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The Importance of Second-Order Partial Derivatives in the Theory of High-Energy-Electron Diffraction from Imperfect Crystals

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The dynamical equations of high-energy-electron diffraction from imperfect crystals are reduced to the usual first-order hyperbolic system of partial differential equations by neglecting second-order partial derivatives. This system is then converted to an integral equation from which an iterative solution is obtained. Next, a second-order parabolic system of partial differential equations is considered. An equivalent integral equation is constructed, and by an asymptotic expansion is compared with the integral equation for the first-order system. Finally an explicit correction term is given as a measure of the validity of ignoring the second-order partial derivatives in deriving the first-order equation.

1. Introduction

In transmission electron microscopy the usual descriptions of high-energy-electron diffraction from imperfect crystals (*e.g.* Takagi, 1962, 1969; Lewis & Villagrana, 1972), that are used to describe diffraction-contrast images, neglect second-order partial derivatives. By comparing contrast calculations made both with and without second-order partial derivatives, Howie & Basinski (1968) have questioned this approximation for certain diffraction conditions. Since numerical calculations using the complete dynamical diffraction equations are quite lengthy, it is desirable to have an analytical method to assess the importance of second-order partial derivatives. In this paper we shall set forth such a criterion for judging the importance of these derivatives.

First, we shall derive an integral equation from which we obtain an iterative solution for the first-order hyperbolic system one obtains when second-order partial derivatives are neglected in the dynamical equations (Takagi formalism). Next, we shall obtain an equivalent integral equation to the complete dynamical equations. Then by means of an asymptotic expansion we obtain the solution for this system, so that we can compare it to the solution of the first-order diffraction equations. The difference between these two solutions provides a measure of the validity of ignoring second-order partial derivatives in the dynamical equations.

2. The imperfect-crystal equations

If we were to stress any of the words of the title of this section, the emphasis would be on the word crystal. The reason for this is that we are considering electron diffraction from substances whose underlying structure is clearly and unmistakeably crystalline. This is not to imply, of course, that the crystal does not contain imperfections such as point defects or dislocations, but merely the existence of a well defined reference lattice. It is this well defined reference lattice that accounts for the coarse structure in an electron-diffraction pattern from an imperfect crystal.

What is this coarse structure, and how can we most naturally incorporate it into a diffraction theory? In order to answer the first question, we suggest that the diffraction pattern from the substances that we are considering must contain the clear imprint of the reference crystal. By this we mean that there exist well localized diffraction maxima separated from each other by regions of negligible intensity, and that these maxima are arranged in an array that images a portion of the reference reciprocal lattice. (In an imaginary world, where we might have at our disposal an infinitely large sample of perfect crystal and detection instruments of unlimited resolution, these maxima would shrink to the limiting case of the mathematical points of the reciprocal lattice.)

In response to our second question, we suggest that the localized nature of the imperfect-crystal diffraction pattern motivates us to consider a resolution of the various functions that would have been spatially periodic in the perfect crystal into a series of terms, each of which has a Fourier transform that has support in a different region of Fourier (reciprocal) space. Clearly the disjoint nature of this support and the completeness of reciprocal space suggests that we are dealing with a unique expansion of an arbitrary function into orthogonal terms. To be explicit, we shall expand the Schrödinger wavefunction of the scattered electrons as

$$\Phi(\mathbf{r}) = \sum_{g} d_g(\mathbf{r}) \exp (i\mathbf{k}_g \cdot \mathbf{r}) \tag{1}$$

where **g** (and later **h**) is a compressed notation for the reciprocal-lattice vector corresponding to the diffract-

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ing planes (hkl), $|\mathbf{g}| = 2\pi/d$, d is the atomic spacing of the planes (hkl), $\mathbf{k}_g \equiv \mathbf{k}_0 + \mathbf{g}$, where $\mathbf{k}_0$ points in the direction of the transmitted beam, $|\mathbf{k}_0| = 2\pi/\lambda$, and λ is the electron wavelength. It is important to point out that the Fourier transform of $d_g(\mathbf{r})$ has support only within the first Brillouin zone for all $\mathbf{g}$. This expansion for the wave function can be achieved for any reasonable $\Phi(\mathbf{r})$ and it is, of course, equivalent to writing $\Phi(\mathbf{r})$ as the Fourier transform of another function; however we feel that in view of our previous remarks this expansion is more natural and more susceptible to physical interpretation than a Fourier transform. Also, equation (1) has the important advantage of maintaining a very close notational connection with the Fourier series one would use for the limiting case of the perfect crystal, while simultaneously allowing one to relax the constraint of translational invariance. The main task of the theory will be to calculate the unknown functions $d_g(\mathbf{r})$.

The precise connection between the expansion given in equation (1) and the more usual Fourier transform is easily outlined. First, we define the Fourier transform of $\Phi(\mathbf{r})$ through the equation

$$\Phi(\mathbf{r}) = \int_{-\infty}^{\infty} \tilde{\Phi}(\mathbf{k}) \exp(i\mathbf{k} \,.\, \mathbf{r}) \mathrm{d}\mathbf{k} \tag{2}$$

where $\mathrm{d}\mathbf{k} \equiv \mathrm{d}^n k$ and n is the dimensionality. Clearly this integral can be broken up into a sum of integrals, one for each reciprocal-lattice point, where the corresponding region of integration is restricted to a reciprocal cell, equivalent to the first Brillouin zone, centered on a reciprocal-lattice point (we shall refer to the cell centered on the origin of reciprocal space as the first cell). In order to do this efficiently, let us define the notation $[k_g]$ to mean the reciprocal-lattice point closest to the vector $\mathbf{k}_g$ (this vector is not in general a reciprocal-lattice vector). Also, we will make use of the characteristic function $f_g(\mathbf{k})$, which equals one when $\mathbf{k}$ lies in the cell centered on $\mathbf{g}$ and zero otherwise. Our definition of $d_g(\mathbf{r})$ is then

$$d_g(\mathbf{r}) = \exp(-i\mathbf{k}_g \,.\, \mathbf{r}) \int_{-\infty}^{\infty} f_{[k_g]}(\mathbf{k}) \tilde{\Phi}(\mathbf{k}) \exp(i\mathbf{k} \,.\, \mathbf{r}) \mathrm{d}\mathbf{k} \,. \tag{3}$$

The integral in equation (3) is, of course, not really over the entire reciprocal space, but rather over one cell because of the presence of the characteristic function. By comparing the expansion of equation (1) to that of equation (2), making use of our definition of $d_g(\mathbf{r})$, one readily sees that the two expansions are equivalent. Furthermore, by using a simple shift of the variables of integration in equation (3), we have

$$d_g(\mathbf{r}) = \int_{-\infty}^{\infty} f_{[k_g]}(\mathbf{k} + \mathbf{k}_g) \tilde{\Phi}(\mathbf{k} + \mathbf{k}_g) \exp(i\mathbf{k} \,.\, \mathbf{r}) \mathrm{d}\mathbf{k} \,. \tag{4}$$

Inspection of the indices of the characteristic function in equation (4) tells us that $d_g(\mathbf{r})$ has support only in the first cell.

We shall resolve the imperfect-crystal potential, $V(\mathbf{r})$, in the same manner as the wave function:

$$V(\mathbf{r}) = \sum_g v_g(\mathbf{r}) \exp(i\mathbf{g} \,.\, \mathbf{r}) \,. \tag{5}$$

Next, by requiring that the wavefunction be a solution of the time-independent Schrödinger equation, we obtain

$$\begin{aligned} \sum_g \Big[& \frac{-i}{2k_{gz}} \nabla^2 d_g(\mathbf{r}) + \frac{\partial}{\partial z} d_g(\mathbf{r}) \\ & + \frac{k_{gx}}{k_{gz}} \frac{\partial}{\partial x} d_g(\mathbf{r}) + \frac{k_{gy}}{k_{gz}} \frac{\partial}{\partial y} d_g(\mathbf{r}) \\ & - \frac{i}{2k_{gz}} (X^2 - k_g^2) d_g(\mathbf{r}) - \frac{i}{2k_{gz}} \sum_h u_{g-h}(\mathbf{r}) d_g(\mathbf{r}) \Big] \\ & \times \exp(i\mathbf{k}_g \,.\, \mathbf{r}) = 0 \end{aligned} \tag{6}$$

where $u_g(\mathbf{r}) \equiv \hbar^2 v_g(\mathbf{r})/2m$, $\mathbf{X}$ is the wave vector of the electron in vacuum, and m is the relativistically corrected electron mass.

At this point in our derivation we make our first and principle approximation to the Schrödinger equation, so that we can obtain 'simple' local differential equations for the functions $d_g(\mathbf{r})$. We shall assume that the Fourier transform of each of the terms enclosed in brackets in equation (6) has support in the first cell. Now according to our previously defined construction the Fourier transform of each of these terms, with the possible exception of the product term $-i\sum_h u_{g-h}(\mathbf{r}) d_g(\mathbf{r}) / 2k_{gz}$, has support in the first cell. Since the Fourier transform of the product term is a convolution, it can have support in the first cell as well as higher-order cells. Therefore, our approximation amounts to neglecting the overlap of the transformed product term into higher-order cells. This approximation is rigorously exact for the perfect crystal, and for the imperfect crystal its degree of validity depends on the magnitude of the lattice distortion. If, for example, the Fourier transforms of both $u_{g-h}(\mathbf{r})$ and $d_g(\mathbf{r})$ do not extend appreciably past the first half of the first cell, then there is essentially no overlap whatsoever.

Once the overlap of the transformed product term is neglected the entire term in brackets has support in the first cell. Consequently, equation (6) represents an expansion of zero into a series of orthogonal terms, telling us that each term of the series must equal zero. Thus, we are led to a set of approximate local differential equations for the unknown functions $d_g(\mathbf{r})$.

Since we are interpreting the functions $d_g(\mathbf{r})$ as describing diffraction into disjoint regions of reciprocal space, the experimental existence of only a finite number of maxima in the diffraction pattern suggest another well known approximation, the n-beam approximation. In this approximation we retain only a finite subset of the local differential equations. We shall also simplify our analysis of these equations, without loss of generality, by restricting the coordinate dependence to two coordinates (in Fig. 1, x is the transverse coordinate and z is the parallel coordinate). We then have the following system of n equations:

$$-\frac{i}{2k_{gz}}\nabla^2 d_g(x,z)+\frac{\partial}{\partial z}d_g(x,z)+\frac{k_{gx}}{k_{gz}}\frac{\partial}{\partial x}d_g(x,z)$$
$$-\frac{i}{2k_{gz}}(X^2-k_g^2)d_g(x,z)-\frac{i}{2k_{gz}}\sum_h u_{g-h}(x,z)$$
$$\times\, d_g(x,z)=0\,. \tag{7}$$

To summarize, equation (7) is an approximation whose solutions are approximations to the exact $d_g(\mathbf{r})$. Being approximations they do not in general have compact support. The validity of the approximation leading to equation (7) is measured by the overlap of the Fourier transform of the product term into higher-order cells. As pointed out by Howie & Basinski (1968), this approximation must be questioned when the lattice distortion varies so rapidly with position that diffuse scattering is visible in regions mid-way between the Bragg maxima in the diffraction pattern. In this case one must use a more rigorous formulation of the dynamical theory (*e.g.* Kuriyama, 1972) to describe the diffraction process.

In order to facilitate further manipulations, we shall rewrite equation (7) in matrix form:

$$-i\mathbf{C}\,\nabla^2\mathbf{D}(x,z)+\left(\mathbf{I}\frac{\partial}{\partial z}+\mathbf{B}\frac{\partial}{\partial x}\right)\mathbf{D}(x,z)$$
$$=i\mathbf{A}(x,z)\mathbf{D}(x,z) \tag{8}$$

where $\mathbf{C}$ is a matrix with elements $C_{gh}=\delta_{gh2}k_{gz}$, $\mathbf{D}(x,z)$ is a column vector with elements $d_g(x,z)$, $\mathbf{I}$ is the identity matrix, $\mathbf{A}(x,z)$ is a matrix with elements

$$A_{gh}=\begin{cases}\dfrac{1}{k2_{gz}}(X^2+u_0-k_g^2) & \text{for}\quad g=h\\[2ex] \dfrac{1}{2k_{gz}}u_{g-h}(x,z) & \text{for}\quad g\neq h\end{cases}$$

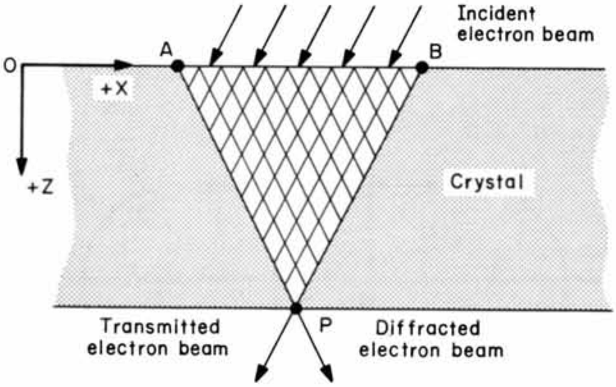

Fig. 1. Two-beam region of determinancy. The triangle *PAB* and its mesh are generated by the characteristics of the hyperbolic system and define the region of determinancy for the point *P*. The coordinate system used in this work is also indicated.

and $\mathbf{B}$ is a matrix with elements $B_{gh}=k_{gx}\delta_{gh}/k_{gz}$. We shall refer to equation (8) as the second-order equation of high-energy-electron diffraction from an imperfect crystal.

Since we have assumed that the terms in equation (6) are orthogonal, we expect that the $d_g(x,z)$ will be slowly varying on the scale of a unit cell. Because of this, we shall initially neglect the term involving $\nabla^2\mathbf{D}(x,z)$ in equation (8). Thus, we obtain the hyperbolic system

$$\hat{\mathbf{L}}\mathbf{D}(x,z)=i\mathbf{A}(x,z)\mathbf{D}(x,z) \tag{9}$$

where $\hat{\mathbf{L}}=(\mathbf{I}\partial/\partial z+\mathbf{B}\partial/\partial x)$ and the operator $\hat{\mathbf{L}}$ is hyperbolic and in normal form. We shall refer to this equation as the first-order equation of high-energy-electron diffraction from an imperfect crystal.

3. The first-order equations

As we have noted, the operator $\hat{\mathbf{L}}$ is hyperbolic; that is to say the elements of $\hat{\mathbf{L}}$ are directional (interior) derivatives along the characteristic curves

$$\frac{\mathrm{d}x_g(z)}{\mathrm{d}z}=\tan\theta_g \tag{10}$$

where θ_g is the Bragg angle of the gth reflection, and the $x_g(z)$ are merely straight lines in the x–z plane, since the Bragg angles of the diffracted waves are constant parameters. As shown in Fig. 1, the region of determinancy for the solution $\mathbf{D}(x,z)$ at a point P in the crystal consists of the interior of the triangle bounded by the characteristics with the greatest and least slopes passing through P, and the base $z=0$.

One also notices that in equation (8), the inverse of the wave vector plays the role of a coupling constant. The higher the energy of the incident wave, the larger $\mathbf{k}_g$, and hence, the smaller the coupling to the crystal potential. It is for this reason that it seems useful to construct an iterative solution to equation (9) in powers of the $\mathbf{A}(x,z)$ matrix. We shall do this by finding a Green matrix for $\hat{\mathbf{L}}$, that is a matrix $\mathbf{G}^{\mathrm{I}}(x,z;x',z')$ which satisfies

$$\hat{\mathbf{L}}\mathbf{G}^{\mathrm{I}}(x,z;x',z')=\delta(x-x')\delta(z-z')\mathbf{I}\,. \tag{11}$$

Then by the usual device of treating the term of the right-hand side of equation (9) as a source, we may construct an equivalent integral equation and exhibit its solution by iterating the integral.

We would point out that constructing the Green matrix is really unnecessary for merely turning equation (9) into an integral equation. Because $\hat{\mathbf{L}}$ represents directional differentiation along the characteristics, its inverse is merely directional integration along the characteristics and so the integral equation may be written down directly. However, we present the Green function for two reasons: (i) it may be compared to the Green function that results when one does not neglect the term involving $\nabla^2\mathbf{D}(x,z)$ in equation (8), and (ii) it is notationally difficult to express the inverse of $\hat{\mathbf{L}}$

in matrix form, so the explicit use of the Green matrix is a helpful indexing aid when iterating the integral equation.

We seek a matrix $\mathbf{G}^{\mathrm{I}}(x,z;\,x',z')$ which satisfies equation (11). Since our crystal has infinite extent in the x direction and a boundary surface at $z=0$, we are motivated to transform the equation with a Fourier transform in x and a Laplace transform in z. Without loss of generality, we shall take $\mathbf{G}^{\mathrm{I}}(x,0;\,x',z')=0$. These transformations will then render the solution transparent.

Transforming equation (11) we obtain

$$(s\mathbf{I}+ik\mathbf{B})\tilde{\mathbf{G}}^{\mathrm{I}}(k,s;\,x',z') = \frac{1}{2\pi}\exp(-ikx')\exp(-sz')\mathbf{I} \quad (12)$$

where $\tilde{\mathbf{G}}^{\mathrm{I}}(k,s;\,x',z')$ is the transformed Green matrix. Hence we may write

$$\mathbf{G}^{\mathrm{I}}(x,z;\,x',z')=\frac{1}{4\pi^2 i}\int_{-\infty}^{\infty}\int_{c-i\infty}^{c+i\infty}\frac{1}{(s\mathbf{I}+ik\mathbf{B})} \times\exp[ik(x-x')]\exp[s(z-z')]\mathrm{d}s\mathrm{d}k \quad (13)$$

where $1/(s\mathbf{I}+ik\mathbf{B})=(s\mathbf{I}+ik\mathbf{B})^{-1}$ and c is to the right of all poles of this matrix. We shall evaluate the s integral with the generalized Cauchy relation for a matrix $\mathbf{Q}$,

$$\frac{1}{2\pi i}\oint\frac{f(s)}{s\mathbf{I}-\mathbf{Q}}\,\mathrm{d}s=f(\mathbf{Q}),$$

assuming $f(s)$ is analytic in the domain including the eigenvalues of $\mathbf{Q}$. (Since the matrices are diagonal here, we do not really need this relation; we present it as a useful tool for more sophisticated manipulations.) Again, referring to the s integral, we note that all the poles are on the imaginary s axis, since the elements of $\mathbf{B}$ are real, and so we must only require that $c=\varepsilon$, where $\varepsilon>0$. For $z<z'$, we must enclose this contour on the right, obtaining zero for the integral. For $z>z'$, we must enclose on the left and the simple poles contribute their residues (the integration contours are shown in Fig. 2). So we have

$$\mathbf{G}^{\mathrm{I}}(x,z;\,x',z')=\frac{\theta(z-z')}{2\pi} \times\int_{-\infty}^{\infty}\exp\{ik[(x-x')\mathbf{I}-(z-z')\mathbf{B}]\}\mathrm{d}k \quad (14)$$

where $\theta(z-z')$ is the usual unit step function. The Fourier inversion is similarly trivial and we have for equation (14)

$$\mathbf{G}^{\mathrm{I}}(x,z;\,x',z')=\theta(z-z')\mathbf{E}(x,z;\,x',z') \quad (15)$$

where $\mathbf{E}(x,z;\,x',z')$ is a matrix with elements $E_{gh}=\delta[(x-x')-(z-z')\tan\theta_g]\delta_{gh}$.

The Green matrix is a diagonal matrix that is singular on the characteristics emanating in the forward $(z>z')$ direction from the source location (x',z'). That is, z behaves formally as a time variable, and through our choice of $\varepsilon>0$ we have constructed the physical retarded Green matrix. One sees in the result how hyperbolic operators tend to propagate discontinuities down their characteristics; the point singularity at (x',z') has been transported down each one of the n characteristics by the appropriate component of $\hat{\mathbf{L}}$. Since our differential operator is only first-order, and our source a delta function of second-order we could have anticipated the singular behavior of the Green matrix.

We may now write an equivalent integral equation for equation (9)

$$\mathbf{D}(x,z)=\mathbf{D}(0)+i\int_0^z\int_{-\infty}^{\infty}\mathbf{E}(x,z;\,x',z') \times\mathbf{A}(x',z')\mathbf{D}(x',z')\mathrm{d}x'\mathrm{d}z' \quad (16)$$

where $\mathbf{D}(0)$ is a column vector with elements $d_g(x,0)=\delta_{g0}$ which are specified by the usual plane-wave boundary conditions at $z=0$. Now because of the delta functions in $\mathbf{G}^{\mathrm{I}}(x,z;\,x',z')$, the integral over x' in equation (16) may be performed immediately leaving only an integration in one parameter. The final result, as we have already mentioned, is merely an integration along the characteristics.

In component form, the integral equation becomes

$$d_g(x,z)=d_g(x,0)+i\sum_h\int_0^z A_{gh}[x-(z-z')\tan\theta_g,z'] \times d_h[x-(z-z')\tan\theta_g,z']\mathrm{d}z'. \quad (17)$$

We may exhibit equation (17) in matrix form by defining a retarded distance, through $x_g^{\mathrm{ret.}}=x-(z-z')\tan\theta_g$. Then always keeping in mind that the index on $x_g^{\mathrm{ret.}}$ is the same as the index implied by $d_g(x,z)$ on the left-hand side of equation (17), we may write

$$\mathbf{D}(x,z)=\mathbf{D}(0)+i\int_0^z\mathbf{A}(x^{\mathrm{ret.}},z')\mathbf{D}(x^{\mathrm{ret.}},z')\mathrm{d}z'. \quad (18)$$

As we have mentioned, displaying the integral equation in matrix form presents the notational problem

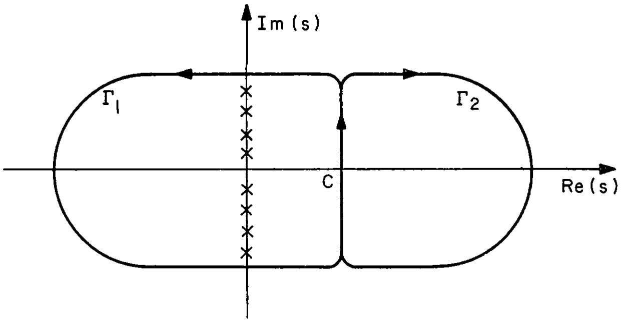

Fig. 2. The complex s-plane showing the contours (Γ_1 for $z>z'$ and Γ_2 for $z<z'$) used to perform the Laplace inversion.

that we have tried to remedy above, albeit not very successfully. It is for this reason that we suggest using equation (16) when constructing the iterative solution. Then after one has written the nth iterated integral, one may then perform all the x integrals; the result in component form is the expansion

$$d_g(x,z)=d_g(x,0)+d_g^{(1)}(x,z) + d_g^{(2)}(x,z)+\ldots+d_g^{(n)}(x,z) \quad (19)$$

where

$$\begin{aligned} d_g^{(n)}(x,z)= & \\ \times \sum_{h_1,h_2,\ldots h_n} & \int_0^z \int_0^{z_1} \ldots \int_0^{z_{n-1}} A_{gh_1}[x-(z-z_1)\tan\theta_g, z_1] \\ \times & A_{h_1h_2}[x-(z-z_1)\tan\theta_g-(z_1-z_2)\tan\theta_{h_1}, z_2] \\ \times & \ldots \\ \times & A_{h_{n-1}h_n}[x-(z-z_1)\tan\theta_g-(z_1-z_2)\tan\theta_{h_1} \\ - & \ldots-(z_{n-1}-z_n)\tan\theta_{h_{n-1}}, z_n] \\ \times & d_{h_n}(0)\mathrm{d}z_1,\ \mathrm{d}z_2\ldots\mathrm{d}z_n\,. \end{aligned}$$

We see from equation (19) that if the $\mathbf{A}(x,z)$ matrix becomes independent of position, we recover the solution to the perfect-crystal case:

$$\mathbf{D}^p(z)=\exp(i\mathbf{A}^pz)\mathbf{D}(0) \quad (20)$$

where the superscript p stands for perfect. In the general case, we see how each term in equation (19) serves to 'fill in' the characteristic triangle (see Fig. 1), with vertex at point (x,z), with successively higher orders of scattering. That is to say, if we construct for ourselves a mesh within the triangle by drawing lines parallel to the characteristics, each of the above terms serves to increase the density of the mesh.

4. The second-order equations

We would now like to examine the validity of the approximation involved in ignoring the term involving $\nabla^2\mathbf{D}(x,z)$ in the second-order equations. First, let us rewrite equation (8) as

$$\left[-i\mathbf{C}\left(\frac{\partial^2}{\partial z^2}+\frac{\partial^2}{\partial x^2}\right)+\left(\mathbf{I}\frac{\partial}{\partial z}+\mathbf{B}\frac{\partial}{\partial x}\right)\right]\mathbf{D}(x,z) = i\mathbf{A}(x,z)\mathbf{D}(x,z)\,. \quad (21)$$

Ordinarily we drop the second-order derivatives in this equation to yield the first-order hyperbolic system. This is a reasonable approximation because (i) the elements of $\mathbf{D}(x,z)$ are normally slowly varying for near-perfect crystals and (ii) the elements of $\mathbf{C}$ are small in the units appropriate to the scale of high-energy-electron diffraction. However, as we shall see later in this section, these may not be valid arguments for crystals with defects thousands of Å in thickness; also it has been reported by Howie & Basinski (1968) that in some diffraction conditions, the first-order system is inadequate in describing the diffraction process in imperfect crystals. For these reasons, we will now examine the relation between the full dynamical equations and the first-order hyperbolic system we have treated in the previous section.

For the case of high-energy-electron diffraction in the Laue geometry, the z direction (see Fig. 1) is approximately the direction of energy flow in the crystal. Because of this fact and because the kinetic energy of the electron is much greater than the potential energy of the crystal (by a factor of $\sim 10^4$), we expect that the variations in the $d_g(x,z)$ may become rapid in the x direction but not in the direction of the energy flux.

We have shown that in the case of a perfect crystal the $\mathbf{D}(x,z)$ are given by equation (20). Roughly speaking, this tells us that $\mathbf{D}^p(z)$ will oscillate with depth, z, at a rate determined by the functions $\exp[i(\gamma_i-\gamma_j)z]$ where γ_i and γ_j are eigenvalues of $\mathbf{A}^p$. This is just the well known Pendellösung behavior, and typically $(\gamma_i-\gamma_j)\sim(200\text{ Å})^{-1}$ at 100 keV. Of course, in the distorted crystal we must generalize to $\gamma_i(x,z)$ and $\gamma_j(x,z)$ but the important thing is that for slowly varying distortions we would still expect these terms to retain the same order of magnitude. Consequently, the oscillation distance will retain the same order of magnitude and remain several hundred Å. As a result of this, we may neglect in equation (21) the term involving $\partial^2\mathbf{D}(x,z)/\partial z^2$ and thus obtain the following second-order parabolic system:

$$\left(-i\mathbf{C}\frac{\partial^2}{\partial x^2}+\mathbf{I}\frac{\partial}{\partial z}+\mathbf{B}\frac{\partial}{\partial x}\right)\mathbf{D}(x,z) = i\mathbf{A}(x,z)\mathbf{D}(x,z)\,. \quad (22)$$

We shall now consider this parabolic system with the intention of showing the relation between its solution and the solution we obtained for the first-order hyperbolic system. By a procedure entirely analogous to the method used in the previous section, we can convert equation (22) into an integral equation. Again using the Fourier and Laplace transforms to construct the Green matrix, we arrive at

$$\mathbf{D}(x,z)=\mathbf{D}(0)+i\int_0^z\int_{-\infty}^{\infty}\mathbf{G}^{\mathrm{II}}(x,z;x',z') \times\mathbf{A}(x',z')\mathbf{D}(x',z')\mathrm{d}x'\mathrm{d}z' \quad (23)$$

where

$$\mathbf{G}^{\mathrm{II}}(x,z;x',z') = [4\pi i(z-z')\mathbf{C}]^{-1/2}\exp[-i\mathbf{M}^2/4(z-z')\mathbf{C}]$$

and $\mathbf{M}$ is a matrix with elements $M_{gh}=[(x-x')-(z-z')\tan\theta_g]\delta_{gh}$. The particular functional form of equation (22) is made possible by the fact that the matrices $\mathbf{C}$ and $\mathbf{M}$ are diagonal. Since $\mathbf{M}$ is a diagonal matrix, the matrix exponential is also diagonal. Thus, the Green matrix is again diagonal, as it was for the hyperbolic equations. Now, however, instead of having delta-function singularities along the characteristics (here we refer to the characteristics of the hyperbolic system), the Green matrix is non-zero for all values of the parameters. Effectively, the x' dependence is just a phase which is zero and stationary along the characteristics of the hyperbolic system, and rapidly varying away from the characteristics. We can see that the phase is rapidly varying away from the characteristics because (i) **C** is small and (ii) the phase is quadratic in the distance from a characteristic. Fig. 3 shows graphically the behavior of a typical term of this Green matrix.

As an aside at this point, it is of value to show how the Green operator $\hat{\mathbf{G}}^{\mathrm{II}}$ reduces to the Green operator for the hyperbolic system in the limit as $\mathbf{C}\rightarrow 0$. The Green matrix $\mathbf{G}^{\mathrm{II}}(x,z;\,x',z')$ acts like a matrix of delta functions $\mathbf{G}^{\mathrm{I}}(x,z;\,x',z')$ inside the integral as $\mathbf{C}\rightarrow 0$. We can see this behavior intuitively by recalling the method of stationary phase for evaluating integrals (see Copson, 1965). When we have integrals of the form

$$\int f(x)\exp\,[i\nu\varrho(x)]\mathrm{d}x$$

where ν is a large parameter, we know that the rapidly oscillating phase term effectively washes out contributions to the integral except at the stationary phase point, that is the point where $\partial\varrho(x)/\partial x=0$. Thus the rapidly oscillating phase acts like a delta function at the stationary phase point when it is in an integral. Looking at equation (23) we see that $1/\mathbf{C}$ is a large parameter and so the x' integral is of the form where the stationary phase method is applicable. From the analysis of the previous section and this section, we can construct the formal identity

$$\delta(\beta)=\lim_{N\rightarrow 0}\,(4\pi iN)^{-1/2}\exp\,[-i(x-\beta)^2/4N]\,.$$

Returning to a more careful treatment of our integral equation, we are motivated to try a stationary phase expansion for the integral in x'. We might expect the initial terms of such an expansion to yield the hyperbolic system and we shall see that it does. The remainder provides implicit correction terms.

We want to expand the following integral in a stationary phase expansion:

$$\mathbf{J}=i\int_{-\infty}^{\infty}\exp\,(-i\nu M^2)\,\mathbf{A}(x',z')\mathbf{D}(x',z')\mathrm{d}x' \qquad (24)$$

where $\nu=1/4(z-z')\mathbf{C}$. Now, in order to simplify the notation, we define the column vector $\mathbf{P}(x',z')\equiv i\mathbf{A}(x',z')\mathbf{D}(x',z')$; then expanding in a Taylor series about the stationary phase point $\mu_g=x-(z-z')\times\tan\theta_g$ we obtain for each element of **J**:

$$\begin{aligned}\mathbf{J}_g=&\int_{-\infty}^{\infty}\exp\,[i\nu(x'-\mu_g)^2]\\&\times\left[P_g(\mu_g,z')+(x'-\mu_g)\frac{\partial}{\partial x}P_g(\mu_g,z')+\ldots\right]\mathrm{d}x'\\&\sim\sqrt{\pi}\left[\left(\frac{\nu}{-i}\right)^{-1/2}P_g(\mu_g,z')-\frac{1}{4!}\left(\frac{\nu}{-i}\right)^{-3/2}\right.\\&\qquad\left.\times\frac{\partial^2}{\partial x^2}P_g(\mu_g,z')+\ldots\right] \qquad (25)\end{aligned}$$

where this is an asymptotic expansion that is valid as $\nu\rightarrow\infty$.

Now if we substitute this expression for **J** back into equation (23), we obtain

$$\begin{aligned}\mathbf{D}(x,z)\sim&\,\mathbf{D}(0)+i\int_0^z\mathbf{A}(x^{\mathrm{ret.}},z')\mathbf{D}(x^{\mathrm{ret.}},z')\mathrm{d}z'\\&+\int_0^z\left\{(z-z')\mathbf{C}\frac{\partial^2}{\partial x^2}[\mathbf{A}(x^{\mathrm{ret.}},z')\mathbf{D}(x^{\mathrm{ret.}},z')]\right.\\&\left.+\ldots\right\}\mathrm{d}z'. \qquad (26)\end{aligned}$$

Writing equation (23) in this form enables us to see again how the Green matrix $\mathbf{G}^{\mathrm{II}}(x,z;\,x',z')$ reduces to the Green matrix $\mathbf{G}^{\mathrm{I}}(x,z;\,x',z')$, for the hyperbolic system, in the limit as $\mathbf{C}\rightarrow 0$.

For the stationary phase approximation to the integral of equation (23) [*i.e.* the hyperbolic system of equation (9)] to be valid, the third term on the right-hand side of equation (26), which we will call the correction term, should be negligible. In order for this to be true, we see that roughly the same restrictions apply as were cited in the beginning of this section. However, now we have these restrictions in an explicit form. We see that the second x-derivative of $\mathbf{A}(x,z)\mathbf{D}(x,z)$ must be small, but it must be small in the sense that its integral along a characteristic of the hyperbolic system modified by a factor proportional to $(z-z')\mathbf{C}$ provides a negligible contribution to the wavefunction. Thus, even if the solution maintains its diffracted-wave char-

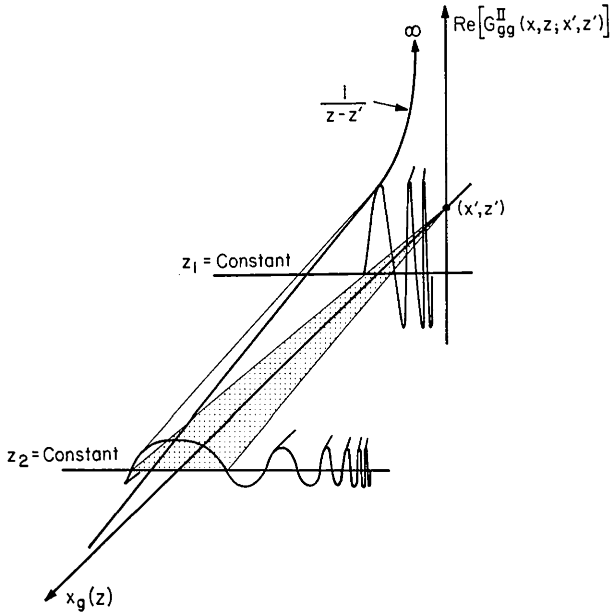

Fig. 3. Schematic plot of the real part of a term of the Green matrix of the second-order equations. Note how the Green function samples primarily along the characteristic line $x_g(z)$, and how the width and amplitude of the sampling depend on the distance from the source (x',z').

acter it is conceivable that the correction term might still become significant if the diffracting region is long. It is difficult to say exactly when the correction term in equation (26) might become important, but it could be a useful tool in numerical calculations to check the validity of ignoring $\partial^2\mathbf{D}(x,z)/\partial x^2$ in the second-order equations. By simultaneously evaluating the first correction term in equation (26) while performing the numerical integration of the hyperbolic system, one can tell immediately when this term becomes a significant correction to $\mathbf{D}(x,z)$.

We see that a good working result is the following: Let $\mathbf{D}^{\mathrm{I}}(x,t)$ be a solution (*e.g.* obtained numerically) to the first-order equation for a crystal of thickness t. Then, we may have confidence in this solution if

$$\left|\int_0^t (t-z')\mathbf{C}\frac{\partial^2}{\partial x^2}[\mathbf{A}(x^{\mathrm{ret.}},z')\mathbf{D}^{\mathrm{I}}(x^{\mathrm{ret.}},z')]\mathrm{d}z'\right| \ll |\mathbf{D}^{\mathrm{I}}(x,t)| \quad (27)$$

for a range of x, and a number of components of $\mathbf{D}^{\mathrm{I}}(x,t)$ for which $\mathbf{D}^{\mathrm{I}}(x,t)$ is numerically significant.

5. Conclusions

By converting the dynamical equations of high-energy-electron diffraction from an imperfect crystal into integral equations we have been able to (i) construct an iterative solution for the Fourier coefficients of the electron wave function for both the first and second-order equations, and (ii) compare these solutions in such a fashion as to obtain an explicit correction term, which is a measure of the validity of ignoring second-order partial derivatives in the dynamical equations.

In concluding this paper, we would like to stress the complementary aspects of the differential equation approach and the integral approach to high-energy-electron diffraction theory. The differential equations have received the most attention to date, undoubtedly owing to the ease by which they can be numerically implemented. On the other hand, the integral equations that we have developed in this paper have definite theoretical advantages. For instance, with regard to the approximation investigated in this paper, it is difficult to look at the differential equation (7) and assess the importance of the $-i\nabla^2 d_g(x,z)/2k_{gz}$ term. Even though the coefficient, $-i/2k_{gz}$, of this term is small, in some sense, we intuitively realize that it must be the specific crystal potential that decides the matter. In other words, there may be cumulative effects that make this term important. These cumulative effects are explicitly displayed in the integral of equation (27) thereby confirming our intuitive feelings.

References

COPSON, E. T. (1965). *Asymptotic Expansions.* Cambridge Univ. Press.
HOWIE, A. & BASINSKI, Z. S. (1968). *Phil. Mag.* **17**, 1039–1063.
KURIYAMA, M. (1972). *Acta Cryst.* A**28**, 588–593.
LEWIS, A. L. & VILLAGRANA, R. E. (1972). *Phys. Rev.* B**6**, 4382–4392.
TAKAGI, S. (1962). *Acta Cryst.* **15**, 1311–1312.
TAKAGI, S. (1969). *J. Phys. Soc. Japan*, **26**, 1239–1253.

Acta Cryst. (1975). A**31**, 227

Use of High-Order Probability Laws in Phase Refinement and Extension of Protein Structures

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High-order covariance matrices are used to show that the maximal determinant rule and the regression equation can be applied successfully to the phase refinement and extension of protein structures. With structure factors calculated from the atomic model of insulin, the use of an order-400 covariance matrix leads to the structure phases with an average error $\Delta\Phi$ of 15°. The method has also been applied to actual data of insulin for phase refinement and for phase extension from 2·8 to 2 Å.

The investigation of the probability law for one structure factor included in a Karle–Hauptman determinant, connected with the regression-plane equation, has been developed recently (de Rango, 1969; Tsoucaris, 1970; de Rango, Tsoucaris & Zelwer, 1974). Here the possibility of applying the regression equation in phase determination of protein structures is investigated in two important cases:

– refinement of the phases approximately known from the isomorphous-replacement method,

– phase extension: determination of new structure-factor phases from approximately known data.

We have already shown that the maximal determinant rule and the regression equation, using high-order covariance matrices, can be applied sucessfully to the phase determination of protein structures (de