at 295°K by Reid & Smith (1970), [B(sodium) = 0·8685; B(fluorine) = 0·8671 Å^2], using force constants derived by fitting a shell model to measured dispersion curves. This shows that the treatment of the extinction-affected reflexions in the least-squares refinement was entirely satisfactory.

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Numerical Evaluation of *N*-Beam Wave Functions in Electron Scattering by the Multi-slice Method

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A method for the numerical evaluation of *N*-beam diffraction amplitudes and intensities which has been successfully employed over the last few years is described. This derives from the multi-slice formulation of Cowley and Moodie. The physical basis of the method and practical approaches to calculation are described.

1. Introduction

The present paper is intended to serve both as a practical guide to calculation of electron-diffraction intensities, and to give a summarized account of the physical basis of the multi-slice method. For the first purpose §§ 1 and 3 to 5 may be read alone.

The feasibility of numerical evaluation of diffraction intensities from the *N*-beam solution for a parallel-sided crystal was demonstrated by Sturkey (1962) using a scattering matrix, and by Wagenfeld (1958) and Howie & Whelan (1961), using Bethe's eigenvalue method (Bethe, 1928).

An analytical solution was obtained by Cowley & Moodie (1957) by applying the slice method to electron diffraction. The solution itself is not suited to direct numerical evaluation, but a numerical method based on the finite-slice approximation (Moodie, 1965) called here the multi-slice method, was tested by Goodman & Lehmpfuhl (1967) and has been since greatly expanded and applied to a large range of problems, including the study of large and complicated unit cells by Lynch & O'Keefe (1972).

Most, if not all, published calculations made for comparison with experimental work have used either this method, or Bethe's eigenvalue method (recent examples of the latter: Lehmpfuhl, 1972; Ayroles & Mazel, 1970; Lally, Humphreys, Metherell & Fisher, 1972). Sturkey's method has been used recently to a limited extent (*e.g.* Melvin, Morris & Bottoms, 1971). It will be shown in § 5 of this paper that economical numerical evaluation by means of the scattering matrix is identical to the multi-slice calculation. Here the term 'scattering matrix' is used to denote Sturkey's formulation, and not a theoretically trivial though convenient rewriting of the eigenvalue method in matrix notation. Leaving aside for the moment the question of computation times, the eigenvalue method appears to be useful for calculations involving a limited number of beams and for some special cases involving symmetry reduction (*e.g.* Blume, 1966). However, this utility is not maintained for large numbers of beams; the size of the computer memory required increases as N^2, and, more seriously, the probability of near coincidence of eigenvalues is increased. As against this, the multi-slice method has proved useful for calculation with several hundred beams, the memory requirement expanding roughly as N. This, and the fact that absorption, faulting and other three-dimensional effects are easily introduced, and that the calculation is not self-normalizing, have combined to make it a useful crystallographic technique.

In the multi-slice method normalization results only if sufficient terms are retained in the calculation, *i.e.* the normalization test is also a test that sufficient N-beam interactions have been included, within the framework of the physically defined problem. Essentially this arises because the phase-grating approximation gives us a very accurate calculation for a very thin crystal, and the unitarity test (defined in § 4) will detect whether the following part of the calculation retains sufficient (but not necessarily all) of the terms from this stage to give a good description of the dynamic interactions. Problems may be looked at in three categories. These are as follows: (*a*) Systematic interactions: this calculation will normalize with inclusion of only the systematic interactions provided the calculation has been made for a one-dimensional projected potential, *i.e.* an artificially averaged structure. (*b*) Two-dimensional interactions: in calculations made from a two-dimensional projected structure sufficient of the two-dimensional array of resulting beams must be retained in the subsequent multi-slice calculation to obtain normalization. (*c*) Three-dimensional interactions: these are automatically included in the multi-slice calculation, and for this reason their correctness is not checked by normalization, *i.e.* their inclusion requires no additional terms in the two-dimensional phase-grating (see later discussion).

Since categories (*b*) and (*c*) include all calculations of real accuracy, and (*a*) is simply a useful approximation, we have an objective means of determining the number of terms required in the dynamic calculation, not available in the eigenvalue method, nor in Sturkey's method by the procedure normally advocated.

Thus, independently of whether the initial Fourier summation contains sufficient terms to give an adequate description of the crystal potential (a point which may be readily checked), the subsequent normalization tests whether sufficient beams have been included in the dynamic calculation. This arises because the phase-grating calculation will generate all higher-order beams *even when those terms have been omitted in the initial kinematic Fourier series.*

Apart from the relative merits of the multi-slice method and the eigenvalue method in obtaining the final results, the two methods have different starting points and therefore give different insights into the diffraction problem. The multi-slice method starts with the complete N-beam expression for a very thin crystal, *i.e.* the thin phase-grating expression. This is also a simple analytical expression. Therefore we are provided at the outset with the thin crystal pattern, which is particularly useful in structure analysis, and for separating the influence of elastic scattering and absorption. The eigenvalue method on the other hand starts with a thickness-independent result, *viz.* eigenvalues, which is useful in the analysis of scattering from thick perfect crystals. The concept of 'Bloch wave scattering' derived from this method has been extensively adopted in studies of absorption; however this concept derives strictly from an N-beam solution obtained before boundary conditions have been applied. The starting point for study of absorption in the multi-slice method is N-beam diffraction from a thin amplitude grating, which has analytical applications particularly (though not exclusively) suited to thin crystal studies (*e.g.* Cowley & Pogany, 1968, and this paper).

Error is introduced in the multi-slice method by having to take finite slices, but this error can be reduced to any arbitrary size by reducing the slice thickness, at the cost of computer time. For example, when the slice thickness is 5 Å an accuracy of 1 % can be maintained in the main beams up to a thickness of 1000 Å in a light-atom structure (MgO), and for heavy atoms the same accuracy can be maintained to 500 Å with about half this slice thickness (Lynch, 1971). The error introduced by taking Δz (slice thickness) finite is analysed below.

The question of the number of beams in a calculation is not a trivial one. In dealing with large and complicated unit cells it has proved necessary to deal with the order of 500 beams to obtain either a qualitative or a quantitative description, while in dealing with small unit cells when accuracy is important, 100 or so beams are needed, at least initially. This is necessary to make sure that the estimation of structure factors is correct. Inadequate calculation results in values being attributed to structure factors which actually include pseudo-potentials deriving from weak-beam interactions (Goodman, 1974).

Computation times for 435 non-equivalent beams have been investigated by Lynch & O'Keefe (1972, and private communication) for different CDC computers. These times are, 15 s per slice for the 3600, 3·5 s per slice for the 6600, and an estimate of less than 0·5 s per slice for the 7600. These times show the big improvement in time with the new computers. Times for a different number of non-equivalent beams can be estimated from the proportionality to N^2. On the other hand multi-slice calculations for 225 beams have been carried out in our laboratory on a small desk computer (HP2114, with 8 K memory) (Lynch, private communication). This is possible because multi-slicing involves only repetitive multiplications, and requires only a small memory.

2. Physical basis of the multi-slice method

The multi-slice formulation was originally used as a means of obtaining an analytical solution, by taking an impulse limit $\Delta z \to 0$, $n \to \infty$, and $n\Delta z \to H$ (Cowley & Moodie, 1957). In order to obtain a formulation suitable for numerical work an earlier stage in the derivation must be used, *i.e.* an approximation with finite Δz.

The material is treated as a series of scattering planes, on to which the potential from the slice between z and $z+\Delta z$ is projected, separated by vacuum gaps Δz, *not* *necessarily corresponding to any planes or spacings of the material structure.*

The phase change in the electron beam produced by passage through a slice is given by

$$\exp\left\{i\sigma\int_{z}^{z_1+\Delta z}\varphi(x,y,z)\mathrm{d}z\right\}=\exp\left\{i\sigma\varphi(x,y)\Delta z\right\},$$

where,

$$\varphi(x,y,z)=\sum_h\sum_k\sum_l V(h,k,l)\times\exp\left[-2\pi i\left\{\frac{hx}{a}+\frac{ky}{v}+\frac{lz}{c}\right\}\right]$$

is the potential distribution within the slice, expressed in V and $\varphi(x,y)$ is the mean value of the potential in V in the region $z_1\rightarrow z_1+\Delta z$. Projected potential may also be defined as the result of the above integration over z, but the unit of projected potential, ${}^P\varphi$, will then be V Å,* *viz*:

$${}^P\varphi(x,y)=\int_{z_1}^{z_1+\Delta z}\varphi(x,y,z)\mathrm{d}z=\varphi(x,y)\Delta z\,.$$

The projected potential is a useful quantity to plot in a calculation, as an indication of the amount of material in a slice.

For the nth slice, the phase change is written

$$\exp\left\{i\sigma\varphi_n(x,y)\Delta z\right\}=\exp\left\{i\sigma{}^P\varphi_n(x,y)\right\}.$$

σ has the dimensions of $(\mathrm{V\,Å})^{-1}$,

$$\sigma=\frac{\pi}{W\lambda}\cdot\frac{2}{1+(1+\beta^2)^{1/2}}\,.$$

W is the accelerating voltage and $\beta=v/c$. This expression, together with the use of the relativistic wavelength for λ incorporates all the relativistic corrections that are necessary.

The phase distribution in the xy plane resulting from propagation between slices is given by,

$$\exp\left\{\frac{ik(x^2+y^2)}{2\Delta z}\right\},\quad\text{where } k=\frac{2\pi}{\lambda},$$

and using the approximation, very good for the range of angles being considered, of a parabolic wave front (Cowley & Moodie, 1957). All errors resulting for the parabolic approximation go to zero for $\Delta z\rightarrow 0$. Thus the wave function for the nth slice is

$$\psi_{n+1}=\left[\psi_n\star\exp\left\{\frac{ik(x^2+y^2)}{2\Delta z}\right\}\right]\exp\left\{i\sigma\varphi_{n+1}\right\}.\qquad(1)$$

z is chosen normal to the bounding surface and $\star$ is the convolution symbol, defined by

$$f_1(x)\star f_2(x)=\int_{-\infty}^{\infty}f_1(w)f_2(x-w)\mathrm{d}w\,.$$

For an ordered crystal structure, $u_n(h,k)$, the Fourier transform of ψ_n, is a set of delta functions, which makes computation relatively simple. Fourier transformation of equation (1) gives a recurrence relation in the momentum space of the (x,y) coordinates, and the direct space of the z coordinates,

$$\begin{aligned}u_{n+1}&=u_n\exp\left\{i2\pi\Delta z\zeta(h,k)\right\}\star q_{n+1}\\&=u_n\exp\left[-i2\pi\alpha(h,k)\right]\star q_{n+1}\\&=u_n\exp\left[-i2\pi\Delta z\,\frac{\lambda}{2}\left\{\frac{h(h-h'')}{a^2}+\frac{k(k-k'')}{b^2}\right\}\right]\star q_{n+1}=u_np_n\star q_{n+1}\,,\end{aligned}\qquad(2)$$

where for simplicity the equations have been given for orthogonal axes, and h'',k'' are the (non-integral) intercepts of the Laue circle on the axes, in units of $(1/a)$, $(1/b)$. q_{n+1} is the Fourier transform of $\exp\left\{i\sigma\varphi_{n+1}\right\}$; and

$$p_n=\exp\left[-i2\pi\Delta z\,\frac{\lambda}{2}\left\{\frac{h(h-h'')}{a^2}+\frac{k(k-k'')}{b^2}\right\}\right]$$

is the Fourier transform of the propagation function. The excitation errors are defined by,

$$\zeta(h,k)=-\lambda/2\left\{\frac{h(h-h'')}{a^2}+\frac{k(k-k'')}{b^2}\right\},$$

and the phase change in terms of 2π between slices of the h,k beam, a useful quantity, is given by

$$\alpha(h,k)=\Delta z\lambda/2\left\{\frac{h(h-h'')}{a^2}+\frac{k(k-k'')}{b^2}\right\}=-\zeta(h,k)\Delta z\,.$$

The sign of $\zeta(h,k)$, the z component of the excitation error for the reflexion (h,k), is fixed by the equation as negative for incident directions (h'',k'') corresponding to (h,k) outside the Ewald sphere.

Iteration of the equation generates the scattering amplitude as a function of thickness.

Separation of the phase change due to material scattering from that due to vacuum propagation in the slice formulation can be justified by deriving the differential equation corresponding to the difference equation (1). In § 7, an argument of Feynman is used to show that equation (1) is a finite difference form of Schrödinger's equation, back-scattering being neglected. The neglect of back-scattering can be justified (Lynch & Moodie, 1972). Equation (2) therefore represents an iterative procedure for the solution of Schrödinger's equation appropriate to the scattering of fast electrons by a plate.

3. Procedure

The numerical procedure involves calculation of the transmission through a thin slice (the 'thin phase grating' calculation), calculation of the vacuum propaga-

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* The whole problem of redefining units in electron diffraction is discussed elsewhere (Dawson, Goodman, Johnson, Lynch & Moodie, 1974).

tion through Δz, followed finally by evaluation in the computer of the iterated form of equation (2),

$$\ldots p_4\{p_3[p_2(p_1q_1 \star q_2) \star q_3] \star q_4\} \star \ldots . \quad (3)$$

as given by Cowley & Moodie (1957); by repeated convolutions and multiplications, up to a given thickness. This calculation must be repeated for each angle of incidence required. Since this final evaluation is a very straight-forward procedure in a digital computer, the main task in starting a calculation is usually the computation of the phase-grating function, q.

Direct evaluation of the phase-grating series in reciprocal space,

$$q(h,k) = \delta(h,k) + (i\sigma\Delta z)V(h,k) + \frac{(i\sigma\Delta z)^2}{2!} \times \sum_{h_1k_1} V(h_1k_1)V(h-h_1,k-k_1) + \ldots ,$$

where Δz is the actual slice thickness, as given by Cowley & Moodie (1959), is too slow in practice. This difficulty is bypassed in the following procedures.

(*a*) *Evaluation from the projected potential* (*real space*)

The phase-grating function may be obtained by Fourier transformation of the expression $\exp[i\sigma . \varphi(x,y) . \Delta z]$, where $\varphi(x,y)$ is the mean potential of the slice. The cosine and sine of ${}^P\varphi(x,y)$ are required, and normal crystallographic structure-factor programs which make use of symmetry reductions may be used on both these functions of the potential for this evaluation. In this way symmetry reduction is introduced not only into the kinematic but also into the dynamic part of the calculation to this stage. One advantage of the real-space calculation is that the projected potential of each slice may be inspected in the course of the calculation. This is valuable in checking for errors, and in relating the final diffraction pattern to structural symmetries.

When absorption is involved, ${}^P\varphi(x,y)$ becomes complex, and then both the phase and the amplitude periodic distributions must be calculated and may be inspected separately.

(*b*) *Evaluation completely in reciprocal space*

A terminated phase-grating series, for example

$$q(h,k) = \delta(h,k) + i\sigma V(h,k)\Delta' z , \quad (4)$$

may be used to obtain the q function for equation (3), provided $\Delta' z$ is made so small that error due to neglect of later terms is negligible. $\Delta' z$ is then too small for use directly in equation (3), but a practical method of computation can be developed from an alternative definition of the exponential

$$\lim_{n\to\infty} \left(1 + \frac{x}{n}\right)^n = \exp(x) . \quad (5)$$

With $x = i\sigma\varphi(x,y)\Delta z$, and $\mathscr{F}$ the Fourier transform operator, the phase-grating series can be written

$$\left[\delta(h,k) + i\sigma\frac{\Delta z}{n}\mathscr{F}\varphi(x,y)\right] \star \left[\delta(h,k) + i\sigma\frac{\Delta z}{n}\mathscr{F}\varphi(x,y)\right] \star \ldots = A \star A \star A \star \ldots ,$$

which, because of the associative nature of convolution, can be written

$$\ldots \{[(A \star A) \star (A \star A)] \star [(A \star A) \star (A \star A)]\} \star \ldots ,$$

a form suitable for numerical evaluation. Thus, if equation (5) is approximated for some finite n, so that $\Delta' z = \Delta z/n$, the convolutions can be arranged to give a geometric progression in thickness.

An estimate for n is obtained by comparing the binomial and the Taylor expansion. These differ in the third terms, which are $x^2/2! - 1/n . x^2 2!$, and $x^2/2!$ respectively. For accuracies meaningful under current experimental conditions, therefore, $n \sim 10^3$. Lynch (1974) shows that this figure leads to acceptable computing times and gives details of computations.

Alternatively, it is of interest to note that if we multi-slice with (4) in single-slice progression, progressive convolutions generate what are approximately equivalent to successive terms in the Born Series, so that for a particular problem the numerical contribution to an intensity of each order process may be estimated.

In calculation by the multi-slice method no additional steps are required for a non-centrosymmetric projection. In calculations with absorption it is necessary to make two calculations of projected slice potential, that is for the phase object and for the amplitude-scattering object. The phase-grating function is then obtained by Fourier transformation of $\{\exp[i\sigma\varphi(x,y) . \Delta z] \exp[-{}^A\varphi(x,y) . \Delta z]\}$ with ${}^A\varphi(x,y)$ representing the absorbing potential, *i.e.*

$${}^A\varphi(x,y) = \sum_h \sum_k V^i_{hk} \exp\left[-2\pi i\left(\frac{hx}{a} + \frac{ky}{b}\right)\right] .$$

From then on the procedure is unchanged. This method gives us a physical picture allowing us to predict the likely effects of the introduction of phenomenological absorption. In other words, we are introducing a periodic amplitude object, which itself introduces further dynamic effects. Using procedure (*b*), absorption is introduced simply by taking complex structure factors.

4. Testing for errors

Calculation for the two-dimensional diffraction pattern represents the general problem, and is one for which true tests of normalization of intensity may be applied. Reduction to the one-dimensional or systematics case is always obvious and often useful provided it is realized that tests of consistency and normalization then only apply within the terms of reference of the problem, *i.e.* a structure composed of uniform planes of potential. Also no internal clue is obtained as to the validity of this approximation.

Limitations of accuracy in the calculation are likely to come from the choice of Δz, and of diffraction aperture (number of beams), and these choices are related.

If Δz is too large there are two possible errors for a certain diffraction aperture: $\exp\,[i\sigma\varphi(x,y)\Delta z]$ becomes too rapidly oscillating for the sampling interval in the inverse Fourier summation, and/or 'false' upper-layer reflexions are generated corresponding to a unit cell with a $c=\Delta z$. On the first point, rather than taking very fine sampling intervals in the xy plane, it is more convenient to subdivide Δz until ${}^{P}\varphi$ is sufficiently small. A phase-grating function is computed for $\Delta' z = 1/n\Delta z$, from which an accurate phase grating for Δz may be obtained by repeated convolution without propagation, *i.e.* application of equation (3) with $p=1$. This is useful, for example, with heavy atoms and/or large diffraction angles, or simply for obtaining a rapid multi-slice procedure by starting with a thick phase grating, to obtain approximate diffraction intensities for special purposes.

On the second point, if Δz is made sufficiently small (and hence slices sufficiently close) the weight of the false upper-layer interactions will tend to zero, while those *neighbouring* the real upper layers will approach the correct three-dimensional result. However, this is a very inefficient approach because the rest of the calculation becomes over-accurate. It is usually an acceptable approximation to take slices through sections of high atomic density, and to propagate through sections of minimum density. This is particularly so for a layer structure with all atoms confined closely to planes perpendicular to the projection.

If for example we take the functions q_1, q_2, q_3 and $\Delta z_1, \Delta z_2, \Delta z_3$, corresponding to interlayer spacings within the unit cell ($\Delta z_1 + \Delta z_2 + \Delta z_3 = c$), we at least ensure that the upper-layer reflexions have the correct reciprocal-lattice coordinates, even though they may be of incorrect weight. Furthermore, the error in weight of upper-layer interactions introduced by this method is likely to be very small, and smaller than other errors of calculation. There are two situations where this is obviously useful. One is in calculations for a layer structure with a long c axis parallel to the incident beam (see Fig. 1), and the other is with a short c axis but with the incident beam at some large angle to the zone axis. In the latter case upper-layer interactions become 'accidental' interactions and their influence is automatically included.

If the diffraction aperture chosen is too small, the calculation will lose energy.

Two tests which must therefore be carried out are as follows:

(1) A unitarity test on the phase-grating function, before it is multi-sliced, *i.e.*

$$\sum_{h'} \sum_{k'} q(h',k')\,.\,q(h+h',k+k') = \delta(h-h',k-k')\,,$$

a summation carried out over the N beams (all h,k). This test includes the test of normalization to unity of the total transmitted intensity. Then, after multi-slicing, the total intensity $\sum I$ should be compared to unity. For this test a calculation must be made without introducing phenomenological absorption, even if this is to be required finally. Such calculations, to lead to good accuracy, should retain at the last slice preferably 90% or so of the original intensity.

(2) A map of propagation phases,

$$\alpha(h,k) = \Delta z\,\frac{\lambda}{2}\left\{\frac{h(h-h'')}{a^2} + \frac{k(k-k'')}{b^2}\right\}$$

(given here for simplicity for orthogonal axes), where h,k are the indices of a reflexion and h'',k'' continuous direction indices for the incident beam, must be plotted for each orientation so that reflexions from other than the first Laue zone ($\alpha_h < 1$) will be detected. The propagation function, $\exp\,(-i2\pi\alpha_h)$, is the function P used to evaluate equation (3).

For a practical calculation the number of beams to be included can be chosen initially on the basis of re-

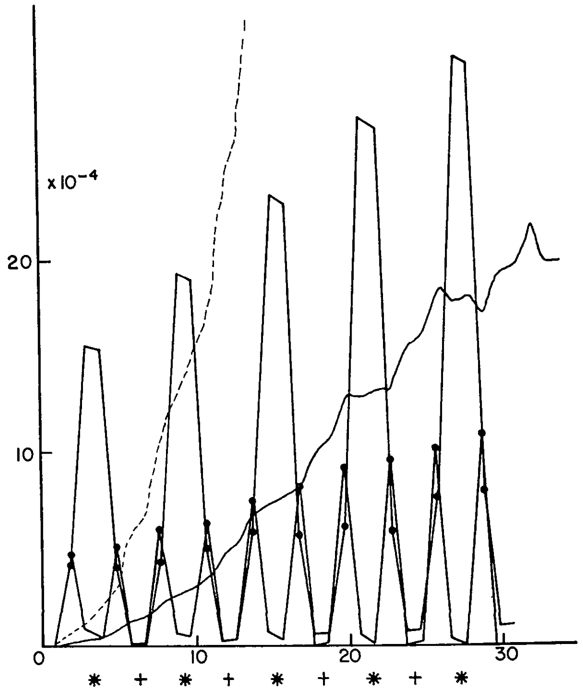

Fig. 1. Intensities of reflexions from MoO_3 computed as a function of thickness for a crystal whose surface is formed by a double octahedral layer, for the [010] zone axis orientation. The broken curve shows the 200 intensity on a scale reduced by 10 relative to the top curves. It is also shown as a full curve reduced 50 times. The other curves are for the 100 reflexion, oscillating with a $\frac{1}{2}$ unit-cell period, and for 001 reflexions, oscillating with a 1 unit-cell period. Crosses and asterisks, correspond to crystal thicknesses commonly observed, which have an integral number of whole and half unit cells respectively.

flexions visible in the diffraction pattern, with the proviso that it is wise not to have a strong reflexion near the edge of the aperture. The normalization test will show if the aperture has been adequate. Δz may be chosen, without detailed examination of the potential, by trying successively smaller values until the final result is not appreciably affected.

If Δz is deliberately made large, *e.g.* to obtain a rapid calculation, the errors will make themselves felt at first at larger scattering angles. With simple structures, having something like a monotonic fall-off in diffraction intensities with angle, these calculations can be useful in obtaining an approximate answer to the main beam intensities in the symmetrical orientation (Johnson, 1968) while giving a poor result for weak high-order reflexions. In these problems one is able to make an optimum choice of Δz based on the information required.

In our experience no atom has been found so heavy as to require sectioning for fast electron diffraction from solids (*e.g.* gold, see Lynch, 1971). Therefore in calculation of $\varphi(x,y)$ the simpler summation $(\sum\limits_h \sum\limits_k V_{hk})$ may always be used for the atoms in each layer, rather than the more complicated summation, $(\sum\limits_h \sum\limits_k \sum\limits_l V_{hkl})$. This will not necessarily be true for gas diffraction or lower-energy diffraction.

5. Summary of procedure

A practical sequence of operations is now given.

(1) *Projected potential*

Assemble kinematic structure factors relevant to the projection, and calculate the projected potentials by Fourier summation. If the calculation is to include phenomenalogical absorption, a similar Fourier summation of the V^{i}_{hk}, must be made to obtain the projected absorbing potential.

(2) *Propagation function*

Given the direction coordinates h'',k'', for the incident beam, calculate and plot the propagation phases,

$$\alpha(h,k)=\Delta z\,\frac{\lambda}{2}\left\{\frac{h(h-h'')}{a^2}+\frac{k(k-k'')}{b^2}\right\}$$

in a two-dimensional array. $\alpha(h,k)$ reaches I at the first Laue circle. If the array reaches and includes this circle it is necessary to ensure that the first upper-layer interactions have been *correctly* included; similarly for higher layers; otherwise the calculation aperture must be reduced to obtain a zero-layer calculation.

For *small* changes in orientation the projected potential need not be recalculated, but the change *must* be introduced in the propagation function. The error introduced in not reprojecting the potential may be simply estimated.

(3) *Calculation of the phase-grating amplitudes*

There are two practical approaches to this calculation.

(*a*) Projected potential method: calculate the Fourier transform of

$$\exp\,\{i\sigma\varphi(x,y)\Delta z\}\,;$$

with phenomenological absorption this becomes the Fourier transform of

$$\exp\,\{i\sigma\varphi(x,y)\Delta z\}\,\exp\,\{-\sigma^A\varphi(x,y)\Delta z\}\,.$$

(*b*) Direct structure-factor method: using very thin slices $\Delta'z(\Delta'z\ll\Delta z)$ take

$$\left.\begin{aligned}q(h,k)&=i\sigma V(h,k,0)\Delta'z\\ q(0,0)&=1\end{aligned}\right\}.$$

(4) *Multi-slice*

Calculate the repetitive convolution of equation (3).

6. Applications

There are now plenty of examples in the literature to provide illustrations of applications in practice, and guidance in choice of parameters. As examples we refer to Goodman & Lehmpfuhl (1967), (1968); Lynch (1971); Johnson (1968); Allpress, Hewat, Moodie & Sanders (1972); Lynch & O'Keefe (1972). In addition two further examples are included in order to show how particular features of the multi-slice method may be exploited. These examples are not intended to explain either the MoO_3 structure or the nature of inelastic scattering, but simply to show the mechanics of the calculation which may be exploited in similar problems.

(1) In diffraction from a parallel-plate crystal, the symmetry of the diffraction pattern is determined by the symmetry of a crystal of finite thickness. The symmetry of the crystal may change with each additional atomic layer, and layers composing the unit cell may themselves belong to different symmetry classes. Because of the very large phase change caused by passing through even one atomic layer, this produces an experimentally observable effect. As an example we show in Fig. 1 calculations for MoO_3, a six-layer structure with three layer types. For MoO_3, $a=3{\cdot}92$, $b=13{\cdot}94$, $c=3{\cdot}66$ Å (orthorhombic), *Pbnm*, and planar group *Cmm* in the (010) projection. Individual MoO_2 layers have the lower symmetry *pm*. Starting, and termination, of the crystal by a particular layer type very strongly influences the intensity of the 100 and 001, (space-group forbidden for *Cmm*) reflexions, while the 200, 002 reflexion intensities are mostly governed by the actual thickness (exhibiting Pendellösung) for the (010) zone-axis calculation. There are two types of phenomena which are shown in the calculation, resulting from dynamic diffraction from the three-dimensional structure. The large oscillation of 100 and 001 intensity with thickness is a projected-potential effect, *i.e.*, the symmetry and (planar) unit-cell size of the projected

potential is an oscillating function of thickness. Kinematically the effect would be small and become vanishingly small with increasing thickness, but with dynamic scattering from a phase object the effect remains significant. This is the main reason for the intensity oscillations shown with $\frac{1}{2}$ and 1 unit-cell periodicity, which continue to large thicknesses. On the other hand differences in diffraction intensities obtained from two crystals containing the same number and identity of layers, but differing in layer sequence, or in identity of the starting (surface) layer, are due to propagation. As a consequence of this effect the 100 and 001 intensities are not the same after traversing equivalent numbers of whole unit cells, in the two crystals represented by Figs. 1 and 2. The intensities are more nearly zero in Fig. 2 because for this crystal the $(\frac{1}{2},\frac{1}{2})$ shift in the structure cancelling out the kinematic structure factors occurs after ~7 Å as against ~14 Å in the crystal corresponding to Fig. 1.

The calculation also showed the very minor role played by absorption in thin crystals. When the calculation was made to include absorbing atoms (assuming the absorption centres coincided with the atom centres) by taking a δ-function absorption model with 0·4 and 0·1 V for Mo and O respectively (giving for example $V^{i}_{002}=2{\cdot}8$ V) no appreciable difference was detected in the thickness curves other than a general damping of the *total* curve.

At intermediate thicknesses absorption introduces intensity changes that are largely separable, but at greater thicknesses the absorption introduces its own dynamic effects which become increasingly difficult to separate out from the effects of phase scattering.

(2) A second example illustrates an application to calculation of diffuse or inelastic scattering from points within the crystal. The use of multi-slice methods for inelastic calculations was first discussed by Gjønnes (1966), and calculations were given by Doyle (1969). Here we must calculate the scattering of the wave up to a point in the crystal, and the subsequent transmission through the remainder of the crystal. However, in calculating by multi-slice for a given angle of incidence and storing all the information up to the exit face, we need only to reassemble this information to obtain the desired result. For a crystal of thickness H, and inelastic scattering from a depth x, we need the diffraction pattern at the depth x, and the subsequent transmission for the depth $H-x$, which is already calculated. We may reassemble this data over all x, either by summing over amplitudes, or intensities. Thus, provided we are content to compute a restricted number of points in reciprocal space, usually points neighbouring the Bragg directions, the multi-slice method may be used economically.

This economy is particularly valuable in calculation for convergent-beam patterns where the calculation must be repeated for a series of incident directions within the incident cone. It is also necessary, in the particular example described, to calculate the incident directions corresponding to the scattering directions of the main Bragg beams. However, further economy is usually possible due to the combination of the reciprocity theorem and the crystal symmetries, *e.g.* in a systematic interaction calculation the number of incident angles calculated may be halved.

In order to obtain the inelastic intensities, a calculation is made both for elastic scattering and for inelastic scattering for a thickness H, for each incident angle. The latter calculation is made by including in the projected potential for the first slice a projected pseudopotential corresponding to the inelastic process represented, or, in the case of phonon scattering, actual atomic displacements may be incorporated into the projected structure. Subsequent slices are for the normal structure.

Hence subsequent convolutions of the calculation propagate separately the elastic, and inelastic beams, through to the exit face. The amplitude and intensity of each beam after each slice is stored. It is noted that the wavelength change may be easily incorporated, but is usually too small to contribute to the observed effects.

The resulting inelastic intensity is calculated by reassembly of the results, as (taking h' to define the scattering direction):

$$\begin{aligned}I^{\text{in}}(h') = {} & I^{\text{in}}(n,h') + I^{\text{in}}(n-1,h_1-h')I^{\text{el}}(1,h_1)\ \ldots \\ & + I^{\text{in}}(n-m,h_1-h')\,.\,I^{\text{el}}(m,h_1)\ \ldots \\ & I^{\text{in}}(1,h_1-h')\,.\,I^{\text{el}}(n-1,h_1)\end{aligned}$$

with the superscripts in and el for inelastic and elastic terms respectively. This gives the contributions from one direction, h_1, to the direction h' or for the total contribution;

$$\begin{aligned}I^{\text{in}}(h')_{\text{total}} = {} & I^{\text{in}}(n,h') + |[u^{\text{in}}(n-1,h_1-h')\,.\,u^{\text{el}}(1,h_1) \\ & + u^{\text{in}}(n-1,h_2-h')u^{\text{el}}(1,h_2) + \ldots]|^2 + \ldots\,.\end{aligned}$$

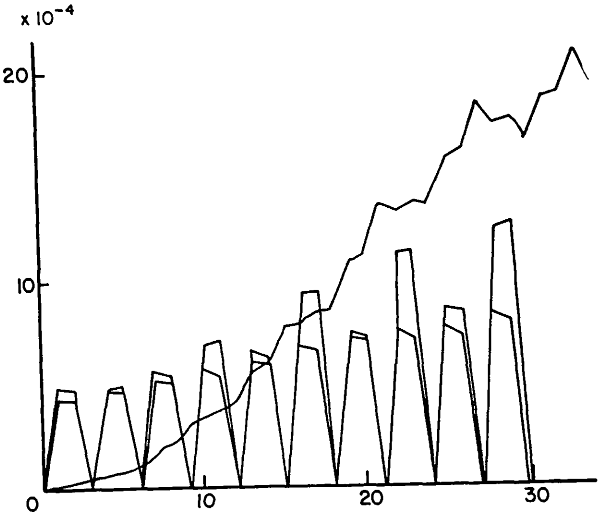

Fig. 2. The corresponding intensity curves for MoO$_3$ in the [010] orientation which start with a single octahedral layer. The diffracted intensities are different, for all thicknesses, from those shown in Fig. 1.

where the summation over contributing beams h_1, h_2 extends only over the strongest beams of the pattern, and not over all beams included in the dynamic calculation.

For a more complete analysis, departure from the Bragg directions and coherence depth in the crystal should be taken as parameters in the calculation, as has been done by Doyle (1969). The principle of this method can also be applied to the economic calculation of elastic scattering from moderately thick crystals. These problems will be described more completely elsewhere.

It might be noted that the multi-slice method is applicable to all problems requiring the N-beam scattering amplitudes. As a further example we quote the calculation of fine-structure associated with diffraction from a wedge crystal. Although it is customary to use the eigenvalue method for this purpose, we have derived this fine structure by integration of the (complex) wave amplitude $u(h,k,z)$ a function of thickness, over a certain thickness range, *i.e.*

$$A(h,k,w) = \int_{z=0}^{z=H} u(h,k,z) \exp\{2\pi izw\}\mathrm{d}z,$$

which is the Fourier transformation of the amplitude u after multiplication with the appropriate step function. In fact we expect this calculation to be more efficient than the eigenvalue method for large numbers of beams. In this equation w is the fine-structure coordinate in reciprocal space, z is crystal thickness at points along the wedge, and A is the fine-structure amplitude for the reflexion hk. The value of H is chosen to suit the experiment.

7. Relationship to other formulations

There are, currently, five formulations describing N-beam scattering. All are equivalent, though for a specific analytical problem one may prove more convenient than another. The connexions between formulations are readily traced, but some of the relationships throw a good deal of light on the efficiencies of the various numerical procedures, and will therefore be considered from this point of view.

In order to clarify expressions the following notation is adopted. Column vectors of arbitrary dimensionality are written in lower-case bold face, matrices in capital bold face, matrix elements as subscripted expressions enclosed in square brackets and a dagger is used to indicate Hermitian transpose. Thus $\mathbf{u}$ is a column vector, $\mathbf{M}$ a matrix, and $[\exp\{i\mathbf{M}^{1/2}z]_{ij}$ is the ijth element of the matrix function enclosed in the square brackets.

An analytical solution is obtained by the multi-slice method on iterating equation (1), and taking the impulse limit. Equation (1), however, can be regarded as the finite difference form of some differential equation that can be derived by Feynman's (1948) method (Path 2, Fig. 3). The number of slices in a crystal of thickness H is $H/\Delta z$, so that, if an error of order $(\Delta z)^2$ is made in each slice, the total error grows as $(H/\Delta z)(\Delta z)^2 = H\Delta z$, which goes to zero in the limit $\Delta z \to 0$. Thus the calculation need be correct only to first order in Δz. Writing the convolution in equation (3) explicitly and expanding $\psi_n(x, -x_1, y-y_1)$,

$$\psi_{n+1} = \exp\{i\sigma\varphi_{n+1}\} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left\{\frac{i\bar{k}(x_1^2+y_1^2)}{2\Delta z}\right\}$$
$$\times \sum_{m=0}^{\infty} \frac{1}{m!}\left(-x_1\frac{\partial}{\partial x} - y_1\frac{\partial}{\partial y}\right)^m$$
$$\times\ \psi_n(x,y)\mathrm{d}x_1\mathrm{d}y_1 .$$

This leads to integrals of the form,

$$\frac{1}{(p+q)!}\frac{\partial^{p+q}}{\partial x^p \partial y^q}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} x_1^p y_1^q \exp\left\{\frac{i\bar{k}(x_1^2+y_1^2)}{2\Delta z}\right\}$$
$$\times\ \mathrm{d}x_1\mathrm{d}y_1 .$$

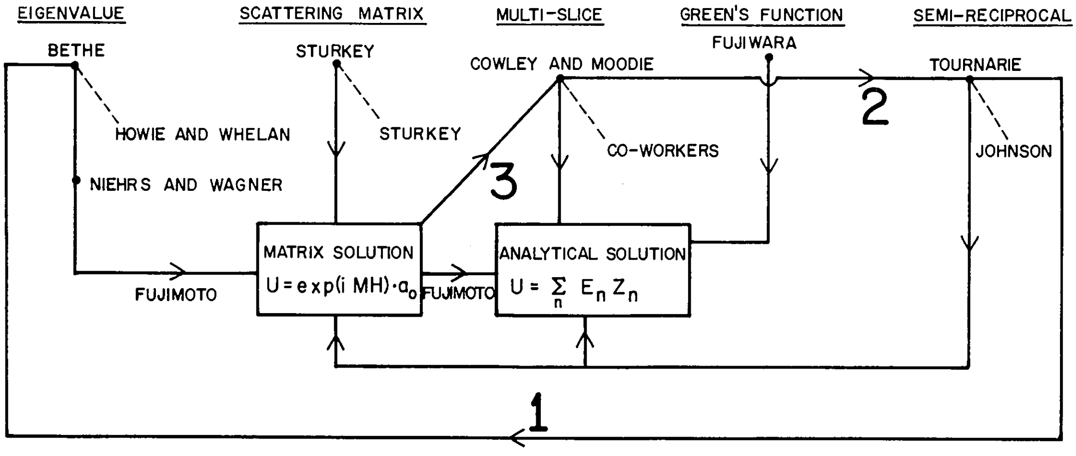

Fig. 3. The relationship between the five principal N-beam formulations. Headings give the principal methods. Boxes show the solutions. Full lines are theoretical treatments; broken lines show numerical applications.

The only non-zero integrals of appropriately low order in Δz are,

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp\left\{\frac{ik(x_1^2+y_1^2)}{2\Delta z}\right\}\mathrm{d}x_1\mathrm{d}y_1=\frac{2\pi i\Delta z}{k}$$

and,

$$\frac{1}{2!}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[x_1^2\exp\left\{\frac{ik(x_1^2+y_1^2)}{2\Delta z}\right\}\frac{\partial^2\psi}{\partial x^2}+y_1^2\exp\left\{\frac{ik(x_1^2+y_1^2)}{2\Delta z}\right\}\frac{\partial^2\psi}{\partial y^2}\right]\mathrm{d}x_1\mathrm{d}y_1$$

$$=\left(\frac{i\Delta z}{k}\right)\left(\frac{2\pi i\Delta z}{k}\right)\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\mathrm{d}y^2}\right).$$

Substituting these values in equation (6), taking, to sufficient accuracy, $\exp\{i\sigma\varphi_{n+1}\Delta z\}=(1+i\sigma\varphi_{n+1}\Delta z)$ and expanding ψ_{n+1} as,

$$\psi_{n+1}=\psi(x,y,z+\Delta z)\approx\psi(x,y)+\frac{\partial\psi}{\partial z}\Delta z\,,$$

$$\psi+\frac{\partial\psi}{\partial z}\Delta z\approx\frac{2\pi i\Delta z}{k}(1+i\sigma\varphi\Delta z)$$
$$\times\left[\psi+\frac{i\Delta z}{k}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)\right].$$

Normalizing and equating coefficients gives,

$$i2k\frac{\partial\psi}{\partial z}=-2k\sigma\varphi\psi-\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right),$$

which is Schrödinger's equation with no back scattering. Fourier transforming this equation with respect to x and y gives Tournarie's semi-reciprocal equation for no back scattering,

$$\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}z}=i\mathbf{M}(z)\mathbf{u}\,, \tag{7}$$

with **u** the column vector of the scattering amplitudes and **M** the matrix with components,

$$\mathbf{M}=\mathbf{K}+\tfrac{1}{2}\mathbf{K}^{-1}\mathbf{V}(z)\,,\quad[\mathbf{K}]_{ij}=\delta_{ij}K_i\,,$$
$$[\mathbf{V}]_{ij}=2k\sigma\sum_{e}V_{i-j}\exp\{2\pi ilz\}\,.$$

K_i is the z component of momentum of a beam scattered in the direction **i**. Equation (7) can be obtained directly by applying Feynman's method to equation (2), that is, equation (2) can be regarded as a finite difference form of equation (7). Broadly, numerical methods based on equation (7) will involve either a direct attack on the set of coupled differential equations, or a transformation of the set into finite difference form, equation (2) being one such form. In fact it is a very efficient form since the set is fundamentally oscillatory and presents classic difficulties to standard relaxation techniques. Johnson (1968) has described methods for the direct solution of equation (4) on an analogue computer. The principal advantage of this method is its speed, which is sufficient to allow the continuous display of scattering amplitudes, or intensities as a function of thickness, or angle of incidence, while parameters in the computation are varied. For any but the largest computers, however, the number of beams that can be included is limited to 10 or 15. Nevertheless the method has been found to be powerful (Goodman, 1971; Lynch, 1971), particularly when used in the survey of parameters for more extensive digital computations, and in utilizing effective potentials determined by digital computation (Goodman, 1974).

If **M** is taken to be independent of z, that is, if upper layer-line interactions are neglected, the solution to equation (7) can be written down immediately as,

$$\mathbf{u}=\exp\{i\mathbf{M}H\}\mathbf{a}_0\,, \tag{8}$$

where H is the crystal thickness and

$$\mathbf{u}(0)=\mathbf{a}_0=\begin{pmatrix}1\\0\\0\\\cdot\\\cdot\\\cdot\end{pmatrix}.$$

Equation (8) is Sturkey's (1962) solution.

Direct computation of the matrix series for **u** is impracticable because of slow convergence. Sturkey solves this problem by using the relation

$$\exp\{i\mathbf{M}H\}=\left[\exp\left\{i\mathbf{M}\frac{H}{n}\right\}\right]^n=[\exp\{i\mathbf{M}\Delta z\}]^n.$$

n is chosen sufficiently large that $\exp\{i\mathbf{M}\Delta z\}$ converges in a few terms, and direct matrix multiplication generates the result for the required thickness. It is a disadvantage of this method that all terms in the scattering matrix must be evaluated by a full-matrix multiplication. With some rearrangement this disadvantage can be overcome at the expense of iterating at equal intervals over the complete range of thickness: in fact, multi-slicing with unit-cell increments in thickness. This can be seen (Path 3, Fig. 3) by making use of a theorem due to Zassenhaus and quoted by Magnus (1954), which states that if **A** and **B** are square matrices of the same dimension,

$$\exp\{\mathbf{A}+\mathbf{B}\}=\prod_{p}\exp\{\mathbf{G}_p\}\,,$$

where the $\mathbf{G}_p$ are elements of a Lie algebra; and that the product series is convergent. The $\mathbf{G}_p$, which increase rapidly in complexity, can be determined by iteration, the first three being, $\mathbf{A},\mathbf{B},-\frac{1}{2}\{\mathbf{AB}-\mathbf{BA}\}=-\frac{1}{2}[\mathbf{A},\mathbf{B}]$. Writing $\mathbf{K}=\mathbf{K}_0+2\pi\mathbf{Z}$, so that

$$[\mathbf{K}]_{ii}=k+2\pi\xi_i\,,\ [\mathbf{K}]_{ij}=0\,,$$

and putting

$$\left.\begin{array}{l}[\mathbf{A}]_{ij}=[\mathbf{K}^{-1}\mathbf{V}]_{ij}=[\mathbf{V}']_{ij}\\ {[\mathbf{A}]_{ii}=0}\end{array}\right\}\left.\begin{array}{l}[\mathbf{B}]_{ij}=0\\ {[\mathbf{B}]_{ii}=k+2\pi\xi_i}\end{array}\right\},$$

then

$$\exp\{i\mathbf{M}\Delta z\}\simeq\exp\{i\mathbf{K}_0\Delta z\}\exp\{i2\pi\mathbf{Z}\Delta z\}$$
$$\times\exp\{i\mathbf{V}'\Delta z\}\exp\left\{-\frac{i}{2}[\mathbf{K}\Delta z,\mathbf{V}'\Delta z]\right\}\ldots,$$

Δz being chosen, in the first instance, sufficiently small to ensure convergence. Since the commutators are necessarily smaller than the constituent elements it will be possible to choose Δz such that

$$\exp\{i\mathbf{M}\Delta z\}\simeq\exp\{i\mathbf{K}_0\Delta z\}\exp\{i2\pi\mathbf{Z}\Delta z\}$$
$$\times\exp\{i\mathbf{V}'\Delta z\}.$$

Hence,

$$\exp\{i\mathbf{M}z\}\mathbf{a}_0=\exp\{i\mathbf{M}n\Delta z\}\mathbf{a}_0=[\exp\{i\mathbf{M}\Delta z\}]^n\mathbf{a}_0$$
$$=[\exp\{i\mathbf{K}_0\Delta z\}\exp\{i2\pi\mathbf{Z}\Delta z\}$$
$$\times\exp\{i\mathbf{V}'\Delta z\}]^n\mathbf{a}_0\ldots. \quad (9)$$

In the analytical solution, *i.e.* for an infinite matrix, the elements of the matrix, $\exp\{i\mathbf{V}'\Delta z\}$, are precisely those of the phase-grating approximation so that the repeated multiplications of equation (9) are precisely the iterations of the multi-slice method. This situation is often approached in current numerical work.

However, when an approximate calculation is required, *i.e.* when the number of beams is deliberately restricted, the two methods will only give identical results when the order and contents of the matrix, and the length of the multi-slice sequence, are made compatible. This situation arises because the number of coupling terms in the calculation is not necessarily the same, and is generally greater than, the number of beams computed.

In calculation for a thick crystal it is possible to drop a number of terms from the calculation after a certain stage and still maintain a consistent accuracy, because the intensities in the outer beams are reduced by propagation.

A point of detail arises in the element of the matrix **M**, given by,

$$\frac{1}{2K_i}2k\sigma V_{i-j}=\frac{\sigma}{\cos\theta_i}V_{i-j},$$

where θ_i is the angle through which the beam is scattered. In the previous sections $\cos\theta_i$ has been approximated as unity, since even the most accurate measurements are so far in error by much more than this amount. In terms of multi-slicing the factor arises from the increasing path length, and hence phase change, with increasing scattering angle.

Sturkey (1962) was the first to point out a rapid method of calculation for a given thickness, involving raising the matrix to the nth power (equation 2.11 of the above reference). In order to use the multi-slice method in an equivalent way, careful attention must be given to those details discussed in connexion with equation (9). In many applications however, intensities or amplitudes are required over a certain range as an almost continuous function of thickness. Because of this, and the points discussed above, Sturkey's method is not usually advantageous numerically compared with the multi-slice method, but his formulation is particularly powerful analytically (*e.g.* Anstis, Lynch, Moodie & O'Keefe, 1973; Lynch & Moodie, 1972).

Upper-layer-line effects can be accurately incorporated into the multi-slice method by making Δz sufficiently small. This suggests that Sturkey's solution can be generalized to include upper-layer-line effects, and this, in fact can be done (and has been, in effect, by Sturkey, 1962), although the solution can no longer be written in a form as simple as equation (8).

The relationship with Bethe's eigenvalue technique (Path 1, Fig. 3) can be obtained by making the change of variable $\mathbf{u}=\mathbf{T}\mathbf{y}$ in equation (8). Then,

$$\frac{d\mathbf{u}}{dz}=\mathbf{T}\frac{d\mathbf{y}}{dz},\quad \mathbf{T}\mathbf{y}(0)=\mathbf{a}_0,$$

$$\frac{d\mathbf{y}}{dz}=i\mathbf{T}^{-1}\mathbf{M}\mathbf{T}\mathbf{y}.$$

Suppose **T** is such that

$$\mathbf{T}^{-1}\mathbf{M}\mathbf{T}=\begin{pmatrix}\lambda_1 & & & \\ & \ddots & & \\ & & \lambda_p & \\ & & & \ddots\end{pmatrix},$$

i.e. the λ_i are the eigenvalues of **M**, then

$$\mathbf{y}=\begin{pmatrix}\exp i\lambda_1 z & & & \\ & \ddots & & \\ & & \exp i\lambda_p z & \\ & & & \ddots\end{pmatrix}\mathbf{T}^{-1}\mathbf{a}_0,$$

$$\mathbf{u}=\mathbf{T}\begin{pmatrix}\exp i\lambda_1 z & & & \\ & \ddots & & \\ & & \exp i\lambda_p z & \\ & & & \ddots\end{pmatrix}\mathbf{T}^{-1}\mathbf{a}_0,$$

giving Fujimoto's (1959) expression,

$$[\mathbf{u}]_h=\sum_p[{}^pt_o^{xp}t_h\exp\{i\lambda_p z\}],$$

where the ${}^pt_h$ are the components of the eigenvectors. From this point of view the eigenvalue formulation uncouples the set of differential equations and gives the solution in terms of the eigenvalues. Apart from the difficulties inherent in deriving accurate eigenvalues for an oscillatory solution derived from many normal modes, the computer memory required increases as the square of the number of beams. Again, this results from working with the full $N\times N$ matrix, when, ultimately only a column of numbers is required.

Thus, in the three main computational methods; the scattering matrix, the eigenvalue, and the multi-slice, the first two require a computer memory porportional to N^2, and the latter, as is shown in § 2, only to N. Ultimately the reason for this is that the multislice numerical method incorporates the boundary conditions from the outset.

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Vibrations des Atomes des Composés III–V. Cas du Phosphure de Gallium

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A simple method of calculating the mean-square displacement $\langle u^2\rangle$ of the different atoms in III–V compounds is given. The method is applied to GaP and the results are compared with experimental values determined by X-ray diffraction. 2500 reflexions were measured at room temperature with an automatic diffractometer. The values of $\langle u^2\rangle^{1/2}$ deduced from experiment, *i.e.* $0{\cdot}067 \pm 0{\cdot}001$ Å for Ga and $0{\cdot}077 \pm 0{\cdot}002$ Å for P, are in agreement with the computed values.

Les amplitudes quadratiques moyennes $\langle u^2\rangle$ des vibrations des atomes du cristal de GaP ont été mesurées par deux équipes différentes (Liang, Guenzer & Bienenstock, 1970; Rosov & Sirota, 1967) en analysant les intensités de rayons X diffusés par une poudre de ce composé. La première équipe trouva $\langle u^2\rangle^{1/2}_{\mathrm{Ga}} = 0{,}074$ Å,