PROMETHEUS-MANUAL PART I

ABSTRACT

This is a manual for the use of the program system PROMETHEUS. PROMETHEUS is designed to carry out sophisticated structure refinements using x-ray as well as neutron data. The most prominent features of the system are: Isotropic correction of thermal diffuse scattering. Absorption correction for sheres and arbitrary shaped crystals. Fast averaging of symmetrical equivalent reflections. Isotropic and anisotropic extinction correction of Zachariasen, Hamilton and Coppens, and Becker and Coppens. Refinement of anharmonic thermal tensors up to the sixth order in the Gram Charlier formalism and up to fourth order in the Edgeworth-, extended Edgeworth-, and the alpha formalism (quasi orthogonalisation formalism). Calculation and plotting of Fourier-, error-fourier-, probability-density-, and effective one particle potentials in arbitrary sections. Computation of mode- and and equilibrium positions. Calculation of Bonds and angles with standard deviations and printing of structure factor lists for publications. All programs are written in FORTRAN. Provisions have been made for an easy implementation on a variety of computers.

PREFACE

The system PROMETHEUS /1/ is a set of inter-related FORTRAN programs for sophisticated structure refinements from X-ray and neutron diffraction data. The system provides routines for isotropic correction for thermal diffuse scattering of first order (method of Skelton and Katz /4/).   *tdscor*

calculation of absorption correction and absorption weighted mean path length for spherical crystals using the results of Flack /5/.   *sphere*

calculation of absorption correction and absorption weighted mean path length for nonspherical crystals.   *absorb*

fast averaging of reflections (with separate treatment of statistic and systematic errors).   *averag*

least-squares refinement of conventional parameters and of anharmonic temperature factors (Gram Charlier formalism up to sixth order /5/, Edgeworth-, extended Edgeworth- /6/, and α (quasi orthogonalisation) /7/ formalism up to fourth order) including corrections for isotropic and anisotropic extinction (Zachariasen /8/. Hamilton and Coppens 9 , and Becker and Coppens /10/ model). The original program allows rigid-body calculations and insertion of special parameters. (The refinement of these special parameters is not supported by the logical structure of prometheus).   *refine*

Fourier- , difference Fourie-, and Patterson calculations   *fourie*

calculation of the standard deviations of the difference Fourier synthesis   *errmap*

calculation of probability density- (pdf) and potential maps using the least-squares estimated thermal tensors in the Einstein approximation /12/.   *pdfmap*

computation of arbitrary sections of all Fourier and the error Fourier maps.   *arbsec*

contour plots of all Fourier-, error Fourier-, pdf-, and potential maps.

plotte

calculation and plotting of the potentials along arbitrary directions, calculation of mode-positions
potcal

calculation of bonds, angles, and rms-displacements (harmonic) as well as thermal corrections of bonds /13/.
bonvib

printing of structure factor lists (adapted from the X-ray system /14/).
listfc

preparation of system descriptions   *predes*

No routines for structure solution are implemented into the system, nevertheless Patterson-maps can be calculated.

The system operates under a main program *monit* which allows ready addition of extra programs into the system. A set of binary data files is used for transmitting the crystallographic informations between the different routines.

This manual is divided into three sections

1. A description of the theoretical background of the performed calculations with some additional comments on practical aspects given for each program.

2. Instructions for the preparation of input data given for each program (card order).

3. Appendices for detailed informations about more internal features of the system.

Disclaimer

Although each program of the PROMETHEUS system has been tested by the authors on several data sets on three different computers no warranty is made as to the functioning and accuracy of the programs and their descriptions. However the authors will greatly appreciate being informed of discrepancies in the programs or desirable options not currenty included.

Distribution

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Updates of the system will be distributed to all users

Note to users

The usual journal reference to calculations done with the system prometheus is as follows

Zucker, U.H., Perenthaler, E ., Kuhs, W.F., Bachmann, R., and Schulz, H. (1983), J. Appl.Cryst.**16**, 358

Arbsec

The purpose of the arbsec program is the calculation of arbitrary sections of Fourier- or pdf-maps using a complete set of sections given in regular intervals parallel to the crystallographic axes. The input sections must be computed with the regular Fourier- or pdfmap program and their results are assumed to be in the input file. To avoid the time consuming calculation of lots of unnecessary points, arbitrary sections may be calculated directly in the routine pdfmap. This program was originally written by L.W.Finger.

The plane of the output section is specified by the coordinates of three points, which belong to the chosen plane. This coordinates may be given in terms of grid coordinates (as defined in the program, which has written the input file) or in fractional coordinates. The fractional coordinates will be initially converted into grid coordinates. The coefficients of the selected plane in the equation

$$a_1\, x + a_2\, y + a_3\, z + a_4\, = 3$$

may be found from the determinant equation

$$\begin{vmatrix} x & y & z & 1 \\ x_1 & y_1 & z_1 & 1 \\ x_2 & y_2 & z_2 & 1 \\ x_3 & y_3 & z_3 & 1 \end{vmatrix} = 0$$

where x ,y and z are the coordinates of the ith point.

This plane will have a line of intersection with each section of the original map. For the value of y and z corresponding to each line and section of the output map, the x coordinate of this point in the plane is determined. A cubic function of the form

$$a\, x^3 + b\, x^2 + c\, x + d$$

is fitted to the four adjacent grid points on the line, and the value of this function at the intersection point is used for the output at the y and z value. This process is repeated until all output points have been determined.

Practical information

The input is reduced to a minimum by transferring all informations previously given via the binary data file. The program itself has several options available. If only a fraction of the unit cell is used as input it will calculate the map in the accessible part only with the remainder replaced by asteriks in the printout. However, if the map for a complete unit translation has been computed, the program will use the translation symmetry to calculate a complete section. No other symmetry operations are taken into account. Following options are available

1. The entire section or a selected portion of it may be calculated and printed.

2. The output can be distorted according to the appropriate angle with regard to the limitations of a conventional   line printer, the program searches automatically for the best approximation to the correct angle.

3. The output may be suppressed optionally for all points within a given interval or the output may be totally suppressed in the case of later plotting.

4. The spacing of the lines may be chosen as single or double spacing.

5. A file is written optionally, which is needed in the case of later plotting.

In any case the geometric conditions of the selected map will be calculated and printed, i.e. the axial length and the interaxial angle of the chosen arbitrary section.

Averag

This program performs averaging of the intensities of symmetrically equivalent reflections. Intensities (and standard deviations) can be corrected for absorption or extinction if correction factors are available. In this case parallel averaging of corrected and uncorrected intensities is executed to allow an easy test of the sense fullness of the correction. Different calculations of the standard deviation can be chosen. Extended statistics are done during averaging to garantee an easy determination of the quality of the data. Two different rejection modes are avaliable.

Transformation of indices and sorting for increasing $\dfrac{\sin\theta}{\lambda}$ is possible.

Formulas

Averaging of the intensities:

$$I_m = \frac{1}{n} \sum_{j=1}^{n} I_j$$

I_m = averaged intensity
n = number of symmetric equivalent reflections
I_j = intensity of measurement j

The different standard deviations:

a) Gaussian error deviation law for the standard deviations read from input data

$$\sigma_{m,count} = \sqrt{\frac{1}{n^2} \sum_{j=1}^{n} \sigma^2_{j,count}}$$

b) Best estimate of the standard deviation calculated with the real deviations from the averaged intensity

$$\sigma_{m,deviation} = \sqrt{\frac{1}{n-1} \sum_{j=1}^{n} (I_m - I_j)^2}$$

(to chose this σ is only meaningful if enough equivalent reflections were measured).

c) Addition of an estimated systematic error.

$$\sigma_{j,systematic} = sysdev\ I_j$$

sysdev = estimated factor defining a systematic error proportional to I_j .

The total standard deviation is calculated in the following way

$$\sigma_{j,total} = \sigma_{j,count} + \sigma_{j,systematic}$$

d) Ignorance factor

The standard deviation σ_{count} can be altered by an ignorance factor e /1/ defined as follows

$$\sigma_{count,new} = \sqrt{\sigma_{count,old}^2 + (e \cdot I)^2}$$

typical values for e are 0.01 ... 0.04

Absorption correction

If absorption correction factors for intensities a* are read from the hkl-cards the correction can be done before averaging as follows

Intensities $\qquad I_{corrected} = I_{uncorrected} \cdot A^*$

Standard deviations $\qquad \sigma_{count,corr.} = \sigma_{count,uncorr.} \cdot A^*$

Extinction correction

If reflection data are read from the Fourier file intensities and standard deviations are divided through the extinction factors y read from the Fourier file

Intensities $\qquad I_{corrected} = \dfrac{I_{uncorrected}}{y}$

Standard deviations $\qquad \sigma_{count,corr.} = \dfrac{\sigma_{count,uncorr.}}{y}$

Calculation of the absorption weighted mean path length (tbar)

If absorption factors (*) but no tbar are read from the hkl-cards tbar is calculated in the following way

$$Tbar = \dfrac{\ln A^*}{\mu}$$

ln = natural logarithm

μ = linear absorption coefficient in μm^{-1}

Averaging of Tbar is always done as follows

$$Tbar_m = \dfrac{1}{n} \sum_{j=1}^{n} Tbar_j$$

Different scale groups

If intensities with different scale factors SCLFAK should be averaged it can be done in the following way

- number the intensities according to the scale factors (see parameter scale group on the hkl-cards).
- if SCLFAK is the scale factor of the first reflection of the data set the intensities of the other scale groups will be changed as follows

$$I_{new} = I_{old} \; \frac{SCLFAK_f}{SCLFAK_j}$$

$$j = 1,2,... \text{ but not equal } f$$

(this means that $SCLFAK_f$ is the scale factor for the averaged data)

Index transformation

Before averaging, the Miller indices can be transformed by a matrix **T**

$$(h_{new}, k_{new}, l_{new}) = \mathbf{T} (h_{old}, k_{old}, l_{old})$$

Reflections for which the new indices are not integer are rejected.

Rejection modes

There are two possibilities of rejecting reflections during the averaging process. They can be rejected

-if the absolute value of $(I_m - I_j)$ is greater than REJ σ_{total}. The factor REJ can be chosen by the user.

-if I_j is less than $(I_s - REJ \; \sigma_{count,s}$ where I_b is the strongest reflection of this symmetric equivalent group and $\sigma_{count,b}$ is the standard deviation I_b.

The latter method is helpful if reflections are shadowed e.g. by cryostats or pressure cells. (The two rejection modes can only be chosen alternatively). Normally before averaging, the reflections are sorted by a very fast sorting program /2/ in a manner, that symmetric equivalent reflections follow each other. Inside such a group the sequence of the reflections can be changed compared to the measurement. After averaging, the data set starts with the reflection with the lowest l, lowest k and lowest h. Then h is increased first. Then k is increased and h starts with the (new) lowest value again. At last l is increased.

If within the symmetric equivalent groups the sequence of the reflections should not be altered (in order to recognise time dependent changes of the intensities during measurement) the fast presorting process can be suppressed. The averaged data will then start with the intensity belonging to the group of the first reflection measured. Then the group of the second reflection (if this did not belong to the group of the first one) follows and so on.

If the lattice parameters are given to the program the printed reflection list is not affected. But on the output file the reflections are sorted for increasing $\frac{\sin(\theta)}{\lambda}$ (θ = sattering angle, λ = wavelength).

Preaveraging possibilities

Before averaging the crystal symmetry, averging of identical or Friedel reflections or both can be done during one program run.

To average first identical reflections is necessary for example for a reference reflection. The symmetric equivalent reflections of a reference reflection are only measured one time. If the reference reflection has a systematic error the influence of this error is not stronger than that of a normal reflection if the preaveraging process is chosen.

Determination of *less than* - reflections

After averaging reflections can be declared as observed or not observed (*less than*). A reflection can be declared as *less than* if the intensity is smaller than a defined multiple of the standard deviation. (Standard deviation means here the deviation which is written onto the output file according to the choice of the user).

Statistics

Q - values:

The Q-value is defined in the following way

$$Q = \frac{I_j - I_m}{\sigma_{total}}$$

Internal R - value:

The internal R-value is calculated for each group of symmetric equivalent reflections

$$R_{group} = \frac{\sum_{j=1}^{n}(I_m - I_j)^2}{\sum_{j=1}^{n}I_j^2}$$

and for the complete data set

$$R_{data\ set} = \frac{\sum_{k=1}^{m}(\sum_{j=1}^{n}(I_m - I_j)^2)_k}{\sum_k \sum_j (I_j^2)_k}$$

j = sum over a symmetric equivalent group
k = sum over symmetric independent reflections

(a weighted internal R-value will be added in a later version)

Literature

(1) N. A.Busing & H.A.Levy, J. Chem. Phys. 26, 563 (57)

(2) N.Wirth, Algorithmen und Datenstrukturen, B.G.Teubner Stuttgart

BONVIB

General description of the programme BONVIB

Written by L.W.Finger and E.Prince

Bond distances

Method of calculation

If x is a column matrix of fractional atomic coordinates for an atom in the asymmetric unit and y is the column matrix of the coordinates of a symmetry related atom, then y and x satisfy the following equation :

$$\mathbf{y} = \mathbf{R}\,\mathbf{x} + \mathbf{t} \qquad (1)$$

where r is a rotation-like opreation in that it involves axis interchanges and t is a translation operation which includes glide and screw components as well as origin shifts. Defining z as a column matrix whose coefficients are the differences in fractional coordinates between an atom x and an atom at y, then

$$\mathbf{z} = \mathbf{x} - \mathbf{y} \qquad (2)$$

If g is defined as the real space metric tensor which has elements

$$g_{ij} = \mathbf{a}_i\ \mathbf{a}_j \qquad (3)$$

where $\mathbf{a}_i$, $\mathbf{a}_j$ (i,j = 1,2,3) are the real space axis vectors, forming the following matrix:

$$\mathbf{g} = \begin{matrix} \mathbf{a}_1{}^2 & \mathbf{a}_1\mathbf{a}_2\cos\gamma & \mathbf{a}_1\mathbf{a}_3\cos\beta \\ \mathbf{a}_2\mathbf{a}_1\cos\gamma & \mathbf{a}_2{}^2 & \mathbf{a}_2\mathbf{a}_3\cos\alpha \\ \mathbf{a}_3\mathbf{a}_1\cos\beta & \mathbf{a}_3\mathbf{a}_2\cos\alpha & \mathbf{a}_3{}^2 \end{matrix}$$

$$(4)$$

If $\mathbf{z}^t$ denotes the transpose of $\mathbf{z}$ which involves an interchange of the rows and columns of $\mathbf{z}$, it may be shown that the square of the bond distance, s^2, between the atoms is determined by the following equation:

$$s^2 = \mathbf{z}\ \mathbf{g}\ \mathbf{z} \qquad (5)$$

In the program, all atoms within a spherical shell centered on each atom in the asymmetric unit are located and the distances are calculated. The size of the spherical shell is determined by the minimum and maximum distances to be considered which are input parameters. The search for the contents of the shell is made efficient by enclosing the central atom with a unit shaped parallelopiped tangent to the sphere with all atomic locations outside this parallelopiped excluded. The position of those atoms which lie within the spherical shell are stored in a table. This table also includes the atom number and the number of the r matrix used to generate this position which is needed to properly compute the partial derivatives of the Bond distances with respect to positional coordinates. These two numbers are stored in packed form in the same storage location. Each time a new atom is generated, this table searched to determine wether this atom has already been included. This search assures that atoms in special positions are properly treated although they may ge generated in several different ways.

Bond angles

All possible bond angles about each atom in the asymetric unit are computed using the table of positions prepared during the bond distance calcuation. Each pair of atoms from this table is checked to determine whether their distances from the central atom are within the limits, and if so, the bond angle is computed. If denotes the column matrix of the central atom with y_1 and y_2 denoting the column matrices of the peripheral atoms, the Bond angle θ for the angle $\mathbf{y} - \mathbf{x} - \mathbf{y}$ can be shown to satisfy the following relationship:

$$\cos\theta = \frac{(y_1 - x)^t g(y_2 - x)}{s_1 x\ s_2 x} \qquad (6)$$

where $\mathbf{g}$ is the real space metric tensor (see equation (4)). s_1x is the Bond distance from the atom at $\mathbf{x}$ to the atom at $\mathbf{y}_1$ and s_2x is the Bond distance from the atom at $\mathbf{x}$ to the atom at $\mathbf{y}_2$.

Ellipsoids of vibration

The conversion of anisotropic thermal coefficients is a problem of finding the characteristic values and characteristic vectors of a particular matrix. Note that characteristic value, proper value, principal value and eigenvalue are equivalent terms. The matrix equation that must be solved is the following:

$$(\mathbf{b} - \Phi \ \mathbf{g}^{-1})\cdot \mathbf{C} = \mathbf{0} \tag{7}$$

where b is the matrix of anisotropic temperature coefficients

Φ is a Eigen value of the equation

$\mathbf{g}^{-1}$ is the reciprocal space metric tensor with elements

$\mathbf{g}^{-1}_{ij} = \mathbf{b}_i \ \mathbf{b}_j$ where $\mathbf{b}_i$ and $\mathbf{b}_j$ are the reciprocal

space axis vectors and C is a column matrix of the coefficients of the caracteristic vector. This is a vector in reciprocal space. If equation (7) is premultipied by g, it is transformed into the standard form of a Eigen value problem.

$$(\mathbf{g} \ \beta - \Phi \ \mathbf{I}) \mathbf{C} = \mathbf{0} \tag{8}$$

Where $\mathbf{I}$ is the identity matrix and $\mathbf{g}$ is the real space metric tensor defined in equations (3) and (4). Equation (8) is a set of homogeneous equations of order 3 which have a solution if the determinant of the coefficients is zero. Thus the characteristic values may be found from the equation:

$$\text{Det} \ (\mathbf{g} \ \beta - \Phi \ \mathbf{I}) = \mathbf{0}$$

The solution of this equation gives three values of Φ which satisfy equation (8). In order to have a meaningful physical situation, it is necessary that the Φs which are the roots of equation (9) are real and positive. If they are not, the set of temperature coefficients is said to be non-positive definite. This is sometimes referred to as complex amplitudes of vibration or negative temperature factors. Each of the roots of equation (9) can then be inserted into equation (8) and the resulting equation solved for the characteristic vector by the method of cofactors. After the coefficients of C are determined, they may be used to form the reciprocal space vector $\mathbf{q}$ and the angle, θ (i) between this vector $\mathbf{q}$ and the real space axis vector $\mathbf{a}_i$ may be found by forming the scalar product of the two vectors:

$$\mathbf{a}_i \cdot \mathbf{q} = |a_i| \ \cdot \ |q| \ \ \cos\theta_i \tag{10}$$

this equation may be simplified since

$$\mathbf{a}_i \cdot \mathbf{q} = \mathbf{a}_i \ (\mathbf{q}_1 \ \mathbf{b}^1 + \mathbf{q}_2 \ \mathbf{b}^2 + \mathbf{q}_3 \ \mathbf{b}^3) \tag{11}$$

and

$$\mathbf{a}_i \ \mathbf{b}^j = d_i^j = \begin{cases} 1 \ \text{for i} = \text{j} \\ 0 \ \text{for i} \neq \text{j} \end{cases} \tag{12}$$

$$\mathbf{a}_i \ \mathbf{q} = \mathbf{q}_i \tag{13}$$

Equation (12) is the definition of the reciprocal space axis vectors. Equation (10) can now be rewritten

$$\cos\theta_i = \frac{q_i}{|a_i| \cdot |q|} \tag{14}$$

The root-mean-sqare amplitude of vibration along the ith charateristic vector is called μ (i) and is found from the ith root, Φ_i of equation (9) by the following relationship:

$$\mu_i = \sqrt{\frac{\Phi_i}{2\pi^2}} \tag{15}$$

Error analysis

If y is a computed value which is a function of experimentally determined variables x_1, x_2, ..., x_n such that:

$$y = y \ (\ x_1 \ , \ x_2 \ , \ ...... , \ x_n \ ) \tag{16}$$

then the variance of y, denoted by $\sigma^2(y)$ is found from the equation

$$\sigma(y) = \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{dy}{dx_i} \frac{dy}{dx_j} \ \text{cov} \ (x_i \ , \ x_j \ ) \tag{17}$$

where cov (x_i, x_j) is the ij^{th} element in the variance covariance matrix of the x.

In crystallographic calculations, the variables for which the variance-covariance matrix elements are known include the unit cell parameters the atomic positions and the temperature factor coefficients. If the dependence of the bond distance on temperature factors is negelcted, as is done in this program, the error in the bond distance will only depend on the cell parameters and the atomic positions. Similarly the ellipsoids will depend only on the unit cell parameters and the temperature factor coefficients. Thus, for crystallographic problems, equation (17) may be rewritten in the form:

$$\sigma(y)^2 = \sum_{i=1} \sum_{j=1} \frac{dy}{da_i} \frac{dy}{da_j} \ \text{cov} \ (a_i \ , \ a_j \ ) \ + \ \sum_{i=1}^{m} \sum_{j=1}^{m} \frac{dy}{dx_i} \frac{dy}{dx_j} \ \text{cov} \ (z_i \ , \ z_j \ ) \tag{18}$$

Where the a s are the unit cell paramerters and the z s are the atomic parameters. The variance-covariance matrix is the inverse of the normal equations least squares matrix. The error formula in equation (18) is a full matrix error formula. The so called diagonal form includes only the terms in equation (18) which have i=j. This approximation usually gives a smaller error. All partial derivatives required for computing the errors are analytically evaluated in this program. This procedure is better than numerical differentiation because it is more accurate easier and faster to do and allows singularities in the derivative to be detected easier. The necessary derivatives are evaluated using the chain rule of derivatives.

Output

1. General output

The first output consists of the information contained on the title card. Then the real space axis length, the cosines of the real space angles, the reciprocal space axis lengths and the cosines of the reciprocal angles are printed. The real space cell volume is also printed. Then the lattice type and centric indicator is printed followed by the symmetry operations. Next, if errors are to be calculated, the standard deviations of the cell parameters and the cell parameter correlation matrix are printed. Then the atomic positions and temperature factors are printed. If ellipsoids and errors are

to be calculated, the standard deviations of the atomic positions and the correlation matrix for the positions are printed. This completes the general output.

2. Bond distance and angle output

For each atom in the asymmetric unit, all atoms within the Bond distance limits are generated. These atoms are added to a table of generated positions. For each Bond distance within the allowable range, the atom identifier, the fractional coordinates, the Bond distance, the error, if calculated, and the number of this atom are printed. In the angle section of the program, all atoms except those in the asymmetric unit will be referenced by this atom number rather than by coordinates. This number makes it easy to determine quickly what angle has been calculated.

The Bond angle section output consists of the atom identifier and coordinates of the central atom which is one of those in the asymmetric unit. The peripheral atoms are each referenced by an atom identifier and an atom table number. The bond angle and its error, if calculated, complete the output for each angle.

3. Ellipsoid of vibration output

For each anisotropic atom, the equivalent isotropic b and its error are calculated and printed. Then for each of the characteristic values, the r.m.s. Amplitude of vibration and the angles that the associated characteristic vector makes with the real cell axes as well as the errors in these quantities are printed. No output occurs for isotropic atoms.

4. Page estimates

The main program will produce approximately one page of output plus $\frac{1}{2}$ page per atom if errors are to be calculated.

The Bond distance and angle subroutine will require about one page for each 60 distances of angles calculated. However, the user should keep the Bond distance limits as small as possible since if n distances are within the limits, the number of angles computed will be approximately $\frac{1}{2}n^2$. The ellipsoids of vibration subroutine will require one page for each three atoms.

FOURIE

The primary purpose of the *FOURIE* program is to calculate the electron (or nuclear) density function ρ(xyz)...

$$\rho(xyz) = \frac{1}{V}\sum_{hkl}(F(hkl)\exp(-2\pi i(hx+ky+lz)))\qquad(1)$$

where   V = volume of the unit cell
        hkl = Miller indizes

The coefficients F(hkl) may be real or complex numbers. Although F(hkl) may be complex, the electron density is everywhere real and can be given (unless anomalous dispersion effects are present) by the following expression

$$\rho(xyz) = \frac{2}{V}\sum_{hkl}A(hkl)\cos(-2\pi i\ (hx+ky+lz) + B(hkl)\sin(2\pi\ (hx+ky+lz))\qquad(2)$$

The summation is here over one-half of the reciprocal space. In centrosymmetric structures B will be zero. The calculation procedure in *FOURIE* is similar to the general method proposed by J.S.Rollett (1) where the points are calculated one by one in lines and sections the Fourier summtion is carried out using the Bevers-Lipson factorization (see e.g. (2)) which allows the conversion of the general expression (2) into simple sums of products. Thereby the number of operations is reduced by some order of magnitude. During the first step of calculation the reflections are read and their structure factors are combined to or the different a's and b's. These values are used as coefficients in the first summation over one index (l) yielding four different intermediate sums for

each value of z. The summation over the second index (k) combines these intermediate sums with the appropriate terms for all values of y. Using again these results the last summation over the third index (h) yields the electron density or a point xyz. The results of the first and second summation are used for the calculation of the next x-value. The procedure runs therefore first over x, second over y and last over z. During the performance of a fourier calculation storage is needed for

1. All involved hkl (in one packed integer word)

2. The Fourier coefficients of all hkl

3. The phase angles of all hkl

4. Four results of fourier summation over the first index

5. Two vectors each equal in length to the number of points in y direction

6. The final ρ-values of one x-y-section

No intermediate files are written.

The following coefficients are presently coded in *FOURIE*

1. F_o - Fourier

2. F_c - Fourier

3. Difference - Fourier $(F_o–F_c)$

4. Patterson - map (F_o^2)

Different inclusion resp. rejection criteria can be used

1. Inclusion of all reflections within two different $\dfrac{\sin(\theta)}{\lambda}$ regions

2. Inclusion of explicitely given reflections hkl only

3. Less-thans may or may not be included in the calculations

The multiplicities of all reflection types must be given or they can be calculated from the symmetry operations by the program. Following reflection types must be considered

```
h 0 0  or  0 k 0
0 0 l
h k 0
h 0 l
0 k l
h h 0
h 0 h
0 k k
h h h
h h l
h k k  or  h k h
h k l
```

A unique set of reflections hkl is expected on the input file (*FOURIE-file*). The necessary information to render possible the automatic generation of symmetry related reflections is contained in the space group symmetry operators, which are transfered to the *FOURIE* program via the Fourie-file. The order of reflections does not influence the efficiency with respect to the computing time.

The printout can be modified if desired with following options..

a. The range and resolution of the map must be given in terms of the initial and final points and the interval between sucessive points in each direction. The intervals are given as number of divisions along one axis, the initial and final points as number of intervals in this direction. In all cases the input is first for the crystallographic x-direction, second for the y-direction and last for the z-direction.

b. The concept of summation order is used, if sections other than standard sections should be printed i.e. The first index summed up is from section-to-section (page-to-page) in the output, the second index summed up is from line-to-line (down the page) and the third index summed up is from point-to-point (horizontally). Six different choices of crystallographic orientations with respect to the summation (and printing) can be made. The necessary transformations are performed automatically.

c. The output can be distorted according to the appropriate angle of non-orthogonal crystal systems. With regard to the limitations of a conventional lineprinter, the program searches automatically for the best approxiation to the correct angle.

d. The output may be scaled with an exaggeration factor to give reasonable numbers.

e. The quantity F000 must be given, so that using the volume of the unit cell (transfered via the fourier-file) the output can be in electrons per $Å^3$.

f. In case of unsufficient space for printing on one page, the output will be divided into parts automatically and printed on succeeding pages.

g. The spacing of the lines may be chosen as single- or double spacing.

Literature

(1) J.S.Rollett (1965) in Computing Methods in Crystallography (ed. J.S.Rollett) Pergamon Press, Oxford, p.82ff

(2) G.H.Stout & L.H.Jensen (1970) X-Ray Structure Determination, Macmillan, London, p.234ff .

LISTFC

This program is an adaption of the X-ray 67 program LISTFC (Stewart et al. 1967) it has been altered to stand alone and read the structure factor file (FOURIE file) created by REFINE. The output of the program has been changed so that the *phase in millicycles* has been replaced by σ (fobs).

Pdfmap

The program *PDFMAP* performs the calculation of the probability density function (*pdf*) (or the corresponding mean effective potential) of a single atom using the least-squares estimated thermal tensors up to the fourth order for the Edgeworth (= special form of cumulant -expansion) and up to the sixth order for the Gram-Charlier expansion. In addition extended pdfs and pdfs using C.K.Johnsons alpha-formalism can be calculated. The program was coded by U.H.Zucker at MPI FKF Stuttgart.

The generalized pdf

A generalized pdf is needed for a description of anharmonicities of atomic thermal motions in crystal structures. A general pdf should comply with the following requirements (1)..

1. The anharmonic description must tend to the harmonic model, if the mean displacements of the atoms become small.

2. The Fouriertransform between pdf and temperature factor (t) must exist and the resulting pdf must be positive definite.

3. The partition function of the corresponding potential energy must exist. And for the practical evaluation of the quantities temperature factor, pdf, and potential V

4. The expressions for T, pdf, and V should be valid for each oblique crystal coordinate system and for each point symmetry.

5. It should be possible to fit the parameters for T by least squares methods and to evaluate pdf and V numerically.

These requirements are fulfilled by a differential expansion of the (harmonic) trivariate Gaussian pdf. The Fourier-transform (FT) of such a trivariate gaussian is the well known anisotropic temperature factor (and vice versa). The trivariate Gaussian pdf is given by

$$\mathbf{P}df(\mathbf{u})_{har} = \frac{Det\mathbf{P}^{\frac{1}{2}}}{(2\pi)^{\frac{3}{2}}} \exp(-\frac{1}{2}(\mathbf{u} - \mathbf{x})_{\mathbf{p}} (\mathbf{u} - \mathbf{x}))$$

$$(1)$$

where a summation over i,j from 1 to 3 is implied and $Det_{\mathbf{P}}$ is the determinant of the matrix $\mathbf{P}$. This matrix $\mathbf{P}$ is given by

$$\mathbf{P} = 2 \ \pi^2 \ \boldsymbol{\beta}^{-1} = \mathbf{u}^{-1} \qquad\qquad (2)$$

where $\boldsymbol{\beta}$ = anisotropic thermal tensor
$\mathbf{u}$ = coordinates of real space
$\mathbf{x}$ = parameters of the mean

As mentioned a general pdf can be approximated by expanding the harmonic pdf into a series of its progressively higher order derivatives with respect to the coordinates of real space (see e.g. (2))

$$pdf(\mathbf{u})_{gnrl} = pdf(\mathbf{u})_{har} (1 - c^j \ d_j + \frac{1}{2} c^{jk} \ d_j \ d_k + \frac{1}{6} c^{jkl} \ d_j \ d_k \ d_l + \frac{1}{24} c^{jklm} \ d_j \ d_k \ d_l \ d_m + ...) \quad (3)$$

where $d_j = \dfrac{d}{du^j}$ etc. (partial derivative)

and c^j = tensorial coefficient (rank 1)

c^{jk} = tensorial coefficient (rank 2) etc.
(to prevent misunderstanding because of the derivative symbol d all tensors are designated here with A c).

Again a summation over j,k,l,m from 1 to 3 is implied, whereby each of these coefficients is invariant to pair-wise interchange of is indices. The introduction of tensorial coefficients allows an application of this expansion for all point symmetries. The given point symmetry can easily be retained by a proper constraining of the elements of the symmetrical tensors. In the general case of symmetry 1 there are 3,6,10,15,21,28 unique elements for the tensors of rank 1 to rank 6. A tabulation of the symmetry restrictions of tensors up to rank 6 for all crystallographic point symmetries is found in /9/.

Using the definition of multidimensional Hermite polynomials /3/

$$H(\mathbf{u})_{jklm...r} \ pdf(\mathbf{u})_{har} = (-1)^r \ d_j \ d_k \ d_l \ d_m...d_r \ pdf(\mathbf{u})_{har} \qquad (4)$$

where $d_j = \dfrac{d}{du^j}$ etc. (partial derivative)

and performing a standardization ($c^j = 0$ and $c^{jk} = 0$, which means that mean and dispersion are given by the mean and dispersion of the harmonic pdf(u)) one obtains from (3) up to the sixth order terms

$$pdf(\mathbf{u})_{gram} = pdf(\mathbf{u})_{har} \ (1 + \frac{1}{6} c^{jkl} h(\mathbf{u})_{jkl} + \frac{1}{24} c^{jklm} h(\mathbf{u})_{jklm}$$
$$+ \frac{1}{120} c^{jklmn} h(\mathbf{u})_{jklmn} + \frac{1}{720} c^{jklmno} h(\mathbf{u})_{jklmno}) \qquad (5)$$

Usually this type is called Gram-Charlier expansion. Its exact FT can be obtained easily (see e.g. /4/). It is given in equation (22) of the *REFINE* description. The least squares estimated thermal tensors **c**,o,e,f are inserted in (5) for a pdf calculation. This calculation is exact to the imposed degree of the expansion within the limits given by the accuracy of estimation of the involved tensors. The Gram-Charlier expansion is coded in *pdfmap* up to the sixth order according to equation (5). The Hermite polynomials used in this calculation can be expressed with equation (2) and

$$w_j = p_{jk} \ u^k \qquad (6)$$

as follows (up to sixth order)/1,4/

$$^0H(\mathbf{u}) \qquad = 1$$

$$^1H(\mathbf{u})_j \qquad = w_j$$

$$^2H(\mathbf{u})_{jk} \qquad = w_j w_k - p_{jk}$$

$$^3H(\mathbf{u})_{jkl} \qquad = w_j \ w_k \ w_l - 3w_j \ p_{kl}$$

$$^4H(\mathbf{u})_{jklm} \qquad = w_j \ w_k \ w_l \ w_m - 6w_j \ w_k \ p_{lm} + 3p_{jk} \ p_{lm} \qquad (7)$$

$$^5H(\mathbf{u})_{jklmn} \qquad = w_j \ w_k \ w_l \ w_m \ w_n - 10w_j \ w_k \ w_l \ p_{mn} + 15w_j \ p_{kl} \ p_{mn}$$

$$^6H(\mathbf{u})_{jklmno} = w_j \ w_k \ w_l \ w_m \ w_n \ w_o - 15w_j \ w_k \ w_l \ p_{no} + 45w_j \ w_k \ p_{lm} \ p_{no} - 15p_{jk} \ p_{lm} \ p_{no}$$

The indices in parenthesis indicate that the term has to be averaged over all permutations of those indices, which produce different terms, remembering that p is a symmetric tensor, e.g.

$$3w_j \, p_{kl} = \frac{3(w_j p_{kl} + w_k p_{lj} + w_l p_{jk})}{3} \tag{8}$$

In the following a second approach to the general expression (3) will be given. If one uses cumulants k defined by (e.g. /5/)

$$FT(pdf_{gnrl}) = T(\mathbf{h}) = \exp \sum_r \frac{k^{j\ldots r}(i^r)h_j\ldots h_r}{r!} \tag{9}$$

with i = imaginary unit, ii= −1
h$_j$, h$_r$... = Miller indices h,k,l

Instead of the tensorial coefficients c, a second form of the general pdf given by equation (3) can be formulated. The tensorial coefficients in (3) can be expressed in terms of cumulants (see e.g. /2/), whereby in the standardized form the terms up to fifth order do not differ formally, while the sixth and higher order terms do

$$c^j = k^j$$

etc.

$$c^{jklmn} = k^{jklmn}$$
$$c^{jklmno} = k^{jklmno} + \frac{1}{72} k^{jkl} k^{mno} \tag{10}$$
$$c^{jklmnop} = k^{jklmnop} + \frac{1}{144} k^{jklm} k^{nop}$$

etc.

Insertion of (10) in (3) yields with (4) e.g. The following standardized expression given up to the first anharmonic antisymmetric order (up to the first anharmonic symmetric order in brackets)

$$pdf(\mathbf{u})_{edgw} = pdf(\mathbf{u})_{har} \left(1 + \frac{1}{6} k^{jkl} H(\mathbf{u})_{jkl} \right.$$

$$\left. \left[+ \frac{1}{24} k^{jklm} H(\mathbf{u})_{jklm} + \frac{1}{72} k^{jkl} k^{mno} H(\mathbf{u})_{jklmno} \right] \right)$$

$$(11)$$

The cross term between the third and fourth order cumulant as well as their higher order multiples are omitted in this expression. A truncated expansion of this type is usually called Edgeworth expansion (= a special form of a cumulant - expansion). The expression (12) is due to F.Y.Edgeworth /6/, who rearranged the terms of equal order in the hermite polynomials from the view point of error statistics with regard to their importance. The FT of (11) is the exponential expansion of (9), which is equivalent to the (truncated) temperature factor expression given in equation (19) of the *REFINE* description. However the FT is exact only as far as the assumptions behind the rearrangement are valid one should keep in mind, that a least-squares estimation of e . g. The third order cumulant contains implicitely further antisymmetrically and symmetrically (sic) terms (e.g. $k^{jkl} k^{mno}$, $k^{jkl} k^{mno} k^{pqr}$ etc.) which do not all appear in a pdf calculation in the form proposed by F.Y.Edgeworth. If these terms are of importance (contrary to the exspectations of statistics) the Edgeworth-expansion is only a more or less satisfactory approximation to the FT of the exponential expansion of the temperature factor. For this reason the interpretation of Edgeworth-maps (and their resulting mean

potentials) should be done with considerable care however it should be pointed out here, that the Gram-Charlier and the Edgeworth-expansion are identical if all terms up to infinity are included.

The Edgeworth-expansion as expressed in equation (11) is coded in *PDFMAP*. The evaluation of an Edgeworth-map is numerically extensiv due to the occurence of the sixth order hermite polynomials. The computational effort is somewhat higher than evaluation of a Gram-Charlier map up to sixth order. Apart from the above mentioned theroretical and practical shortcomings of the Edgeworth-expansion, it was found, that in all investigated structures the Gram-Charlier based structure factor equation yields the better R-factors and the better goodness-of-fit, therefore owing to the advantages in real as well as in reciprocal space, the use of the Gram-Charlier based structure factor equation is strongly recommended.

The extended Edgeworth expansion

C.K.Johnson /7/ suggested the use of an extended version of the Edgeworth-expansion. This extended form is a unstandardized expansion and it is given up to the first anharmonic antisymmetric order (up to the first anharmonic symmetric order in square brackets) by the following expression

$$\text{pdf}(\mathbf{u})_{\text{ext}} = \text{pdf}_{\text{har}} \left(\; 1 + k^j H_j \; {}^j_j + \frac{1}{6} k^{jkl} \, h_{jkl} \right.$$

$$\left. \left[+ \frac{1}{2} k^{jk} H_{jk} + \frac{1}{2} k^j k^k H_{jk} + \frac{1}{6} k^j k^{klm} H_{jklm} + \frac{1}{24} k^{jklm} H_{jklm} + \frac{1}{72} k^{jkl} k^{mno} H_{jklmno} \right] \; \right) \quad (12)$$

$$\text{with } k^j = x^j_{\text{anharm}} - x^j_{\text{harm}} \qquad (13)$$

$$k^{jk} = \beta^{jk}_{\text{anharm}} - \beta^{jk}_{\text{harm}} \qquad (14)$$

where *harm* means terms obtained by purely harmonic calculations and *anharm* terms obtained by calculations using the (anharmonic) Edgeworth-based structure factor equation. The normal and the extended Edgeworth-map are identical in their FT. Therefore the different forms of expansion should yield identical pdfs. Only the convergence behaviour can be expected to be different. However it was shown by U.H.Zucker /1,7/ that there are remarkable numerical discrepancies between the normal and the extended map. Therefore it can be supposed that particularly in cases of large anharmonicities a convergence of the normal Edgeworth-expansions is not really obtained. On the other hand it seems impracticable at least in the case of strong anharmonicities to obtain the true harmonic parameters from a simple harmonic refinement because of the strong interactions of even order resp. odd order harmonic and anharmonic terms. In view of this somehow arbitrary evaluation of the harmonic parameters the extended Edgeworth expansion should be interpreted with care.

The α -formalism

This formalism has been published just recently by C.K. Johnson /9/, but it had been used for many years in the unpublished structure refinement programs of C.K.Johnson. The derivation of this formalism for the coding in the prometheus system was done using secondary publications. For this reason the numerical value of the - orthogonalization-parameter α of C.K. Johnson is just two times the value of the parameter α coded in the PROMETHEUS system. Orthogonalization should be understood in the sense, that the thermal tensors of even order resp. odd order do not interact systematically in the least squares refinement. The pdf in the α -formalism (the *-quasi-orthogonal-* pdf in the notation of C.K.Johnson) is given up to the fourth order by

$$\text{pdf} (\mathbf{u})_{\alpha} = \text{pdf}(\mathbf{u})_{\text{har}} (1 + \text{calph}(\mathbf{u}) + \text{dalph}(\mathbf{u})) \qquad (15)$$

$$\text{with calph} = \frac{c^{jkl}}{6} \; (y_j \, y_k \, y_l - 3(1 - \alpha) y_j \, p_{kl}) \qquad (16)$$

$$\text{dalph} = \frac{d^{jklm}}{24}(y_j\ y_k\ y_l\ y_m\ -6(1-\alpha)y_j\ y_k\ p_{lm}+ 3(1-\alpha)^2 p_{jk}\ p_{lm}) \qquad (17)$$

$$\text{where } y_j = p_{jk}\ u^k \qquad (18)$$

and p is given by equation (2). C and d are the least-squares estimated thermal tensors of rank three and four and α is the least-squares estimated orthogonalization parameter. Equations (15) to (18) are coded in *PDFMAP*. Further comments on this formalism are given in the *REFINE* description and in /1/.

Practical information

The program reads the mainfile (resp. 2 mainfiles in the case of extended map calculations) to get all informations, which are obtainable from the *REFINE* program. According to the structure factor type of the *REFINE* run, the correct series expansion will be calculated using the least-squares estimated thermal tensors (and alphas). The following options can be used for this calculations

A. The thermal tensors can be included individually into the pdf calculation. Inclusion of odd order terms only produces a completely antisymmetric map (approximation in case of Edgeworth expansion see above) while inclusion of even order terms only produces 1 symmetric map. All other combinations are allowed. Inclusion of all least-squares estimated thermal tensors yields the total pdf of the selected atom.

B. The atom selected for a calculation must be indicated by a flag. The sequence of atoms is identical with the sequence used in *REFINE*.

C. Six different choices of crystallographic orientations with respect to the printing can be made. All necessary transformations are performed automatically. The calculation order is first across a page, second down the page and third from page to page.

D. The pdf can be calculated for arbitrarily chosen planes too. The planes are specified by three points. The form of the planes used by *PDFMAP* is always rectangular.

E. The range and resolution of a map must be given in terms of the initial and final points and the interval between sucessive points for each direction. The intervals are inputted as number of divisions along one axis, the initial and final points as number of intervals in this direction. In all cases the input is first for the crystallographic x-direction, second for the y-direction and third for the z-direction (if the while the calculation order is given by the choice of crystallographic orientation of the map.

F. In case one page is insufficient for the output, the output will automatically be devided into two parts and printed on suceeding pages.

G. The output will be distorted automatically according to the appropriate angle of non-orthogonal crystal systems. With regard to the limitations of a conventional line printer, the program searches for the best approximation to the correct angle. Optionally the output can be printed in a conventional rectangular fashion.

H. The reference point for the pdf-calculation can be chosen in grid- or in map-coordinates.

I. The sections can be saved for later plotting. In this case the printing of a map can be suppressed.

J. The printing can be done single- or double-spaced and an exaggeration factor may be chosen. Points between given limits (not including the limits itself) will be suppressed.

K. Optionally one can calculate *potential*-maps which give the the mean (one particle) potentials of the seleted atom. Or further comments see *POTCAL* description.

Further comments and suggestions

All calculated pdf maps should be inspected very carefully. Negative regions of the pdf are physically meaningless. Due to the limited accuracy of the temperature factors, the pdf may have some negative regions with small absolute values and far from the centre of the pdf. If negative regions are obtained in more central parts of the total pdf (possibly with surrounding positive areas) the refined set of cumulants is probably meaningless. That means the number and/or the accuracy of the diffraction data used is not sufficient to allow a proper refinement of the theral tensors. In this case it is wise to reduce the number of refined parameters (e.g. to go back to a conventional harmonic refinement) or to collect a new better data set.

In some cases relatively deep negative regions result from refinements of split-positions (or other overlapping atoms). These negative regions are situated just at the position of the neighbouring atom. Such effects are due to the break down of the one particle approximation, which is used throughout in conventional crystallographic least-squares programs. Therefore the pdf (and the resulting potential) cannot be exactly evaluated in the overlap regions. To overcome these difficulties one can try to use a non-split structural model. The available series expansions involving terms up to high order (i.e. especially the Gram-Charlier series) are able to describe multimodal pdfs. This means that a split position may be described in a one particle form. It should be mentioned that such a description is often physically more realistic in comparsion with the corresponding split-model, although a proper superposition of pdfs may give reasonable results as well.

Finally in the case of X-ray diffraction data one should remember, that the true character of anharmonic motions can be obscured to some extend by the non-spherical nature of the atomic electron distribution. This may be essential especially if lone pair regions or strong covalent bonds are present.

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PLOTTE

The program *PLOTTE* performs the contour plotting of Fourier and pdf-maps. The routines contained in this program have been derived from multiple sources. Program authors are S.H.Zisk & N.M.Brenner of mit Lincoln laboratory (subroutine ICONT), D.V.Ahujo (subroutine INTPLT) and G.Ford of Purdue University (the remaining routines) with modifications of L.W.Finger, U.H.Zucker and W.F.Kuhs.

The present version of the program has been written as machine independent as possible. Only the call to standard plotter functions and to the functions *or* and *and* (used to mark or unmark the least significant bit of data points during the contouring process) are machine specific. It is hoped however that these functions are fairly standard everywhere

The main contouring subroutine (ICONT) takes the function values at the grid points of the map and computes the coordinates of the intersection of a specified contour line with the lines of the grid. Linear interpolation is used in this process. The second contouring subroutine (CPLOT) coordinates the drawing of the contours and produces any desired contour labels. The third contouring routine (INTPLT) produces a smooth curve through the intersections located by icont. Rational cubic polynomials are used to fit a spline-like curve through neighboring points. Two such curves meet smoothly be cause the first and second derivatives are single valued along the composite curve. The plotter line is drawn as a series of straight line segments.

Practical information

The input is reduced to the necessary plotter-specific information. All previously given information is transferrred via the binary data file (plot file) or is recalculated automatically. There are several options to modify the layout of the plot

1. It is possible to plot several sections of a three-dimensional map with one single call of *PLOTTE* as well as to plot different selected sections out of the calculated ones. However care must be taken to the limits of plot size on your local plotting facility.

2. Different section intervals may be chosen, whereby negative contours will be automatically plotted as dashed lines. At each contour line the corresponding height may be written.

3. The plot may optionally be surrounded with lines corresponding to the boundary directions of the selected map.

4. The plot may optionally be completed with lines (to mark e.g. bonds) or crosses (to mark e.g. atom positions) and labels (alphanumeric information) may be written at any desired point of the plot.

5. In addition a title, the label of the corresponding refine run and an index of the contour lines will be plotted on every plot.

Potcal

The program *POTCAL* performs the calculation of mean potentials (= one particle potentials of isolated atoms averaged over time and space due to the measurement conditions) in arbitrary directions using the corresponding probability density function (pdf) for this reason the complete pdf-calculation procedures are implemented in the program (for further details on the pdf-calculations see *PDFMAP* description). *POTCAL* was coded by W.F.Kuhs and U.H. Zucker.

The mean potential

The refinement of a crystal structure yields thermal parameters defined in the reciprocal space, which are unamenable to a direct interpretation. In a pdf calculation these parameters are transformed into real space. Such pdf maps allow the direct in spection of the physical meaning of the refined parameter set. On the other hand the observed density

distribution is connected with the potential of the considered atom. The calculation of these potentials is certainly useful with respect to their great importance in solid state physics.

The general (anharmonic) temperature factor is related to the intensity of bragg scattering into a specific direction (given by the Miller triple h) arising from a vibrating atom (see e.g. /1/)

$$T_j(\mathbf{h}) = <\exp(2\pi\ i\ \mathbf{h}\ \mathbf{u})>_{time} \qquad\qquad (1)$$

where $\mathbf{u}$ is any displacement vector of the atom j and the average is taken over a period of time which is long compared with the period of vibration (i.e. the counting time of the Bragg experiment). The temperature factor gives the weakening of a reflection h due to thermal motion effects. Introducing the space-averaged potential V instead of the time-average of the displacement vectors $\mathbf{u}$ one obtains the following expression

$$T_j(\mathbf{h}) = \frac{\iiint \exp(2\pi i h u j)\exp\dfrac{-V(h_j)}{k_B \cdot T}d^3 u_j}{\iiint \dfrac{\exp(-V_j(u_j)}{k_B \cdot T}d^3 u_j} \qquad\qquad (2)$$

where $\exp\dfrac{-V_j(u_j)}{k_B T}$ = Boltzmann factor resp.

$$\iiint \frac{\exp{-V_j(u_j)}}{k_B T}d^3 u_j = \text{partition function}$$

and k_B = Boltzmann s constant

   T = absolute temperature

Each possible value of $\exp(2\ \pi\ i\ \mathbf{h}\ \mathbf{u})$ is weighted with the Boltzmann factor to obtain its thermodynamic probability. The average of the atomic displacements $\mathbf{u}$ in each direction is given by the corresponding potential V for every temperature T in the classical region (T greater than the Debye temperature).

Expression (2) can be inserted (after lengthy but straightforward transformations /1,2/) into a structure factor equation using a power series expansion of V(u). Then the coefficients of these power series can be refined in a conventional least squares procedure (see e.g./3,4,5/). The calculations were restricted for practical reasons to high-symmetric cases.

However if the pdf is already known, a much easier approach to the potential is available without any restrictions due to the low symmetry. Remembering that the general temperature factor is the Fourier transform (FT) of a general (averaged) pdf

$$T(\mathbf{h}) = \iiint\ pdf_j(\mathbf{u}_j)\exp(2\ \pi\ i\ \mathbf{h}\ \mathbf{u}_j)\ d^3\ u_j \qquad\qquad (3)$$

where $\mathbf{h}$ = Miller index triple
       $\mathbf{u}$ = coordinates in real space of atom j

one obtains by comparsion of (2) and (3)

$$pdf_j(\mathbf{u}_j) = \frac{1}{Z_j}\exp\left(\frac{-V_j(\mathbf{u}_j)}{k_B \cdot T}\right) \qquad\qquad (4)$$

where Z is the partition function of atom j given in (2).

It is convenient to fix the potential V on the energy scale with respect to the deepest point in the potential (i.e. at the mode position of atom j)

$$V_j (\mathbf{u}_{mode}) = 0 \tag{5}$$

then the normalization factor is easily obtained via the pdf

$$Z_j = pdf_j (\mathbf{u}_{mode}) \tag{6}$$

and the resulting mean potential is calculated according to

$$V_j (\mathbf{u}_j) = - k_B \cdot T (\ln(pdf_j (\mathbf{u}_j) - \ln(pdf_j (\mathbf{u}_{mode}))) \tag{7}$$

using equation (7) the mean potential can be calculated point by point.

It is worth mentioning that by no means the mean potentials of crystallographically different atoms in a structure can be compared with regard to their normalization energy, i.e. they can not be brought to an absolute scale.

A prerequisite for the calculation of meaningful mean potentials is the existence of an exact ft as expressed in equation (3). Only the Gram-Charlier expansion form of a general pdf possesses a unequivocal expression of its FT, while the Edgeworth expansion is only approximatively Fourier transformable (see further comments in *PDFMAP* description). Therefore the Gram-Charlier expansion is strongly recommended, if mean potentials will be calculated.

The atomic position

Whenever anharmonic terms are involved in the calculation of temperature factors resp. the calculation of the corresponding pdfs and mean potentials, a distinction has to be made between different expressions for the atomic positions. The *mean position* (or shortly the *mean*) is just simply the first order term in the calculated series expansion. The *mode position* (or shortly the *mode*) is given by a minimum in the potential resp. a maximum in the corresponding pdf. There can be two or even more modes at one atomic position (*multimodal- potentials* resp. pdfs). It should be mentioned in this context, that the use of multimodal distributions may be very useful for a physically meaningful description of some order disorder situations (e.g. in ferroelectrics or fast ionic conductors) /6/. The physically most important positional parameter is the *equilibrium position* $m_{t,j}(\mathbf{u})$, which is the the true mean position of an atom at a given temperature. $m_{t,j}(u)$ may be evaluated for a given direction using the calculated mean potential of (7)

$$m_{t,j} (\mathbf{u}) = \frac{\int exp\dfrac{\mathbf{u}_j(-V_j(\mathbf{u}_j))}{k_B \cdot T}du_j}{\int exp\dfrac{(-V_j(\mathbf{u}_j))}{k_B \cdot T}du_j} \tag{8}$$

In the harmonic case the mean, mode and equilibrium position are identically. If only even order terms of the general pdf are involved, at least the mean and the equilibrium position are identical. In the presence of odd order modifications the mean, mode and equilibrium position may differ. The mode(s) is (are) valuated in *POTCAL* by a systematic search using the method of vector complication. The resulting bond situation (distances and angles) are calculated optionally for convenience. It should be noted however, that this calculated bonds have no striking physical meaning.

Experimental restrictions

Using Bragg diffraction data it is clear, that meaningful mean potentials can be calculated only as far these potentials are sufficiently filled up with exited states. What is sufficient depends on the accuracy of the measurement (and the complexity of the problem), while the filling itself is given primarily by the temperature of the measurement. Considering a harmonic oscillator with its equidistant energy levels, the occupation probability is given by the Bose-Einstein distribution function, which is expressed in the classical limit by

$$F(E) = \exp \frac{-E}{k_B \cdot T} \qquad\qquad (9)$$

In the case of an anharmonic oscillator the energy levels are no longer equidistant and the calculation of the corresponding distribution function is more complicated. However a rough estimation of the *scanning limit* for a given experimental temperature can be obtained in the harmonic approximation. It was found that the accuracy of nowadays available diffraction data allows a scanning up to F(E) values of about 0.01. This limit should be taken not too seriously and has to be changed in the case of strong anharmonicities or not very accurate diffraction data. Anyway these somewhat artificial limit of 0.01 is used for the calculations in *POTCAL* as default. Other limits may be given optionally.

Practical information

The program reads the mainfile (resp. 2 mainfiles in the case of extended map calculations) to get all informations, which are obtainable from the *REFINE* program. According to the structure factor type of the *REFINE* run, the correct series expansion will be used for the potential calculations. The following options can or must be used for the calculations

A. The atom selected for a calculation must be indicated by a flag. The sequence of atoms is identical with the sequence used in *REFINE*.

B. The direction selected for calculation may be given by the fractional coordinates of the last point of calculation or by the crystallographic vector (uvw), whereby the calculation starts optionally at the mean or at the mode position. In addition an arbitrary direction may be given by the fractional coordinates of the first and last point to be calculated. The calculation may also be extended to the opposite direction by simply setting the appropriate flag.

C. The mode position(s) and their bond situation(s) can be evaluated optionally. The highest mode can be used for the normalization of the potential and moreover it may replace the mean as reference point for the evaluation of the chosen direction.

D. The desired spacing in the displacement vector (for printout) may be given in Å units.

E. The calculated potential can be plotted optionally. The size resp. scaling of the plot can be chosen individually.

F. The scanning limit is used as upper boundary for plotting and printout. This limit may be altered optionally.

G. If already known (from prior calculations) the pdf value of the mode can be given as input. This saves the time needed for the search of this mode.

H. The energy units of the output can be chosen as eV or J$\cdot 10^{-19}$.

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(5) M.J.Cooper, K.D.Rouse & B.T.M.Willis (1968) Acta Cryst. A24, 484.

(6) W.F.Kuhs (1983) Acta Cryst. A39, 148-158.

PREDES

This program generates the printed output of the system description as well as any other printed output from an input file following the rules given in the cardorder part of the system description.

REFINE

This performs program full-matrix least-squares refinements of conventional and anharmonic structural parameters in a normal or rigid body treatment with x-ray or neutron data. It is an extensively modified version of the routine RFINE4 written by L.W. Finger /1/ . It was extended to refine extinction parameters in the formalism of Becker & Coppens as well as anharmonic thermal parameters in four diffrent structure factor formulae (Gram Charlier formalism up to sixth order , Edgeworth-, extended Edgeworth- , and α - (quasi orthogonalisation) formalism up to fourth order). In addition the program computes optionally Lorentz and polarisation correction, or after every cycle of refinement bond distances, angles, or thermal ellipsoids.

A scheme of derivative modification and parameter restoration, which eliminates the need for coding special subroutines to treat dependent parameters, is included. This method handles trivial (symmetry dependent) as well as non-trivial (symmetry independent) restrictions on parameters, allowing e.g. the occupancies of a multiposition , in a partially ordered structure to be refined with the occupancies constrained to a particular chemical composition. Provisions have been made for incorporation of *special parameters* (PROMETHEUS is indepted to L.W. Finger for this part of the program) which do not belong to a set used in a conventional least-squares refinement. Groups of atoms may be introduced as rigid bodies with respect to position, orientation (*shape refinement*) and thermal motions.

Anharmonic thermal motion may be treated as higher order modification of the conventional harmonic structure factor formula. The methods used for the description of these anharmonicities are based on series expansions of a normal (Gaussian) trivariate probability density function (pdf). Two different series expansions are particularly suited for this problem, the Edgeworth- and the Gram Charlier -expansion. Their Fourier transforms lead to temperature factors (see below) which are inbedded into the structure factor formula.

In its present form the program allows for a maximum of 60 atoms per asymmetric unit (6th order temperature factors can be refined for the first 6 and 4th order temperature factors for the first 40 atoms) 20 scattering curves and 10 scale factors are allowed for a structure in any space group. The maximum number of simultaneously refined parameters is 200.

The normal equations

The parameters p(1),p(2),...p(n) of a structural model will be adjusted to the actual structural parameters in a linearized least squares procedure by minimising the sum of the squares of the differ-ences between the observed and calculated structure factors F_o and F_c. The refinement is based either on F or on F^2 (for simplicity all equations of this section are written without scale and extinction factors

($F_o(\text{experimental}) = \sqrt{\text{ext. factor} * \text{scalefactor} * F_o}$)

$$M(F) = \sum_{hkl} w \, ||F_o| - |F_c||^2 \quad (w \, (F_o - F_c)^2) \qquad (1)$$

$$M(F^2) = \sum_{hkl} w\,(F_o^{\,2} - F_c^{\,2}) \qquad (2)$$

F_c is a function of all parameters P_i to be determined and the sum is
over all structure factors, which may be weighted with a weight w. For M(F) to be a minimum, the partial derivatives
$\dfrac{dM(F)}{dP_i}$ must be equal to zero.

$$\frac{dM(F)}{dP_i} = 2\sum_i \left(w\,(|F_o - F_c|)\,\frac{(d|F_c|)}{dP_i}\right) = 0 \qquad (3)$$

Since $|F_c|$ is not a linear function of the parameters P_i, the linear least-squares procedure is not applicable. However a linearisation of the problem can be achieved by expanding $(|F_o - F_c|)$ as a function of its parameters by a Taylor-series. With

$$drv(i) = \frac{d(|F_c(P_i)|)}{dP_i} \qquad (4)$$

one has

$$(|F_o - F_c|) = |F_o| - |F_c(P_i)| + \sum_i ((q_i - P_i)drv(i)) + h \qquad (5)$$

where q_i is the true value of the parameter, P_i the initial approximation of this parameter and h represents the higher order terms of the expansion. Assuming the P_i to be close to Q_i the *parameter shifts* S_i

$$S_i = Q_i - P_i \qquad (6)$$

will be close to the true shifts and the higher terms in (3) will be small compared to the linear term and can be set equal to zero in the least-squares procedure

$$(|F_o| - |F_c|) = (|F_o - F_c|) - \sum_i (S_i\,drv(i)) \qquad (7)$$

Obeying the conditions for M(F) to be a minimum, the resulting normal equations are

$$\sum_{hkl} \left(w(|F_o| - |F_c|) - \sum_i (S_i\,drv(i))drv(j)\right) = 0 \qquad (8)$$

thus

$$\sum_i \left(\sum_{hkl} (w\,drv(i)drv(j))S_i\right) = \sum_{hkl} (w\,((|F_o| - |F_c|)drv(j))) \qquad (9)$$

There are n of these equations for j= 1,2..n for the determination of n unknowns. The parameter shift scan be calculated by multiplying the inverted A_{ij} matrix by the *vector* B_j

$$S_i = A_{ij}^{-1} \cdot B_j \qquad (10)$$

where

$$A_{ij} = \sum_{hkl} (w\,drv(i)drv(j)) \qquad (11)$$

$$B_j = \sum_{hkl} (w(|F_o| - |F_c|)drv(j)) \qquad (12)$$

The shifts S_i can be used to correct the initial approximation which gives a new set of parameters closer to the Q_i. The whole process can be repeated until the S_i are sufficiently small.

The procedure implemented in the *REFINE* program is the one proposed by Busing & Levy /2/ and coded by J. Mundstock of the numerical analysis center of the university of Minnesota.

Assuming that convergence has been obtained, that the weights have been correctly chosen (*sic*) and that the errors of the ($|F_o| - |F_c|$) are not correlated (*sic*) /3/, meaningful variances resp. covariances can be calculated from the diagonal resp. off-diagonal elements of the inverted matrix

$$\text{var}(i) = A_{ii}^{-1} \cdot \frac{M(F)}{hkl - n} \tag{13}$$

$$\text{covar}(i,j) = A_{ii}^{-1} \cdot \frac{M(F)}{hkl - n} \tag{14}$$

where

hkl= number of reflections
n   = number of parameters

The estimated standard deviation *esd* and the correlation coefficients *corr* can be obtained from

$$\text{esd}(i) = \text{sqrt}(\text{var}(i)) \tag{15}$$

and

$$\text{corr}(i,j) = \frac{\text{covar}(i, j)}{(\text{esd}(i)\text{esd}(j))} \tag{16}$$

The constraints

In many structures the parameters of a model may not be varied independently. If a parameter is constrained to a constant value, there is no difficulty, the refinement selection flag for the parameter is simply set to zero. The situation is greatly complicated how ever if the model requires a parameter to be equal to a linear combination of the free varaiables. In the least-squares refinement of such structures, the contribution of the dependent parameter to the derivative of the structure factor with respect to the independent variable must be computed if the shifts are to be properly evaluated. Similarly, the correct value of the dependent parameter must be restored at the end of the cycle so that the structure factor is properly computed in the next cycle.The method used to treat the constraints was coded by L.W.Finger /4/ and essentially consists of the application of the chain rule to the derivatives of the structure factor with respect to the parameters of the model. The user must determine the dependecies between parameters using the rules of Levy /5/ for thermal coefficients or the equations of L.W.Finger /4/ for chemical constraints and then give this information to the program. The constraints for tensor elements up to fourth order are given e.g. in the international tables/6/. They are included in Appendix A together with the symmetry restrictions on thermal tensors of rank 5 and 6 which were calculated by W.F.Kuhs /6/. Correlations between odd order tensor elements in non-centrosymmetric structures restrict the number of coefficients which can be refined /7/. All parameters corresponding to a unique non-zero entry in the tabulations mentioned above have to be kept fixed. The program will presently not allow constraining the total occupancy of a site with only one species present. This way be accomplished however, by introducing a second species with a null scattering curve.

The dependent parameter information is read by subprogram.

RDEGN. This routine rearranges the array of relationships in ascending order first of independent atom and parameter designators and then of dependent atom and parameter designators. Special parameters are arbitrarily assigned to atom number 0.

The symmetry operations

The symmetry operations are needed to generate all atoms in the unit cell from one asymmetric set. They must be given in the form tabulated in the first volume of the international tables /8/and they are stored as matrices (rotational parts) and vectors (translational parts) in the binary data file. The identity x,y,z is always expected and must be given. Center of symmetry as well as centering of the lattice are generated by the program.

The scale factor

The scale factor in the program *REFINE* is used to place the value of F_o on the same scale as F_c (division of F_o by the scale factor). There may be up to 10 different scale factors for different groups of data, which can be refined independently.

The temperature factor

The Fourier-transform (*FT*) of the probability density function (*pdf*) or thermal smearing function of an atom j is called the *temperature factor* T of this atom. A trivariate normal distribution (Gaussian distribution) for the pdf gives the conventional anisotropic temperature factor

$$T(\mathbf{h}) = \exp(-(h^2\beta^{11} +...2hk\beta^{12} +...)) \qquad (17)$$

with the Miller indices h,k,l. The β^{ij} are the components of the symmetric thermal tensor (of rank 2). The β^{ik} (used throughout the PROMETHEUS system) are converted to the Cruickshank notation /9/ by

$$u^{ik} = \frac{\beta^{ik}}{2\pi^2 |a_i^*||a_k^*|} \qquad (18)$$

where $|\mathbf{a}^*|$ is a reciprocal axis length.

In the case of a non-Gaussian pdf an anharmonic temperature factor results. In the statistical (=isolated atom) approach an expansion of the Gaussian (=harmonic) pdf is used to describe a general, anharmonic pdf. If the trivariate Gaussian distribution is taken as the developing function and expanded into a series of strictly progressive higher order derivatives the G r a m - C h a r l i e r expansion /10/ results. For mathematical reasons /11/ one also uses the E d g e w o r t h expansion /12/ which is a rearrangement of the Gram-Charlier series.

This *Edgeworth expansion* was introduced in thermal motion analysis by C.K.Johnson/13/. The FT of the Edgeworth expansion for each atom is given by

$$T(h)_{j,ah} = \exp(c_j^{pqr} i^3 h_p h_q h_r + d_j^{pqrs} i^4 h_p h_q h_r h_s + ...) T(h)_j \qquad (19)$$

with $T(h)$ = harmonic temperature factor of atom j

$c \quad = \dfrac{(2\pi)^3}{3!} \cdot c' =$ (skewness-) tensor of rank 3

$d \quad = \dfrac{(2\pi)^4}{4!} \cdot d' =$ (kurtosis-) tensor of rank 4

$h \quad =$ miller indices

$i \quad =$ imaginary unit; $(i \cdot i = -1)$

while the FT of the standardized Gram-Charlier expansion for each atom is given by

$$T(h)_{j,ah} = (1 + \frac{(2\pi i)^3}{6} c_j^{pqr} h_p h_q h_r + \frac{(2\pi i)^4}{24} d_j^{pqrs} h_p h_q h_r h_s + ..) T(h)_j \qquad (20)$$

The corresponding structure factor expression for the Edgeworth type up to the fourth order assumes the form

$$F(h) = \sum_j f_j \exp(i(2\pi x_j^p h_p - c_j^{pqr} h_p h_q h_r) - (\beta_j^{pq} h_p h_q - d_j^{pqrs} h_p h_q h_r h_s)) \qquad (21)$$

and for the Gram-Charlier type up to the sixth order

$$F(h) = \sum_j f_j \exp(2\pi i x_j^p h_p - \beta_j^{pq} h_p h_q)$$

$$[1 - i\frac{4}{3}\pi^3 c_j^{pqr} h_p h_q h_r + \frac{2}{3}\pi^4 d_j^{pqrs} h_p h_q h_r h_s + \qquad (22)$$

$$i\frac{4}{15}\pi^5 e_j^{pqrst} h_p h_q h_r h_s h_t - \frac{4}{45}\pi^6 f_j^{pqrstu} h_p h_q h_r h_s h_t h_u]$$

Equation (20) was coded by L.W.Finger and equation (22) by U.H.Zucker, both are introduced in the *REFINE* program. The least-squares estimates of the elements of the tensors c, d, e, f can be used to calculate the pdf of the atom j with the program *pdfmap*. The pdf gives a physical interpretation of the thermal parameters. It should
It should always be calculated to check the physical significance of the refined data, since a direct interpretation of high rank tensors is rather impracticable. In some cases the pdf becomes negative or otherwise physically meaningless showing the weakness of the model used. In addition provisions were made in the program *REFINE* to allow the computation of *extended* Edgeworth maps /12/ with the program *pdfmap*.
The *α-formalism* of C.K.Johnson /13/ was also implemented in the program *REFINE* by U.H.Zucker. The aim of this formalism is to minimize the (sometimes strong) correlations between harmonic and anharmonic parameters of order n and n+2 by a replacement of the simple powers of h in (21) or (22) by polynomials $g(h,\alpha)$

$$g(h,\alpha_j)_{pqr} = h_p h_q h_r - 3\alpha_j h p(p j_{qr}) \qquad (23)$$

$$g(h,\alpha_j)_{pqrs} = h_p h_q h_r h_s - 6\alpha_j h_p (h_q p j_{rs}) +$$

$$3(\alpha_j^2)pj_{pq}(pj_{rs})$$

$$pj = p_j$$

(24)

where the indices in parentheses indicate that the term has to be averaged over all permutations which produce different terms. P is a symmetric tensor and is related to the anisotropic displacement tensor β by

$$\mathbf{P} = 2\pi^2\boldsymbol{\beta}^{-1}$$

(25)

The parameter α can be adjusted in the least-squares refinement for all atoms j individually. For α equal to zero the structure factor formula is identical to the one for the Gram-Charlier expansion. It should be noted that for historical reasons the parameter α used in the PROMETHEUS system is just one half of the parameter alpha in C.K.Johnson's work. In addition the refinement procedures are slightly different. In C.K.Johnson's program p is evaluated only once at the beginning of the procedures using the starting values of β (and therefore rather arbitrarily). In refine p is recalculated in every cycle. It was found that a slight reduction of correlations can be achieved with values of α between 0.1 and 0.2 (PROMETHEUS notation).

General remarks and suggestions

The Edgeworth and Gram-Charlier expansions are identical if all terms up to infinity are included. Therefore neither is theoretically superior to the other, if a general pdf is considered. However it is found, that in all structures investigated the Gram-Charlier based structure factor formula yields the better R-values and the better goodness-of-fit. Moreover, the Fourier transform of the Gram-Charlier expansion can be evaluated numerically without approximation, whereas the Fourier transform of the Edgeworth expansion is only an approximation. This makes a detailed interpretation of the Edgeworth-map doubtful. Therefore the use of the Gram-Charlier expansion is recommended to all users. Finally it should be mentioned that no calculation using the α-formalism yielded a better fit to the data than calculations using the Gram-Charlier expansion. Moreover, the convergence was bad, if the α parameters were refined. Correlations are lowered, however they enter into the refined α parameters. If due to correlation different sets of cumulants are obtain and they give similar pdfs, the correlation should not be taken too seriously.

The extinction correction

In the kinematical limit the weakening of a reflection by energy transfer between the incident and the reflected beam is called *extinction*. A suitable correction for this effect is necessary and may be very important especially for strong low order reflections (which strongly influence e.g. the determination of site occupancies or of valence electron distributions). The lack of detailed information on the perfection of the investigated crystal only allows for a correction via a refinement of the *extinction factor* y

$$F_c+ = \mathrm{sqrt}\ (y)\ \ F_c$$

(26)

where F_c+ is the extinction affected calculated structure factor.

All extinction corrections implemented in the program *REFINE* are based on Darwin's model of a mosaic crystal (=ensemble of mosaic blocks of certain size which are misaligned against one another) in the formulation of W.H.Zachariasen /14/ with the important extensions made by P.J.Becker & P.Coppens /15,16,17/. In the case of small mosaic blocks the energy transfer occurs always once in one block (*secondary extinction*), while in the case of larger mosaic blocks - larger than the extinction length /18/ - the beam is multiply reflected in one block (*primary extinction*)

The Zachariasen-formalism

The extinction factor y of the Zachariasen-formalism as extended and revised by P.Coppens & W.C.Hamilton /19/ is given by

$$y = \frac{1}{1 + B(\theta) \cdot GF_c^2} \tag{27}$$

with

$$B(\theta) = \frac{e^4 \lambda^3}{M^2 c^4 V^2 \sin_2\theta} \text{ Tbar2 } \frac{\cos_2 d + \sin_2 d \cos_2 M + (\sin_2 d + \cos_2 d \cos_2 M)\cos_4 t}{\cos_2 d + \sin_2 d \cos_2 M + (\sin_2 d + \cos_2 d \cos_2 M)\cos_2 t} \tag{28}$$

where $\cos_2 d \quad = \quad \cos^2\delta$

$\quad\quad\quad \sin_2 d \quad = \quad \sin^2\delta$

$\quad\quad\quad \cos_2 M \quad = \quad \cos^2 2\theta_M$

$\quad\quad\quad \cos_2 t \quad = \quad \cos^2 2\theta$

$\quad\quad\quad \cos_4 t \quad = \quad \cos^4 2\theta$

with δ = dihedral angle

$\quad\quad \theta_M$ = scattering angle of the monochromator

$\quad\quad \theta$ = scattering angle of the reflection

for X-rays and

$$B(\theta) = \frac{\lambda^3 a^2}{V^2 \sin 2\theta} \text{ Tbar2} \tag{29}$$

for neutrons, where

$\quad\quad \lambda \quad$ = wavelength of radiation

$\quad\quad e \quad$ = charge of the electron

$\quad\quad m \quad$ = mass of the electron

$\quad\quad c \quad$ = velocity of light

$\quad\quad a \quad$ = unit scattering length

$\quad\quad V \quad$ = volume of the unit cell

$\quad\quad th \quad$ = Bragg angle

The absorption weigthed mean path length Tbar is given as

$$\text{Tbar} = \frac{1}{A*} d \frac{A*}{d\mu} \tag{30}$$

with

A* = reciprocal of absorption factor μ = linear absorption coefficient. G is the refined parameter in the case of isotropic extinction. If the extinction is anisotropic one can choose between two models. Model 1 assumes the extinction to depend only on the mosaic spread (*type I crystal*). Using the mosaic spraed description of F.R. Thornley & R.J.Nelmes [20] G in (27) has to be replaced by

$$R* = \frac{1}{\sqrt{d^t R d}} \tag{31}$$

where **d** is a unit vector perpendicular to the plane which contains incident and diffracted beam and **dt** is its transpose. In this case the elements of the symmetric second order tensor **R** will be refined. Model 2 assumes the extinction to depend on the particle shape (i.e. the anisotropy of the domain size), whereby the natural width of the reflection from a single domain is greater than the mosaic spread. (*type II crystal*) in this case G in (27) has to be replaced by

$$R^* = \frac{1}{\sqrt{n^t Wn}} \qquad\qquad (32)$$

where **n** is a unit vector in the plane of incident and diffracted beam and perpendicular to the incident beam. **Nt** is its transpose. In this case the elements of the symmetric second order tensor W will be refined. The reference coordinate system for R and W is attached to the crystal and has its x-axis parallel to the incident beam and its z-axis vertical when all diffractometer angles are 0. Thereby it is assumed that the UB-matrix is (a) either from a Philips PW 1100 diffractometer, i.e. x is along the incident beam, y is both in the diffraction plane and the plane of the chi-circle (+y is defined so that a reflection measured at an angle $+2\theta$ lies in the +x, +y quadrant) and z is normal to x and y to yield a rigth-handed system or (b) from a diffractometer with Busing&Levy geometry, i.e. y is along the incident beam, x is both in the diffraction plane and the plane of the chi-circle (+y is defined so that a reflection measured at an angle $+2\theta$ lies in the +x, +y quadrant) and z is normal to x and y to yield a righthanded system.

Scheme of refineable parameters in Zachariasen's treatment

Case	extinction	distribution	type	parameter(s)
1	secondary	Gauss	isotropic	G
2	secondary	Gauss	anisotr.I	R11,R22,R33,R12,R13,R23
3	secondary	-	anisotr.II	W11,W22,W33,W12,W13,W23

The R_{ij} and W_{ij} parameters are printed as R^*_{ij} both, and G as R^* in the output of *REFINE*. A part of the Zachariasen formalism was implemented in the system by L.W.Finger. It was completed and generalized for easier calculation and input by U.H.Zucker.

Notes on the Zachariasen correction

There are some shortcomings in the extinction correction of Zachariasen. (1)In all types of this formalism it is assumed that primary extinction is negligible. (2) Crystals are likely to be intermediate in their type of extinction i.e. they should be described as an anisotropic general type which however is not implemented in the system. Moreover, the classification in type I and type II crystals itself is not very well defined because in the case of strong extinction at very small Bragg angles the particle size always becomes the dominant effect. (3) The expression for y shows an improper angular dependence for type II crystals, which yields wrong corrections for strong reflections at high Bragg angles. Therefore the Zachariasen correction should only be used for crystals of type I and weak extinction (y greater than 0.8). In these cases the Zachariasen correction fits the data as well as the more extended formalism of Becker & Coppens. The latter is recommended for general use.

The Becker & Coppens formalism

The total extinction correction factor y, which is applied to F_c is defined as

$$y = y_p(x_p)\ y_s(y_p(x_p)x_s) \qquad\qquad (33)$$

where y_p and y_s are the contributions to y from primary and secondary extinction resp. They are determined from the parameters x_p and x_s which are functions of the refinable parameters R and/or G and/or Z_{ij}. Y_p solely depends on the

parameter R and is calculated only in the general case (simultaneous refinement of R and G or Z_{ij}). In all the other cases y_P is set to 1.0.

The polarisation correction (including the pre-polarisation of the beam at the monochromator) is handled in a way that y_p and y_s are resolved into parallel and perpendicular components of the electric field

$$y = \frac{y_{per}\cos^2 2\theta_M + y_{per}\cos^2 2\theta}{\cos^2 2\theta_M + \cos^2 2\theta}$$ (34)

where θ_M is the Bragg angle for the monochromator.

The general formulation of y_p and y_s can be given by the following analytical expression

$$y_i = \frac{1}{\sqrt{1 + c_i\, x_i + \dfrac{A_i(\theta)x_i^2}{1 + B_i(\theta)x_i}}}$$ (35)

with i = p or s and x_p is given by..

$$x_p = k^2 \cdot \gamma_p \cdot F_c^2 \cdot R_o^2$$ (36)

with $R_o = \dfrac{R}{\lambda}$, where R is the refinable domain size parameter.

xs is given as

$$x_s = k^2 \cdot \gamma_p \cdot F_c^{\ 2} \cdot \psi$$ (37)

where ψ depends on the chosen mosaic spread distribution function. For a Gaussian distribution ψ is given by

$$\psi_G = \frac{r_o}{\sqrt{\dfrac{1 + r_o^2 \cdot \sin^2 2\theta}{G^2}}}$$ (38)

and for a Lorentzian distribution

$$\psi_L = \frac{r_o}{\sqrt{\dfrac{1 + r_o \cdot \sin 2\theta}{G}}}$$ (39)

where G is the refinable mosaic spread parameter; k is a polarisation correction term which is equal to cos2θ for the perpendicular component of the x-ray electric field, and l in all other cases.
γ_p is given by

$$\gamma_p = \frac{3\lambda^4 a^2}{2v^2}$$ (40)

and γ_s by

$$\gamma_s = \frac{\lambda^3 a^2 \text{Tbar}}{v^2}$$ (41)

with $a = \dfrac{e^2}{mc^2}$ for x-rays and a = unit scattering length for neutrons.

The c_i in (35) are constants and are equal to 2.0 except for c_s which equals 2.12 for a Gaussian distribution. The A_i and B_i are functions of the angle 2θ. A tabulation of these functions is given in /15/. To simplify the calculations a reasonable analytical evaluation of the θ dependence of A_i and B_i were evaluated in the same work. These expressions are included in the program *REFINE*.

If the extinction is anisotropic the refinable tensor **Z** resp. **E** has to be introduced. The mosaic spread is then given as

$$G = \frac{1}{\sqrt{\mathbf{d^t Z d}}} \qquad\qquad (42)$$

for a Gaussian and a Lorentzian distribution in the description of F.R.Thornley and R.J.Nelmes /20/, where **d** is the unit vector normal to the diffraction plane and $\mathbf{d^t}$ is its transpose. The particle size parameter R has to be replaced by

$$R = \frac{1}{\sqrt{\mathbf{u^t E u}}} \qquad\qquad (43)$$

whereby **u** is the unit vector along the diffracted beam and $\mathbf{u^t}$ is its transpose. Again in the necessary calculations it is assumed that the UB-matrix used is from a Philips PW 1100 diffractometer or from a diffractometer with Busing & Levy geometry (see comments in the explanation of the Zachariasen-formalism).

Practical hints on the Becker & Coppens correction

The Becker & Coppens formalism allows for 10 different ways of correcting for extinction. Basically one may refine the secondary extinction of type 1 (mosaic spread dominated) or type 2 (particle size dominated), or use a combination of both types with inclusion of primary extinction (*general case*). The options are such that one may refine either isotropically or anisotropically with the possibility of converting from one type to the other. For type I and general case refinements, the mosaic angular distribution can be chosen as either Gaussian or Lorentzian. These may be interchanged if desired.

Scheme of refinable parameters in Becker & Coppens treatment

case	extinction	distribution	type	parameter(s)
1	s	Gauss	isotrop 1	G
2	s	Lorentz	isotrop 1	G
3	s	-	isotrop 2	R
4	s,p	Gauss	iso. gnrl	R,G
5	s,p	Lorentz	iso. gnrl	R,G
6	s	Gauss	anisotr.l	Z11,Z22,Z33,Z12,Z13,Z23
7	s	Lorentz	anisotr.l	Zl 1,Z22,Z33,Z12,Z13,Z23
8	s	-	anisotr.2	Zl 1,Z22,Z33,Z12,Z13,Z23
9	s,p	Gauss	anis.gnrl	Zl 1,Z22,Z33,Z12,Z13,Z23,R
10	s,p	Lorentz	anis.gnrl	Zl 1,Z22,Z33,Z12,Z13,Z23,R

Note that the tensor of type 2 is in the PROMETHEUS output also printed with the letter Z. S and p are secondary and primary extinction resp. In all cases the parameters can be refined or fixed individually. However, dependencies are not possible in the present version.

For input and output the refinable parameters are multiplied by 10^{-4}. In the anisotropic cases, use is made of the relative vectors defining the directions of the incident and diffracted beams in real space. For this calculation the UB-

matrix (which is assumed to be from a Philips PW 1100 or a diffractometer with Busing & Levy geometry) must be given. Because anisotropic extinction needs not to be the same for equivalent reflections and for nonspherical crystals not even for Friedel reflections, this correction must be applied before the averaging procedure. In the system routine *AVERAG* the F_o are then corrected for extinction before averaging.

The extinction correction of Becker & Coppens was implemented using the coding of the ray 80 system (written by M.G.Vincent & H.D.Flack), and a damping procedure added by U.H.Zucker.

Notes and further suggestions on the Becker & Coppens correction

1. When extinction is severe, it is dominated by type 1, except for very low Bragg angles.
2. A choice between extinction dominated by type 1 or type 2 is usually possible on the basis of the R-values.
3. In the case of anisotropic extinction the quality of the extinction correction can be tested comparing the internal R-values of equivalent reflections.

4. The mosaic angular distribution seems more frequently to be Lorentzian than Gaussian.

5. The correction is accurate to within 2 per cent for crystals whose ratio of maximum to minimum dimensions is less than 2.

6. A procedure for calculating the eigenvalues of the extinction tensor is implemented. The results are put out together with the corresponding mosaic spread and particle size respectively.

7. The derivatives of the extinction parameters have been considered in the limiting case of zero extinction and are implemented in the program, i.e. one can start the refinement with zero extinction.

8. The divergence tendency in a least-squares refinement with anisotropic extinction parameters has been reduced by introducing a parameter damping routine. Physically unreasonable parameters (resulting in negative extinction corrections) will be damped with the smallest possible value (to give the fastest possible convergence).

9. The present treatment which uses the absorption weigthed mean path length Tbar as the absorption dependent parameter is exact for μr values less than about 1 (in the case of strong reflections at medium Bragg angles for μr values less than 0.25). Higher values of μr yields more and more an incorrect description of extinction in the present coding, which does not contain the absorption dependence of the A_i and B_i in (35).

10.It is advisable to measure all symmetrical equivalents of these reflections, which are most strongly influenced by extinction. This facilitates the refinement (i.e. the convergence) of anisotropic extinction parameters.

The anomalous dispersion correction

The effect of anomalous dispersion depends on the photoelectric absorption cross section. Since only the most tightly bound electrons have resonance frequencies of approximately the same magnitude as the vibrational motion imposed on an electron by x-ray photon stimulation the dispersion factors may be considered independent of the Bragg angle. Thus in practice the real and imaginary dispersion terms $\Delta F'$ and $\Delta F''$ resp. depend only on the x-ray avelength.

$$F = F(0)+\Delta F'+i\,\Delta F'' \tag{44}$$

where F is the atomic form factor. In *REFINE* anomalous dispersion terms are included in all x-ray structure factor and derivative calculations. The use of the anomalous dispersion correction terms calculated by D.T.Cromer & D.Liberman /21/, given also in a tabulation in the international tables /22/ is recommended.

The Lorentz- and polarisation correction

The $\frac{1}{LP}$ correction in the case of x-ray data resp. the $\frac{1}{L}$ correction for neutron data is carried out for each reflection individually. In case of diffractometer measurements using a crystal monochromator, the θ-value of the monochromator and the *dihedral angle* between the diffraction planes of sample crystal and monochromator must be given. Then the polarisation correction including the prepolarisation at the crystal monochromator can be calculated with the formula given by L.I.Azaroff /23/

$$P = \frac{\cos^2\delta + \sin^2\delta\cos^2 2\theta_M + (\sin^2\delta + \cos^2\delta\cos^2 2\theta_M)\cdot\cos^2 2\theta}{1 + \cos^2 2\theta} \tag{45}$$

with δ = dihedral angle
  $2\theta_M$ = scattering angle of the monochromator
  2θ = scattering angle of the reflection

The Lorentz-correction is given by

$$L = \frac{1}{\sin 2\theta} \tag{46}$$

The residual or reliability factors (*R-factors*) give the reflection-by-reflection agreement between observation and calculation. They are important criteria for both the quality of the refined model and the quality of the measurement and the corrections applied to the the reflection data. The R-factors are calculated and printed in every cycle before the calculated shifts are added to the parameters. Therefore the final R-factors must be calculated in an additional cycle omitting the least-squares procedure. The weighted R-factors are defined /24/ as

$$R_w = \sqrt{\frac{\sum w|F_o - F_c|^2}{\sum wF_o^2}} \tag{47}$$

for refinements on F_o and

$$R_w = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum wF_o^4}} \tag{48}$$

for refinements on F_o^2. The unweighted R-factor is defined as

$$R = \sum \frac{(|F_o - F_c|)}{F_o} \tag{49}$$

In addition the ranges of variation of F_o and $\frac{\sin(\theta)}{\lambda}$ are each divided into eight subranges and the sums needed for the eight *interval R-factors* are accumulated in the subroutine RCALC. If the weighting scheme is correct, the expression $\frac{1}{m}\sum w(F_o - F_c)^2$, where the sum is taken over a subset of the full data set containing m reflections, should be independent of the composition of the subset. $R_{intervall}$ is calculated as follows

$$R_{intervall} = \frac{\frac{1}{m}\sum w(F_o - F_c)^2}{\frac{1}{n}\sum w\, F_o^2} \qquad (50)$$

where n is the total number of reflections in the data set. $R_{intervall}$ can be considered as the average contribution to R_w from the reflections in each subset. The $R_{intervall}$-factors of the 8 subsets in F_o resp. $\frac{\sin\theta}{\lambda}$ are printed in addition to the above mentioned R-factors every cycle (except before the first cycle). The use of significance-test on the R-factors is recommended to all users who want to know whether a structure model A yields a significantly lower R-factor than a structure model B. The use of two different tests is suggested depending on the kind of problem. If two models with different numbers of parameters are compared, the R-factor test of W.C.Hamilton /24,25/ is appropriate. For models with the same number of parameters the *jack-knive* test /26/ can be used.

The goodness-of-fit

The estimated standard deviation of an observation of unit weight is a measure of the goodness of fits /27/

$$S = \sqrt{\frac{\sum w(F_o - F_c)^2}{hkl - n}} \qquad (51)$$

where   hkl   =   number of reflections
                  n   =   number of independent parameters
therefore   hkl−n   =   number of degrees of freedom

The goodness-of-fit S should have a value close to 1, if both the weighting scheme and the chosen model are correct. For a complete and correct structure model the deviation of S from 1 is a measure of the validity of the weight assignement. A quantitative comparison is possible via the statistical χ^2. The expected values of S^2 are given by a reduced χ^2 distribution

$$\chi^2_{red,p}(hkl - n) = \frac{\chi^2_p}{hkl - n} \qquad (52)$$

where p is a probability point of the χ^2 distribution. Then the *confidence intervals* can be obtained

$$U_p = \sqrt{\frac{S^2}{\chi^2_{red,p}}} \qquad (53)$$

$$U_{p-1} = \sqrt{\frac{S^2}{\chi^2_{red,1-p}}} \qquad (54)$$

A goodness-of-fit within these limits means that the chosen weight assignement is correct with a probabiltiy of p (a correct structural model supposed). A new tabulation of the confidence intervals for hkl−n between 10 and 10000 is given in Appendix B.

The weights

The method of least-squares is based on the hypothesis, that the best description of a dataset is one which minimizes the w e i g h t e d sum of squares of deviations of the observed data from the calculated data. Therefore it is important to use the correct weigths for the calculations. Apart from initial refinements (where it is sometimes helpful for getting a better convergence) the use of unit weights is a bad choice. At least in the
final stages of a structure refinement the weights must reflect the accuracy of the data. The best choice of weights yielding parameters of the lowest variance is

$$w = \frac{1}{(\sigma(F_o))^2} \tag{55}$$

when refining on F_o and

$$w = \frac{1}{(\sigma(I_o))^2}$$

when refining on $F_o{}^2$

where $\sigma(F_o)$ and $\sigma(I_o))$ is the standard deviation of F_o and the scaled intensity I_o resp. correct $\sigma(I_o)$ can be calculated from the standard deviation of repeated intensity measurements of one reflection. In the case of a spherical crystal and negligible anisotropy of extinction, the intensity measurements of symmetry related reflections can be treated as repeated measurements of one reflection. In other cases where the true standard deviations are not known, the estimated standard deviation (*esd*) of the intensities obtained from counting statistics can be used. Especially in the case of strong reflections these esd s should be altered by a so-called *ignorance factor* /28/ to obtain a better estimation of σ (i_o)

$$\sigma(I_o) = sqrt(esd(I_o)^2 + p^2\, I_o{}^2) \tag{56}$$

where   p = ignorance factor (ca.0.01 - 0.05)

Using the true or estimated $\sigma(I_o)$ the corresponding $\sigma(F_o)$ can be calculated according to B.Rees /29/.

$$\sigma(F_o) = \frac{\sigma(I_o)}{2F_o} \quad \text{if } I_o \text{ greater than } \sigma(I_o) \tag{57}$$

$$\sigma(F_o) = \frac{\sqrt{\sigma(I_o)}}{2} \quad \text{if } I_o \text{ less equal } \sigma(I_o) \tag{58}$$

Then the weights can be calculated according to (55). A test on the validity of the weight assignment can be done via the goodness-of-fit. It is adviseable to check further if the weighted sum of differences F_o–F_c has constant averages in groups of increasing F_o resp. $\frac{\sin(\theta)}{\lambda}$. This can be tested via the interval R-value. If the structural model and the weights are correct, the average value of $w(F_o–F_c)$ must be independent of the subset over which the average is calculated. If not so, either the model or the weight assignement should be changed. However an application of weighting schemes which forces constant averages over $w(F_o–F_c)$ should be done with great care. This artificial weighting may have drastic effects on the scale and thermal parameters of the structure model (but it is less important for the coordinates). In addition the use of incorrect weights can easily falsify the calculated variances of the structure parameters by 10 p.c. or even more. It is wise to introduce such weighting schemes only in cases, where one can be sure that the reasons or the deviations are not caused by an incorrect structural model.

The weight assignement may be examined in a more detailed way by looking at the distribution of $w(F_o-F_c)$ of each reflection by calculation of *normal probability plots* in which the differences are compared with the theoretical value for a standardized normal distribution /30/.

The partial structure factor

The calculation of *partial* Fourier maps using *partial* structure factors may be useful in some cases for a better presentation of results. Only a set of (one or more) selected atoms will constribute to the calculated densities
In addition the series termination effects will be reduced to some extend.
The partial structure factor is calculated using a structural model with omission of the selected atom(s). This structure factor is written on the Fourier file instead of F_c and a subsequent calculation of a difference Fourier synthesis is actually the wanted partial fourier map. However a serious problem arises due to the incertainity in the phase factor. The phase factor actually used in the fourier summation is the phase of the complete structural model. This choice may be incorrect even in centrosymmetric structures and it is very doubtful in non centrosymmetric cases. Therefore partial fourier maps should be calculated only, if the phases of the remaining (not omitted) part is in sufficient agreement with the phases of the complete structural model.

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SPHERE

This program calculates the absorption factor a* and the absorption weighted mean path length Tbar for a spherical crystal. The values are computed by interpolating table values.

Tables of a* and tbar as a function of μ r (linear absorption coefficient× radius of the crystal) and $\frac{\sin\theta}{\lambda}$ are included in the program. The table of a* contains values of high precision obtained by C.W.Dwiggins /1/ and H.O. Flack and G.Vincent /2/.

Since the approximate formula for the absorption weighted mean path length

$$\text{Tbar} = \frac{\ln(a*)}{\mu}$$

is inappropriate for values of μ r greater than 0.25 (P.J.Becker and P.Coppens, /3/), a second table contains the correct values of tbar. They were calculated from the values of a* using the correct formula

$$\text{Tbar} = \frac{1}{a*} \frac{d(a*)}{d(\mu)}$$

(d means differentiation) with the program SPHCOR written by H.O.Flack and M.G.Vincent/4/

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TDSCOR

This program performs the correction of isotropic thermal diffuse scattering of first order using the formalism of Skelton and Katz /1/. For this correction the elastic constants (stiffness or compliance tensor) or the mean squared sound velocity of the substance must be known.

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