Book Reviews

Works intended for notice in this column should be sent direct to the Book-Review Editor (J. H. Robertson, School of Chemistry, University of Leeds, Leeds LS2 9JT, England). As far as practicable books will be reviewed in a country different from that of publication.

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Mathematical techniques in crystallography and materials science. By EDWARD PRINCE. Pp. 192. New York, Heidelberg, Berlin: Springer-Verlag, 1982. Price DM 55, *ca* US$ 25.60.

This attractive book of nine chapters and seven appendices covers many of the mathematical topics encountered in crystallography including geometrical aspects, statistics and refinement.

The opening chapter on matrices is beautifully clear and includes some 21 definitions which do much to clarify the jargon which seems inescapable in works on matrices. If I have a criticism here it is that the discussion of orthogonal matrices is barely minimal. The Eulerian system, introduced as 'one of the most common and most convenient' ways of constructing a general three-dimensional rotation matrix, is the only one presented but its suitability and limitations in relation to various problems is not discussed. It is ideal for diffractometry, as its primitive rotations correspond to those of one common type of instrument. However, it would not be a suitable description of the orientation of a rigid body when this is being optimised, since this situation requires quasi linear behaviour for all small rotations, *i.e.* the three primitive rotations must be about axes which are initially orthogonal. It can be used, however, as described in chapter 9, provided these angles are whole rather than incremental and χ is not near zero. Likewise, the form which describes a rotation about an arbitrary axis in terms of the direction cosines of that axis and the angle of rotation would have been well worth including, together with the solution of the converse problem of finding these from a given matrix. The discussion of the Eulerian system is also somewhat marred by insufficient labelling in the relevant diagram. The 33 element of the matrix on page 18 and the expression for G^{-1} on page 19 are incorrect, but otherwise accuracy is good.

Chapter 2 on the *Symmetry of finite objects* was for me a disappointment, though I think the fault must be my own, because I failed to understand an unfamiliar treatment of a very familiar topic. The treatment is a formal one based on group theory which tends to lead the subject away from entrenched crystallographic views. In this treatment the number of poles of the general form appears as a more important basis of classification than the restrictions imposed by the symmetry on the underlying lattice. Thus a single group (in the sense of this book) may have several representations, each of which is a crystallographic point group, and these need not necessarily even be from the same crystal system. Thus the triclinic $\bar{1}$ and the monoclinic m and 2 comprise a single group, as do the monoclinic $2/m$ and orthorhombic $mm2$ and 222. One must be wary also of group-theoretic meanings for words such as 'class' and 'isomorphous' which are different from their crystallographic meanings. But the biggest mystery is with the character tables. We are told that 'The character of a group operation is just another name for the trace of the matrix representing that operation', yet the character tables presented appear to contain eigenvalues of these matrices rather than their traces and the basis of their organisation is not made clear. Nor is their relationship, if any, to the multiplication tables with which the chapter opens.

Chapter 3, on space-group symmetry, is clear and straightforward being largely confined to an explanation of the entries in *International Tables for X-ray Crystallography*.

Chapter 4 on vectors is also straightforward and well presented, though it is a pity that $\mathbf{a}\,.\,\mathbf{d}^*$ (p. 53) is given as unity when, by definition, it should be h. I would also have liked more discussion of the underlying reasons why some vectors are axial and others polar, rather than handling this topic by illustration alone. Included here also is a useful introduction to the matrices involved in setting diffractometers.

Chapter 5 on tensors gives a clear and detailed presentation of selected topics involving tensors, especially thermal motion ellipsoids, with a discussion of the effects of symmetry and of the cell parameters. This treatment is then extended through an account of moments and cumulants to include third- and fourth-rank tensor terms in the probability density distributions for atomic motions. This theory is very nicely presented and one of the clearest accounts I have seen. The chapter concludes by relating the foregoing to the thermal motion of rigid groups in terms of the libration, translation and screw correlation tensors.

Chapter 6, on data fitting, begins with a discussion of robustness and resistance of procedures for estimating the parameters of an interpretive model. The issues involved are clearly brought out, though I found the presentation marred by some inconsistencies. For example, at the foot of page 80 we are given

$$\varphi(y)=(1/y)(\mathrm{d}/\mathrm{d}y)\rho(y)$$

but it should be either

$$\varphi(y)=(1/\sigma^2y)(\mathrm{d}/\mathrm{d}y)\rho(y)$$

with y corresponding to the foregoing R/σ, as it does in the preceding equation, or

$$\varphi(y/\sigma)=(1/y)(\mathrm{d}/\mathrm{d}y)\rho(y/\sigma)$$

with y corresponding to the foregoing R. (R_i is the unweighted observational discrepancy at data point i.) So the reader is left in some confusion as to whether the argument of φ is the weighted or unweighted observational discrepancy. The next sentence states 'If $\rho(y)=y^2/2$, corresponding to least squares, $\varphi(y)=1/\sigma_i^2,\ldots$'. Here the 'correspondence with least squares' implies that y corresponds to R/σ rather than R, in which case the right-hand side of the given equation for φ is wrong. Furthermore, substitution of the given value of ρ in the given equation gives $\varphi(y)=1$, not $\varphi(y)=1/\sigma_i^2$, though the latter result would be correct. Nowhere is y defined, so the reader has to rely on implication in the presence of an error. Moreover, the same symbol is also used for observations before the formation of observational differences.

Having convinced oneself that y corresponds to R/σ (and that a minor error is present) one finds examples of ρ and φ on page 81 which are related according to $\varphi = (1/y)(\partial\rho/\partial y)$ suggesting that y corresponds to R after all. Whether y is R or R/σ, of course, is immaterial if σ_i is independent of i, but we expect a general treatment here.

Despite these criticisms of presentation this chapter contains much that is good and is full of ideas and suggestions which may be extremely helpful when carefully applied. This is particularly true in relation to techniques of solution and to the recognition and handling of local minima.

Chapter 7 is concerned with the statistics of the estimation of errors and provides a comprehensive treatment of the normal error case together with some useful comments relating to non-normal distributions and robust/resistant treatments of these. My only criticisms here are minor ones in that the procedure recommended on page 96 for estimating σ should be avoided when σ/μ is very small since the procedure, which is analogous to determining the smallest side of a right-angled triangle by measuring the two longer sides, becomes very susceptible to round-off errors in computation when σ/μ is small. The other is in the presentation of the χ^2 distribution on page 100, where some explanation of χ as a radius in a ν-dimensional hyperspace containing a spherical Gaussian distribution would be conceptually helpful. Appendix D, however, which deals with the associated algebra, is excellent.

Chapter 8, on significance and accuracy, gives a very good account of correlation amongst the parameters of a problem, together with some useful hints on how to avoid or minimise the effects of correlation by a suitable choice of parameters in the first place. However, it stops short of treatments which depend on determining eigenvalues and eigenvectors of the Hessian – an approach which, though more expensive, may be relied on to characterise fully the inter-dependencies of the parameters and to produce uncorrelated shifts of the transformed variables. This is alluded to in the example of the use of Chebychev polynomials, but not developed for the general case. The discussion of the possible effects of unmodelled parameters is most enlightening.

The final chapter, on constrained crystal-structure refinement, discusses this topic mainly in terms of the proper parameterisation of the problem and draws on the work of previous chapters to explain tests, including Hamilton's R-factor ratio test, which may be applied to determine the necessity or otherwise of including certain parameters in a model. Quite properly in my view, discussion of Lagrange undetermined multipliers is avoided in preference to the use of constraint matrices which serve to describe the problem in terms of a subspace section of parameter space, though I would like to have seen this topic expanded a little further. I also felt that it would have been appropriate here to relate penalty functions (touched on in chapter 6) to the formal representation of an *a priori* probability density distribution in parameter space and to show that their use leads formally to an *a posteriori* probability density distribution with variances and covariances properly described by the matrix which is the sum of the usual Hessian and the matrix of coefficients in the penalty functions.

Refinement of the orientation of rigid bodies in terms of Eulerian angles is discussed here and some of the work of chapter 1 is repeated, but with sign reversals in each of the angles (which presumably arise from the distinction between rotating an object and rotating the axes to which the object is referred, but the sign change appears without comment).

Much of the emphasis throughout the book is on statistical aspects and it is in this connection that I think the book is particularly good. This is supported by a number of appendices which develop the basic theory and also provide Fortran source code for a number of useful statistical functions.

Although I was conscious of a number of misprints, I consider it very good value at DM 55.

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Crystallographic statistics: progress and problems. Edited by S. RAMESESHAN, M. F. RICHARDSON and A. J. C. WILSON. Pp. 313. Bangalore: Indian Academy of Sciences, 1982. Price US$ 18 (£9) for institutions; US$ 9 (£5) for individuals.

This volume contains the proceedings of the symposium on Progress and Problems in Crystallographic Statistics held prior to the Twelfth Congress of the International Union of Crystallography, Ottawa, 1981. In a short introduction A. J. C. Wilson draws a brief historical background of the beginning of crystallographic statistics. A good overview of the statistical properties of the intensities of X-rays scattered by a crystal is given by H. Hauptman. The main topics: Bayesian statistics, intensity statistics, measurability of Bijvoet differences, statistics of recorded counts, variations on least-squares and Wiener–Kolmogorov methods are treated in twelve subsequent full papers and three abstracts; they give the present state of knowledge, as well as provide a useful reference source for the specialist. In addition, the extended subject index makes the book very useful. The book is of interest for scientists who carry out structure-determination work in all fields of crystallography. However, the more elaborate treatment of the intensity statistics requires a high mathematical level; the non-specialist will find a general introduction in the excellent book by Srinivasan & Parthasarathy: *Some statistical applications in X-ray crystallography*, Pergamon Press, Oxford, 1976.

The low price of the book, the remarkable printing and the solid binding with hard plastic cover make it an excellent purchase.

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