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Phase Determination and Patterson Maps from Multiwavelength Powder Data

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Dedicated to Professor K. Fischer on the occasion of his 65th birthday.

Abstract

In the limit of unrestricted resolution, with Friedel pairs as the only coincidences, phase angles or signs can be determined uniquely from powder diffraction data using multiple-wavelength techniques. For a centrosymmetric structure one anomalously scattering species of atoms and data taken at two λ 's are sufficient. In the acentric case one needs two different anomalous scatterers and measurements at three λ 's. The anomalous scatterers can be localized from difference Patterson maps: their peaks can be discriminated against the peaks due to non-anomalous scatterers.

I. Introduction

Anomalous scattering effects in X-ray powder data have been taken into account so far mostly as corrections of the form factor for the profile refinement,

e.g. in the program by Young, Mackie & Von Dreele (1977). In a powder diagram reflections H and $-H$ coincide exactly. Bijvoet differences as well as Bijvoet ratios can therefore not be determined from powder data, and so all methods of phase determination based on either quantity cannot be applied. Another practical restriction of the powder method at conventional X-ray sources has been the limited resolution which causes, in addition to the Friedel pairs, further coincidences. The availability of high-resolution powder diffractometers at synchrotron X-ray sources has improved the experimental situation in several respects:

(i) The resolution has been improved substantially above conventional diffractometers: line widths (FWHM) of $\Delta(2\theta) \leq 0.025^\circ$ in $30 \leq 2\theta \leq 80^\circ$ have been reported by Wroblewski, Ihringer & Maichle (1988). Reinhardt (1989) found these line widths smaller by a factor ≈ 5 than corresponding values from a high-resolution Guinier diffractometer.

(ii) The continuous spectral distribution of a synchrotron source makes it necessary in any case to select one energy/wavelength by a monochromator, and the inherent good collimation of the source $(\Psi^2)^{1/2} \approx 0.1$ mrad provides for a narrow spectral resolution of the monochromatic beam as long as monochromator crystals with a sufficiently small mosaic angle η are used. So one of the components λ/n in the monochromatic beam may be chosen to be close to the absorption edge of the atoms in the sample in many cases.

(iii) Ideal crystals are not needed. Freund (1988) discusses the possibilities of applying mosaic crystals as monochromators at synchrotron sources. Schneider, Goncalves, Rollason, Bonse, Lauer & Zulehner (1988) report the improvement of the reflectivity of silicon crystals containing small amounts of oxygen.

(iv) A λ/n contribution in the polychromatic 'monochromatic' beam may be used also as a non-resonant reference radiation. Polychromatic powder diagrams have been taken simultaneously at up to three different wavelengths by Limper, Ihringer, Knorr, Prandl & Wroblewski (1989).

With these experimental advances at hand multiple-wavelength methods for powders will be discussed in the present paper for phase-angle determination as well as for Patterson methods. For the single-crystal case, phase-angle determination with two wavelengths has been reviewed recently by Klop, Krabbendam & Kroon (1989). Fischer (1987) discusses difference Patterson functions calculated from single-crystal data taken at three or four wavelengths as the 'lambda technique'. Ramachandran & Srinivasan (1970) cover the earlier literature in a comprehensive way.

II. Notation, abbreviations

a.s., a.s.a., a.s. σ	anomalous scatterer, anomalously scattering atom, anomalously scattering atom of the chemical species σ
$g * f$	convolution of g and f
$f_s \equiv f_{os}$	form factor for normal scatterers; $s = 1, \dots, N$
$f_\sigma = f_{o\sigma} + \Delta'_\sigma + i\Delta''_\sigma$	form factor for the a.s. of type σ ; $\sigma = 1, \dots, \Sigma$
$f_{os}, f_{o\sigma}$	high-energy limit of the form factors: $E \gg E_K$
$\delta_\sigma^2 = \Delta_\sigma'^2 + \Delta_\sigma''^2$	squared 'length' of the anomalous contribution to f_σ . $\Delta'_\sigma, \Delta''_\sigma$ and δ_σ depend on λ
T_s, T_σ	isotropic temperature factor for normal and anomalous scatterers
$\hat{x} = x \cdot T$	the caret $\hat{}$ above a variable x stands for the product $x \cdot T$. Here $x = f_{os}, f_{o\sigma}, \Delta'_\sigma, \Delta''_\sigma, \delta_\sigma$
$\mathbf{r}_{si}, \mathbf{r}_{\sigma j}$	position vectors for normal and anomalous scatterers, respectively

$$F_{o\pm} \equiv F(\pm \mathbf{H}) = A \pm iB \\ = |F_o|(\cos \Phi \pm i \sin \Phi) \\ F_{\sigma\pm} = F_\sigma(\pm \mathbf{H})$$

$$R_\sigma + iJ_\sigma = L_\sigma (\cos \Psi_\sigma + i \sin \Psi_\sigma)$$

$$= \sum_{j=1}^{N_\sigma} \exp 2\pi i \mathbf{H} \mathbf{r}_{\sigma j} \\ L_\sigma^2 = R_\sigma^2 + J_\sigma^2 \\ \tan \Psi_\sigma = J_\sigma / R_\sigma$$

N_σ

ρ
 $\rho_{K\sigma}, \rho_s$

$$I_o = |F_{o+}|^2 + |F_{o-}|^2$$

$$I_\sigma = |F_{\sigma+}|^2 + |F_{\sigma-}|^2$$

$P_o(\mathbf{u})$

$P_\sigma(\mathbf{u})$

$\Pi_\sigma(\mathbf{u})$

$\mathcal{F}_-\{\dots\}$

structure factors in the high-energy limit
structure factors with anomalous contribution due to a.s.
 σ
trigonometric part of the structure factor for the a.s. atoms

$L_\sigma \geq 0$

Ψ_σ : phase angle of the a.s. atoms

number of sites occupied by the a.s. σ

electron density of the crystal atomic K -shell density, total atomic electron density

intensity=integrated intensity of a powder line $|\mathbf{H}|$ corrected with the appropriate Lorentz, polarization and absorption factors. See § VII, *Scaling*.

Patterson density of the crystal structure calculated from non-resonant intensities.

Patterson density of the crystal structure from data containing contributions due to a.s. σ .

Patterson density of the a.s. σ , calculated for pointlike atoms.

Fourier inversion

III. The calculation of phase angles from powder data

In the high-energy limit $E \rightarrow \infty, \lambda \rightarrow 0$ with no anomalous dispersion effects the structure factors are given by

$$F_{o\pm} = \sum_{si} \hat{f}_{os} \exp(\pm 2\pi i \mathbf{H} \mathbf{r}_{si}) \\ = |F_o| \cos \Phi \pm i |F_o| \sin \Phi. \quad (1)$$

Here the quantities \hat{f}_{os} are form factors including an (isotropic) temperature factor

$$\hat{f}_{os} = f_{os} \cdot T_s. \quad (2)$$

The same notation will be used for the anomalous parts $\Delta'_\sigma, \Delta''_\sigma$. Close to the K, L, \dots absorption edges of the atoms of type σ the structure factor is modified to

$$F_{\sigma\pm} = F_{o\pm} + (\hat{\Delta}'_\sigma + i\hat{\Delta}''_\sigma)(R_\sigma \pm iJ_\sigma). \quad (3)$$

In a powder diagram the intensities without and with the inclusion of anomalous contributions, I_o and I_σ , respectively, are

$$I_o = 2|F_o|^2 \quad (4)$$

$$I_\sigma = 2|F_o|^2 \{1 + 2\hat{\Delta}'_\sigma (R_\sigma / |F_o|) \cos \Phi \\ + 2\hat{\Delta}''_\sigma (J_\sigma / |F_o|) \sin \Phi + \hat{\delta}_\sigma^2 (L_\sigma^2 / |F_o|^2)\}. \quad (5)$$

I_o and I_σ are directly accessible from the scaled (§ VII) integrated intensities of single powder lines

after the usual corrections: Lorentz, polarization factors, multiplicity and absorption. We write R_σ and J_σ in terms of L_σ and the angles Ψ_σ and obtain the differences

$$I_\sigma - I_o = 4|F_o|L_\sigma\hat{\Delta}'_\sigma (\cos \Psi_\sigma \cos \Phi + \sin \Psi_\sigma \sin \Phi) + 2\hat{\delta}_\sigma^2 L_\sigma^2. \quad (6)$$

We assume at the present stage that the atomic positions $\mathbf{r}_{\sigma i}$ are known (see § VI for the determination of $\mathbf{r}_{\sigma i}$). With this assumption the L_σ and Ψ_σ can be calculated.

Defining intensity ratios

$$r_\sigma = I_\sigma / I_o, \quad (7)$$

we arrive from (6) at an equation for the differences between the unknown and the known angles, Φ and Ψ_σ , respectively:

$$\cos(\Phi - \Psi_\sigma) = X_\sigma \quad (8)$$

with

$$X_\sigma = \frac{|F_o|}{2L_\sigma\hat{\Delta}'_\sigma} \left(r_\sigma - 1 - \hat{\delta}_\sigma^2 \frac{L_\sigma^2}{|F_o|^2} \right). \quad (9)$$

IV. Centrosymmetric structures

For centrosymmetric structures the problem simplifies appreciably, since only the phase angles 0 and π may occur. Therefore

$$\left. \begin{array}{l} \cos \Phi = s = \pm 1 \quad \cos \Psi_\sigma = s_\sigma = \pm 1 \\ \sin \Phi = 0 \quad \sin \Psi_\sigma = 0. \end{array} \right\} \quad (10)$$

The signs $s \equiv s(\pm \mathbf{H})$ are given from (9) by

$$s = \frac{|F_o|}{2R_\sigma\hat{\Delta}'_\sigma} \left(r_\sigma - 1 - \hat{\delta}_\sigma^2 \frac{R_\sigma^2}{|F_o|^2} \right). \quad (11)$$

On the r.h.s. of (11) all quantities are known either from tables ($\hat{\Delta}'$, $\hat{\delta}_\sigma^2$) or from two measurements at λ_o and λ_σ . The unknown temperature factors T_σ contained in $\hat{\Delta}'_\sigma$ and $\hat{\delta}_\sigma^2$ may be approximated by an overall temperature factor which can be estimated by, for example, Wilson's method. For a centrosymmetric structure the phase or sign problem can, therefore, be solved uniquely from two powder diagrams taken at the appropriate wavelengths using only one type of a.s. atom. Actually, (11) can be simplified further by using only the signs of the relevant terms:

$$s = \text{sign}(R_\sigma) \text{sign}(\hat{\Delta}'_\sigma) \times \text{sign}[r_\sigma - 1 - \hat{\delta}_\sigma^2(R_\sigma^2/|F_o|^2)]. \quad (12)$$

This simplification can, of course, be expected to give correct results only as long as $|s| \approx 1$ from (11). With only one a.s.a. located in the inversion center $\bar{1}$ at $\mathbf{r} = \mathbf{r}_{\sigma 1} = \mathbf{0}$ one further obtains $\text{sign}(R_{\sigma 1}) = 1$.

V. Acentric structures

It is clear from (8) that with a single type of a.s. $\sigma = 1$ the phase angles are not unique since

$$\Phi = \Psi_\sigma \pm \arccos(X_\sigma). \quad (13)$$

If only one a.s. atom is present in the unit cell we are free to choose its position in $\mathbf{r}_{\sigma=1} = \mathbf{0}$. Then all $\Psi_\sigma \equiv 0$ and $\Phi = \pm \arccos X_\sigma$. In this case only the real parts of the structure factors

$$A(\mathbf{H}) = |F_o(\mathbf{H})| \cos \Phi(\mathbf{H}) \quad (14)$$

are uniquely determined from the experimental data and may be used for the calculation of the superimposed Fourier densities $\bar{\rho}$ with

$$\bar{\rho}(\mathbf{r}) = \rho(\mathbf{r}) + \rho(-\mathbf{r}). \quad (15)$$

In other words, with only one a.s. a centrosymmetric solution made up of the density and its inversion image is obtained for an acentric crystal.

The complete solution of the phase problem in the acentric case can be obtained if at least two (or more) different types of a.s. atoms are at hand. In this case (6) and (9) can be expressed as

$$\cos \Psi_\sigma \cos \Phi + \sin \Psi_\sigma \sin \Phi = X_\sigma \quad \sigma = 1, 2 \quad (16)$$

which can be solved for $\sin \Phi$ and $\cos \Phi$ provided the determinant of (16), $\det = \sin(\Psi_2 - \Psi_1)$, is nonzero:

$$\begin{aligned} \begin{vmatrix} \cos \Phi \\ \sin \Phi \end{vmatrix} &= [\sin(\Psi_2 - \Psi_1)]^{-1} \\ &\times \begin{vmatrix} \sin \Psi_2 & -\sin \Psi_1 \\ -\cos \Psi_2 & \cos \Psi_1 \end{vmatrix} \begin{vmatrix} X_1 \\ X_2 \end{vmatrix}. \end{aligned} \quad (17)$$

For three or more different types of a.s. atoms (16) is overdetermined. In this case a least-squares solution is appropriate. It should be emphasized that varying Δ'_σ , Δ''_σ of only one type of a.s. by fine tuning of λ_σ close to the absorption edge would make the matrix of (16) singular with no chance for a solution for both $\cos \Phi$ and $\sin \Phi$.

VI. Patterson maps from powder data: the localization of the anomalous scatterers

From a completely resolved powder diagram taken in the high-energy limit we can calculate the usual Patterson density by Fourier inversion:

$$\begin{aligned} P_o(\mathbf{u}) &= \sum_{\mathbf{H}} |F_o(\mathbf{H})|^2 \cos(2\pi\mathbf{H}\mathbf{u}) \\ &= \sum_{\mathbf{H}} I_o(\mathbf{H}) \cos 2\pi\mathbf{H}\mathbf{u} \equiv \mathcal{F}_- \{I_o\}. \end{aligned} \quad (18)$$

We rewrite the intensity differences (6) slightly:

$$I_\sigma - I_o = 4[A(\mathbf{H})\hat{\Delta}'_\sigma R_\sigma(\mathbf{H}) + B(\mathbf{H})\hat{\Delta}'_\sigma J_\sigma(\mathbf{H})] + 2\hat{\delta}_\sigma^2 L_\sigma^2(\mathbf{H}). \quad (19)$$

Since $A(\mathbf{H})R_\sigma(\mathbf{H})$, $B(\mathbf{H})J_\sigma(\mathbf{H})$ and $L_\sigma^2(\mathbf{H})$ are symmetric under the inversion $\mathbf{H} \rightarrow -\mathbf{H}$, the Fourier inversion of (19) is real, and contains essentially two different contributions $T_{\sigma_1}(\mathbf{u})$ and $T_{\sigma_2}(\mathbf{u})$:

$$\mathcal{F}_-\{I_\sigma - I_o\} \equiv P_\sigma(\mathbf{u}) - P_o(\mathbf{u}) = T_{\sigma_1}(\mathbf{u}) + T_{\sigma_2}(\mathbf{u}) \quad (20)$$

$$T_{\sigma_1}(\mathbf{u}) = \mathcal{F}_-\{4\hat{\Delta}'_\sigma[A(\mathbf{H})R_\sigma(\mathbf{H}) + B(\mathbf{H})J_\sigma(\mathbf{H})]\} \quad (21)$$

$$T_{\sigma_2}(\mathbf{u}) = \mathcal{F}_-\{2\hat{\delta}_\sigma^2 L_\sigma^2(\mathbf{H})\}. \quad (22)$$

In (22) the terms $2\hat{\delta}_\sigma^2 L_\sigma^2(\mathbf{H})$ are the powder intensities of a - fictitious - structure consisting only of a.s. σ . In addition, because of the $\hat{\delta}_\sigma$ term, only the K - (or L -, depending on λ_σ) shell scattering contributes. Therefore,

$$T_{\sigma_2}(\mathbf{u}) = (\rho_{K\sigma} * \rho_{K\sigma}) * \Pi_\sigma(\mathbf{u}). \quad (23)$$

Since $R_\sigma + iJ_\sigma$ is the structure factor of the anomalous structure taken with point-like atoms, $\Pi_\sigma(\mathbf{u})$ is made up of δ peaks. The peaks in $T_{\sigma_2}(\mathbf{u})$ are autoconvolutions of the K - (L -)shell densities.

To understand $T_{\sigma_1}(\mathbf{u})$ we rewrite the r.h.s. of (21)

$$\begin{aligned} & \hat{\Delta}'_\sigma(AR_\sigma + BJ_\sigma) \\ &= \hat{\Delta}'_\sigma \sum_{sij} \hat{f}_{os} (\cos 2\pi \mathbf{H} \mathbf{r}_{si} \cos 2\pi \mathbf{H} \mathbf{r}_{sj} \\ & \quad + \sin 2\pi \mathbf{H} \mathbf{r}_{si} \sin 2\pi \mathbf{H} \mathbf{r}_{sj}) \\ &= \hat{\Delta}'_\sigma \sum_{sij} \hat{f}_{os} \cos 2\pi \mathbf{H}(\mathbf{r}_{si} - \mathbf{r}_{sj}). \end{aligned} \quad (24)$$

$\hat{\Delta}'_\sigma$ and \hat{f}_{os} are essentially Fourier transforms of the K (L) shell and of the total atomic electron densities, $\rho_{K\sigma}$ and ρ_s respectively. Since the inner shells are much less extended than ρ_s we may approximate

$$\mathcal{F}_-\{\hat{\Delta}'_\sigma \hat{f}_{os}\} = \rho_{K\sigma} * \rho_s \approx n_\sigma \rho_s, \quad (25)$$

where n_σ is the number of electrons in the K (L) shell.

Combining (21), (24) and (25) we arrive at

$$\begin{aligned} T_{\sigma_1}(\mathbf{u}) &= 4n_\sigma \sum_{sij} \rho_s * \frac{1}{2} \{ \delta[\mathbf{u} - (\mathbf{r}_{si} - \mathbf{r}_{sj})] \\ & \quad + \delta[\mathbf{u} + (\mathbf{r}_{si} - \mathbf{r}_{sj})] \}. \end{aligned} \quad (26)$$

$T_{\sigma_1}(\mathbf{u})$ has atomic peaks with the shape ρ_s at positions $\pm(\mathbf{r}_{si} - \mathbf{r}_{sj})$ or, expressed differently,

$$T_{\sigma_1}(\mathbf{u}) = 2n_\sigma \sum_j \rho(\mathbf{u} - \mathbf{r}_{\sigma j}) + \rho_-(\mathbf{u} - \mathbf{r}_{\sigma j}) \quad (27)$$

where $\rho(\dots)$ is the electron density of the complete crystal and $\rho_-(\dots)$ its inversion image. Every a.s. atom introduces in $T_{\sigma_1}(\mathbf{u})$ one image of the electron density shifted by $(-\mathbf{r}_{\sigma j})$ together with its inverse shifted by $+\mathbf{r}_{\sigma j}$; that is, in both images the a.s. atom creating the image occurs at the origin of the coordinate system.

In order to make the discussion more transparent we analyse the centrosymmetric and the acentric case separately.

(a) Centrosymmetric structures

(aa) *Only one a.s. per unit cell.* In this case $\mathbf{r}_{\sigma=1,1}$ coincides with one of the inversion centres and defines the origin. $T_{\sigma_2}(\mathbf{u})$ contains only the trivial centre peak. $\mathcal{F}_-\{I_\sigma - I_o\} = T_{\sigma_1} + T_{\sigma_2}$ is, up to a scale factor, identical with the complete electron density with one minor exception: the peak at $\mathbf{u} = \mathbf{0}$ is the superposition of $\rho_{K\sigma}$ and ρ_σ , the K (L) shell and the total electron density of the anomalous scatterer.

(ab) *Two a.s. at positions $\mathbf{r}_{\sigma_1} = +\mathbf{r}_\sigma$ and $\mathbf{r}_{\sigma_2} = -\mathbf{r}_\sigma$ related by an inversion centre.* $\mathcal{F}_-\{I_\sigma - I_o\}$ contains two sharp peaks at $\pm 2\mathbf{r}_\sigma$ [interatomic vectors for a.s. atoms due to $T_{\sigma_2}(\mathbf{u})$] together with two copies of $\rho(\mathbf{r})$ having normal atomic peaks ρ_s shifted by $\pm\mathbf{r}_\sigma$. The problem of structure determination is solved as soon as the narrow peaks at $\pm\mathbf{r}_\sigma$ have been identified. If this is not possible, the autocorrelation function of $\mathcal{F}_-\{I_\sigma - I_o\}$ may be used: this function will show large peaks at shift vectors $\pm 2\mathbf{r}_\sigma$. The size and shape of these peaks are identical with the centre peak at $\mathbf{0}$.

(b) Acentric structures

(ba) *One a.s. atom of one kind per unit cell.* In $\mathcal{F}_-\{I_\sigma - I_o\}$ the T_{σ_2} part shows only the centre peak. In $T_{\sigma_1}(\mathbf{u})$ the density ρ with \mathbf{r}_{σ_1} as the origin and its inverse ρ_- with the centre of inversion at $\mathbf{r}_{\sigma_1} = \mathbf{0}$ occur. This result is familiar from and identical with image seeking in a Patterson map with one (known) interatomic vector only.

(bb) *Two a.s. of the same kind at $\mathbf{r}_{\sigma_1,1}$ and $\mathbf{r}_{\sigma_1,2}$ per unit cell.* $\pm(\mathbf{r}_{\sigma_1,1} - \mathbf{r}_{\sigma_1,2})$ may be found from $T_{\sigma_2}(\mathbf{u})$, but otherwise the situation (ba) occurs again with two shifted images and their inverses.

(bc) *Two different a.s. of two kinds occurring with one atom per cell at $\mathbf{r}_{\sigma_1,1}$ and $\mathbf{r}_{\sigma_2,1}$.* $T_{\sigma_1,2}(\mathbf{u})$ and $T_{\sigma_2,2}(\mathbf{u})$ are trivial again: only a sharp peak at $\mathbf{u} = \mathbf{0}$. In a (cross) convolution $T_{\sigma_1,1} * T_{\sigma_2,1}$ two large peaks will occur at $\pm(\mathbf{r}_{\sigma_1,1} - \mathbf{r}_{\sigma_2,1}) = \pm\mathbf{d}$. With \mathbf{d} given one is free to choose, for the phase-angle calculation, a new origin for the structure, e.g. either $\mathbf{r}_{\sigma_1,1} = \mathbf{0}$ and $\mathbf{r}_{\sigma_2,1} = \mathbf{d}$ or $\mathbf{r}_{\sigma_1,1} = -\mathbf{d}/2$ and $\mathbf{r}_{\sigma_2,1} = +\mathbf{d}/2$. From either choice the angles $\Psi_1 \equiv \Psi_1(\mathbf{H}) = 2\pi \mathbf{H} \mathbf{r}_{\sigma_1,1}$ and $\Psi_2 \equiv \Psi_2(\mathbf{H}) = 2\pi \mathbf{H} \mathbf{r}_{\sigma_2,1}$ in the system of equations (16), (17) are defined, and the phases $\Phi(\mathbf{H})$ can be calculated uniquely. One has of course to bear in mind that the two selected origins, either (α) $\mathbf{r}_{\sigma_1,1} = \mathbf{0}$ or (β) $\mathbf{r}_{\sigma_1,1} + \mathbf{r}_{\sigma_2,1} = \mathbf{0}$, will give two different, internally consistent, sets of phases which are related by

$$\Phi_\alpha(\mathbf{H}) = \Phi_\beta(\mathbf{H}) + \pi \mathbf{H} \mathbf{d}. \quad (28)$$

The choices of signs suggested here for case (α) or (β) will select one out of the two possible absolute configurations of the crystal structure which are compatible with the powder data.

(bd) We will not discuss any more complicated situations in detail. We should, however, emphasize that in the general case with two groups σ_1 and σ_2

containing Σ_1 and Σ_2 a.s. atoms, respectively, the analysis is simplified appreciably if the structural fragments σ_1 and σ_2 are known *a priori*, e.g. from chemical considerations. In this case the well known Patterson search routines are at hand for the analysis of $\mathcal{F}\{I_\sigma - I_o\}$.

VII. Scaling

The intensity ratios r_σ and the differences $I_\sigma - I_o$ defined in (7) and (19), respectively, are accessible from the experimental data after scaling:

$$I_\sigma = q_\sigma I_\sigma^{\text{EXP}} \quad (29)$$

where I_σ^{EXP} is the observed integrated powder line intensity after L_p and absorption correction (see § II) and q_σ takes into account all instrumental effects: spectral density, wavelength dependence of the detector efficiency *etc.* Absolute intensities are not required, either for the phase angles or for the Patterson maps. All intensities may, therefore, be referred to one wavelength, e.g. to λ_o . So we may put $q_o = 1$. We discuss briefly two methods: intrinsic and external scaling.

Intrinsic methods use only data of the sample itself. A simple estimate is

$$q_\sigma \approx \sum_{\mathbf{H}} I_o^{\text{EXP}} / \sum_{\mathbf{H}} I_\sigma^{\text{EXP}} \quad (30)$$

where the sums extend to the highest-order reflection \mathbf{H}_M common to both spectra. A more detailed analysis shows that wavelength-dependent corrections depending on $|\mathbf{H}_M|$ have to be included. If the overall contribution of the a.s. atoms to the intensities is small then a better choice is to include in (30) only a few strong low-index intensities.

External scaling uses a standard material either added to the sample or prepared on a separate sector of the surface of a rotating sample holder as suggested by Ritter, Maichle, Eder, Ihringer & Prandl (1989). In the latter case sample and reference data are registered separately: the rotation of the sample holder is used for gating two electronic counters and any overlap between sample and reference reflections is avoided. The possibility of anomalous contributions to the reference intensities has, of course, to be taken into account. Even for standards containing only low-order atoms these contributions may become

important in accurate data, as shown by Zachariasen (1965) in the case of quartz.

VIII. Concluding remarks

Polychromatic data from high-resolution powder patterns in which Friedel pairs ($\pm\mathbf{H}$) are the only systematic coincidences can be used in principle for a complete solution of the phase problem. In centrosymmetric structures two data sets, one with no anomalous effects and one having contributions from one a.s., are sufficient for the localization of the a.s., as well as for the sign determination. With only one a.s. located at an inversion centre the Fourier density of the electronic structure is given by the difference of the two Patterson densities $P_\sigma(\mathbf{u}) - P_o(\mathbf{u})$. In the acentric case one needs at least three different data sets: one with no a.s. effects (the high-energy limit), and two containing contributions from two different types of anomalous scatterers. Again the simplest case occurs if only one atom of the a.s. σ_1 and σ_2 is present in the unit cell. The present paper applies, strictly speaking, to the triclinic system. Higher symmetries will be treated separately.

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