

The determination of hydrogen positions in materials was of such interest to ORNL crystallographers that a separate program was established in the Chemistry Division under Henri Levy to study hydrogen bonding in crystals. Levy and Selmer Peterson were pioneers in developing the neutron scattering technique for detailed structural analysis of single crystals. William Busing, Harold Smith, Ray Ellison, Dan Danford, George Brown, Carroll Johnson, Paul Agron, Bill Thiessen, and Al Narten joined the Chemistry Division program later and developed a very strong program in X-ray crystallography.

Henri A. Levy - President of ACA, 1965

William R. Busing - President of ACA, 1971

Carroll Johnson - President of ACA, 1977



Levy at the Picker 4-circle diffractometer

Crystallography programs
ORFLS
ORTEP and others

This Week's Citation Classic

**Busing W R, Martin K O & Levy H A. *OR FLS, a FORTRAN crystallographic least-squares program.* Oak Ridge, TN: Oak Ridge National Laboratory, August 1962, ORNL-TM-305. 75 p.
[Chemistry and Mathematics Divisions, Oak Ridge National Laboratory, Oak Ridge, TN]**

This report describes a computer program to perform the least-squares refinement of crystal structure parameters based on x-ray or neutron diffraction measurements. The program is written mostly in the FORTRAN language to facilitate modification and to permit its use on various machines. Detailed instructions for its use are included, and the required card decks may be obtained from the authors. [The *SCI*[®] indicates that this paper has been cited over 3,035 times since 1962.]

“Crystallographers measure the intensities of many x-ray or neutron reflections from a crystal (sometimes several thousand) and use various techniques to deduce the approximate atomic arrangement. Finally, the structure is refined by adjusting the coordinates of the atoms and parameters which describe their thermal motion so as to produce the best agreement between observed and calculated intensities. Our 1962 report describes a least-squares computer program for performing this refinement.

William R. Busing
Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, TN 37830

"I arrived at Oak Ridge National Laboratory in 1954 and began learning crystallography, neutron diffraction, and computing from Henri Levy. We had access to the ORACLE, a vacuum tube computer with 1,024 40-bit words of cathode-ray tube memory and paper tape input and output. Programming was done in hexadecimal machine language. We wrote a least-squares program to refine the two coordinates and six temperature factors of calcium hydroxide¹ based on 53 neutron diffraction intensities. We then generalized this program to handle other problems under study at Oak Ridge. It was capable of adjusting a maximum of 30 parameters, and when they doubled the memory to 2,048 words, we were able to increase this number to 54.

"Following the acquisition of an IBM 704 with 8 k words of memory in 1957, we re-wrote the program for that machine using assembly language. A computing conference at the National Bureau of Standards in November of that year made it clear that many crystallographers had access to this machine, so we made binary card decks available to them and wrote a report² with instructions for its use.

"In 1961, with the arrival of the IBM 7090, and with other computers on the horizon, it became apparent that it would be worth rewriting the program in FORTRAN. Kay Martin of the mathematics division worked closely with us and did the actual programming and testing. Again, a report was written to provide instructions, and this is the work which has been highly cited. The program has been greatly improved by various users so that the present version lists nine coauthors. It is often used to adjust from 200 to 400 parameters. Instructions are now included as part of the source program, so the users generally identify it by citing the 1962 report. Apparently it has been successful because it is a versatile program with test examples and clear instructions, and because it performs a job which is routinely needed.

Commun. ACM 5(8):

445-446 (1962)

[Association for
Computing Machinery]

A Procedure for Inverting Large Symmetric Matrices

By WILLIAM R. BUSING AND HENRI A. LEVY

Chemistry Division, Oak Ridge National Laboratory,
Oak Ridge, Tennessee*

We are solving for changes in parameters. Remember that F_i^c is the i^{th} calculated structure factor for a given set of trial atom parameters (eg 200) and F_i^o is the magnitude of the structure factor as actually observed. In a typical modern structure analysis there may be many thousand observed structure factors (eg 2000). The elements of the matrix \mathbf{D} are simply the derivatives of each structure factor with respect to each parameter. That is:

$$D_{ij} = \frac{\partial F_i}{\partial p_j}$$

$$\Delta \mathbf{p} = (\mathbf{D}^T \mathbf{D})^{-1} \mathbf{D}^T (\mathbf{F}^c - \mathbf{F}^o)$$

$\Delta \mathbf{p}$	=	$(\mathbf{D}^T \mathbf{D})^{-1}$	\mathbf{D}^T	$(\mathbf{F}^c - \mathbf{F}^o)$
200x1		200x200	200x2000	2000x1

Even for a medium structure most time is spent doing the multiplication of matrix \mathbf{D} times its transpose. There are 200 by 200 elements of this (only half independent) and each is a sum of 2000 products.

Choleski inversion routine (used by Levy):

Every symmetric matrix that is positive definite can be written as a product of a lower triangular matrix times its transpose ($D^T D$ is symmetric, why?).

$$D^T D = L L^T$$

So we find and store L

There is a straight forward process to invert a lower triangular matrix.

So we find and store L^{-1}

Premultiply L^{-1} by its transpose to get the inverse of S

$$(D^T D)^{-1} = (L^{-1})^T L^{-1}$$

In the least squares handout we showed that the variance-covariance matrix is given by

$$\mathbf{S} = \left(\frac{\mathbf{R}}{n - m} \right) (\mathbf{X}^T \mathbf{X})^{-1}$$

$$\mathbf{S} = \{s_{ij}\}$$

That is, it is just related to the inverse matrix of the product of derivatives multiplied by a scale factor (the agreement factor divided by the number of observations minus the number of variance parameters). The elements of this matrix are used to calculate the errors in values derived from the refined parameters (such as bond lengths and angles).

$$s_{ij} = \sigma_i \sigma_j c_{ij} = \text{covariance (or variance) of parameters } i \text{ and } j$$

The general equation for an error in a function f calculated from n uncorrelated variables x_1, x_2, \dots, x_n is $\sigma_f = \left[\sum_{j=1}^n \left(\frac{\partial f}{\partial x_j} \right)^2 \sigma_j^2 \right]^{1/2}$

You can write this as a matrix/vector equation:

$\sigma^2(f) = \mathbf{d}^T \mathbf{S} \mathbf{d}$, where $d_j = \delta f / \delta x_j$ and \mathbf{S} is the diagonal matrix of variances. In general s_{ij} is the i, j^{th} element of the variance/covariance matrix and this equation then includes correlation between the positional or other refined parameters.

TABLE 18.1 Normal Distribution^a

p	λ	p	λ
1.00	0.000	0.30	1.04
0.90	0.126	0.20	1.28
0.80	0.253	0.10	1.65
0.70	0.385	0.05	1.96
0.60	0.524	0.01	2.58
0.50	0.674	0.001	3.29
0.40	0.842	0.0001	3.89

^aThe probability that a quantity x differs from its mean value in either direction by more than $\lambda\sigma$ is equal to p .

Some rules of thumb:

If difference is less than σ , not significant

If difference is between one and two σ , maybe significant

If difference is greater than three σ , significant.

**Bond distance.
What does it mean?
How reliable?
Estimated error?**

Your structure has a resolution of 1 Å from data at 125 K and the error a C-N bond distance found to be 1.166 Å has a listed error of 0.002 Å. You explain to Dr. Hollander that this is evidence for π back bonding in your cyanide structure and he snorts at you. Why?

The refined P-F bond distance in your PF_6 salt are all shorter than expected. Due to lattice packing?

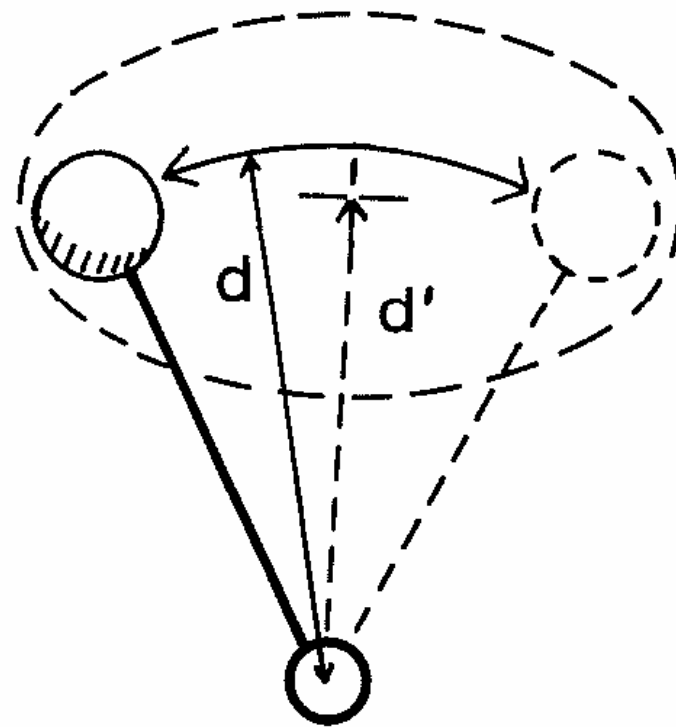


Fig. 12.1. Illustration of the apparent shortening of a bond length by strongly anisotropic vibration.

- What is the Mn-F₁ distance and error?
- What is the Mn-F₂ distance and error?
- What is the trans F₂-F₂ distance and error?
- What is the trans F₁-F₁ distance and error?

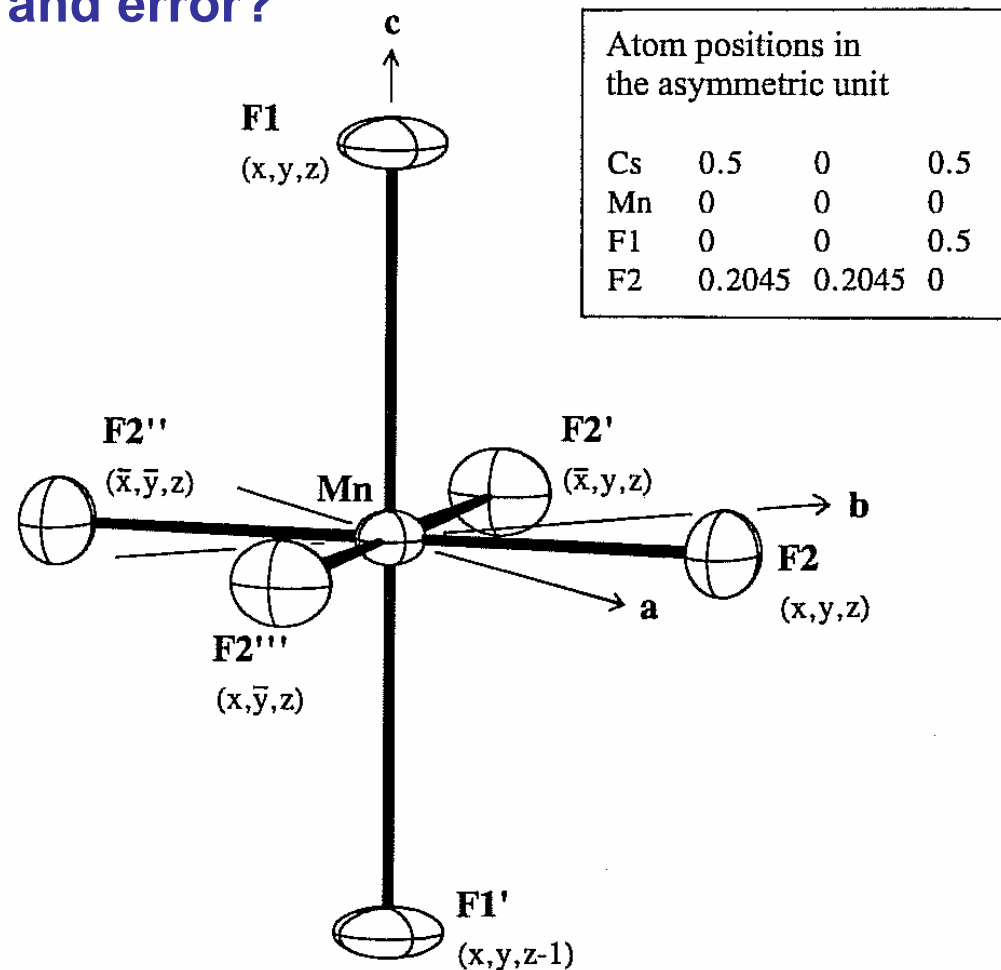


Fig. 12.4. Illustration of symmetry-equivalent positions in an $[\text{MnF}_6]^{3-}$ ion in Cs_2MnF_5 , space group $P4/mmm$, $a = 6.420$, $c = 4.229$ Å.

Bond angle.
Least squares plane (weighted).
Dihedral angle
Torsion angle
Ring midpoint

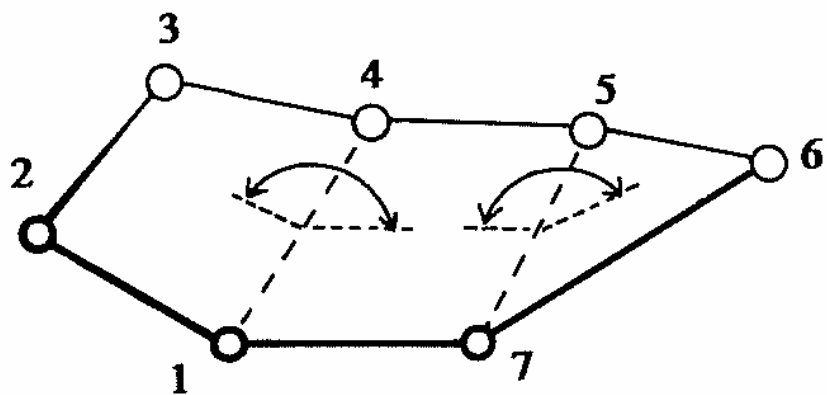


Fig. 12.2. Folding angles in a seven-membered ring.

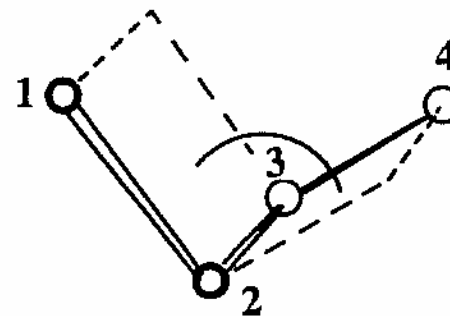


Fig. 12.3. The definition of a torsion angle.

Anomalous scattering and chirality

How do we know the chirality of a chiral crystal structure?

$$f_o^{\text{anom}} = f_o + \Delta f' + i \Delta f'' = f' + i \Delta f''$$

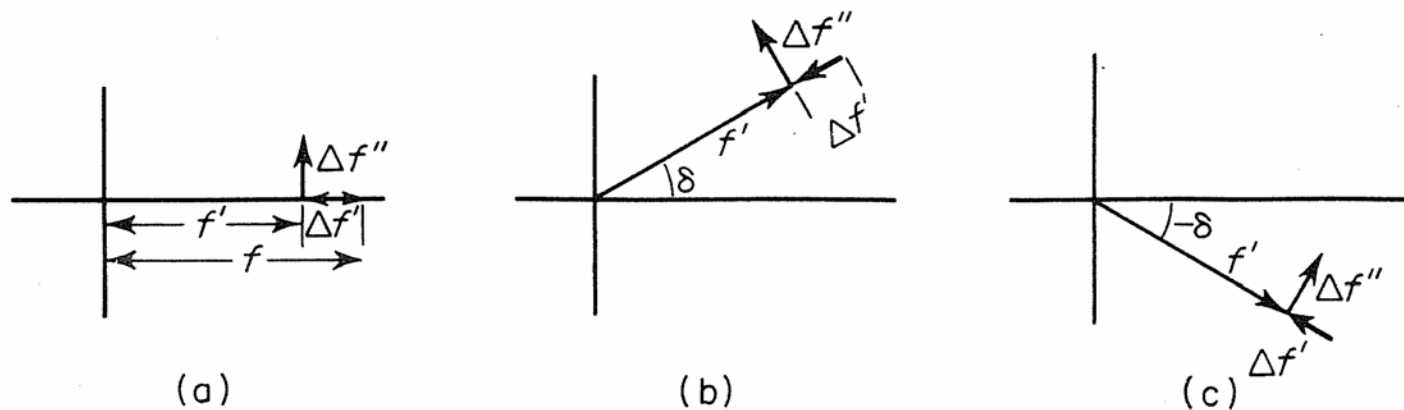


Figure 8.11. Vector representation of f , $\Delta f'$, and $\Delta f''$ for an atom showing anomalous scattering. (a) At the origin; (b), (c) at other positions in the unit cell.

Anomalous scattering is X-ray wavelength dependent
 Discontinuity at absorption maximum
 Note that the imaginary term is not dependent on $\sin\theta/\lambda$
 so relative importance increases with $\sin\theta/\lambda$

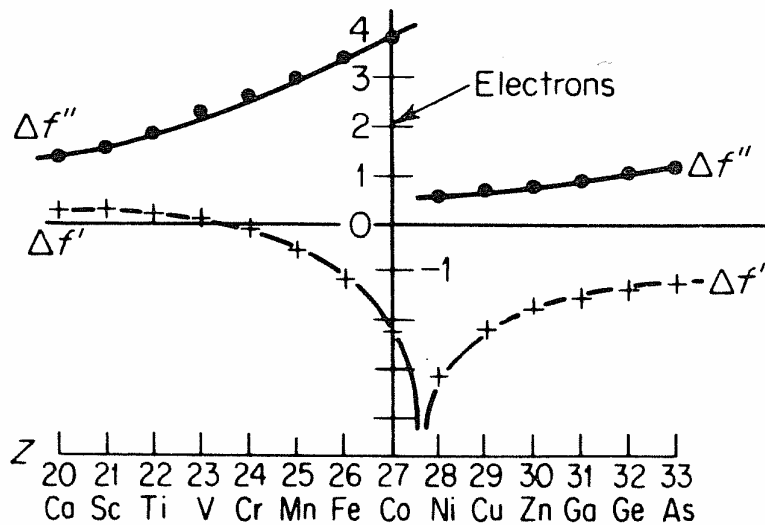


Figure 8.12. $\Delta f'$ (+) and $\Delta f''$ (·) plotted as a function of atomic number for Cu K_α radiation.

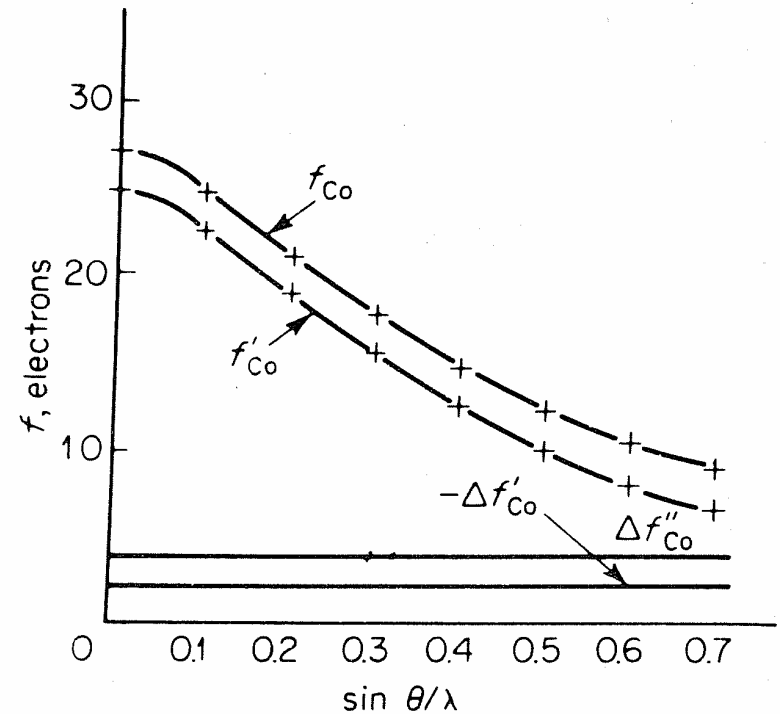
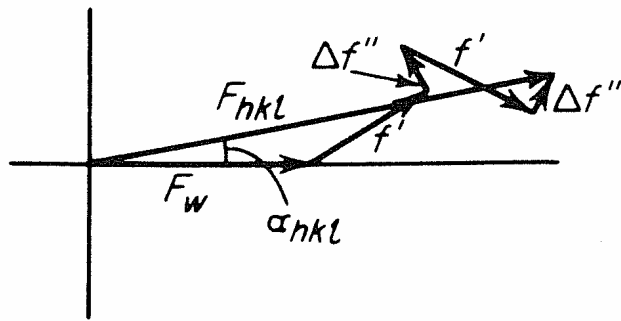
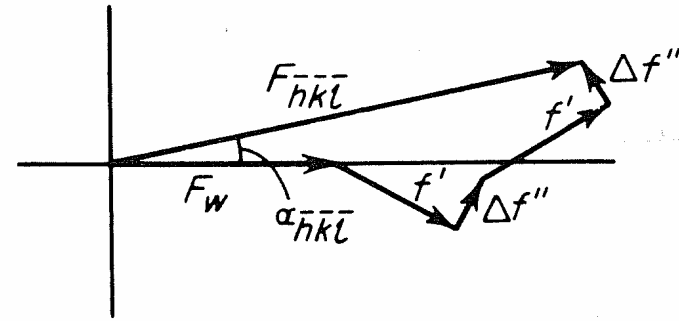


Figure 8.13. f_{Co} , f'_{Co} , $-\Delta f'_{Co}$, and $\Delta f''_{Co}$ for Cu K_α radiation as functions of $(\sin\theta)/\lambda$.



(a)



(b)

Figure 8.14. Vector representation showing anomalous scattering for a Friedel pair in a centrosymmetric structure; $F_{hkl} = F_{\bar{h}\bar{k}\bar{l}}$.

Note:

If F_w is the scattering from all the atoms with no anomalous scattering consider what happens when there is one additional atom that has anomalous scattering. The scattering from the two inversion related atoms reflects the f' across the real axis, so the vertical components cancel. But the $\Delta f''$ term, at a left 90 degree angle from the f' scattering, does not have the vertical components cancel.

F now has an imaginary component (i.e. the phase angle is not just 0 or π)

But the Friedel pairs still have exactly the same magnitude

The Flack (or perhaps better, Rogers') parameter, η :

Using the known anomalous scattering factors for the atoms in the structure, add another variable to enable the change of sign of all the $\Delta f''$ values. Changing η from +1 to -1 is equivalent to changing the chirality of the structure.

$$f_o^{\text{anom}} = f_o + \Delta f' + i\eta \Delta f''$$

[Stout and Jensen]

Refinement of η is expected to tend strongly to +1, indicating that the model has the correct hand, or -1, indicating that it needs to be reversed. The method appears to be very successful and is being increasingly incorporated into refinement programs.²⁵ It has the particular advantage of being little affected by the details of experimental conditions, even including uncorrected absorption.^{26,27}

G. Bernardinelli and H. D. Flack, *Acta Cryst.* (1985). A41, 500-511
H. D. Flack, *Acta Cryst.* (1983). A39, 876-881