PHILLIPS, J. C. (1968). *Phys. Rev.* **168**, 912–917.
PRICE, P. F., MASLEN, E. N. & MAIR, S. L. (1977). *Acta Cryst.* A. In the press.
REED, W. A. & EISENBERGER, P. (1972). *Phys. Rev.* B**6**, 4596–4604.
STEWART, R. F. (1972). Unpublished.
STEWART, R. F. (1973*a*). *J. Chem. Phys.* **58**, 1668–1676.
STEWART, R. F. (1973*b*). *J. Chem. Phys.* **58**, 4430–4438.
TRUCANO, P. & CHEN, R. (1975). *Nature (London)*, **258**, 136–137.

Acta Cryst. (1978). A**34**, 94–102

The Scattering of High-Energy Electrons. I. Feynman Path-Integral Formulation

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The Feynman path-integral formulation of quantum mechanics is used to investigate the theoretical problem of the propagation of high-energy electrons through thin crystalline specimens. The primary objective is to find a satisfactory scattering approximation that accurately describes the transmitted (elastically scattered) wave, and still retains a mathematically invertible relation between the transmitted wave function and the specimen structure. It is shown that the path-integral method leads naturally to an invertible, higher-order, phase-object approximation, in addition to the usual kinematic approximation and the usual phase-object approximation. The higher-order phase-object approximation in turn leads to the noninvertible, multislice approximation of Cowley & Moodie, which had previously been derived by those authors from a semi-classical, physical-optics point of view.

Introduction

As early as 1928, Bethe developed the dynamical theory of electron diffraction. The theory gives, however, a solution which is highly complicated and also tedious to be applied to cases where more than two diffracted beams are considered. In subsequent years, the problem of dynamical scattering of electrons has been approached by a variety of theoretical methods, including the 'physical-optics' method of Cowley & Moodie (1957), an extension of Bethe's eigenvalue method (*i.e.* the Bloch wave method) by Howie & Whelan (1961), use of the Born series as developed by Fujiwara (1959), and use of the scattering-matrix method as given, for example, by Sturkey (1962) and by Fujimoto (1959). A full quantum-field theoretical method has also been applied (Ohtsuki & Yanagawa, 1966). A comparison of these approaches has recently been discussed in some detail by Goodman & Moodie (1974). Only recently have rigorous attempts been made to use the multislice dynamical theory of Cowley & Moodie (1957) for interpretation of electron images (Allpress, Hewat, Moodie & Sanders, 1972; Lynch, Moodie & O'Keefe, 1975). Up to now the work has been limited to inorganic crystals.

In this paper we present the derivation of four different high-energy electron-scattering approximations, following the Feynman path-integral formulation of quantum mechanics. The four approximations are, in order of increasing complexity, the kinematic approximation, the phase-object approximation, a higher-order phase-object approximation (not previously described) and the multislice approximation of Cowley & Moodie (1957). The conditions under which each of these approximations has a useful degree of validity is explored by representative, numerical calculations in the subsequent papers of the series. It is worth noting that these approximations, except for the multislice formulation, give an invertible relation between the transmitted wave function and the projected object potential. Thus the projected potential can be retrieved from the wave function, which can, in principle, be determined from the image intensities (see for example Misell, Burge & Greenaway, 1974; Lannes, 1976).

The path-integral formulation of quantum mechanics developed by Feynman (1948) and Feynman & Hibbs (1965) appears to be a logical as well as an intuitive way of dealing with the scattering problem for high-energy electrons. The classical limit arises naturally in this formulation as a special case of quantum mechanics, when the quantities such as mass and velocity are so large that Planck's constant can be considered infinitesimal (Feynman & Hibbs, 1965). The path-integral formulation has been shown to be

consistent with the Schrödinger equation (Nelson, 1964; Feynman & Hibbs, 1965).

The path-integral method not only gives a kind of simplicity that is often lost in the ordinary quantum-mechanics approach but also has the advantage of showing clearly the physical assumptions that lead to the various approximate scattering formulas. In *Kinematic approximation*, the concept of the Feynman path-integral formulation is introduced. The kinematic scattering approximation is rederived here in order to illustrate the interpretational simplicity developed through the derivation. In the following section, the phase-object approximation is derived on the basis of the near forward nature of the scattering. This approximation assumes that the scattering can be described by a single straight-line path. Improvement of the approximation can be made by considering the paths which cascade along this straight-line path. A new dynamical approximation, the higher-order phase-object approximation, was developed under these assumptions. The validity of each of these approximations is expected to be limited by crystal thickness. In the final section, the multislice dynamical approximation of Cowley & Moodie (1957), which previously was developed on the basis of a 'physical-optics' method, is also obtained by the Feynman path-integral approach. The remaining limitations of the multislice approximation can easily be seen in the Feynman path-integral approach, where they were not previously so evident from the 'physical-optics' derivation.

Kinematic approximation*

The kinematic approximation or the first Born approximation (Scott, 1963; Schiff, 1955) was first derived by a perturbation-theoretical treatment of scattering (Born, 1926). First-order perturbation theory assumes that the scattered waves are weak compared with the initial wave. The far-field, Fraunhofer-scattered wave can be shown to be a spherical wave with amplitude proportional to the Fourier transform integral of the perturbing potential field. The derivation gives, however, no clear physical interpretation of the approximation. We rederive the kinematic approximation following the path-integral formulation. With this method it is well known that the kinematic approximation can be clearly interpreted as corresponding to a single scattering process.

The wave function of the electron, $\Psi(\mathbf{r},t)$, under the influence of a potential field such as that of an atom or a crystal lattice, can be described by the following integral equation:

$$\Psi(\mathbf{r},t) = \int \Psi_0(\mathbf{r}_0,t_0)\, P(\mathbf{r},t;\, \mathbf{r}_0,t_0)\, \mathrm{d}\mathbf{r}_0 \qquad (1)$$

where $P(\mathbf{r},t;\ \mathbf{r}_0,t_0)$ is called the propagator of the electron wave and $\Psi_0(\mathbf{r}_0,t_0)$ is the initial wave function.

The propagator depends on the strength of the potential field and on the kinetic energy of the electron. It can be written as the path integral in going from the initial point $(\mathbf{r}_0,t_0)$ to the final point $(\mathbf{r},t)$, as follows:

$$P(\mathbf{r},t;\, \mathbf{r}_0,t_0) = \int_{\mathbf{r}_0}^{\mathbf{r}} \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} L(\mathbf{r}',\dot{\mathbf{r}}',t')\, \mathrm{d}t'\right] \mathrm{D}\mathbf{r}'$$

and

$$L(\mathbf{r}',\dot{\mathbf{r}}',t') = \tfrac{1}{2}m\dot{\mathbf{r}}'^2 - eV(\mathbf{r}',t')\cdot$$

where m, e, V and $\hbar$ are respectively the electron mass, the electron charge, the object potential, and Planck's constant divided by 2π; $\mathrm{D}\mathbf{r}'$ denotes the continuous sum of integrals over all possible paths. If the reader is not previously familiar with the conceptual and mathematical definition of a path integral, he should consult Feynman & Hibbs (1965) for reference.

For high-energy electrons and weak object potential, such that

$$\left|\frac{i}{\hbar}\int_{t_0}^{t} eV(\mathbf{r}',t')\mathrm{d}t'\right| \ll 1;$$

the portion of the exponential function which depends upon the object potential can be expanded in a power series. The propagator can thus be written as

$$P(\mathbf{r},t;\, \mathbf{r}_0,\, t_0) = \int_{\mathbf{r}_0}^{\mathbf{r}} \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t}\frac{1}{2}\, m\dot{\mathbf{r}}'^2\, \mathrm{d}t'\right)$$

$$\times\left[1 + \frac{i}{\hbar}\int_{t_0}^{t} eV(\mathbf{r}',t)\, \mathrm{d}t' + \text{higher-order terms}\right] \mathrm{D}\mathbf{r}'. \quad (3)$$

In the case where the sum of the higher-order terms in the potential is much smaller than the first-order term,† the propagator can be approximated in the following form:

$$P(\mathbf{r},t;\, \mathbf{r}_0,t_0) = \int_{\mathbf{r}_0}^{\mathbf{r}} \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t}\frac{1}{2}m\dot{\mathbf{r}}'^2\mathrm{d}t'\right) \mathrm{D}\mathbf{r}'$$

$$+ \frac{i}{\hbar}\int_{\mathbf{r}_0}^{\mathbf{r}} \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t}\frac{1}{2}m\dot{\mathbf{r}}'^2\mathrm{d}t'\right)\int_{t_0}^{t} eV(\mathbf{r}',t'')\, \mathrm{d}t''\, \mathrm{D}\mathbf{r}'. \quad (4)$$

We have replaced the variable t' in the integral of $V(\mathbf{r}',t')$ by the variable t'' in order to avoid confusion with the time variable in the integral over the kinetic energy. The order of the integration over the variable

* The derivation of this approximation by the path-integral method has been outlined by Feynman & Hibbs (1965). The derivation given here follows their outline closely.

† In crystalline objects, the contribution from the sum of many higher-order terms in the potential to the large-angle reflections may be quite significant because the amplitudes of the corresponding first-order reflection may be very small to begin with.

$\mathbf{r}'$, and that over t'' can be interchanged, and (4) becomes then

$$P(\mathbf{r},t;\mathbf{r}_0,t_0)=\int_{\mathbf{r}_0}^{\mathbf{r}}\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t}\frac{1}{2}m\dot{\mathbf{r}}'^2\,dt'\right)\mathbf{D}\mathbf{r}'$$
$$+\frac{i}{\hbar}\int_{t_0}^{t}\int_{\mathbf{r}_0}^{\mathbf{r}}\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t''}\frac{1}{2}m\dot{\mathbf{r}}'^2\,dt'\right)$$
$$\times eV(\mathbf{r}'',t'')\exp\left(-\frac{i}{\hbar}\int_{t''}^{t}\frac{1}{2}m\dot{\mathbf{r}}'^2dt'\right)dt''\,\mathbf{D}\mathbf{r}' \qquad (5)$$

where $\mathbf{r}''$ is a position at $t'=t''$, $\mathbf{D}\mathbf{r}'$ includes the notion of integration for all paths between the position and time $(\mathbf{r}_0,t_0)$ to $(\mathbf{r}'',t'')$ as well as between $(\mathbf{r}'',t'')$ to $(\mathbf{r},t)$ and also the integration over all possible positions $\mathbf{r}''$ at the time t''. The first term on the right-hand side of (5) can be interpreted as the propagator of a free electron. The second term is associated with the scattering by the potential field and can be interpreted as the superposition of all possible amplitudes for an electron starting from the incoming position and time $(\mathbf{r}_0,t_0)$, moving as a free particle to a point $\mathbf{r}''$ at a given time $t'=t''$, and then being scattered by the potential field of the object, $V(\mathbf{r}'',t'')$, after which it moves as a free particle to the point $(\mathbf{r},t)$.

By substituting this propagator into (1), the wave function for the outgoing electron can be written as

$$\Psi(\mathbf{r},t)=\int\Psi_0(\mathbf{r}_0,t_0)\left\{\int_{\mathbf{r}_0}^{\mathbf{r}}\exp\left(-\frac{i}{\hbar}\right.\right.$$
$$\left.\times\int_{t_0}^{t}\frac{1}{2}m\dot{\mathbf{r}}'^2\,dt'\right)\mathbf{D}\mathbf{r}'\Bigg\}d\mathbf{r}_0+\frac{i}{\hbar}\int\Psi_0(\mathbf{r}_0,t_0)$$
$$\times\left[\int_{t_0}^{t}\int_{\mathbf{r}_0}^{\mathbf{r}}\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t''}\frac{1}{2}m\dot{\mathbf{r}}'^2\,dt\right)\right.$$
$$\left.\times eV(\mathbf{r}'',t'')\exp\left(-\frac{i}{\hbar}\int_{t''}^{t}\frac{1}{2}m\dot{\mathbf{r}}'^2\,dt'\right)dt''\mathbf{D}\mathbf{r}'\right]d\mathbf{r}_0 \qquad (6)$$

where $\Psi_0(\mathbf{r}_0,t_0)$ is the initial wave function of the electron.

The wave function for an incoming electron with momentum $\hbar\mathbf{k}_0$ and energy E_0 can be described by

$$\exp\left(i\mathbf{k}_0\cdot\mathbf{r}-\frac{i}{\hbar}E_0t\right).$$

In (6), the propagator for an electron going from the interaction point $\mathbf{r}''$ at the time t'' to the final point $\mathbf{r}$ at the time t in the forward direction can be represented by the following equation (Feynman & Hibbs, 1965):

$$P(\mathbf{r},t;\mathbf{r}'',t'')=\left[\frac{m}{2\pi i\hbar(t-t'')}\right]^{3/2}\exp\left[-\frac{im(\mathbf{r}-\mathbf{r}'')}{2\hbar(t-t'')}\right]. \qquad (7)$$

Substituting these expressions into (6), we can write then the wave function for the outgoing electron as

$$\Psi(\mathbf{r},t)=\exp\left(-i\mathbf{k}_0\cdot\mathbf{r}+\frac{i}{\hbar}E_0t\right)$$
$$+\frac{i}{\hbar}\int_{t_0}^{t}\int_{\mathbf{r}_0}^{\mathbf{r}}\exp\left(-i\mathbf{k}_0\cdot\mathbf{r}'+\frac{i}{\hbar}E_0t''\right)\,eV(\mathbf{r}'',t'')$$
$$\times\left[\frac{m}{2\pi i\hbar(t-t'')}\right]^{3/2}\exp\left[-\frac{im(\mathbf{r}-\mathbf{r}'')}{2\hbar(t-t'')}\right]dt''\,d\mathbf{r}'. \qquad (8)$$

We have assumed in this equation that the initial position is such that $\mathbf{k}_0\cdot\mathbf{r}_0=0$ at the time $t_0=0$, so that the initial wave function can be replaced by unity. The first term on the right-hand side of (8) is the wave function of the free electron which passed through the potential field without being scattered, and the second term is the scattered wave function.

For a potential of very large extent (see the discussion below for the case of a potential field of restricted spatial extension) and for the far-field region such that $\mathbf{r}\to\infty$ at the time $t\to\infty$, the integral over t'' for the scattered wave function can be performed in closed form when the potential is independent of time. After performing this integration, we can write the outgoing wave function of the electron as follows (Appendix):

$$\Psi_\infty(\mathbf{r},t)=\exp\left(-i\mathbf{k}_0\cdot\mathbf{r}+\frac{i}{\hbar}E_0t\right)+\exp\left(\frac{i}{\hbar}E_0t\right)\left(\frac{me}{2\pi\hbar^2}\right)$$
$$\times\int\exp(-i\mathbf{k}_0\cdot\mathbf{r}'')\,V(\mathbf{r}'')\,\frac{\exp(-ik|\mathbf{r}-\mathbf{r}''|)}{|\mathbf{r}-\mathbf{r}''|}\,d\mathbf{r}''. \qquad (9)$$

For a potential that falls off rapidly enough for large $\mathbf{r}''$, we can simplify the outgoing wave function by using the following approximation:

$$\frac{\exp(-ik|\mathbf{r}-\mathbf{r}''|)}{|\mathbf{r}-\mathbf{r}''|}\cong\exp(i\mathbf{k}.\mathbf{r}'')\,\frac{\exp(-ikr)}{r}. \qquad (10)$$

Thus we can write the wave function as

$$\Psi_\infty(\mathbf{r},t)=\exp\left(-i\mathbf{k}_0\cdot\mathbf{r}+\frac{i}{\hbar}E_0t\right)$$
$$-\frac{me}{2\pi\hbar^2}\exp\left(\frac{i}{\hbar}E_0t\right)\Phi(\mathbf{s})\frac{\exp(-ikr)}{r} \qquad (11)$$

where $\Phi(\mathbf{s})$ is the Fourier transform of the potential and is directly proportional to the diffracted wave function, and $2\pi\mathbf{s}=\mathbf{k}_0-\mathbf{k}$. Elastic scattering requires that $|\mathbf{k}_0|=|\mathbf{k}|$. This means that the Fourier transform integral should be evaluated only on the spherical surface in Fourier space, which is called the Ewald sphere in X-ray diffraction theory.

We next review here the formulation for describing the diffracted wave function for a finite crystal, even though this formulation is a well known one in crystallography. We hope, by reviewing the formula-

tion for the single-scattering approximation, that we will gain some physical understanding of the limitation of the dynamical scattering approximations derived in the later sections.

For a crystalline object whose limited dimensions can be described by a shape function, the diffracted wave function can be written as the convolution of the diffracted wave function of the infinite crystal and the shape transform. The shape transform itself is the Fourier transform of the shape function. In mathematical notation, the coefficient of the spherical wave in (11) becomes

$$F(\mathbf{k},\mathbf{k}_0) = \frac{me}{2\pi\hbar^2}\,[\Phi(\mathbf{s}) * \Sigma(\mathbf{s})]' \qquad (12)$$

where $F(\mathbf{k},\mathbf{k}_0)$ is the diffracted wave function, $\Phi(\mathbf{s})$ is the Fourier transform of the infinite crystal potential, the symbol * denotes a convolution operator, $\Sigma(\mathbf{s})$ is the shape transform, and the prime indicates that the resulting convolution integral is evaluated only on the Ewald sphere. For a finite crystal, each reciprocal-lattice point is spread out by the shape-transform function. The Ewald sphere may intersect the reciprocal-lattice point, which has been extended in reciprocal space by the shape-transform function, and give a diffracted beam.

The kinematic approximation can describe the geometrical pattern of the diffracted electron beams, but fails in most cases to give correct amplitudes and especially, phases of these beams. The fact that the kinematic approximation is inadequate even for heavy-atom gas molecules was realized first by Schomaker & Glauber (1952) and Glauber & Schomaker (1953), who tried to explain the anomalies in the gas diffraction pattern from UF_6 molecules. Recent results in a test study with the crystalline structure of β-glycine (Quon, 1970) have also shown the kinematic approximation can be insufficient for the description of the scattering of electrons by organic crystals.

Phase-object approximation and higher-order phase-object approximation

A. Phase-object approximation

Since the wavelength of an electron in the high-voltage microscope is very small and since the object potential can be assumed to vary slowly over a single electron wavelength, the electron can be considered to propagate through the object following the classical path. The classical approach may therefore be quite sufficient to describe electron diffraction by crystals for the high-voltage microscope.

In the classical approximation, the single, classical path is the only one which contributes to the path integral, instead of a continuous sum of integrals over all paths. For this case, the propagator from $(\mathbf{r}_0,t_0)$ to $(\mathbf{r},t)$ can be written as the single-path integral:

$$P(\mathbf{r},t;\,\mathbf{r}_0,t_0) = \exp\left[-\frac{i}{\hbar}\underbrace{\int_{t_0}^{t}\frac{1}{2}m\dot{\mathbf{r}}'^2\,\mathrm{d}t'}_{\text{classical path}} - \frac{i}{\hbar}\underbrace{\int_{t_0}^{t} eV(\mathbf{r}')\mathrm{d}t'}_{\text{classical path}}\right]. \qquad (13)$$

In the second term within the argument of the exponential function, the integral over the time t' can be converted to an integral over the electron trajectory by the use of the following approximate relation between the electron velocity, v, position and time:

$$\mathrm{d}t' = \frac{1}{v}\,\mathrm{d}r'. \qquad (14)$$

The propagator can then be written as

$$P(\mathbf{r},t;\,\mathbf{r}_0,t_0) = \exp\left[-\frac{i}{\hbar}\underbrace{\int_{t_0}^{t}\frac{1}{2}m\dot{\mathbf{r}}'^2\,\mathrm{d}t'}_{\text{classical path}} - \frac{i}{\hbar v}\underbrace{\int_{\mathbf{r}_0}^{\mathbf{r}} eV(\mathbf{r}')\mathrm{d}\mathbf{r}'}_{\text{classical path}}\right] \qquad (15)$$

where the integral is taken along the classical-path trajectory.

For high-energy electrons, the scattering is confined to a small angle. Thus, we can assume that the classical-line path can be approximated by a straight-line path parallel to the incident beam direction (Fig. 1). The first term in (15) is again the propagator for the free electron. For a path length much greater than the electron wavelength, this term can be described by the plane wave:

$$\exp\left[-i\mathbf{k}.(\mathbf{r}-\mathbf{r}_0) + \frac{i}{\hbar}E(t-t_0)\right.$$

With such an approximation, the propagator without the time factor,

$$\exp\left[\frac{i}{\hbar}E_0(t-t_0)\right],$$

can be written as

$$P(\mathbf{r};\,\mathbf{r}_0) = \left\{\exp[-i\mathbf{k}.(\mathbf{r}-\mathbf{r}_0)]\cdot\right.$$
$$\left.\times\exp\left[-\frac{i}{\hbar v}\int_{Z_0}^{Z} eV(\boldsymbol{\rho},Z')\mathrm{d}Z'\right]\right\}\delta(x-x_0)\,\delta(y-y_0) \qquad (16)$$

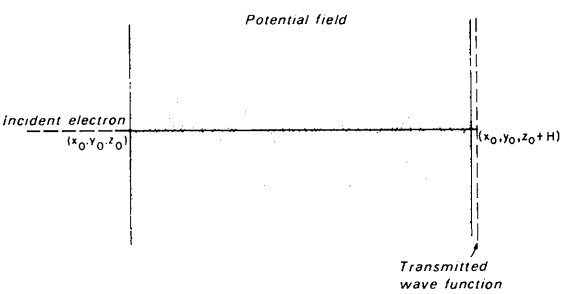

Fig. 1. Schematic diagram illustrating the single, straight-line path used in deriving the phase-object approximation.

where δ is the Dirac delta function and $\boldsymbol{\rho} = (x,y)$. In (16), we have assumed that the incident-beam direction is along the z axis.

The straight-line path approximation is valid only when both the integral of the potential as well as the kinetic energy over the classical-line path at a small angle from the incident-beam direction can be approximated by the integral over the straight-line path parallel to the incident-beam direction. In other words, the straight-line path approximation is justified if and only if the following two conditions are satisfied. (1) The difference in path length between the classical-line path at a small angle and the straight-line path parallel to the incident beam direction is much smaller than the electron wavelength, *i.e.*

$$\frac{H\theta^2}{2} \ll \lambda. \tag{17}$$

In (17), θ is the scattering angle, H is the object thickness and λ is the electron wavelength. The strong condition in (17) is also required for the stationary-phase approximation (Schiff, 1956). (2) The potential does not change appreciably within the column diameter, d, associated with the angle of the stationary phase approximation (*i.e.* $d = H\theta$).

The transmitted wave function, for a slab of a potential field of thickness H, can be obtained by substituting the propagator into (1). Noting the Dirac delta function in the propagator, we can write the wave function as

$$\psi(\boldsymbol{\rho}) = \exp(-ikH)\exp\left[-\frac{i}{\hbar v}\int_{Z_0}^{Z_0+H} eV(\boldsymbol{\rho},\mathbf{Z}')\mathrm{d}Z'\right] \tag{18}$$

where $\psi(\boldsymbol{\rho})$ is the transmitted wave function at the exit face of the slab.

Equation (18) is, of course, the transmitted wave function of the phase-object approximation. The validity of this approximation depends on the electron wavelength, the deviation from the average potential (*i.e.* the strength of the Fourier coefficients), the thickness of the object and the scattering angle.

Unlike the first Born approximation, the phase-object approximation takes multiple scattering processes into account. The scattered wave in the phase-object approximation is assumed to propagate in the same direction as the incoming electron wave. To the first order in the potential, the phase-object approximation is therefore not exactly the same as the first Born approximation. The phase-object approximation can be loosely described by saying that its Ewald sphere is approximated as a plane, although it is known that the Ewald-sphere construction cannot ordinarily be used to predict the amplitude of the diffracted beam intensity in the dynamical electron-scattering approximation.

B. Higher-order phase-object approximation

The phase-object approximation was derived under the condition that the electron propagates through the object following a straight-line path. The validity of this approximation is limited to a very small angle and to a very thin object. For an object of sufficient thickness the phase-object approximation fails to describe the electron-scattering process. The need for an approximation which can be used for larger object thickness is therefore in demand. The expected approximation must, however, give an invertible relation between the transmitted wave function and the object potential so that it can be used for correction of the dynamical scattering effect on the electron-micrograph image. We develop here a higher-order phase-object approximation which has the required improvement in behavior.

The propagator for an electron influenced by the potential field $V(\mathbf{r})$ can be written as the separate sum of path integrals over the straight-line and non-straight-line paths. The propagator can then be described by

$$P(\mathbf{r},t;\mathbf{r}_0,0) = \frac{1}{N}\exp[-i\mathbf{k}.(\mathbf{r}-\mathbf{r}_0)]$$
$$\times \exp\left[-\frac{i}{\hbar v}\int_{Z_0}^{Z_0+H} eV(\boldsymbol{\rho},\mathbf{Z}')\mathrm{d}\mathbf{Z}' + \frac{i}{\hbar}E_0 t\right]\delta(x-x_0)\,\delta(y-y_0)$$
$$+\int' \exp\left[-\frac{i}{\hbar v}\int_{\mathbf{r}_0}^{\mathbf{r}} eV(\mathbf{r}')\mathrm{d}\mathbf{r}' - \frac{i}{\hbar}\int_0^t \frac{1}{2}m\dot{\mathbf{r}}'^2\mathrm{d}t'\right]\mathrm{D}\mathbf{r}' \tag{19}$$

where the prime in the integral sign indicates that the integral is taken over all possible non-straight-line paths, and N is a normalizing factor.

Let us assume that only a certain subset of paths, which initially follow the incident-beam direction in a straight-line path and then cascade along this path with subsequent straight-line propagation, give significant contributions to the propagator of an electron

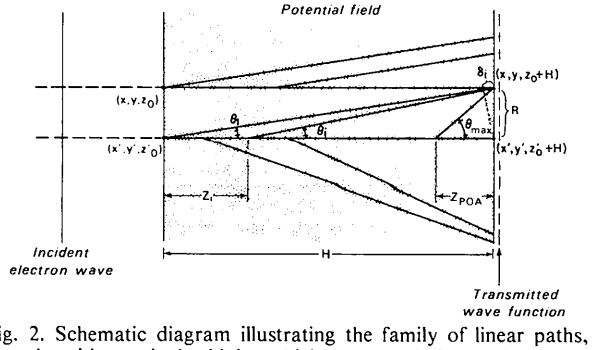

Fig. 2. Schematic diagram illustrating the family of linear paths, each with a single kink, which are used for deriving the higher-order phase-object approximation. Each path is characterized by its point of entry at the plane $Z = Z_0$; its point of deflection and the corresponding angle θ_i; and the associated increase in path length, δ_i. $\theta_{\max}$ is defined in terms of the thickness, Z_{POA}, for which the phase-object approximation is an adequate description.

passing through a lamellar volume of potential field of thickness H (Fig. 2). The transmitted wave function derived by including these paths in the evaluation of the propagator can be expected to be of superior accuracy in comparison with that of the phase-object approximation. Let us further assume that the scattering is limited to a small angle. For electron microscopy at high energy, this assumption is justified for reasonably thick objects because the electron momentum used is much larger than the momentum change due to interaction with the object's potential field. However, as the object thickness becomes very large the number of electrons which undergo multiple scattering increases, and a large number of electrons are scattered at a large angle. In this case, the assumptions above will break down.

For a potential that is weak compared with the kinetic energy of the electron, the integral of the potential along any one of these non-straight-line paths can be approximated by the integral along the straight-line-path parallel to the incident beam direction. The path integral of the kinetic energy can, however, be quite different for these two different path lines. The difference in path length between the straight-line and non-straight-line path can be approximately described by

$$\delta_i = R(\boldsymbol{\rho},\boldsymbol{\rho}') \cdot \frac{\theta_i}{2}$$

and

$$\theta_i = \frac{R(\boldsymbol{\rho},\boldsymbol{\rho}')}{(H - Z_i)} \tag{20}$$

where $R(\boldsymbol{\rho},\boldsymbol{\rho}') = [(x - x')^2 + (y - y')^2]^{1/2}$ and H is the object thickness. With this approximation, the propagator in (19), without the time factor $\exp(iE_0 t/\hbar)$, can then be written as

$$P(\mathbf{r},\mathbf{r}_0) = \frac{1}{N} \exp\left[-\frac{i}{\hbar v} \int_{Z_0}^{Z_0+H} eV(\boldsymbol{\rho},Z')\mathrm{d}Z' - ikH \right] \times \left\{ \lim_{n\to\infty} \frac{1}{n} \sum_{i=1}^{n} \exp\left[-ikR(\boldsymbol{\rho},\boldsymbol{\rho}') \frac{\theta_i}{2} \right] \right\} \tag{21}$$

where N is the normalizing factor and n is the total number of paths. The term $1/n$ is used to normalize the sum of the series. With this normalization, the propagator converges to that of the phase-object approximation, when θ_i approaches zero.

The sum over the angle θ_i should be restricted to some maximum value, in order to be consistent with the earlier assumption that the scattering angle is small. However, as Z_i approaches the object thickness, θ_i approaches a maximum value $\pi/2$. We know that the scattering of high-energy electrons is confined mostly to a cone of a very small angle, and we are then left with the dilemma of how to specify this maximum angle.

In the case of the phase-object approximation, we have assumed that the contributions of these non-straight-line paths are negligible. The non-straight-line path is insignificant for an object thickness where the phase-object approximation is valid. With this idea in mind, we can set the maximum angle as

$$\theta_{\max} \cong \frac{R(\boldsymbol{\rho},\boldsymbol{\rho}')}{\Delta Z_{\mathrm{POA}}} \tag{22}$$

where ΔZ_{POA} is the object thickness for which the phase-object approximation is valid, or for which the contributions of non-straight-line paths are negligible, up to the desired resolution.

The sum of the series, depending on θ_i, in (21) can be expressed as an integral over θ as follows:

$$\lim_{n\to\infty} \frac{1}{n} \sum_{i=1}^{n} \exp\left[-ikR(\boldsymbol{\rho},\boldsymbol{\rho}') \frac{\theta_i}{2} \right] = \int_{\theta_1}^{\theta_{\max}} \exp\left[-ikR(\boldsymbol{\rho},\boldsymbol{\rho}') \frac{\theta}{2} \right] \mathrm{d}\theta \Big/ \int_{\theta_1}^{\theta_{\max}} \mathrm{d}\theta$$

where $\theta_1 = R(\boldsymbol{\rho},\boldsymbol{\rho}')/H$. After performing this integration, we can substitute the result into (21). We have then

$$P(\mathbf{r},\mathbf{r}_0) = \frac{1}{N} \exp\left[-\frac{i}{\hbar v} \int_{Z_0}^{Z_0+H} eV(\boldsymbol{\rho},\mathbf{Z}')\mathrm{d}\mathbf{Z}' - ik_0 H \right] \times \frac{\exp\left[-ikR(\boldsymbol{\rho},\boldsymbol{\rho}') \frac{\theta_{\max}}{2} \right] - \exp\left[-ikR(\boldsymbol{\rho},\boldsymbol{\rho}') \frac{\theta_1}{2} \right]}{-ikR(\boldsymbol{\rho},\boldsymbol{\rho}')(\theta_{\max} - \theta_1)} . \tag{23}$$

Substituting the propagator into (1) and also using (22) for $\theta_{\max}$, the transmitted wave function $\psi(\boldsymbol{\rho})$ can be described by the following integral, which is carried out over the initial plane,

$$\psi(\boldsymbol{\rho}) = \frac{1}{N} \int \exp\left[-\frac{i}{\hbar v} \int_{Z_0}^{Z_0+H} eV(\boldsymbol{\rho}',\mathbf{Z})\mathrm{d}\mathbf{Z} - ikH \right] \times \left\{ \frac{\exp\left[\frac{-ikR^2(\boldsymbol{\rho},\boldsymbol{\rho}')}{2H} \right] - \exp\left[\frac{-ikR^2(\boldsymbol{\rho},\boldsymbol{\rho}')}{2\Delta Z_{\mathrm{POA}}} \right]}{\frac{-ikR^2(\boldsymbol{\rho},\boldsymbol{\rho}')}{2} \left(\frac{1}{H} - \frac{1}{\Delta Z_{\mathrm{POA}}} \right)} \mathrm{d}\boldsymbol{\rho}' \right\} \tag{24}$$

for $H > \Delta Z_{\mathrm{POA}}$. In this equation, we have assumed that the wave function at the initial plane $Z_0 = 0$ can be described by $\exp(-i\mathbf{k}.\mathbf{Z}_0) = 1$. Equation (24) is the transmitted wave function for the higher-order phase-object approximation. In order to be consistent with the small-angle approximation, the integral in (24) should be limited to values corresponding to a small angle. However, for large angles the path difference described

by (20) will be extremely large, and the phase change due to this difference in path length will oscillate very rapidly. As a result, the contribution from the large angles to the integral will be insignificant (Goodman, 1968). The integral in (24) can be performed then over all possible values without making a significant error in the transmitted wave function.

The complex wave amplitude of the diffracted electrons can be written as the Fourier transform of the object's transmitted wave function. We then have

$$F(\mathbf{k},\mathbf{k}_0) = \exp(-ikH)\,\mathcal{F}\left\{\frac{1}{N}\exp\left[-\frac{i}{\hbar v}\times\int_{z_0}^{z_0+H} eV(\boldsymbol{\rho},\mathbf{Z})\mathrm{d}\mathbf{Z}\right] * \left[\frac{\exp\left(-ik\frac{\rho^2}{2H}\right)-\exp\left(-ik\frac{\rho^2}{2\Delta Z_{\mathrm{POA}}}\right)}{\frac{-ik\rho^2}{2}\left(\frac{1}{H}-\frac{1}{\Delta Z_{\mathrm{POA}}}\right)}\right]\right\} \tag{25}$$

for $H > \Delta Z_{\mathrm{POA}}$ where $*$ denotes a convolution, $\mathcal{F}$ is a Fourier transform operator, N is the normalizing factor and $R(\boldsymbol{\rho},0)$ has been replaced by ρ. This is the diffracted wave for the higher-order phase-object approximation. Its validity can be expected to depend on the strength of the potential, the object thickness and the scattering angle.

Multislice dynamical approximation

The multislice dynamical approximation was first developed by Cowley & Moodie (1957) on the basis of the theory of physical optics. In their formulation, they considered that the electron wave passing through the potential field of a finite domain suffers a phase modification not only due to the effect of the potential field but also due to the spread of the wave by the Fresnel propagation processes. They have also shown that, for a periodic potential, the multislice dynamical approximation reduces to Bethe's two-beam dynamical formulation in the case where one considers that only the forward scattered beam and one diffracted beam have dominant amplitudes (Cowley & Moodie, 1957). Furthermore, Fujiwara (1959) has shown that application of the higher-order Born approximation to obtain the general solution for electron scattering by crystals is consistent with the multislice approximation. Fujimoto (1959) has also demonstrated that the scattering-matrix theory gives a formulation which is identical with the multislice dynamical formulation. By comparison of observed diffraction intensities and/or image intensities with the corresponding intensities calculated according to the Cowley & Moodie theory, much important information about the object has been obtained (Allpress *et al.*, 1972; Anstis, Lynch, Moodie & O'Keefe, 1973).

It should be expected that the path-integral formulation of quantum mechanics can be used to derive the multislice approximation. The multislice dynamical approximation is therefore rederived here in order to demonstrate the unity of the scattering approximations treated in this paper.

The propagator of an electron passing through a slab of a potential field can be described by the path-integral equation (2). The path integral can be obtained by dividing the potential field into n slices of thickness ΔZ. Within each slice, we assume that only the straight-line paths at various angles will give a significant contribution to the propagator (Fig. 3). The validity of this assumption depends upon the thickness of the slice taken as well as upon the strength of the potential field. The difference in path length between the electron passing through the straight-line path (*i.e.* perpendicular to the slice) and the one scattered at a certain angle is

$$\Delta_i = [R_i^2(\boldsymbol{\rho}_i,\boldsymbol{\rho}'_{i-1}) + \Delta Z_i^2]^{1/2} - \Delta Z_i \tag{26}$$

where $R_i(\boldsymbol{\rho}_i,\boldsymbol{\rho}'_{i-1}) = [(x_i - x'_{i-1})^2 + (y_i - y'_{i-1})^2]^{1/2}$, $\boldsymbol{\rho} = (x,y)$ and ΔZ_i is the thickness of the ith slice. Let us assume that the slice is very thin and that the electron momentum is much larger than the change of the momentum due to interaction with the potential field. The electrons can be said to be scattered mostly into a small angle. The difference in path length can then be approximated as

$$\Delta_i \cong \frac{R_i^2(\boldsymbol{\rho}_i,\boldsymbol{\rho}'_{i-1})}{2\Delta Z_i} = \frac{\Delta Z_i \theta_i^2}{2}. \tag{27}$$

This path difference contributes an additional phase change to the propagator of the phase-object approximation. This phase change is due to the contribution from the potential energy as well as from the kinetic energy of the electron. Since the object potential is assumed throughout to be small compared with the kinetic energy of electrons, the contribution from the potential energy, because of the very small difference in

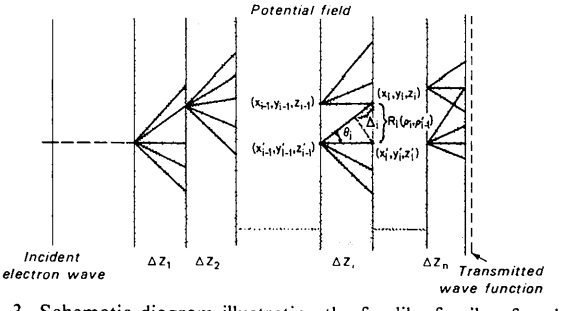

Fig. 3. Schematic diagram illustrating the fan-like family of paths which branch out within individual slabs of the specimen, and which form the basis for deriving the Cowley–Moodie multislice approximation.

path length, can therefore be neglected. The propagator $P(\mathbf{r}_i,\mathbf{r}'_{i-1})$ following the straight-line path from a point $\mathbf{r}_{i-1}$ at the entrance face of the slice to a point $\mathbf{r}_i$ at the exit face can then be written as

$$P(\mathbf{r}_i,\mathbf{r}'_{i-1}) = \frac{1}{N}\exp\left[\frac{i}{\hbar v}\int_{z_{i-1}}^{z_i} eV(\rho'_{i-1},\mathbf{Z}')\,\mathrm{d}\mathbf{Z}' - ik(\Delta Z_i + \Delta_i)\right] \tag{28}$$

where $\rho'_{i-1} = (x'_{i-1},y'_{i-1})$ and Z_{i-1}, Z_i are respectively, the z coordinates of the entrance and the exit face of the ith slice, and N is a normalizing factor.

The transmitted wave function emerging from the exit face of the ith slice can be described by the following equation:

$$\psi_i(\boldsymbol{\rho}_i) = \int \psi_{i-1}(\boldsymbol{\rho}'_{i-1})\,P(\mathbf{r}_i,\mathbf{r}'_{i-1})\mathrm{d}\boldsymbol{\rho}'_{i-1} \tag{29}$$

where $\psi_i(\boldsymbol{\rho}_i)$ and $\psi(\boldsymbol{\rho}_{i-1})$ are respectively, the transmitted wave function emerging from the exit face of the ith and the $(i-1)$th slice. We have then

$$\psi_i(\boldsymbol{\rho}_i) = \int \psi_{i-1}(\boldsymbol{\rho}'_{i-1})\frac{1}{N}\exp\left\{-\frac{i}{\hbar v}\int_{z_{i-1}}^{z_i} eV(\boldsymbol{\rho}_{i-1},\mathbf{Z}')\,\mathrm{d}\mathbf{Z}' - ik\left[\Delta Z_i + \frac{R_i^2(\boldsymbol{\rho}_i,\boldsymbol{\rho}'_{i-1})}{2\Delta Z_i}\right]\right\}\mathrm{d}\boldsymbol{\rho}'_{i-1} \tag{30}$$

where ΔZ_i is the slice thickness of the ith slice. The integral over $\boldsymbol{\rho}_{i-1}$ should be limited to values which are associated with a small angle. As in the case of the higher-order phase-object approximation, the rapid phase change at a large angle makes it possible for the integration to be performed over all possible values of $\boldsymbol{\rho}'_{i-1}$ without giving significant error to the transmitted wave function.

Equation (30) can be rewritten as

$$\psi_i(\boldsymbol{\rho}) = \exp(-ik\Delta Z_i)\left\{\psi_{i-1}(\boldsymbol{\rho}) \times \exp\left[-\frac{i}{\hbar v}\int_{z_{i-1}}^{z_i} eV(\boldsymbol{\rho},\mathbf{Z}')\mathrm{d}\mathbf{Z}'\right] * \frac{i}{\lambda\Delta Z_i}\exp\left(-\frac{ik\rho^2}{2\Delta Z_i}\right)\right\} \tag{31}$$

where $*$ represents a convolution. This is the recursion relation for the transmitted wave in the multislice approximation. The transmitted wave function for a sequence of n slices may be described by successive applications of the equation.

The validity of the multislice approximation depends on the electron energy relative to the strength of the object potential and on the thickness of the slice taken. Goodman & Moodie (1974) have demonstrated that in the limiting case when the slice thickness goes to zero and the number of slices goes to infinity (such that this product remains constant and equal to the object thickness) the multislice approximation then becomes consistent with the conventional quantum-mechanics description for forward electron scattering.

Conclusions

The path-integral formulation of quantum mechanics, when compared with conventional quantum mechanics, gives a clear physical picture for high-energy electron-scattering processes. The kinematic approximation can, in the path-integral formulation, be easily identified as a single-scattering approximation. Furthermore, the path-integral formulation gives clearly the various physical assumptions that lead to the different dynamical scattering approximations. For instance, the phase-object approximation was obtained from the assumption that a single straight-line path is sufficient to describe high-energy electron scattering. It can be expected to be valid when the scattering angle is extremely small. Improvement can be made by considering the non-straight-line paths. The higher-order phase-object approximation was developed under this consideration. Further improvement can be made by considering all possible straight line paths limited to forward directions, and this results in the so-called 'multislice dynamical approximation'. The validity of the multislice approximation depends therefore on the forward scattering nature of high-energy electrons. With increasingly small slice thickness, the multislice approximation can be expected to give a correct description for the forward scattering approximation.

The phase-object approximation and higher-order phase-object approximation give an attractive solution for the retrieval of the projected potential when the scattered wave function is known. The validity of these approximations is evaluated in the subsequent papers of this series. Within certain validity domains these approximations can therefore be properly used for the structure analysis of crystals.

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APPENDIX
Evaluation of the integral [in equation (8)]

For the far-field region and for the case where the potential $V(\mathbf{r},t)$ is independent of t, (8) can be written as

$$\psi(\mathbf{r},t) \underset{r\to\infty}{=} \exp\left(-i\mathbf{k}_0\cdot\mathbf{r} + \frac{i}{\hbar}E_0 t\right) + \frac{i}{\hbar}\int F(|\mathbf{r}-\mathbf{r}'|,t')\,eV(\mathbf{r}')\exp(-i\mathbf{k}_0\cdot\mathbf{r}')\mathrm{d}\mathbf{r}' \tag{a}$$

and

$$F(|\mathbf{r}-\mathbf{r}'|,t) = \int_0^t\left(\frac{m}{2\pi\hbar t'}\right)^{3/2} \times \exp\left(\frac{-im|\mathbf{r}-\mathbf{r}'|^2}{2\hbar t}\right)\exp\left(\frac{i}{\hbar}E_0 t'\right)\mathrm{d}t' \tag{b}$$

where t is the time required for the electron to travel from the initial point $\mathbf{r}_0$ to the final position $\mathbf{r}$. For a limited potential field and for a large value of $t(t \to \infty)$, we can then write (b) as

$$F(|\mathbf{r}-\mathbf{r}'|,t) \underset{\substack{r\to\infty \\ t\to\infty}}{=} \int_0^\infty \left(\frac{m}{2\pi\hbar t'}\right)^{3/2} \times \exp\left(\frac{-im|\mathbf{r}-\mathbf{r}'|^2}{2\hbar t'}\right) \exp\left(\frac{i}{\hbar}E_0 t'\right) dt'. \qquad (c)$$

To simplify the integral, we substitute

$$\left(\frac{im|\mathbf{r}-\mathbf{r}'|^2}{2\hbar t'}\right)^{1/2}$$

by the variable μ. We have then

$$F(|\mathbf{r}-\mathbf{r}'|,t) \underset{t\to\infty}{=} \left(\frac{im}{\pi^{3/2}\hbar}\right) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \int_0^\infty \exp\left(-\mu^2 - \frac{a^2}{\mu^2}\right) d\mu \qquad (d)$$

and

$$a^2 = -\frac{m|\mathbf{r}-\mathbf{r}'|^2}{2\hbar^2} E_0 .$$

The definite integral can be integrated in closed form (see, for example, *Standard Mathematical Tables*, 1965). This equation can be rewritten as

$$F(|\mathbf{r}-\mathbf{r}'|,t) \underset{t\to\infty}{=} \frac{im}{2\pi\hbar}\left(\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right) \times \exp\left[-\frac{i}{\hbar}(2mE_0)^{1/2}|\mathbf{r}-\mathbf{r}'|\right]. \qquad (e)$$

Noting that E_0 is the energy of the free electron, we can write $E_0 = (\hbar k)^2/2m$ where $|\mathbf{k}| = |\mathbf{k}_0|$. Equation (e) can then be represented as

$$F(|\mathbf{r}-\mathbf{r}'|,t) \underset{t\to\infty}{=} \frac{im}{2\pi\hbar}\frac{1}{|\mathbf{r}-\mathbf{r}'|} \exp(-ik|\mathbf{r}-\mathbf{r}'|). \qquad (f)$$

Substituting this relation into (a), we can finally write (a) as follows:

$$\psi_\infty(\mathbf{r},t) = \exp\left(-i\mathbf{k}_0.\mathbf{r} + \frac{i}{\hbar}E_0 t\right) - \frac{me}{2\pi\hbar^2}\int \exp(-i\mathbf{k}_0.\mathbf{r}')\, V(\mathbf{r}')\, \frac{\exp(-ik|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'.$$

References

ALLPRESS, J. G., HEWAT, E., MOODIE, A. F. & SANDERS, J. V. (1972). *Acta Cryst.* A**28**, 528–536.

ANSTIS, G. R., LYNCH, D. F., MOODIE, A. F. & O'KEEFE, M. A. (1973). *Acta Cryst.* A**29**, 138–147.

BETHE, H. (1928) *Ann. Phys. (Leipzig)*, **87**, 55–129.

BORN, M. (1926). *Z. Phys.* **37**, 863–867; **38**, 803–827.

COWLEY, J. M. & MOODIE, A. F. (1957). *Acta Cryst.* **10**, 609–619.

FEYNMAN, R. P. (1948). *Rev. Mod. Phys.* **20**, 367–387.

FEYNMAN, R. P. & HIBBS, A. R. (1965). *Quantum Mechanics and Path Integrals*. New York: McGraw-Hill.

FUJIMOTO, F. (1959). *J. Phys. Soc. Jpn*, **14**, 1558–1568.

FUJIWARA, K. (1959). *J. Phys. Soc. Jpn*, **14**, 1513–1524.

GLAUBER, R. & SCHOMAKER, V. (1953). *Phys. Rev.* **89**, 667–671.

GOODMAN, J. W. (1968). *Introduction to Fourier Optics*, McGraw-Hill Physical and Quantum Electronic Series, pp. 59–60. San Francisco: McGraw-Hill.

GOODMAN, P. & MOODIE, A. F. (1974). *Acta Cryst.* A**30**, 280–290.

HOWIE, A. & WHELAN, M. J. (1961). *Proc. R. Soc. London*, A**263**, 217–237.

LANNES, A. (1976). *J. Phys. D*, **9**, 2533–2544.

LYNCH, D. F., MOODIE, A. F. & O'KEEFE, M. A. (1975). *Acta Cryst.* A**31**, 300–307.

MISELL, D. L., BURGE, R. E. & GREENAWAY, A. H. (1974). *J. Phys. D*, **7**, L27–L30.

NELSON, E. (1964). *J. Math. Phys. (NY)*, **5**, 332–343.

OHTSUKI, Y. H. & YANAGAWA, S. (1966). *J. Phys. Soc. Jpn*, **21**, 326–335.

QUON, W. K. (1970). PhD Thesis, Univ. of California, Berkeley.

SCHIFF, L. I. (1955). *Quantum Mechanics*. New York: McGraw-Hill.

SCHIFF, L. I. (1956). *Phys. Rev.* **103**, 443–453.

SCHOMAKER, V. & GLAUBER, R. (1952). *Nature (London)*, **170**, 290–291.

SCOTT, W. T. (1963). *Rev. Mod. Phys.* **35**, 231–313.

Standard Mathematical Tables (1965). 14th ed., p. 345. Cleveland, Ohio: Chemical Rubber Publishing Co.

STURKEY, L. (1962). *Proc. Phys. Soc.* **80**, 321–354.