References

BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst.* **A31**, 417-425.
BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180-187.
CAMPBELL, I. E. (1956). *High-Temperature Technology.* Electrochemical Society. New York: John Wiley & Sons.
CHITRA, S., VEMPATI, C. S. & JACOBS, P. W. (1983). *Cryst. Lattice Defects Amorphous Mat.* **10**, 9-17.
CLINE, C. F., DUNEGAN, H. L. & HENDERSON, G. W. (1967). *J. Appl. Phys.* **38**, 1944-1948.
CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.
DOWNS, J. W., ROSS, F. K. & GIBBS, G. V. (1985). *Acta Cryst.* **B41**, 425-431.
FUKAMACHI, T. & HOSOYA, S. (1970). *J. Phys. Soc. Jpn*, **28**, 161-167.
HASHIMOTO, M. & SANTRY, D. P. (1978). *Theor. Chim. Acta*, **50**, 39-48.
HEWAT, A. (1972). *J. Phys. C*, **5**, 1309-1316.
HUGGINS, M. L. & SAKAMOTO, Y. (1957). *J. Phys. Soc. Jpn*, **12**, 241-251.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht, The Netherlands.)
JEFFREY, G. A., PARRY, G. S. & MOZZI, R. L. (1956). *J. Chem. Phys.* **25**, 1024-1031.
JULG, A. (1978). *Phys. Chem. Miner.* **3**, 45-53.
KARA, M. & KURKI-SUONIO, K. (1981). *Acta Cryst.* **A37**, 201-210.
KINGERY, W. D., FRANCH, J., COBLE, R. L. & VASILOS, T. (1954). *J. Am. Ceram. Soc.* **37**, 2, 107.
KURKI-SUONIO, K. (1968). *Acta Cryst.* **A24**, 379-390.
KURKI-SUONIO, K. (1977). *Isr. J. Chem.* **16**, 115-123, 132-136.
KURKI-SUONIO, K., MERISALO, M. & PELTONEN, H. (1979). *Phys. Scr.* **19**, 57-63.
KURKI-SUONIO, K. & SÄLKE, R. (1984). *Local Density Approximations in Quantum Chemistry and Solid State Physics*, edited by J. P. DAHL & J. AVERY, pp. 713-733. New York and London: Plenum Press.
KURKI-SUONIO, K. & SÄLKE, R. (1985). Report Series in Physics, HU-P-240, Univ. of Helsinki, Finland.
MAIR, S. L. & BARNEA, Z. (1975). *Acta Cryst.* **A31**, 201-207.
MIURA, M., MURATA, H. & SHIRO, Y. (1977). *J. Phys. Chem. Solids*, **38**, 1071-1073.
MIURA, M., MURATA, H. & SHIRO, Y. (1978). *J. Phys. Chem. Solids*, **39**, 669-673.
MIURA, M., SATÔ, T., MURATA, H. & SHIRO, Y. (1980). *J. Phys. Chem. Solids*, **41**, 189-197.
MOSS, G. & BARNEA, Z. (1976). *J. Appl. Cryst.* **9**, 510-511.
MUCILLO, R. & BLACK, A. R. (1980). *Int. Symp. on Electrets and Dielectrics*, São Carlos, Brazil, 1-6 September 1975, pp. 357-364. Rio de Janeiro: Academia Brasiliera de Ciencias.
NUSIMOVICI, A. (1968). Thesis, Univ. of Paris, France.
PRYOR, A. W. & SABINE, T. M. (1964). *J. Nucl. Mater.* **14**, 275-281.
RANI, N., GUPTA, D. K. & GUPTA, H. C. (1981). *Ind. J. Pure Appl. Phys.* **19**, 316-318.
SABINE, T. M. & DAWSON, B. (1963). *Int. Conf. on Beryllium Oxide*, Newport, Sydney, Australia, 21-25 October 1963.
SABINE, T. M. & HOGG, S. (1969). *Acta Cryst.* **B25**, 2254-2256.
SÄLKE, R. & KURKI-SUONIO, K. (1984). Report Series in Physics, HU-P-233, Univ. of Helsinki, Finland.
SANGER, P. L. (1969). *Acta Cryst.* **A25**, 694-702.
SMITH, D. K., NEWKIRK, H. W. & KAHN, J. S. (1964). *J. Electrochem. Soc.* **111**, 78-87.
VIDAL, J. P. & VIDAL-VALAT, G. (1986). *Acta Cryst.* **B42**, 131-137.
VIDAL, J. P., VIDAL-VALAT, G., GALTIER, M. & KURKI-SUONIO, K. (1981). *Acta Cryst.* **A37**, 826-837.
VIDAL, J. P., VIDAL-VALAT, G., GALTIER, M. & KURKI-SUONIO, K. (1982). *Sagamore VII Conf. on Charge, Spin and Momentum Densities*, Nikko, Japan. Abstr. p. 26.
VIDAL, J. P., VIDAL-VALAT, G. & ZEYEN, C. M. E. (1985). *Nucl. Instrum. Methods*, **228**, 569-575.
VIDAL-VALAT, G., VIDAL, J. P. & KURKI-SUONIO, K. (1975). Report Series in Physics, No. 107, Univ. of Helsinki, Finland.
VIDAL-VALAT, G., VIDAL, J. P. & KURKI-SUONIO, K. (1978). *Acta Cryst.* **A34**, 594-602.
VIDAL-VALAT, G., VIDAL, J. P., ZEYEN, C. M. E. & KURKI-SUONIO, K. (1979). *Acta Cryst.* **B35**, 1584-1590.
WHITELEY, B., MOSS, G. & BARNEA, Z. (1977). *Phys. Lett. A*, **60**, 429-439.
WHITELEY, B., MOSS, G. & BARNEA, Z. (1978). *Acta Cryst.* **A34**, 130-136.
WITH, G. DE, HARKEMA, S. & FEIL, D. (1976). *Acta Cryst.* **B32**, 3178-3184.

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An Algorithm for Generating the Moduli of Normal Order Statistics for Half-Normal Probability Plots

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Abstract

A simple relationship has been developed for determining values for the moduli of normal order deviates for sample size n from the values of the normal order deviates for sample size $2n+1$. This relationship can be expressed as a quadratic 'correction' to the normal order values. This approximation is in error by $<0{\cdot}001$ for values of $n>8$.

Introduction

Although the use of probability plots for data and parameter analysis is well known in crystallography (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972; Abrahams, 1974; Abrahams, Bernstein, Bugg & Hvoslef, 1978), programs for performing the analysis are not routinely included in the commonly available crystallographic program packages. Such a

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program was needed for work being done in this laboratory; so the design and structure of the required algorithms were explored.

A program for probability plot analysis, as applied to crystallographic problems, needs to incorporate algorithms for calculating: (i) the percentage points of the normal distribution, $P(X_i)$, (ii) the values for the ranked normal deviates, $\xi(i/n)$, and (iii) the values for the ranked moduli of normal deviates, $\xi_{1/2}(i/n)$. These algorithms need to be accurate, fast and general if they are to be useful in a program intended for routine use. Examination of the literature showed published methods for accurately approximating the values needed in (i) (Beasley & Springer, 1977) and (ii) (Royston, 1982) but did not reveal any procedure for calculating the quantities in (iii) to similar levels of accuracy. Only two methods seemed to be available for acquiring $\xi_{1/2}$ values: approximation to the values with the normal distribution curve, *i.e.* $\xi_{1/2} \simeq X_i$, or use of tables of $\xi_{1/2}$ values for various sample sizes as listed in the literature (*International Tables for X-ray Crystallography*, 1974).

In the first of these methods the required values may be approximated by that X_i which is defined by*

$$P(X_i) = (6n-3i+2)/(6n+1) \qquad (1)$$

but, as has been pointed out (Hamilton & Abrahams, 1972), values calculated by this type of approximation are appreciably in error, particularly for the extreme values of i, for values of n up to 400.

The second method, using tables of $\xi_{1/2}$ values, avoids any calculations but the tables do not list all sample sizes nor are all the values of the larger sample sizes included in the tables.

These difficulties led to the development of a procedure, described herein, that does not require the numerical integration of the defining equation but does accurately determine the values of $\xi_{1/2}(i/n)$ for all reasonable sample sizes ($n>10$) and for any desired value of i in that sample size.

Method of calculation

It was noticed that, to a first approximation, the values for $\xi_{1/2}(i/n)$ are similar to the values for $\xi(i/j)$ where $j=2n+1$. Thus it was felt that developing a correction term as a function of i and n would suffice to allow reasonable values for $\xi_{1/2}(i/n)$ to be calculated from the values for $\xi(i/j)$. A series of plots of $[\xi(i/j)-\xi_{1/2}(i/n)]$ *versus* i (with the ξ and $\xi_{1/2}$ values determined by numerical integration) for selected values of n from 10 to 120 showed that the difference could be expressed, to a reasonable approximation, as a quadratic function of i, $a+bi+ci^2$, where the values of the coefficients a, b and c are constants for any given sample size n. Additional plots of each of these coefficients as functions of n showed that they could be expressed by the following equations:

$$a = 0{\cdot}071n^{-0{\cdot}980}$$

$$b = 0{\cdot}099n^{-1{\cdot}877}$$

$$c = -\exp(-2{\cdot}090-2{\cdot}856\ln n),$$

which leads to the full approximation being expressed as

$$\xi_{1/2}(i/n) = \xi(i/j)-(a+bi+ci^2). \qquad (2)$$

The discrepancies between the values for $\xi_{1/2}(i/n)$ calculated by the above method and those determined by numerical integration are largest for the smallest sample sizes and for the largest deviates within a given sample size. Thus the error in $\xi_{1/2}(i/n)$ reaches a maximum value of 0·014 when $n=2$ and $i=1$. This error is reduced to less than 0·001 by the time $n=8$. Table 1 lists the value of $\xi_{1/2}$ for $i=1$ for some of the smaller sample sizes.

Table 1. *$\xi_{1/2}$ values for some small sample sizes and $i=1$*

n	$\xi_{1/2}$ (approx.)*	$\xi_{1/2}$ (approx.)†	$\xi_{1/2}$ (exact)‡
2	1·019	1·114	1·128
4	1·405	1·460	1·465
6	1·606	1·652	1·654
8	1·741	1·782	1·783
10	1·841	1·880	1·881
12	1·920	1·958	1·958

* Calculated using approximation (1).

† Calculated using approximation (2) with the values of ξ calculated by the approximation of Royston (1982). These ξ values differ from the exact values by as much as 0·003 for $n=2$ although the difference is $<0{\cdot}001$ for $n>8$.

‡ Calculated by numerical integration.

Concluding remarks

It has been shown that equation (2) yields accurate values for the ranked moduli of normal deviates for all values of i and n in a computationally effective manner. Use of this method of approximation in a computer program eliminates the need for time-consuming numerical integration routines or the internal storage of large tables of values for all the likely sample sizes.

A Fortran program has been written to calculate both ξ values [using the approximation of Royston (1982)] and, incorporating the methods discussed herein, the $\xi_{1/2}$ values. This program functions in conjunction with the files of the Enraf–Nonius (1979) *SDP* program package to produce a variety of probability plots. A copy of the program is available from the author upon request.

* The original approximation of Hamilton & Abrahams (1972) is $(2n-2i+1)/2n$ which is based on using the two-tailed cumulative normal distribution function. A more accurate approximation is given by Abrahams (1974) (see the footnote on p. 266) which when modified to use the one-tailed cumulative normal distribution function gives the equation as presented.

References

ABRAHAMS, S. C. (1974). *Acta Cryst.* **B30**, 261-268.
ABRAHAMS, S. C., BERNSTEIN, J. L., BUGG, C. E. & HVOSLEF, J. (1978). *Acta Cryst.* **B34**, 2981-2985.
ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157-165.
BEASLEY, J. D. & SPRINGER, S. G. (1977). *Appl. Statist.* **26**, 118-121.
Enraf-Nonius (1979). *Structure Determination Package.* Enraf-Nonius, Delft.
HAMILTON, W. C. & ABRAHAMS, S. C. (1972). *Acta Cryst.* **A28**, 215-218.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 293-310. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht, The Netherlands.)
ROYSTON, J. P. (1982). *Appl. Statist.* **31**, 161-165.

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Generalization of the Classical 'Parallel' Condition: Zero-Wavelength-Dispersion 'Counter' Profile Measurement

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Abstract

In the classical two-crystal system with monochromator (M) and specimen (c) crystal axes parallel, measurement with zero-wavelength dispersion (ZWD) is possible at only one value of scattering angle, $\theta_c = \theta_M$, the so-called 'parallel' condition. The procedure is highly selective and therefore of limited applicability. If one examines the situation where the ω rotation axis of c is rotatable (Φ) about the monochromator beam incident on c, the condition can be generalized so that appropriate choice of Φ will allow ZWD measurement anywhere in the range $0 \leq \theta_c \leq \theta_M$, thus releasing this valuable procedure from its earlier severe constraints. The setting condition for Φ is $\cos \Phi = -(\tan \theta_c)/(\tan \theta_M)$.

Introduction

Recently, we have shown how measurements of 'film' profiles,

$$I(\Delta 2\theta) = \int_{\Delta\omega_1}^{\Delta\omega_2} I(\Delta\omega, \Delta 2\theta^{(0)}) \mathrm{d}(\Delta\omega),$$

can be carried out so that they do not involve wavelength dispersion (Mathieson & Stevenson, 1986*b* - hereafter MS86*b*). With this procedure, Bragg reflections from a small single crystal, c, are intercomparable irrespective of the scattering angle, θ_c. As a result, variation of the reflectivity curve [=mosaic spread distribution for imperfect crystals; see Mathieson (1984)] from reflection to reflection can be identified and a more direct estimation of the reflectivity curve for individual reflections in a given orientation is feasible (see Mathieson & Stevenson, 1986*a*). The procedure proposed in MS86*b* for 'film' profiles is applicable also where a monochromator is involved.

'Counter' profiles – examination from the $\Delta\omega$, $\Delta 2\theta$ viewpoint

The question arises as to whether a similar type of capability is feasible for the measurement of 'counter' profiles,

$$I(\Delta\omega) = \int_{\Delta 2\theta_1}^{\Delta 2\theta_2} I(\Delta\omega, \Delta 2\theta^{(0)}) \mathrm{d}(\Delta 2\theta).$$

The analysis in MS86*b* shows that, for the non-monochromator case, the wavelength dispersion component makes a contribution at all θ_c (except $\theta_c = 0°$) and so, apart from that trivial case, the zero-wavelength-dispersion (ZWD) condition is not attainable.

When a monochromator crystal is introduced between the source and the specimen single crystal, interaction of the dispersion of the two crystals offers the potential to overcome that limitation. In the classical treatment of the two-crystal spectrometer (diffractometer) (Compton & Allison, 1935) which deals with extended-face crystals and the configuration where the two crystal axes are parallel, it was shown that the ZWD condition does exist but that it is highly selective, occurring only at the so-called 'parallel' condition where $\theta_c = \theta_M$. At any other value of θ_c, the wavelength dispersion makes a systematic contribution to the 'counter' profile.

Consider (Fig. 1) the more general situation where the ω rotation axis of the small specimen single crystal, c, and hence the associated zero-layer diffraction

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