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The role of projection operators in the theory of *N*-beam diffraction and the inversion of three-beam elastic scattering intensities

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Dedicated to Professor A. F. Moodie on the occasion of his 75th birthday

Abstract

Commencing from a projection-operator description of *N*-beam diffraction, the mathematical basis for the recovery of phase and amplitude information from a three-beam convergent-beam electron diffraction pattern is given for both the centrosymmetric and noncentrosymmetric cases. The algebra is available in *Mathematica* Notebook form from the URL ftp://ftp.physics.uwa.edu.au/pub/EMC/3BeamAlgebra.nb.

1. Introduction

The direct problem in scattering theory is the determination of the scattered beam, in amplitude and phase, as a function of the direction of scattering given the distribution of electron charge density, electric potential and nuclear positions responsible for the scattering. In principle, this direct problem is always soluble in a straightforward way although the calculations may become difficult and complicated. The inversion problem – that of deducing the distribution of scattering elements from the observed beam intensity as a function of direction – is much more complex. A classic example is the so-called phase problem in the scattering of X-rays, which may prevent the straightforward calculation of a crystal structure from the observed intensities of the diffracted beams. Recently, Spence (1998) and Allen *et al.* (1998) have considered factors relevant to *N*-beam inversion and have explored iterative schemes for structure analysis.

We consider *N*-beam elastic scattering of electrons by crystals investigated by the convergent-beam technique. Here the general resolvent operator and the related projection operators into the eigenspaces of the *S* matrix provide powerful analytic tools. In particular, in the three-beam case, they lead to a simple direct inversion for centrosymmetric crystals and a rather more complex and difficult inversion for noncentrosymmetric crystals.

An alternative approach for the case of noncentrosymmetric crystals is presented by Moodie *et al.* (1997).

2. Theory

The *N*-beam diffraction equations (with neglect of upper-layer lines) may be expressed in terms of a scattering matrix $S(z)$ which satisfies

$$S(0) = I, \quad \mathrm{d}S/\mathrm{d}z = iMS, \tag{1}$$

where I is the identity matrix, z is the crystal thickness and

$$M = \begin{pmatrix} 0 & V_{\bar{g}} & V_{\bar{h}} & \cdots \\ V_g & \zeta_g & V_{g-h} & \cdots \\ V_h & V_{h-g} & \zeta_h & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{2}$$

is a constant Hermitian matrix with a characteristic equation

$$\lambda^N - \Sigma_1\lambda^{N-1} + \Sigma_2\lambda^{N-2} + \ldots + (-1)^N\Sigma_N = 0, \tag{3}$$

whose roots $\lambda_1, \lambda_2, \ldots$ are all real.

In this formulation, the orientation of the incident beam is specified by the excitation errors $\zeta_g, \zeta_h, \ldots$ and the initial state is always the fixed vector $\langle 0| = (1, 0, 0, \ldots)$. For brevity, we have absorbed 2π into $\zeta_g, \zeta_h, \ldots$ and used $V_g = \sigma e_g$, where σ is the interaction constant and $e_g, e_h, \ldots$ the Fourier coefficients of the crystal potential.

The formal solution of (1), namely

$$S = \exp(iMz), \tag{4}$$

may be reduced using the general resolvent

$$\exp(iMz) = \frac{1}{2\pi i}\oint \frac{\exp(i\lambda z)}{\lambda I - M}\,\mathrm{d}\lambda \tag{5}$$

to the form

$$S = \sum_{k=1}^{N} P_k \exp(i\lambda_k z), \tag{6}$$

where P_k, the projectors into the eigenspaces of M (and S), are explicit functions of M and the roots of the characteristic equation (3):

$$P_k = \prod_{l\neq k=1}^{N} \frac{M - \lambda_l I}{\lambda_k - \lambda_l}. \tag{7}$$

These expressions, especially (6), (7) and various forms of (5), have proved very convenient and powerful in deriving series solutions (Hurley *et al.*, 1978) in terms of the invariants $\Sigma_1, \Sigma_2, \ldots$, and the components of M. Once the scattering matrix is available, the wave function for any beam (g say) is given by

$$u_g = \langle g|S|0\rangle, \tag{8}$$

where $\langle g| = (0, 1, 0, \ldots)$.

For $N = 2$, we obtain from (6), (7) and (8) the two-beam wave function in the form

$$u_g = V_g \frac{\exp(i\lambda_1 z) - \exp(i\lambda_2 z)}{\lambda_1 - \lambda_2}. \tag{9}$$

When the roots λ_1, λ_2 are evaluated explicitly from (2) and (3), we find for the two-beam intensity the well known expression

$$I_g = u_g^* u_g = |V_g|^2 \frac{4\sin^2[(z/2)(\zeta^2 + 4|V_g|^2)^{1/2}]}{\zeta^2 + 4|V_g|^2}. \tag{10}$$

3. Centrosymmetric crystals

We notice that the two-beam intensity (10) is invariant under the substitution $\zeta \to -\zeta$, that is, is symmetrical about $\zeta = 0$. Since in a convergent-beam pattern ζ plays the role of a directional coordinate, this symmetry is readily detectable experimentally. This forms the basis for a simple three-beam inversion in the centrosymmetric case where we may choose M to be real as well as Hermitian, so that, in (2), $V_{\bar{g}} = V_g^* = V_g, \ldots$.

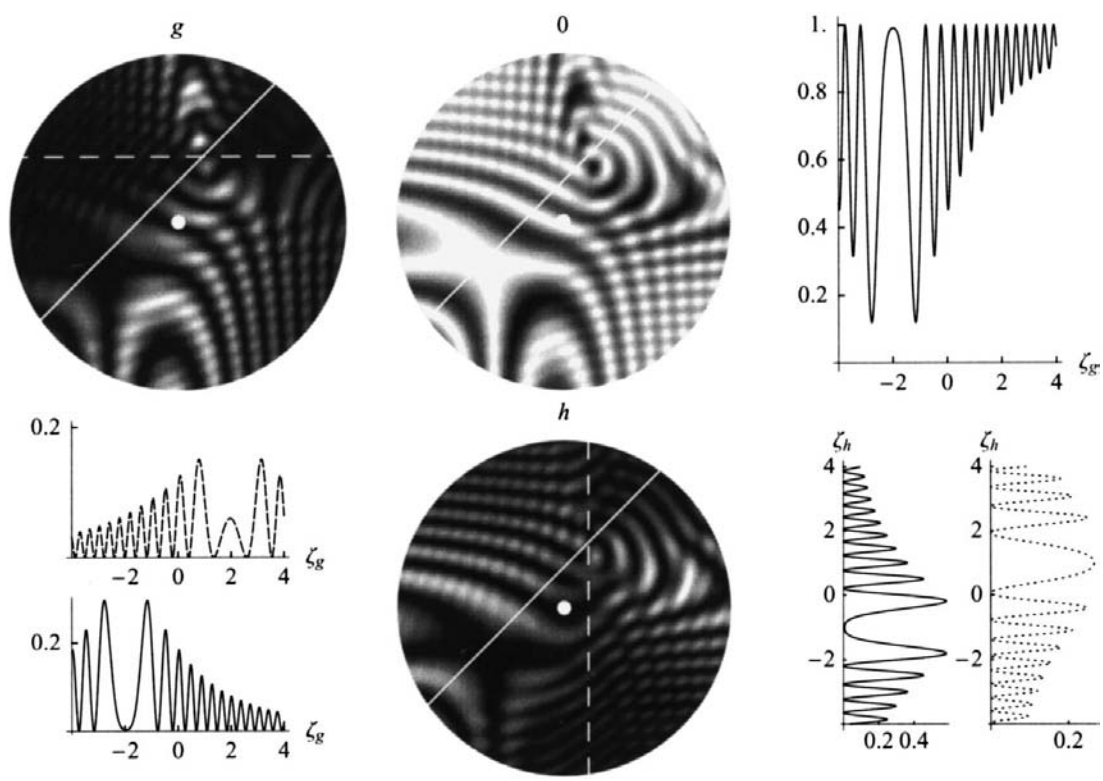

Fig. 1. A convergent-beam pattern computed using equation (8) (and the appropriate modifications for beam h and the central beam) with $N = 3$ for the parameters $V_g = 0.64$, $V_h = 0.9$, $V_{h-g} = 1.4$ and $z = 20$. The horizontal axis is ζ_g and the vertical axis ζ_h. The pattern is drawn with the reciprocal-lattice vectors g and h perpendicular and equal, simply for convenience. The centre of each disc is the point $\zeta_g = \zeta_h = 0$ and the radius is 4. For an accelerating voltage of 100 kV, these parameters are equivalent to $e_g = 6.4$, $e_h = 9$, $e_{h-g} = 14$ V (the last value made large to emphasize the displacement of the point of confluence), a thickness of 2164 Å and the excitation error at the disc edge being 0.00588 Å^{-1}. The continuous lines mark the loci of equation (17) and the dashed lines in discs g and h mark the locus (16). Three-beam calculations along these lines are displayed in plots adjacent to the respective discs and are clearly two-beam in character. The displacements of the centres of these distributions in beam g is ±1.97 along the ζ_g axis as predicted by the value of G for the above parameters.

We now seek loci in ζ_g, ζ_h space along which the three-beam intensities reduce to two-beam form. Geometrical features of these loci then yield the amplitudes V_g, V_h, V_{g-h} and their relative phase.

Specifically, the wave function for the g beam appears in the three-beam case as [*cf.* (6), (8)]

$$u_g = \exp(i\lambda_1 z)\langle g|P_1|0\rangle + \exp(i\lambda_2 z)\langle g|P_2|0\rangle + \exp(i\lambda_3 z)\langle g|P_3|0\rangle, \quad (11)$$

which will reduce to two-beam form if

$$0 = \langle g|P_1|0\rangle = \langle g|M^2|0\rangle - (\lambda_2 + \lambda_3)\langle g|M|0\rangle, \quad (12)$$

where we have used (7) with $N = 3$, $k = 1$ to evaluate P_1. Using the explicit form (2) for the matrix M, the condition (12) may be reduced to

$$\lambda_1 = \zeta_h - V_h V_{g-h}/V_g. \quad (13)$$

The root λ_1 must also satisfy the characteristic equation (3) for the case $N = 3$, that is,

$$\lambda_1^3 - \Sigma_1\lambda_1^2 + \Sigma_2\lambda_1 - \Sigma_3 = 0. \quad (14)$$

Eliminating λ_1 from (13) and (14) and using (2) to evaluate Σ_1, Σ_2 and Σ_3 explicitly, we find, for real M, the condition

$$0 = (\zeta_h + C - G)(\zeta_g - \zeta_h + G - H), \quad (15)$$

where

$$G = V_h V_{h-g}/V_g, \quad H = V_g V_{h-g}/V_h, \quad C = V_g V_h/V_{h-g}.$$

Hence, if the point (ζ_g, ζ_h) lies on either of the straight line loci

$$\zeta_h = G - C \quad (16)$$

or

$$\zeta_g - \zeta_h = H - G, \quad (17)$$

the three-beam wave function (11) reduces to a two-beam form, which may be expressed by

$$u_g \exp[-(i/2)z(\lambda_2 + \lambda_3)] = V_g \frac{2i\sin[(z/2)(\lambda_2 - \lambda_3)]}{(\lambda_2 - \lambda_3)}. \quad (18)$$

At the intersection of the lines (16) and (17), we have the point

$$\zeta_g = H - C \equiv \Gamma_1, \quad \zeta_h = G - C \equiv \Gamma_2, \quad (19)$$

at which two roots of the cubic equation (14) are equal, that is, we have a confluence (Gjønnes & Høier, 1971). It is important to note that, at all other points on the loci (16) and (17), equation (14) is not confluent but, nevertheless, beam g reduces to the two-beam form (18). The further reduction of this form is different for the two loci; for the line (16), we find that

$$(\lambda_2 - \lambda_3)^2 = (\zeta_g - G)^2 + 4(V_g^2 + V_{g-h}^2), \quad (20)$$

whereas for the line (17)

$$(\lambda_2 - \lambda_3)^2 = (\zeta_g + G)^2 + 4(V_g^2 + V_h^2). \quad (21)$$

From (20), (21) and (18), we see that the centres of the two-beam distributions are displaced equal and opposite distances G along the ζ_g axis. Similarly, in the h beam there are two two-beam loci that may be obtained by interchanging the subscripts g and h, an interchange that leaves line (17) invariant. This is shown in the calculated pattern of Fig. 1, which also indicates that (17) is the only two-beam locus in the central beam.

Thus, in a three-beam diffraction pattern for a centrosymmetric crystal, we may identify the unique pair of symmetry lines in either diffracted beam and hence determine Γ_1, Γ_2 and G; the sign of G phases the structure amplitudes and their moduli are given by

$$V_g^2 = (G - \Gamma_2)(G + \Gamma_1 - \Gamma_2), \quad V_h^2 = G(G - \Gamma_2), \quad V_{h-g}^2 = G(G + \Gamma_1 - \Gamma_2). \quad (22)$$

The loci in the other diffracted beam and the single locus in the central beam provide checks. The convergent-beam pattern of intensity at a single unknown thickness is sufficient for the inversion in this case (Hurley & Moodie, 1980).

4. Noncentrosymmetric crystals

Here it is impossible to satisfy the basic condition (13) since λ_1 and ζ_h are necessarily real whereas $V_g^{-1}V_h V_{g-h}$ is, in general, complex. A different strategy is needed for the inversion. The intensity $I_g = u_g^* u_g$ of the g beam may be obtained from (11); subtracting the corresponding expression for the setting where M is replaced by M^T $(= M^*)$, we obtain

$$\Delta \equiv I_g(M) - I_g(M^T) = 4K[\sin(\mu_1 z) + \sin(\mu_2 z) + \sin(\mu_3 z)]/\mu_1\mu_2\mu_3, \quad (23)$$

where we have put $\mu_1 = \lambda_2 - \lambda_3$, $V_g = v_g \exp(i\theta_g)$ *etc.* and

$$K = v_{g-h} v_g v_h \sin(\theta_{g-h} - \theta_g + \theta_h). \quad (24)$$

We now use the expression

$$\mu_n = 2(-\sigma_2)^{1/2}\cos[(\theta + 2n\pi)/3]$$

for $n = 0, 1, 2$, with

$$\theta = \cos^{-1}[(1 + 27\sigma_3^2/4\sigma_2^3)^{1/2}]$$

for the μ's in terms of the coefficients of the reduced characteristic equation of M,

$$\lambda^3 + \sigma_2\lambda - \sigma_3 = 0, \quad (25)$$

and the expansion (Watson, 1944)

$$\sin[z\cos(\theta)] = 2\sum_{k=0}^{\infty}(-1)^k J_{2k+1}(z)\cos[(2k+1)\theta],$$

to transform (23) to the form

$$\Delta = -12K(-\sigma_2)^{-3/2}\sum_{p=0}^{\infty}(-1)^p J_{6p+3}[2z(-\sigma_2)^{1/2}] \times \cos[(2p+1)\theta]/\cos(\theta). \quad (26)$$

The quantity (26) may be determined experimentally, at least in principle, as a continuous function $\Delta(\zeta_g, \zeta_h, z)$ of the excitation errors ζ_g, ζ_h and the thickness z. The inversion may then be achieved as follows:

(i) In a plot of $-\frac{1}{2}z^{-3}\Delta(0, 0, z)$ as a function of $z^2/4$ for small values of the thickness z, the limiting value for zero thickness yields K of equation (24), whereas the initial gradient gives the quanity $K\sigma_2$ and hence

$$\sigma_2(0, 0) = -(v_g^2 + v_h^2 + v_{g-h}^2). \quad (27)$$

(ii) From (3), (14), and (25), we now obtain σ_2 for all values of the excitation errors ζ_g $(= x)$ and ζ_h $(= y)$

$$\sigma_2 = \Sigma_2 - \tfrac{1}{3}\Sigma_1^2 = \tfrac{1}{3}(xy - x^2 - y^2) - (v_g^2 + v_h^2 + v_{g-h}^2). \quad (28)$$

(iii) Using the orthogonality relations (Watson, 1944)

$$\int_0^{\infty}[J_{6p+3}(t)J_{6q+3}(t)/t]\,\mathrm{d}t = \delta_{p,q}/(12p+q),$$

we may extract the individual terms in the expansion (26):

$$\cos[(2p+1)\theta]/\cos(\theta) = [(-1)^p(12p+q)/K]\int_0^{\infty}\Delta(z)J_{6p+3}[2z(-\sigma_2)^{1/2}]/z\,\mathrm{d}z. \quad (29)$$

In particular, we obtain, for $p = 1$, $\cos(3\theta)/\cos(\theta) = -3 + 4\cos^2(\theta)$ and hence the value of $\cos(\theta)$ and the invariant σ_3 for all values of x $(= \zeta_g)$ and y $(= \zeta_h)$.

$$\begin{aligned}\sigma_3 = {} & \tfrac{1}{27}(2x^3 - 3yx^2 - 3y^2x + 2y^3) \\ & + 2\cos(\theta_g - \theta_{g-h} - \theta_h)v_g v_{g-h} v_h \\ & + \tfrac{1}{3}x(v_g^2 + v_{g-h}^2 - 2v_h^2) \\ & - \tfrac{1}{3}y(2v_g^2 - v_{g-h}^2 - v_h^2). \end{aligned} \quad (30)$$

(iv) We now substitute $y = mx + c$ in (30) and choose m to eliminate the cubic term in x. This yields $m = -1, 2$ or $\frac{1}{2}$. For each of these directions, the variation of σ_3 with x is expressed as a perfect square. Thus, for $m = -1$, we find $3\sigma_3 = c(x - x_c)^2 + \text{constant}$, where

$$x_c = \tfrac{1}{2}[c + 3(v_h^2 - v_g^2)/c]. \quad (31)$$

The quantities c and x_c appearing in (31) may be identified by an inspection of a contour plot of $\sigma_3(x, y)$, so that an analysis of the case $m = -1$ yields the value of $v_h^2 - v_g^2$. Similarly, the cases $m = 2$ and $\frac{1}{2}$ lead to values of $v_g^2 - v_{g-h}^2$ and $v_h^2 - v_{g-h}^2$, respectively. These quantities, together with K of (24) and $\sigma_2(0, 0)$ of (28) give us v_g, v_h, v_{g-h} and the single phase angle $\theta_{g-h} - \theta_g + \theta_h$. This is *all* the information about the V's contained in $\Delta(\zeta_g, \zeta_h, z)$. By spanning the whole reciprocal lattice by a sequence of three-beam settings, all the v's and their phases (θ) may be determined.

5. Conclusions

The centrosymmetric scattering problem can be inverted in the three-beam approximation and from convergent-beam data – that is, knowledge of the intensity distribution as a function of angle of incidence – to recover explicitly and uniquely all crystallographic parameters, V_g, V_h, V_{h-g}, and the origin-independent phase.

The applicability of the technique to structure analysis will be described in another publication but, in summary, it can be claimed, at least in favourable cases, that the technique is practical.

APPENDIX *A*

Mathematica was used to check the algebraic manipulations in §§3 and 4 and to generate Fig. 1. The associated algebra is available as a *Mathematica* Notebook from ftp://ftp.physics.uwa.edu.au/pub/EMC/3BeamAlgebra.nb.

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Regretfully, one of the authors, Dr Andrew Hurley, passed away during the progress of this work.

AWSJ is priveleged to dedicate his contribution to Professor A. F. Moodie, a fine teacher, supervisor and colleague, on the occasion of his 75th birthday.

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