Summary and concluding remarks

Using simple model calculations, the diffuse intensities of X-rays scattered from the substitutionally disordered monoclinic form of 9-bromo-10-methylanthracene have been analysed. Qualitative agreement between observed and calculated diffuse intensity distributions was obtained using four primary correlation coefficients. Correlation coefficients between other molecular sites were assumed to be products of these coefficients.

The correlation coefficients obtained from this analysis showed that correlations between molecular sites increased the number of short-range bromine–methyl contacts and decreased the number of bromine–bromine and methyl–methyl contacts relative to the random distribution of molecules over the molecular sites.

The procedures used for this analysis are completely general and are readily implemented. They complement optical-simulation techniques since the latter are necessarily restricted to analyses of only zero-layer intensity distributions.

The present method is semi-quantitative in that only qualitative features of the observed diffuse intensity distributions have been reproduced. More quantitative procedures must rely on the separation of thermal diffuse scattering (neglected in the present study) from the diffuse scattering resulting from substitutional disorder. Such a separation would then allow correlation coefficients to be determined *via* a least-squares analysis of the measured diffuse intensities. Studies in these directions are proceeding.

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Treatment of Equations of Constraint in Least-Squares Refinement

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Abstract

With a least-squares program organization, as described by Busing [*Acta Cryst.* (1971), A**27**, 683–684], the constraints have to be put into a form where the dependent parameters are expressed by the independent ones and, possibly, by further constants. Difficulties may arise if (1) several linear or non-linear constraints refer simultaneously to several parameters, and (2) if the constraints are not linear and cannot be

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solved analytically for the dependent parameters. For both cases a solution is offered which is based on the application of the well known solution of linear equations. Non-linear constraints are linearized. If all constraints are linear, Busing's organization is retained; if they are (partly) non-linear, Busing's organization has to be changed in the main program, and the user's subroutine *SETP* has to be written according to a different concept. Hints concerning programming are given and some examples are discussed.

Introduction

Busing (1971), hereafter BUS, when he described the organization of his program, left it up to the user to program the constraints on the parameters in a subroutine *SETP*. The derivatives between the parameters, $\partial x_i/\partial x_j$, which are needed for structure-factor calculation, are then calculated in the main program by numerical differentiation. This procedure implies that the dependent parameters are specified and expressed by the remaining (independent) parameters and, possibly, by further constants. In many cases this does not pose any problem, *e.g.* with symmetry constraints of a simple type like $x_2 = x_1$, *etc.*

The dependent parameters are, however, not immediately given (1) if several linear (or non-linear) constraints simultaneously refer to some parameters, and (2) if the constraints are non-linear in the parameters and cannot analytically be solved for the dependent parameters. An example for the second case is the constraint that three bonds at a given atom are equally long; here the author would not know how to eliminate two parameters analytically or even numerically. It is the purpose of this paper to give a simple and generally applicable solution for both cases.

There are two different ways of introducing physical information into the refinement: (1) the information is described by equations of constraint on the standard parameters, (2) the information leads to the definition of an extra set of appropriate independent parameters. Usually one of the two ways is clearly preferable. Well known examples for extra independent parameters are the rigid-body positional (Scheringer, 1963) and thermal parameters (Cruickshank, 1956; Schomaker & Trueblood, 1968), and parameters for imposing non-crystallographic symmetry and the identical-molecule constraint (Pawley, 1972). The above mentioned examples can be handled with the user's subroutine *SETP* as defined in BUS's program organization. This paper is mainly concerned with the first way of describing physical information.

Our approach centres in applying the classical solution of linear equations (see *e.g.* Smirnow, 1954). Non-linear constraints are linearized. If all constraints are linear in the parameters, BUS's program organization can be retained. If the constraints are (partially) non-linear, then, with our proposal, BUS's organization must be altered in the main program and the user's subroutine *SETP* must be written according to a different concept. In the following, we treat linear and non-linear constraints separately, give hints concerning programming and discuss some examples.

Linear constraints

Let the set of the n parameters x_i be constrained by m linear equations of the form

$$\mathbf{A}\mathbf{x} = \mathbf{C}. \tag{1}$$

$\mathbf{A}$ is of order $m \times n$, $\mathbf{x}$ of order $n \times 1$, and $\mathbf{C}$ of order $m \times 1$. In order to evaluate the dependent parameters $\mathbf{x}^{\text{dep}}$, we apply the solution of linear equations which has been known for a long time (see *e.g.* Smirnow, 1954). We choose $n - m = k$ independent parameters $\mathbf{x}^{\text{indep}}$ out of the set x_i; for simplicity of notation we count these parameters first. We now divide $\mathbf{A}$ into two submatrices $\mathbf{A}_1$ and $\mathbf{A}_2$ which refer to the parameters $\mathbf{x}^{\text{indep}}$ and $\mathbf{x}^{\text{dep}}$ and we can then rewrite (1) in the form

$$\mathbf{A}_1\,\mathbf{x}^{\text{indep}} + \mathbf{A}_2\,\mathbf{x}^{\text{dep}} = \mathbf{C}. \tag{2}$$

$\mathbf{A}_1$ is an $m \times k$ matrix, $\mathbf{A}_2$ a non-singular $m \times m$ matrix, $\mathbf{x}^{\text{indep}}$ of order $k \times 1$ and $\mathbf{x}^{\text{dep}}$ of order $m \times 1$. Multiplication by $\mathbf{A}_2^{-1}$ from the left then leads to

$$\mathbf{x}^{\text{dep}} = -\mathbf{A}_2^{-1}\,\mathbf{A}_1\,\mathbf{x}^{\text{indep}} + \mathbf{A}_2^{-1}\,\mathbf{C}. \tag{3}$$

Equation (3) constitutes the prescription for writing *SETP*. The dependent parameters have to be specified from which $\mathbf{A}_2$ is defined. In many cases (with most of the symmetry constraints), $\mathbf{A}_2$ is diagonal and *SETP* can immediately be written. The elements of $-\mathbf{A}_2^{-1}\,\mathbf{A}_1$ are the derivatives $\partial x_i^{\text{dep}}/\partial x_j^{\text{indep}}$ which are needed for structure-factor calculation. Thus, these derivatives need not be calculated in the main program by numerical differentiation.

Raymond (1972) has also established a procedure for calculating the derivatives $\partial x_i^{\text{dep}}/\partial x_j^{\text{indep}}$. In the Appendix, we compare our result (3) with Raymond's and show that our procedure is simpler in principle and usually simpler to apply.

Non-linear constraints

Instead of analyzing the non-linear constraints explicitly in *SETP*, we linearize them. This means that the now linearized constraints do not refer to the parameters themselves but only to (small) changes of the parameters (Scheringer, 1965). Hence, the problem of determining the dependent parameters is now posed in a different form and it is advantageous that we can apply the solution of linear equations.

Let the m non-linear functions of the parameters $\mathbf{x}$ be contained in the column matrix $\mathbf{C}(\mathbf{x})$, and the m values which these functions should assume in the column matrix $\mathbf{C}_0$. Then the m constraints have the form

$$\mathbf{C}(\mathbf{x}) = \mathbf{C}_0. \tag{4}$$

In order to linearize these equations, we assume that the given parameters $\mathbf{x}$ satisfy (4) approximately, *i.e.* $\mathbf{C}(\mathbf{x}) \simeq \mathbf{C}_0$. We expand the difference between $\mathbf{C}_0$ and $\mathbf{C}(\mathbf{x})$ into a Taylor series up to linear terms in the changes $\Delta\mathbf{x}$, and obtain

$$\partial\mathbf{C}(\mathbf{x})/\partial\mathbf{x}\,\Delta\mathbf{x} = \mathbf{C}_0 - \mathbf{C}(\mathbf{x}). \tag{5}$$

By analogy with (1), we denote the derivatives $\partial\mathbf{C}(\mathbf{x})/\partial\mathbf{x}$ by $\mathbf{A}$ and specify the dependent parameters again in such a way that we can subdivide $\mathbf{A}$ according to $\mathbf{A} = (\mathbf{A}_1 | \mathbf{A}_2)$. Then the solution of (5) yields

$$\Delta\mathbf{x}^{\text{dep}} = -\mathbf{A}_2^{-1}\,\mathbf{A}_1\,\Delta\mathbf{x}^{\text{indep}} + \mathbf{A}_2^{-1}[\mathbf{C}_0 - \mathbf{C}(\mathbf{x})]. \tag{6}$$

In contrast to the case of linear constraints, the elements of $\mathbf{A}$ are no longer constants, and $\mathbf{A}_1$ and $\mathbf{A}_2$ and $\mathbf{C}(\mathbf{x})$ have to be recalculated in every cycle of refinement. The dependent parameters are obtained from

$$\mathbf{x}_{\text{new}}^{\text{dep}} = \mathbf{x}_{\text{old}}^{\text{dep}} + \Delta\mathbf{x}^{\text{dep}}, \tag{7}$$

where $\mathbf{x}_{\text{old}}^{\text{dep}}$ are the input parameters for a given cycle of refinement. The constraints are introduced by iteration, *i.e.* with the cycles of refinement. The differences $\mathbf{C}_0 - \mathbf{C}(\mathbf{x})$, which may deviate from zero for the input parameters, are reduced in each cycle according to (6) and (7). In this way, the linear approximation which we have made with (5) becomes more and more valid, and the constraints are exactly fulfilled after a few cycles of refinement (in our experience with bond-length constraints, in no more than three cycles).

The advantage of this procedure is that it is generally applicable and that only the functions $\mathbf{C}(\mathbf{x})$ have to be differentiated with respect to the parameters $\mathbf{x}$.

Programming

We have written two program versions for (only) linear and non-linear constraints respectively. Both versions are essentially organized as described by BUS. In the first version, *SETP* has to be written according to (3). In the second version, we have altered the main program and *SETP* according to (6) and (7). The parameter changes are used instead of the parameters. In the following, we refer to BUS's description (BUS, Fig. 1, steps 1–16, 28). Since in the beginning of a cycle no shifts $\Delta\mathbf{x}^{\text{indep}}$ are known, these shifts are set to zero in step 2 before *SETP* is called. In steps 2 and 28, the new dependent (and independent) parameters are calculated according to (7) after *SETP* is called. *SETP* has to be programmed according to (6). Since, with the calculation of the derivatives $\partial x_i^{\text{dep}}/\partial x_j^{\text{indep}}$ in step 8, *SETP* is called in a loop, it is recommended that the elements of $-\mathbf{A}_2^{-1}\,\mathbf{A}_1$ and $\mathbf{A}_2^{-1}[\mathbf{C}_0 - \mathbf{C}(\mathbf{x})]$ are put in a second user's subroutine which we named *SETAC*, and pass these elements as constants into *SETP* (otherwise loop 8 may become unnecessarily time consuming). *SETAC* is only called in steps 2 and 28, before *SETP*.

We may comment on a difference in the meaning of the 'numerical differentiation' in BUS's and our non-linear programs. With BUS, for non-linear constraints, the derivatives $\partial x_i/\partial x_j$ are generated in the main program for the first time; with us, these derivatives are already known as elements of $-\mathbf{A}_2^{-1}\,\mathbf{A}_1$ and are used in *SETP*. In our programs, the purpose of steps 4–16 is only to select and store those derivatives which are actually needed in a given cycle. Since, with (6), this follows an equation which is linear in the changes $\Delta\mathbf{x}$, the increments of the 'numerical differentiation' can be large (we have used values of unity), whereas BUS has to keep the increments sufficiently small (he used values of 2^{-10}).

Finally, we draw attention to a strategy for selecting the dependent parameters. Often there are several possibilities for the selection. In order to facilitate inversion of $\mathbf{A}_2$ and keep the expressions obtained for (3) and (6) as small as possible, those parameters should be chosen as dependent ones which make $\mathbf{A}_2$ as much as possible (block) diagonal and which place as many as possible zero elements into $\mathbf{A}_2$. In this way, a computer inversion of $\mathbf{A}_2$ can often be avoided and *SETAC* and *SETP* can be programmed directly.

Examples

Here we give three examples where several parameters are constrained simultaneously by (partly) non-linear constraints.

The first example refers to the refinement of charge distribution models. Recently, we wanted to impose the neutrality condition for the charge parameters q_i, $\sum q_i = 0$, in conjunction with the condition that the molecular dipole moment assumes a fixed value (Scheringer, 1982). This gives rise to the three further conditions $\sum \mathbf{x}_i q_i = \boldsymbol{\mu}$ (one for each component of the dipole moment) on the positional and charge parameters. Generally, $\mathbf{A}_2$ is of order 4×4 and has, at best, three zero elements.

Our second example, mentioned already in the introduction, is the condition that three bond lengths are equally long. Let these be three C–H bond lengths at the same C atom, and the constraints have the form

$$C_1(\mathbf{x}) = d^2_{\text{calc}}[\text{C–H(1)}] - d^2_{\text{calc}}[\text{C–H(2)}] = 0,$$

$$C_2(\mathbf{x}) = d^2_{\text{calc}}[\text{C–H(1)}] - d^2_{\text{calc}}[\text{C–H(3)}] = 0,$$

where d^2_{calc} is the square of the bond length as calculated from the given parameters. $\mathbf{A}_2$ is of order 2×2. To get $\mathbf{A}_2$ diagonal the first dependent parameter has to be chosen from H(2) and the second from H(3). The worst choice in this case is to take the dependent parameters only from the C and/or H(1) atoms. The dependent parameters must depend strongly on the bond lengths, *i.e.* their direction should not be (approximately) perpendicular to the bond direction; otherwise the corresponding element of $\mathbf{A}_2$ is (approximately) zero and $\mathbf{A}_2$ is (ill-conditioned) singular.

Our third example is established from the structure of urea which we have refined recently (Guth, Heger, Klein, Treutmann & Scheringer, 1980). Here we have the symmetry constraints $y = x + \frac{1}{2}$ in the tetragonal system. In addition, we introduce bond-length constraints for the N–C and one N–H bond. We discuss this example in detail, firstly, to show that writing of *SETP* is not always trivial although it may appear so and, secondly, to illustrate that 'simplifications' in the treatment lead to insufficient convergence. Let d^2 be the square of the fixed bond length, then

$$\mathbf{C}_0 = \begin{pmatrix} \frac{1}{2} \\ d^2(\text{N–C}) \\ d^2(\text{N–H}) \\ \frac{1}{2} \end{pmatrix},$$

$$\mathbf{C}(\mathbf{x}) = \begin{pmatrix} y(\text{N}) - x(\text{N}) \\ [\mathbf{x}(\text{N}) - \mathbf{x}(\text{C})]^T\, \mathbf{g}[\mathbf{x}(\text{N}) - \mathbf{x}(\text{C})] \\ [\mathbf{x}(\text{N}) - \mathbf{x}(\text{H})]^T\, \mathbf{g}[\mathbf{x}(\text{N}) - \mathbf{x}(\text{H})] \\ y(\text{H}) - x(\text{H}) \end{pmatrix}, \quad (8)$$

where $\mathbf{g}$ is the metric tensor. With the C atom, only the z parameter can be varied. The derivatives $\partial\mathbf{C}(\mathbf{x})/\partial\mathbf{x}$ are easily obtained in the tetragonal system as $\partial d^2[\mathbf{x}(\text{N}), \mathbf{x}(\text{C})]/\partial x(\text{N}) = 2g_{11}[x(\text{N}) - x(\text{C})]$, *etc.* We denote these derivatives as A_{ij} and (5) assumes the form

$$\begin{pmatrix} -1 & 1 & 0 & 0 & 0 & 0 & 0 \\ A_{11} & A_{12} & A_{13} & -A_{13} & 0 & 0 & 0 \\ A_{21} & A_{22} & A_{23} & 0 & -A_{21} & -A_{22} & -A_{23} \\ 0 & 0 & 0 & 0 & -1 & 1 & 0 \end{pmatrix} \Delta\mathbf{x} = \mathbf{C}_0 - \mathbf{C}(\mathbf{x}),$$

$$x(\text{N})\; y(\text{N})\; z(\text{N})\; z(\text{C})\; x(\text{H})\; y(\text{H})\; z(\text{H}) \quad (9)$$

where the expressions from (8) have to be substituted into (9). The sequence of the parameters is written below the matrix of (9). In order to obtain a non-singular matrix $\mathbf{A}_2$ we have to choose two of the dependent parameters from $x(\text{N})$, $y(\text{N})$ and $x(\text{H})$, $y(\text{H})$. In this case, it does not matter and we choose $y(\text{N})$ and $y(\text{H})$. The best choice for the other two dependent parameters is $z(\text{C})$ and $z(\text{H})$. $z(\text{N})$, $x(\text{N})$ or $x(\text{H})$ could also be used, but then $\mathbf{A}_2$ has more non-zero elements [with $x(\text{N})$ and $x(\text{H})$ three more], the inversion of $\mathbf{A}_2$ takes more effort and the expressions obtained for (6) become longer. Since, in our case, A_{13} and A_{23} are large enough and $\mathbf{A}_2$ is well conditioned with them, we choose $z(\text{C})$ and $z(\text{H})$ as further dependent parameters. The corresponding columns of the matrix in (9) form the matrix $\mathbf{A}_2$, and its inverse reads

$$\mathbf{A}_2^{-1} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ A_{12}/A_{13} & -1/A_{13} & 0 & 0 \\ 0 & 0 & 0 & 1 \\ A_{22}/A_{23} & 0 & -1/A_{23} & -A_{22}/A_{23} \end{pmatrix}. \quad (10)$$

According to (6), we find the following four equations which have to be programmed in *SETAC* and *SETP*

$$\Delta y(\text{N}) = \Delta x(\text{N}) + \tfrac{1}{2} + x(\text{N}) - y(\text{N}), \quad (11a)$$

$$\Delta z(\text{C}) = \frac{A_{11} + A_{12}}{A_{13}} \Delta x(\text{N}) + \Delta z(\text{N}) + \frac{A_{12}}{A_{13}} [\tfrac{1}{2} + x(\text{N}) - y(\text{N})] - \{d^2(\text{N–C}) - d^2_{calc}[\mathbf{x}(\text{N}), \mathbf{x}(\text{C})]\}/A_{13}, \quad (11b)$$

$$\Delta y(\text{H}) = \Delta x(\text{H}) + \tfrac{1}{2} + x(\text{H}) - y(\text{H}), \quad (11c)$$

$$\Delta z(\text{H}) = \frac{A_{21} + A_{22}}{A_{23}} \Delta x(\text{N}) + \Delta z(\text{N}) - \frac{A_{21} + A_{22}}{A_{23}} \Delta x(\text{H}) + \frac{A_{22}}{A_{23}} [\tfrac{1}{2} + x(\text{N}) - y(\text{N})] - \frac{A_{22}}{A_{23}} [\tfrac{1}{2} + x(\text{H}) - y(\text{H})] - \{d^2(\text{N–H}) - d^2_{calc}[\mathbf{x}(\text{N}), \mathbf{x}(\text{H})]\}/A_{23}. \quad (11d)$$

Obviously, the symmetry constraints (11*a*) and (11*c*) are not affected by the bond-length constraints. This may lead one to conclude that the symmetry and bond-length constraints are independent of each other. This is not so because $\mathbf{A}_2$ is not (and cannot be made) a 2×2 block diagonal. We purposely set the two types of constraints to be independent of each other [all terms with A_{12} and A_{22} vanish in (11)] and then looked at the convergence. The correct minimum is not reached and the bond-length constraints are not exactly introduced (only to about 0·001–0·0001 Å) because the dependent shifts are not correctly calculated. With the correct form of (11), the constraints were introduced after the third cycle with an error of less than 10^{-5} Å (with the

input parameters, the bond lengths deviated by 0·040 and 0·008 Å from their desired values, the symmetry constraints were exactly satisfied). Errors or simplifications in the terms $-\mathbf{A}_2^{-1}\mathbf{A}_1$ and $\mathbf{A}_2^{-1}[\mathbf{C}_0 - \mathbf{C}(\mathbf{x})]$ mean that the constraints are not exactly introduced and that convergence is impaired. As a control, we recommend printing the elements of $\mathbf{C}_0$ and $\mathbf{C}(\mathbf{x})$ in *SETAC*.

With bond-length constraints, we used the squares of the bond lengths because they can be more easily obtained. Theoretically one could also use the bond lengths themselves. Then the elements A_{ij} would also change but the derivatives $\partial\Delta x_i/\partial\Delta x_j$ remain unchanged (as it should be) because all constant factors cancel in $-\mathbf{A}_2^{-1}\mathbf{A}_1$. The expressions $\mathbf{C}_0 - \mathbf{C}(\mathbf{x})$, however, differ from those calculated according to (8), but this does not matter since they converge to zero anyway.

APPENDIX
Comparison with Raymond's (1972) procedure of calculating the derivatives

Raymond (1972), hereafter RAY, treated the calculation of derivatives between the parameters, for linear and non-linear constraints. Here we compare his results with ours contained in (3) and (6). RAY writes the equations of constraint in the form

$$\mathbf{A}\,\mathrm{d}\mathbf{x} = \mathbf{0} \qquad (A1)$$

[RAY(2)], where $\mathbf{0}$ is the null matrix, and chooses $n - m = k$ independent parameters v_j which need not necessarily be a subset of the given parameters x_i. Then he puts

$$\mathbf{B}\mathbf{x} = \mathbf{v}, \quad \mathbf{B}\,\mathrm{d}\mathbf{x} = \mathrm{d}\mathbf{v} \qquad (A2)$$

[RAY(3)], where $\mathbf{B}$ is of order $k \times n$, and $\mathbf{v}$ of order $k \times 1$. Now RAY combines $(A1)$ and $(A2)$ according to

$$\begin{pmatrix}\mathbf{B}\\ \mathbf{A}\end{pmatrix}\mathrm{d}\mathbf{x} \equiv \mathbf{Q}\,\mathrm{d}\mathbf{x} = \begin{pmatrix}\mathrm{d}\mathbf{v}\\ \mathbf{0}\end{pmatrix}, \qquad (A3)$$

[RAY(4)], whereby $\mathbf{Q}$ is defined. The derivatives $\partial x_i/\partial v_j$ are, with RAY, all contained in the left $n \times k$ submatrix of $\mathbf{Q}^{-1}$.

With RAY's approach, the independent parameters $\mathbf{v}$ may be chosen quite generally. Our approach is defined by $\mathbf{v} = \mathbf{x}^{\mathrm{indep}}$, and then $\mathbf{B} = (\mathbf{E}|\mathbf{0})$, where $\mathbf{E}$ is the unit matrix. We prove the mathematical equivalence of both approaches (for this choice of $\mathbf{v}$) as follows. We use $\mathbf{A} = (\mathbf{A}_1|\mathbf{A}_2)$, and invert $\mathbf{Q}$ algebraically. Then

$$\mathbf{Q} = \begin{pmatrix}\mathbf{E} & \mathbf{0}\\ \mathbf{A}_1 & \mathbf{A}_2\end{pmatrix},$$

which gives

$$\mathbf{Q}^{-1} = \begin{pmatrix}\mathbf{E} & \mathbf{0}\\ -\mathbf{A}_2^{-1}\mathbf{A}_1 & \mathbf{A}_2^{-1}\end{pmatrix}, \qquad (A4)$$

as can be shown by multiplying out $\mathbf{Q}\mathbf{Q}^{-1} = \mathbf{E}$. Equation $(A4)$ shows that the derivatives, as they were determined in (3) and (6), $-\mathbf{A}_2^{-1}\mathbf{A}_1$, are identical to the lower left block of $\mathbf{Q}^{-1}$ (the upper block contains only the trivial derivatives unity and zero which are known in advance). Hence, the equivalence is proved. We remark that there is always a numerical solution with our procedure if there is one for RAY's because $\mathbf{A}_2$ is a principal submatrix of $\mathbf{Q}$, and thus $\mathbf{A}_2$ is always as well conditioned as is $\mathbf{Q}$.

The comparison also shows that, with $\mathbf{v} = \mathbf{x}^{\mathrm{indep}}$, $\mathbf{B} = (\mathbf{E}|\mathbf{0})$, with RAY's procedure too large a matrix is inverted and that the use of $\mathbf{A}_2$ instead of $\mathbf{Q}$ should offer advantages, particularly when the matrix inversion is done by hand. The choice of $\mathbf{v} = \mathbf{x}^{\mathrm{indep}}$, $\mathbf{B} = (\mathbf{E}|\mathbf{0})$ does not imply a limitation in the treatment of the constraints (this choice is also preferred by RAY in his examples) but rather represents the simplest solution that can be used in actual practice.

In order to demonstrate the advantage gained with the use of $\mathbf{A}_2$ instead of $\mathbf{Q}$, we discuss RAY's first example. There are six occupation factors $x_1, \ldots, x_6$ which are subjected to the three constraints $x_5 = x_4$, $x_6 = 2x_4$, and

$$12\cdot2(x_1 + x_2) + 14x_3 + 8(x_4 + x_5 + x_6) = C. \qquad (A5)$$

RAY has put $v_1 = x_1$, $v_2 = x_2$, $v_3 = x_3$ and has then set up and inverted the 6×6 matrix $\mathbf{Q}$. With a computer inversion of $\mathbf{Q}$, the choice of the dependent parameters does not matter. With our approach this problem can easily be solved by hand. $\mathbf{A}_2$ is of order 3×3. The inspection of $\mathbf{A}$ shows that, with RAY's choice of the dependent parameters, seven elements of $\mathbf{A}_2$ are non-zero. The better choice is $v_3 = x_4$, and now $\mathbf{A}_2$ has only five non-zero elements. Although $\mathbf{A}_2$ is not diagonal, the inversion is now trivial. With $v_3 = x_4$, two equations are already in the solved form which we are looking for, *i.e.* $x_5 = v_3$, $x_6 = 2v_3$. Hence, only the third equation has to be solved for x_3 which yields immediately

$$x_3 = -12\cdot2(v_1 + v_2)/14 - 32v_3/14 + C/14. \qquad (A6)$$

With our treatment there are only five derivatives $\partial x_i/\partial v_j$ which are different from 0 and 1, with RAY's there are nine (with $v_3 = x_3$). The solution for this simple example can, of course, be found without discussing it in terms of $\mathbf{A}_2$. But we point out that the inspection of $\mathbf{A}$ and the appropriate specification of the dependent parameters and $\mathbf{A}_2$ always enables one to find the simplest solution.

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Determination of the One-Particle Potential for an Atom with Highly Anharmonic Thermal Motion

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Abstract

Analytical expressions are derived relating the coefficients (α, β, γ, and δ) of the anharmonic one-particle-potential (OPP) model at a cubic site to the parameters of the higher cumulant expansion of the Debye–Waller factor. These expressions are used to derive the shape of the potential for the Al(4) site in the structure of $VAl_{10.42}$ from refinements of X-ray data measured at 100 K and room temperature, including third and fourth cumulant thermal parameters. Reasonable potentials are obtained at both temperatures. A negative value of β indicates a softening of the potential in the $\langle 111 \rangle$ directions in contradiction to the results of previous pseudopotential calculations. A single set of potential parameters is obtained by least-squares fit to the cumulants at both temperatures. Deviations from the fit indicate a lower temperature dependence for the anharmonic terms than predicted by the OPP model. Corrections for quantum statistical effects are small at both temperatures.

Introduction

Aside from interest in anharmonic motion itself, an accurate description of the thermal motion is required in many applications which utilize precise diffraction data, such as measuring the electron density distribution in crystals. When high-resolution measurements are present in the data set, the neglect of anharmonic motion will introduce additional noise in experimental density maps (see, for example, Stevens, 1979; Stevens, DeLucia & Coppens, 1980). In addition, multipole modeling, which may be used to derive an estimate of the static electron distribution, requires a proper model of thermal smearing to avoid correlations with parameters describing the electron distribution.

Deviations from harmonic thermal motion may be accounted for in the temperature factor in several ways. A general expansion of the temperature factor in terms of higher cumulants has been introduced by Johnson (1969),

$$T(\mathbf{h}) = \exp\left\{\frac{i^2}{2!}\,{}^{(2)}\kappa^{ij} h_i h_j + \frac{i^3}{3!}\,{}^{(3)}\kappa^{ijk} h_i h_j h_k + \frac{i^4}{4!}\,{}^{(4)}\kappa^{ijkl} h_i h_j h_k h_l + \ldots\right\}, \quad (1a)$$

or equivalently,

$$T(\mathbf{h}) = \exp\left\{-2\pi^2 b^{ij} a_i^* a_j^* h_i h_j - i\frac{4\pi^3}{3} c^{ijk} a_i^* a_j^* a_k^* h_i h_j h_k + \frac{2\pi^4}{3} d^{ijkl} a_i^* a_j^* a_k^* a_l^* h_i h_j h_k h_l + \ldots\right\}, \quad (1b)$$

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