General Calculation of the Polarization Factor for Multiple Coherent Scattering of Unpolarized and Plane-Polarized X-rays*

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Abstract

The polarization factor for coherent scattering from a crystalline or non-crystalline sample can be calculated easily for any number of pre- and post-sample scatterers of any orientation. No complicated visualization is necessary. Either an analytical or a numerical method can be used. Simple repeated matrix multiplication is used to determine the polarization factor. The technique is illustrated for a Bonse–Hart instrument having 13 scattering processes.

Introduction

When only one or two scattering processes are considered, the ideal polarization factor often can be derived easily considering the orientation and components of the electric vector before and after each scattering process. The ideal polarization factor is the usual one used in kinematical diffraction theory. For more complicated cases the geometry can become very difficult to visualize, and analytical equations for the ideal polarization factor P can become very complicated.

Vincent (1982) derived equations for calculating the ideal polarization factor for any number of pre-sample scatterers, with the restriction that all scattering planes are either normal or parallel to all other scattering planes for all of the pre-sample scatterers. He indicates that equations can be derived for other orientations of planes, but the resulting equations become complicated. Post-sample scatterers were not considered.

A general method for determining the ideal polarization factor has existed for many years. The origin of it is over a century old (Stokes, 1852). The Stokes parameters describe the state of polarization of radiation. Since this early work, a large number of persons have developed methods for calculating ideal polarization factors based on matrix operations on the Stokes parameters. McMaster (1961) reviewed this

subject and gave several references. The matrix method has seldom been used in X-ray scattering studies, although it was used to derive the intensity of secondary scattering in non-crystalline materials (Dwiggins & Park, 1971; Dwiggins, 1972). An advantage of using such a matrix method is that either numerical or analytical expressions can be determined using only simple matrix multiplication.

In this paper the matrix method is adapted for X-ray scattering studies used for investigations of structure. Only coherent radiation is considered at first, but incoherent radiation will be discussed. Although X-ray tubes produce unpolarized characteristic radiation, completely polarized radiation is allowed because synchrotron radiation that is nearly completely polarized now is used for some studies (Vincent, 1982). Circular polarization is not allowed, although it is possible to include it, because the resulting equations would be much more complicated and because high-intensity X-ray sources with circular polarization are not yet available.

When strongly diffracting crystals are used as monochromators, as often is the case in single-crystal structure studies, dynamical rather than kinematical theory applies and the degree of perfection can influence the polarization factor greatly (Jennings, 1981; Mathieson, 1982). This requires a modification in McMaster's matrix treatment.

Theory

The review paper of McMaster (1961) should be consulted for details concerning the matrix method for determining polarization factors. The general form of the matrix method involves matrix multiplication of sets of four different types of matrices. In this paper, matrices will be indicated by bold-face capital type, while vectors will be indicated by bold-face lower-case type.

A brief description of how the Stokes parameters are used in matrix form follows using the formalism of McMaster (1954).

The state of photons is characterized by four

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parameters that usually are given in column matrix form but are given in row matrix form here to save space. The matrix giving the Stokes parameters is (I, p_1, p_2, p_3). The I represents intensity, and it often is normalized to unity. The three p parameters specify the state of polarization. An unpolarized beam is represented by $(1,0,0,0)$. A coordinate system can be found such that a plane-polarized beam is represented either by $(1, \pm 1, 0, 0)$ or by $(1, 0, \pm 1, 0)$. A beam with circular polarization is represented by $(1, 0, 0, \pm 1)$ in some coordinate systems. Partial polarization results in non-zero terms in both p_1 and p_2 that cannot be eliminated by rotation of the coordinate system.

The Stokes parameters depend on the choice of axes. Thus, when one rotates from one scattering plane to another scattering plane the Stokes parameters must be converted to a new coordinate system. This is done using a four-dimensional matrix $\mathbf{M}$ such that the Stokes parameters in a new primed coordinate system are related to those in the old system by $(I', p_1', p_2', p_3') = \mathbf{M}(I, p_1, p_2, p_3)$.

The polarization factor P is multiplied by intensities obtained from theory so that they can be compared with observed intensities, or $1/P$ is multiplied by experimental intensities to eliminate the polarization effect.

If there are n scatterers including the sample identified by the subscript s, then the unnormalized polarization factor P is given by a matrix product

$$P = (\mathbf{DT}_n \mathbf{M}_{n,n-1} \cdots \mathbf{T}_{s+1})(\mathbf{M}_{s+1,s} \mathbf{T}_s \mathbf{M}_{s,s-1})$$
$$\times \ (\mathbf{T}_{s-1} \ldots \mathbf{M}_{2,1} \mathbf{T}_1 \mathbf{U}). \tag{1}$$

The $\mathbf{T}$ represents scattering, and the $\mathbf{M}$ represents rotations of the scattering planes. The $\mathbf{D}$ represents detection, and the $\mathbf{U}$ represents the X-ray source.

McMaster's (1961) treatment is kinematical, but dynamical scattering theory often applies for thick crystals used for pre- and post-sample scatterers.

For structural studies the sample must be kept small enough to be described by kinematical theory or by making small corrections for dynamical effects such as extinction. Differences between kinematical and dynamical scattering occur in the elements of the $\mathbf{T}$ matrices.

The term enclosed in the first set of parentheses in (1) is defined as $\mathbf{D}_c$, and that enclosed in the last set of parentheses is defined as $\mathbf{U}_c$. In most experiments all of the scatterers represented by $\mathbf{T}$ in $\mathbf{D}_c$ are rigidly attached to one another, and likewise for the scatterers in $\mathbf{U}_c$. Thus, $\mathbf{D}_c$ and $\mathbf{U}_c$ do not vary as the scattering angle for the sample is changed. Using the defined terms, (1) is rewritten

$$P = \mathbf{D}_c \mathbf{M}_{s+1,s} \mathbf{T}_s \mathbf{M}_{s,s-1} \mathbf{U}_c. \tag{2}$$

Usually it is necessary to determine $\mathbf{D}_c$ and $\mathbf{U}_c$ only once for a fixed experimental arrangement, and thus

calculation of P for a large number of points is simplified.

Because circular polarization is not allowed, and only coherent scattering is considered at this point, the matrices are simplified greatly from those given by McMaster (1961).

The matrix $\mathbf{T}_i$ representing scattering process i simplifies to

$$\mathbf{T}_i = \begin{vmatrix} a_i & c_i & 0 \\ c_i & a_i & 0 \\ 0 & 0 & b_i \end{vmatrix}. \tag{3}$$

For the ideal case, the value of the elements of $\mathbf{T}_i$ are

$$a_i = (1 + \cos^2 2\theta_i)/2, \ b_i = \cos 2\theta_i, \ c_i = (\sin^2 2\theta_i)/2,$$

where $2\theta_i$ is the total scattering angle for scattering process i.

When some of the scattering processes are not ideal, a more general expression must be used with

$$a_i = (1 + K_i)/2, \quad b_i = K_i^{1/2}, \quad c_i = (1 - K_i)/2.$$

The term K_i is the polarization ratio for scattering process i. For the ideal case, $K_i = \cos^2 2\theta_i$. For a perfect crystal, $K_i = |\cos 2\theta_i|$. When a thick crystal scattering with high intensity is used, then K_i for it must either be determined experimentally, or some experimental arrangement must be found that causes K_i to cancel.

The matrix $\mathbf{M}_{i+1,i}$ represents rotation from the plane of scattering process i to the plane of scattering process $i + 1$, and it simplifies to

$$\mathbf{M}_{i+1,i} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & d_{i+1,i} & f_{i+1,i} \\ 0 & -f_{i+1,i} & d_{i+1,i} \end{vmatrix}. \tag{4}$$

The elements of $\mathbf{M}_{i+1,i}$ are

$$d_{i+1,i} = \cos 2\gamma_{i+1,i}, \quad f_{i+1,i} = \sin 2\gamma_{i+1,i}.$$

The angle $\gamma_{i+1,i}$ is the angle of right rotation required to rotate the plane of scattering process i to the plane of scattering process $i + 1$. In the special case that both the i and $i + 1$ scattering processes are in the same plane, $\mathbf{M}_{i+1,i} = \mathbf{1}$, and thus this matrix can be deleted.

The polarization of the incident X-ray beam is described by the matrix $\mathbf{U}$ that gives the Stokes parameters in column matrix form. The $\mathbf{U}$ matrix often will be written in row form to save space.

If the incident X-rays are unpolarized, $\mathbf{U}$ simplifies to $\mathbf{U} = |1, 0, 0|$.

Some synchrotrons produce plane-polarized X-radiation. The term $\mathbf{U}$ for a plane-polarized X-ray beam is $\mathbf{U} = |1, \cos 2\varphi, -\sin 2\varphi|$.

Let the incident X-ray beam be $\mathbf{s}_0$ and the beam scattered by the first scattering point be $\mathbf{s}_1$, with both vectors having the first scattering point as their origin.

The normal to the first scattering plane thus is given by the vector product, $\mathbf{p} = \mathbf{s}_0 \times \mathbf{s}_1$. Consider a reference plane through the first scattering point that is perpendicular to $\mathbf{s}_0$. The normal $\mathbf{p}$ and the electric vector $\mathbf{e}$ of the incident polarized X-ray beam will both be in the reference plane. The angle φ is given by

$$\varphi = \cos^{-1}\{\mathbf{p}.\mathbf{e}(|\mathbf{p}||\mathbf{e}|)^{-1}\}.$$

The matrix $\mathbf{D}$ is a row matrix representing detection. For the usual X-ray detectors that are not polarization sensitive, such as counters and films, then $\mathbf{D}$ simplifies to $\mathbf{D} = |1,0,0|$.

The polarization factor must be normalized so that it is equal to unity for zero scattering angle for the sample. In the less general case with no scatterers after the sample (Azaroff, 1955; Vincent 1982) normalization is done by division of P by the intensity just before the sample. In this general case, normalization can be done by division of P by the value of P obtained with $2\theta_s = 0$. Thus the normalized polarization factor P_n is given by

$$P_n = \frac{\mathbf{D}_c\mathbf{M}_{s+1,s}\mathbf{T}_s\mathbf{M}_{s,s-1}\mathbf{U}_c}{\mathbf{D}_c\mathbf{M}_{s+1,s}\mathbf{T}_{0,s}\mathbf{M}_{s,s-1}\mathbf{U}_c}. \tag{5}$$

The matrix $\mathbf{T}_{0,s}$ is the matrix $\mathbf{T}_s$ with $2\theta_s = 0$.

If there is a very complicated geometry of pre- and post-sample scatterers, then numerical solution of (5) is simpler than obtaining a very lengthy analytical expression. One must know all of the $2\theta_i$ and corresponding K_i values so that a_i, b_i, and c_i can be calculated. All of the values of $\gamma_{i+1,i}$ must be known so that $d_{i+1,i}$ and $f_{i+1,i}$ can be calculated. Also φ must be known if the incident X-ray beam is polarized. With this numerical information one calculates $\mathbf{D}_c$ and $\mathbf{U}_c$ using numerical matrix multiplication. Finally, P_n is calculated using (5) for each data point. The time required to do these simple matrix multiplications is trivial using a modern computer.

In many cases of interest, fairly simple analytical equations can be obtained. Thus some simplifications resulting for special cases will be examined next.

In the special case that *all* scattering processes are in the same plane and a polarization-insensitive detector is used, all $\mathbf{M}_{i+1,i}$ can be deleted and all remaining matrices can be reduced to two-dimensional ones by deleting all third rows and columns.

If there are q successive identical scattering processes in the same plane, then a term $\mathbf{T}^q$ occurs in (5), which is given by

$$\mathbf{T}^q = \begin{vmatrix} \alpha & \beta & 0 \\ \beta & \alpha & 0 \\ 0 & 0 & b^q \end{vmatrix}. \tag{6}$$

The term α is

$$\alpha = (1 + K^q)/2. \tag{7}$$

The term β is

$$\beta = (1 - K^q)/2. \tag{8}$$

The term K refers to the identical values of this term in a sequence of q matrices of type $\mathbf{T}$.

The Appendix gives a general method for calculating the terms $2\theta_i$ and $\gamma_{i+1,i}$.

Example

A Bonse–Hart unit used by the author (Dwiggins, 1978, 1980) has six pre- and six post-sample scatterers. If the 13 scattering processes were all in different planes an analytical expression could be obtained using matrix multiplication, but it would be several pages long. In such a case the numerical matrix multiplication method previously mentioned would be much easier to use.

Since all of the scattering processes are in the same plane, all $\mathbf{M}_{i+1,i}$ matrices can be deleted. Because the detector is not sensitive to polarization, all remaining matrices thus reduce to two-dimensional ones. Also, all values of $2\theta_i$, except for $2\theta_s$ for the sample, are identical and will be labeled 2θ. Thus, $\mathbf{D}_c = \mathbf{D}\mathbf{T}^6$ and $\mathbf{U}_c = \mathbf{T}^6\mathbf{U}$.

Application of (7) and (8) results in

$$\alpha = (1 + K^6)/2, \quad \beta = (1 - K^6)/2.$$

Thus the elements of $\mathbf{T}^6$ can be determined using (6). Application of (5) gives $P_n = a_s + 2c_s\alpha\beta(\alpha^2 + \beta^2)^{-1}$ for an unpolarized X-ray source with $\mathbf{U} = |1,0,0|$.

Nearly perfect germanium crystals are used in the Bonse–Hart instrument, so a value of $K = |\cos 2\theta|$ for the perfect crystals probably is closer to the correct value than is $K = \cos^2 2\theta$ for ideal scattering.

The Bonse–Hart instrument uses 12 germanium 220 reflections, giving $2\theta = 45\cdot34°$ for the Cu $K\alpha$ radiation used. Solving for P_n for both the ideal scattering and the perfect-crystal cases gives $P_n = 1$ for all scattering angles $2\theta_s$ for the sample to within $1\cdot43\%$. The maximum allowed $2\theta_s$ for the instrument is $10°$, and $P_n = 1$ to within $0\cdot022\%$ for this range. Thus, for the described Bonse–Hart instrument, the polarization factor can be neglected at all scattering angles for practical applications.

If the incident X-radiation is completely polarized in a direction normal to the first scattering plane, then $\varphi = 0$ and $\mathbf{U} = |1,1,0|$. Solving in the same manner as for the unpolarized beam gives $P_n = 1$ exactly for all values of $2\theta_s$. This is in agreement with the results for a more simple case (Templeton, Templeton, Phillips & Hodgson, 1980).

If the polarized radiation is in the direction of the first scattering plane, then $\varphi = \pi/2$ and $\mathbf{U} = |1,-1,0|$. In this case, $P_n = \cos^2 2\theta_s$ for a sample that scatters ideally. This is in agreement with the results for a more simple case (Vincent, 1982).

If $\varphi = \pi/4$, then $\mathbf{U} = |1,0,-1|$. But in the special case

for the Bonse–Hart instrument, it was shown that all third rows and columns can be eliminated in the matrices. Thus the value obtained for P_n is exactly the same as for the unpolarized X-ray beam.

The conclusion is that no polarization corrections need be made for the described Bonse–Hart instrument and using a polarized radiation source offers no advantages. However, for cases when P_n can vary considerably, using polarized radiation can eliminate errors caused by uncertainty in the correct K for thick highly reflecting crystals.

Discussion

The sample can be a liquid or gas as well as a crystal. However, low-atomic-number elements can produce a very high intensity of incoherent radiation at high scattering angles. The polarization correction for incoherent scattering is not the same as that for coherent scattering. At wavelengths usually used for structural studies, often 1·54 Å, the difference in the coherent and incoherent polarization factors can be neglected. McMaster (1961) gives the full **T** matrix for incoherent scattering, but using it adds considerable complexity and should be necessary only when radiation with a wavelength considerably less than 1 Å is used. A more important correction at shorter wavelengths is for the difference in the absorption for coherent and incoherent radiation (Dwiggins & Park, 1971).

Using either the ideal polarization factor or the one for a perfect crystal often can be grossly in error for the crystals of high reflecting power often used as monochromators in single-crystal structural studies. Determining the correct polarization ratio K from experiment can be complicated and subject to several errors, some of which can be rather subtle (Mathieson, 1982; Jennings, 1981; LePage, Gabe & Calvert, 1979; Evans, Hine, Richards & Tichy, 1980; Vincent & Flack, 1980). If the K cannot be determined with confidence, then either no monochromator should be used or a special geometry should be used that eliminates the polarization effect for the monochromator, such as the method of Mathieson (1978).

It is unlikely that synchrotron sources of polarized X-radiation will be available for the bulk of routine structure determinations soon. Thus, using polarized radiation to eliminate K will be available only to a few. However, it is possible that polarized radiation might be helpful in determining K for crystals to be used as monochromators for unpolarized X-ray sources, because K is the same for both polarized and unpolarized radiation when $\varphi = \pi/4$ while the effect of K is completely eliminated for polarized radiation for $\varphi = 0$ or for $\varphi = \pi/2$.

If a sample is studied for which full dynamical theory is required, using radiation polarized normal to the plane of scattering of the sample will eliminate K for the sample and thus any uncertainty in the polarization correction for the sample. This is not likely to be of much use for structural studies, because corrections for other dynamical effects often cannot be made accurately for somewhat imperfect crystals.

APPENDIX

The objective is to determine $2\theta_i$ and $\gamma_{i+1,i}$ values from the known geometry of the scattering process. A good illustration of the angle γ is given in Fig. 4 of McMaster (1961), who labels the angle φ.

Let the ends of the vectors $\mathbf{m}_j$ give the locations of the n scatterers in space in any instrumental coordinate system that is convenient. Let $\mathbf{m}_0$ be the location of the X-ray source and $\mathbf{m}_{n+1}$ be the location of the detector. Then the vectors $\mathbf{t}_j$ connecting the points $\mathbf{m}_j$ to points $\mathbf{m}_{j+1}$ are

$$\mathbf{t}_j = \mathbf{m}_{j+1} - \mathbf{m}_j. \qquad (A1)$$

Using the vector scalar product, the total scattering angle $2\theta_i$ for the scatterer i is

$$2\theta_i = \cos^{-1}\{(\mathbf{t}_{i-1}.\mathbf{t}_i)(|\mathbf{t}_{i-1}||\mathbf{t}_i|)^{-1}\}. \qquad (A2)$$

Let $\mathbf{n}_1$ be a normal to the plane defined by $\mathbf{t}_{i-1}$, $\mathbf{t}_i$ and $\mathbf{n}_2$ be a normal to the plane defined by $\mathbf{t}_i$, $\mathbf{t}_{i+1}$. Thus, if the coordinate system is right-handed and the usual right-handed convention is used for the vector product, the angles between the defined planes can be obtained by using the vector scalar products between the normals to the planes, resulting in

$$\gamma_{i+1,i} = \cos^{-1}\{(\mathbf{n}_1.\mathbf{n}_2)(|\mathbf{n}_1||\mathbf{n}_2|)^{-1}\} \qquad (A3)$$
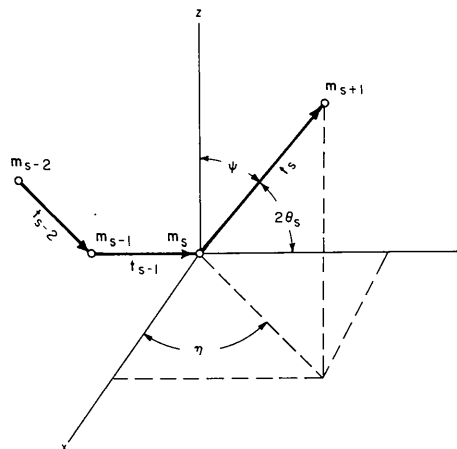

Fig. 1. Example of scattering geometry with the sample $\mathbf{m}_s$ located at the origin of a Cartesian coordinate system. See text for definitions.

with

$$\mathbf{n}_1 = \mathbf{t}_{i-1} \times \mathbf{t}_i$$

and

$$\mathbf{n}_2 = \mathbf{t}_i \times \mathbf{t}_{i+1}.$$

The method described will work in a mechanical manner without requiring elaborate geometrical constructions. A simple example perhaps will be useful.

In Fig. 1, the sample is at the origin of Cartesian coordinates in which components of vectors are expressed by (x,y,z). Suppose that point $\mathbf{m}_{s+1}$ is variable and is measured experimentally by the spherical coordinate system with components $[r,\psi,\eta]$ which is related to the Cartesian coordinate system by $x = r \sin \psi \cos \eta$, $y = r \sin \psi \sin \eta$, and $z = r \cos \psi$.

Let the scatterer $\mathbf{m}_{s-1}$ be located at $(0,-3,0)$, and let the scatterer, or X-ray source, $\mathbf{m}_{s-2}$, be located at $(0,-6,3)$.

Application of $(A1)$ gives

$$\mathbf{t}_s = r \sin \psi \cos \eta \mathbf{i} + r \sin \psi \sin \eta \mathbf{j} + r \cos \psi \mathbf{k};$$

$$\mathbf{t}_{s-1} = 3\mathbf{j}; \quad \mathbf{t}_{s-2} = 3\mathbf{j} - 3\mathbf{k}.$$

The terms $(\mathbf{i},\mathbf{j},\mathbf{k})$ are unit vectors in the Cartesian coordinate system.

The term $\mathbf{n}_1$ is determined by

$$\mathbf{n}_1 = \mathbf{t}_{s-2} \times \mathbf{t}_{s-1} = \begin{Vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ 0 & 3 & -3 \\ 0 & 3 & 0 \end{Vmatrix} = 9\mathbf{i}.$$

In the same manner, $\mathbf{n}_2$ is found to be

$$\mathbf{n}_2 = 3r \cos \psi \mathbf{i} - 3r \sin \psi \cos \eta \mathbf{k}.$$

All of the quantities necessary to solve $(A2)$ and $(A3)$ have been determined. Use of $(A2)$ results in the

two total scattering angles $2\theta_{s-1} = \pi/4$ and $2\theta_s = \cos^{-1}(\sin \psi \sin \eta)$.

Use of $(A3)$ results in the angle of rotation between the scattering planes

$$\gamma_{s,s-1} = \cos^{-1}\{(1 + \tan^2 \psi \cos^2 \eta)^{-1/2}\}.$$

Note added in proof. It is emphasized that inverse cosines and square roots result in both a positive and a negative solution. The definitions used allow the correct signs to be selected, but explicit rules may be helpful. The negative solution of $(A3)$ is used if $\mathbf{n}_1 \times \mathbf{n}_2 = L\mathbf{t}_i$ with L positive. The angle φ is negative if $\mathbf{e} \times \mathbf{p} = N\mathbf{s}_0$ with N positive. Also, b must be positive if $2\theta < \pi/2$ and negative if $2\theta > \pi/2$.

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Extrapolative Filtering.
II. Formalism for a Maximum-Entropy Enhancement of Resolution in n Dimensions

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Abstract

An extrapolative filtering formalism is used to determine a high-resolution positive-definite density estimator. In an example, comparison with results from Fourier transformation of structure factors shows a resolution enhancement factor of 1·3 for the density estimator. The density estimator satisfies a maximum-entropy criterion and is the direct-space representation of a maximum determinant of structure factors as used in phase determination.

1. Introduction

In a previous paper (Collins, 1978), hereafter referred to as paper I, a foundation was laid for extraction of