f_i(\mathrm{Lp})^{\frac{1}{2}}$ can be made up for each atom for the complete data, since $(\mathrm{Lp})^{\frac{1}{2}}$ is a function of θ only. However if Weissenberg-type geometry is used the modified scattering curves are dependent also on the inclination angle and different layers must be calculated with different form factor tables.

An additional complication arises if attenuators are used in the experiment. Suppose the attenuation factor is α, then

$$R_1 = \sum_{\mathbf{h}} \frac{4\mathrm{Lp}\alpha}{K} \{|F_o(\mathbf{h})| - |F_c(\mathbf{h})|\}^2$$

$$= \sum_{\mathbf{h}} 4\{N(\mathbf{h})^{\frac{1}{2}} - (1/K^{\frac{1}{2}})|\sum_{\mathbf{i}} (f_i(\mathrm{Lp}\alpha)^{\frac{1}{2}} \exp 2\pi j \mathbf{h} \, . \, \mathbf{x}_i|\}^2 .$$

It is obvious that each group of differently attenuated counts must be treated separately.

It is interesting to note that since $w_1 \propto \mathrm{Lp}\alpha$, if no attenuators are used the weighting function which has infinite value at $\sin\theta = 0$ falls to unit value at $\sin\theta = 0{\cdot}7$ and then rises again to infinite value at $\sin\theta = 1$. This implies that high weighting is given to the low order reflexions which define the gross features of the structure and also to the high order reflexions which define the detail of the structure, provided the data are collected over the full range of $\sin\theta$. An instrument which only collects data to a $\sin\theta$ value of $0{\cdot}5$ will have a weighting function which decreases with increase in $\sin\theta$. This, it should be emphasized, is not overcome by using a shorter wavelength radiation. It would appear that to obtain the most advantageous weighting for those reflexions which define the detail of the structure, an instrument should be used that collects data over nearly the complete sphere of reflexions and a wavelength of the radiation should be chosen such that thermal cut-off occurs at $\sin\theta$ as nearly as possible equal to one. The use of attenuators at low $\sin\theta$ values will also help to weight down what might otherwise become predominant weighting on low order reflexions, particularly when it is realized that extinction or errors in crystal setting may have produced substantial inaccuracies in the measurements of these reflexions, giving non-random errors substantially greater than the counting statistics errors.

If the background counts are not negligible then

$$\sigma\{|F_o(\mathbf{h})|\}^2 = \left\{\frac{K}{\mathrm{Lp}}\right\}^{\frac{1}{2}} |F_o(\mathbf{h})|$$

$$\left\{\frac{\text{Integrated counts} + \text{background counts}}{\text{Integrated counts} - \text{background counts}}\right\}^{\frac{1}{2}}$$

and the subsequent analysis is similar to the above.

Constant-count, variable-time experiments

The standard deviation of $|\Delta_2(\mathbf{h})|$ for this type of experiment is

$$\sigma\{|F_o(\mathbf{h})|\}^2 \simeq \frac{K}{\mathrm{Lp}t\alpha} \; N(\mathbf{h})^{\frac{1}{2}} = \frac{|F_o(\mathbf{h})|^2}{N(\mathbf{h})^{\frac{1}{2}}}$$

and

$$R_2 = \sum_{\mathbf{h}} \left\{\frac{N(\mathbf{h})^{\frac{1}{2}}}{|F_o(\mathbf{h})|^2}\right\}^2 |\Delta_2(\mathbf{h})|^2$$

and

$$R_1 = \sum_{\mathbf{h}} \frac{4N(\mathbf{h})}{|F_o(\mathbf{h})|^2} |\Delta_1(\mathbf{h})|^2 \, .$$

The form of R_1, which is recognized as one of the usual forms for least squares, is not dependent on diffractometer geometry or on the use of attenuators, and weights the strongest structure factors least. The use of this technique will also lead to a reliability index which is reasonably constant throughout regions of reciprocal space.

Many diffractometers do not operate on the constant count principle but a very close approximation can be obtained to this mode of operation by arranging the time spent on each reflexion to be such that near constant counts are obtained.

Conclusion

It is clearly desirable to design an experiment for which the subsequent least-squares technique is geometry-independent. This being so, the mode of operation to be preferred should be constant count, variable time.

It is of interest to note that this technique is the diffractometer analogue of the much used multiple-film photographic technique where the intensities are measured in a relatively small optical density range.

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The Crystal Structure of Deuterated Oxalic Acid Dihydrate, $(COOD)_2.2D_2O$, by X-ray Analysis

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(*Received* 4 *October* 1966)

Crystals of deuterated oxalic acid dihydrate, $(COOD)_2.2D_2O$, are monoclinic with $a=10{\cdot}021$, $b=5{\cdot}052$, $c=5{\cdot}148$ Å, $\beta=99{\cdot}27°$, $Z=2$, space group $P2_1/a$. They are not isomorphous with those of $(COOH)_2.2H_2O$. The structure was determined by Harker–Kasper inequalities and Fourier method using visually estimated Cu $K\alpha$ data. Positional and anisotropic thermal parameters were refined by the full-matrix least-squares method, the final R index being 0·073 for 506 observed reflexions. The oxalic acid molecules and the water molecules are linked with hydrogen bonds which make three-dimensional networks. The hydrogen bond distances O–D···O are 2·540, 2·854 and 2·822 Å.

Introduction

Ubbelohde and his coworkers have done extensive work on the isotope effect of deuterium substitution on structures of hydrogen bonded crystals (Robertson & Ubbelohde, 1939; Ubbelohde, 1939; Ubbelohde & Woodward, 1942; Dickson & Ubbelohde, 1950; Gallagher, Ubbelohde & Woodward, 1954). They reported that the maximum isotope effects were found to lie near the directions of the short hydrogen bonds and concluded that these short hydrogen bonds were subjected to a considerable expansion by the deuterium substitution, while for the long hydrogen bonds no appreciable effect was observed. These conclusions were derived, however, from the variations of the unit-cell dimensions alone, and no attempt was made to determine the positional parameters of the deuterated crystals.

It is widely known that the crystal structures of compounds containing hydrogen are not affected by the substitution of hydrogen by deuterium. However, in some exceptional cases the effect of substituting deuterium for hydrogen is so large as to give rise to the spontaneous crystallization of a different structure, as in the case of potassium dihydrogen phosphate (Ubbelohde & Woodward, 1939) or resorcinol (Robertson, 1936, 1938).

In the case of the crystals of oxalic acid dihydrate, $(COOH)_2.2H_2O$, an investigation of the isotope effect was also carried out by Robertson & Ubbelohde (1939). They reported that the crystals of deuterated oxalic acid dihydrate, $(COOD)_2.2D_2O$, are isomorphous with those of $(COOH)_2.2H_2O$ (Robertson & Woodward, 1936), and that the short hydrogen bonds are expanded by the substitution of deuterium. The crystal structure of $(COOH)_2.2H_2O$ was further refined (Ahmed & Cruickshank, 1953; Garrett, 1954) although the result was not essentially different from the structure previously reported (hereafter called the α form). Recently a nuclear magnetic resonance study was made for a single crystal of deuterated oxalic acid dihydrate (Chiba, 1964), and it was found that the O–D direction in this crystal could not be interpreted on the basis of the ordinary structure of $(COOH)_2.2H_2O$. By an X-ray study it was shown that the crystal of $(COOD)_2.2D_2O$ represents a new modification (hereafter called the β form) (Fukushima, Iwasaki & Saito, 1964; Fukushima, Iwasaki, Saito, Sato & Hoshino, 1965).

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