Theory of Low-Energy Electron Diffraction

I. Application of the Cellular Method to Monatomic Layers

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A method for calculating the intensities of diffracted waves in low energy electron diffraction by crystals is proposed. The elastic multiple scattering is fully taken into account. The cellular method of KOHN and ROSTOKER in the band theory of metals is applied to the integral equation of the scattering by two dimensional lattices, particularly by monatomic layers. The solution is expanded in spherical harmonics on the surface of spheres, within which the atomic potential is assumed to be confined.

The dynamical theory of electron diffraction by BETHE [1] is based on the representation of electron waves in crystals as a superposition of BLOCH waves. If it is applied to low-energy electrons, however, the strong interaction between the electrons and the crystal atoms causes bad convergence in the expansion of the BLOCH waves in plane waves.

In the band theory of metals, which is concerned also with the motion of slow electrons in a periodic field, the so-called cellular method (or GREEN's function method) has been developed (KORRINGA [2], KOHN and ROSTOKER [3], MORSE [4], HAM and SEGALL [5]), in which the above difficulty is avoided by expanding the BLOCH waves in spherical harmonics instead of plane waves. This can be realized conveniently by using the so-called "muffin tin" model (HAM and SEGAL [5]). The crystal is divided into separate spherical regions, in each of which an atom is represented by a spherically symmetric potential. In the space between the spherical regions the potential is assumed to be constant. The summation over the plane-wave components is then absorbed in the calculation of the GREEN's function. The difficulty of convergence is successfully overcome by means of EWALD's ϑ-transformation method [6]. The expansion of the wave function in spherical harmonics has proved to be rapidly convergent owing to the well-known fact, that the partial-wave method for the scattering by single atoms is rapidly convergent for slow electrons.

In the present theory the same technique is applied to the problems of low-energy electron diffraction. If we wanted, we could follow BETHE [1] and calculate BLOCH functions by applying the above method. However, it appears to be more reasonable to apply the method directly to the integral equation of scattering by crystals [7]. This integral equation has a form somewhat different from that of BLOCH functions [3]. The direct application appears to be particularly advantageous if the atoms build up only one or two layers, or if the surface is not flat but has steps. In fact, in these cases BETHE's method [1] would be hardly applicable.

The method is at first applied to flat monatomic layers as the simplest case. It will be extended in Part II to multi-layers. The scattering problem by monatomic layers has been treated by VON LAUE [8] who has used the first BORN approximation. MCRAE [9] has developed a more exact calculation using the distorted wave method. The present calculation is the most exact one, as far as we admit the muffin tin model. Quite recently MCRAE [10] has developed a theory based on the multiple-scattering approach by LAX [11]. This theory is essentially equivalent to the present one, although the apparent formulations are considerably different. In fact, the two theories have proved to render completely identical results for s-wave scatterers.

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§ 1. Scattering by Monatomic Layers

The atoms are assumed to be confined in spheres within which the spherically symmetric potential is given. The solution of the SCHRÖDINGER equation [12]

$$[\nabla^2 + \varkappa^2 - V(\boldsymbol{r})]\,\psi(\boldsymbol{r}) = 0 \qquad (1)$$

within the sphere is assumed to be already obtained for a given value of $\varkappa$ by the usual method of partial waves. We put

$$\psi(\boldsymbol{r}) = \psi(r, \vartheta, \varphi) = \sum_{lm} C_{lm} R_l(r)\, Y_{lm}(\vartheta, \varphi), \qquad (2)$$

where Y_{lm} are spherical harmonics (KOHN–ROSTOKER [3])

$$Y_{lm}(\vartheta, \varphi) = \left[\frac{2l+1}{4\pi}\,\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}} \cdot P_l^{|m|}(\cos\vartheta)\, e^{im\varphi}. \qquad (3)$$

The radial function $R_l(r)$ should be calculated for each kind of atom.

If the values of $\psi(\boldsymbol{r})$ on the surface of the sphere [in other words, the values of C_{lm} in (2)] were given, then, putting $r = r_i$ (r_i: radius of the sphere), we could obtain at once the radial gradient of ψ on the surface as

$$\left(\frac{\partial\psi}{\partial r}\right)_{r=r_i} = \sum_{lm} C_{lm} \left(\frac{\mathrm{d}R_l}{\mathrm{d}r}\right)_{r=r_i} Y_{lm}(\vartheta, \varphi). \qquad (4)$$

Since $Y_{lm}(\vartheta, \varphi)$ build up an ortho-normal system, it follows

$$\left(\frac{\partial\psi}{\partial r}\right)_{r=r_i} = \sum_{lm} \frac{(\mathrm{d}R_l/\mathrm{d}r)_{r=r_i}}{R_l(r_i)}\, Y_{lm}(\vartheta, \varphi) \cdot \int_0^{2\pi} \mathrm{d}\varphi' \int_0^{\pi} \sin\vartheta'\, \mathrm{d}\vartheta'\, Y_{lm}^*(\vartheta', \varphi')\, \psi(r_i, \vartheta', \varphi'). \qquad (5)$$

Thus the solution inside the sphere determines the relation between ψ and $\partial\psi/\partial r$ on the surface. This relation should be regarded as the boundary condition for the solution outside the sphere, because the latter should have the same values of ψ and $\partial\psi/\partial r$ on the surface.

The space outside the spheres is assumed to be vacuum, the potential being zero. The SCHRÖDINGER equation reduces in this range to the HELMHOLTZ equation

$$\nabla^2\psi + \varkappa^2\,\psi = 0. \qquad (6)$$

[12] The symbols are, as far as possible, same as those of KOHN and ROSTOKER [3], with the only exception that we use for the reciprocal-lattice vectors the symbol $\boldsymbol{B}_{pt}$ [see (21)] instead of $\boldsymbol{K}_n$, since the latter is reserved for wave vectors in vacuum.

The spheres are considered to build up a regular two-dimensional array which is extended to infinity in two directions. We imagine two "surfaces" of this monatomic layer taking two planes parallel to the layer in such a way that they lie totally in vacuum (Fig. 1). Then we divide the "layer", the space between the surfaces, in two-dimensional "cells" putting "walls" perpendicular to the two surfaces in such a way that they lie just half-way between the nearest-neighbour atoms (Fig. 1). This is done in a similar way as in the cellular method of the band theory [3], but only in two-dimensions. We assume that each of the equivalent cells contains only one atom.

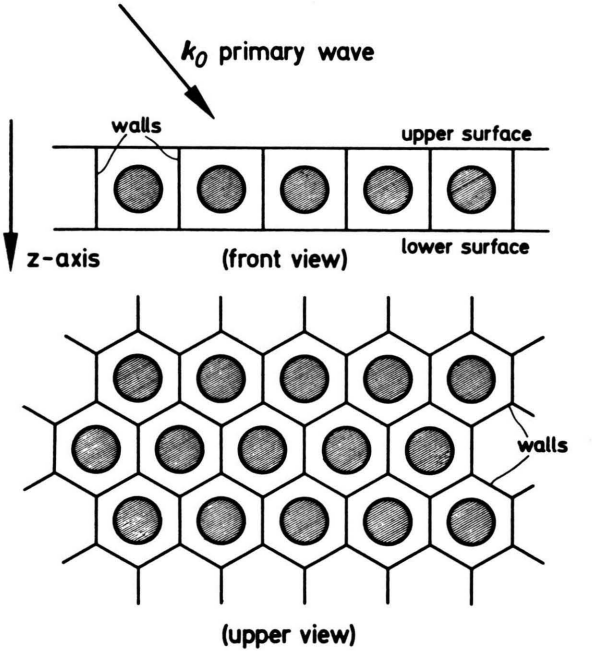

Fig. 1. Monatomic layer; an example of (111) surface atoms of a cubic crystal.

We want now to calculate the scattering of a plane wave with the wave vector $\boldsymbol{K}_0$ ($|\boldsymbol{K}_0| = \varkappa$) falling on the upper surface of the layer (Fig. 1). Thus, the problem is only a particular case of GI [7], so that we can apply the results obtained there to our problem. The choice of our cell instead of the usual two-dimensional unit cell in GI has no influence on the application.

According to GI [7] the solution should have a periodic property

$$\psi(\boldsymbol{r} + \boldsymbol{a}_{nt}) = \exp\{i\,\boldsymbol{K}_{0t}\cdot\boldsymbol{a}_{nt}\}\,\psi(\boldsymbol{r}), \qquad (7)$$

where $\boldsymbol{K}_{0t}$ is the component of $\boldsymbol{K}_0$ tangential to the surface, and $\boldsymbol{a}_{nt} = n_1 \boldsymbol{a}_1 + n_2 \boldsymbol{a}_2$ is an arbitrary two-dimensional lattice vector, $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ being the basis vectors. The form (7) indicates that the scattered waves in the upper and lower vacuum are sets of discrete plane waves. The solution inside the layer must be found only in one arbitrarily chosen cell. The solution in other cells follows then by (7).

§ 2. Integral Equation

According to GI [7] the solution in the cell should satisfy the integral equation

$$\psi(\boldsymbol{r}) = \psi^{(0)}(\boldsymbol{r}) + \int_{\text{cell}} G(\boldsymbol{r}, \boldsymbol{r}')\, V(\boldsymbol{r}')\, \psi(\boldsymbol{r}')\, \mathrm{d}\tau', \tag{8}$$

where $\psi^{(0)}(\boldsymbol{r})$ is the primary wave

$$\psi^{(0)}(\boldsymbol{r}) = \exp\{i\, \boldsymbol{K}_0 \cdot \boldsymbol{r}\}, \tag{9}$$

and $G(\boldsymbol{r}, \boldsymbol{r}')$ is GREEN's function, which satisfies

$$\nabla_r^2 G(\boldsymbol{r}, \boldsymbol{r}') + \varkappa^2 G(\boldsymbol{r}, \boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}') \tag{10}$$

and the same boundary conditions as the function $\psi(\boldsymbol{r}) - \psi^{(0)}(\boldsymbol{r})$ [not $\psi(\boldsymbol{r})$!] The explicit form of $G(\boldsymbol{r}, \boldsymbol{r}')$ will be given in § 4.

Since we assume that $V(\boldsymbol{r}) = 0$ outside the sphere, the integral range of (8) can be reduced to the volume of the sphere. If the point $\boldsymbol{r}$ lies outside the sphere, we obtain, on applying (1), (10) and GREEN's theorem (MORSE–FESHBACH [13], p. 803)

$$\begin{aligned} &\int_{\text{sphere}} G(\boldsymbol{r}, \boldsymbol{r}')\, V(\boldsymbol{r}')\, \psi(\boldsymbol{r}')\, \mathrm{d}\tau' \\ &= \int G(\boldsymbol{r}, \boldsymbol{r}')\, (\nabla_{r'}^2 + \varkappa^2)\, \psi(\boldsymbol{r}')\, \mathrm{d}\tau' \\ &= \int [G(\boldsymbol{r}, \boldsymbol{r}')\, \nabla_{r'}^2 \psi(\boldsymbol{r}') - \psi(\boldsymbol{r}')\, \nabla_{r'}^2 G(\boldsymbol{r}, \boldsymbol{r}')]\, \mathrm{d}\tau' \\ &= \int \left[G(\boldsymbol{r}, \boldsymbol{r}') \frac{\partial}{\partial r'} \psi(\boldsymbol{r}') - \psi(\boldsymbol{r}') \frac{\partial}{\partial r'} G(\boldsymbol{r}, \boldsymbol{r}') \right] \mathrm{d}s'. \end{aligned} \tag{11}$$

The last integral should be taken on the surface of the sphere. We have then from (8)

$$\psi(\boldsymbol{r}) = \psi^{(0)}(\boldsymbol{r}) + \int_{\text{sphere}} \left(G \frac{\partial \psi}{\partial r'} - \psi \frac{\partial G}{\partial r'} \right) \mathrm{d}s' \tag{12}$$

if the point $\boldsymbol{r}$ lies inside the cell but outside the sphere. This equation should be satisfied also in the limit that the point $\boldsymbol{r}$ approaches the surface of the sphere, giving an inhomogeneous integral equation in two dimensions. Strictly speaking, this is a linear *functional* equation, since $\partial\psi/\partial r'$ is a functional of ψ according to (5).

If we have found the solution of (12) on the sphere, the same equation gives the values of ψ in the whole cell outside the sphere. From these values we can easily find the amplitudes of scattered waves going out from the layer.

§ 3. Expansion in Spherical Harmonics

Since the integral in Eq. (12) is taken on the sphere, it is advantageous to expand (12) in spherical harmonics. The origin of polar coordinates is taken at the center of the sphere and the polar axis (z-axis) is taken downwards perpendicular to the surfaces (Fig. 1).

From (9) and the well-known expansion formula of plane waves [KOHN–ROSTOKER [3] Eq. (A 2. b)] we have

$$\psi^{(0)}(\boldsymbol{r}) = 4\pi \sum_{lm} i^l\, Y_{lm}^*(\vartheta_{K_0}, \varphi_{K_0})\, j_l(\varkappa r)\, Y_{lm}(\vartheta, \varphi), \tag{13}$$

where $j_l(\varkappa r)$ are spherical BESSEL functions and $\varkappa (= |\boldsymbol{K}_0|)$, ϑ_{K_0}, φ_{K_0} are the polar coordinates of the vector $\boldsymbol{K}_0$.

Following the same procedure as in KOHN and ROSTOKER [3] we find also in our case that $G(\boldsymbol{r}, \boldsymbol{r}')$ should have the form (note that $r' < r$)

$$G(\boldsymbol{r}, \boldsymbol{r}') = \sum_{lm} \sum_{l'm'} [\delta_{ll'}\, \delta_{mm'}\, \varkappa\, n_l(\varkappa r)\, j_l(\varkappa r') + A_{lml'm'}\, j_l(\varkappa r)\, j_{l'}(\varkappa r')]\, Y_{lm}(\vartheta, \varphi)\, Y_{l'm'}^*(\vartheta', \varphi'), \tag{14}$$

where $A_{lml'm'}$ are "structure constants" which will be calculated in § 4. n_l are spherical NEUMANN functions.

Inserting (2), (13), and (14) into (12), and putting $r = r_i$, we obtain

$$\beta_{lm} = X_{lm} + \sum_{l'm'} \alpha_{lml'm'}\, X_{l'm'}, \tag{15}$$

where

$$X_{lm} = C_{lm}\, R_l(r_i), \quad \beta_{lm} = 4\pi\, i^l\, Y_{lm}^*(\vartheta_{K_0}, \varphi_{K_0})\, j_l(\varkappa r_i), \tag{16), (17}$$

[13] P. M. MORSE and H. FESHBACH, Methods of Theoretical Physics, 2 Vols., McGraw-Hill, New York 1953.

and
$$\alpha_{lm\,l'm'} = r_i^2[\delta_{ll'}\,\delta_{mm'}\,\varkappa\, n_l(\varkappa r_i)\; j_l(\varkappa r_i) + A_{lm\,l'm'}\, j_l(\varkappa r_i)\; j_{l'}(\varkappa r_i)] \times\left[\frac{1}{j_{l'}(\varkappa r_i)}\left(\frac{\mathrm{d}j_{l'}}{\mathrm{d}r}\right)_{r=r_i} - \frac{1}{R_{l'}(r_i)}\left(\frac{\mathrm{d}R_{l'}}{\mathrm{d}r}\right)_{r=r_i}\right]. \tag{18}$$

We can write, introducing the phase shift η_l (KOHN–ROSTOKER [3], MORSE–FESHBACH [13], p. 1068),

$$\alpha_{lm\,l'm'} = [\delta_{ll'}\,\delta_{mm'}\, n_l(\varkappa r_i) + \varkappa^{-1} A_{lm\,l'm'}\, j_l(\varkappa r_i)] \times \frac{\tan\eta_{l'}}{j_{l'}(\varkappa r_i) - n_{l'}(\varkappa r_i)\tan\eta_{l'}}. \tag{19}$$[13a]

Eq. (15) is an *infinite* system. However, the function $(\mathrm{d}R_l/\mathrm{d}r)/R_l$ should approach $(\mathrm{d}j_l/\mathrm{d}r)/j_l$ rapidly, in other words, η_l should decrease rapidly to zero with increasing l, if the energy of the incident electron is not very large and the atoms are not very heavy. Accordingly the quantity $\alpha_{lm\,l'm'}$ should approach zero rapidly with the increase of l'. We expect then that the system (15) can be solved sufficiently accurately by taking only a limited number of unknowns X_{lm} into account.

§ 4. Calculation of the Structure Constants

To obtain the structure constants $A_{lm\,l'm'}$ according to (14) we should known the explicit form of GREEN's function. We find in GI [7] the expression

$$G(\boldsymbol{r},\boldsymbol{r}') = \frac{1}{A}\sum_p \frac{1}{2\,i\,\Gamma_p}\exp\{i\,\Gamma_p\,|z-z'|+i\,\boldsymbol{K}_{pt}\cdot(\boldsymbol{r}_t-\boldsymbol{r}_t')\} \tag{20}$$

where $\boldsymbol{r}_t(\boldsymbol{r}_t')$ and $z(z')$ are the tangential and normal components of $\boldsymbol{r}(\boldsymbol{r}')$ with respect to the surfaces, and

$$\boldsymbol{K}_{pt} = \boldsymbol{K}_{0t} + \boldsymbol{B}_{pt} \quad \text{where} \quad \boldsymbol{B}_{pt} = p_1\,\boldsymbol{B}_{1t} + p_2\,\boldsymbol{B}_{2t}, \tag{21), (22}$$

p representing a pair of integers p_1 and p_2. $\boldsymbol{B}_{1t}$ and $\boldsymbol{B}_{2t}$ are the reciprocal basis vectors which satisfy

$$\boldsymbol{B}_{it}\,\boldsymbol{a}_j = 2\pi\,\delta_{ij}\,(i,j=1,2). \tag{23}$$

Γ_p is given by

$$\Gamma_p = +\sqrt{\varkappa^2 - |\boldsymbol{K}_{pt}|^2} \quad \text{if} \quad \varkappa^2 > |\boldsymbol{K}_{pt}|^2, \qquad \Gamma_p = +i\sqrt{|\boldsymbol{K}_{pt}|^2 - \varkappa^2} \quad \text{if} \quad \varkappa^2 < |\boldsymbol{K}_{pt}|^2. \tag{24}$$

We assume that $\Gamma_p \neq 0$ for all values of p (cf. GI [7]). A is the area of the two-dimensional unit cell and equal to the area of the cross-section of our cell.

The expression (20) is valid only for $z \neq z'$. It can be modified, in order to include the case $z = z'$, to the form

$$\begin{aligned} G(\boldsymbol{R}) = &-\frac{1}{2\pi A}\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\sum_p \exp\{i\,\boldsymbol{K}_{pt}\cdot\boldsymbol{R}_t\}\int_{\omega}^{\infty\exp\{i\varphi_p\}}\zeta^{-\frac{1}{2}}\exp\left\{\frac{1}{2}\left(\Gamma_p^2\,\zeta - \frac{Z^2}{\zeta}\right)\right\}\mathrm{d}\zeta \\ &-\frac{1}{4\pi^2}\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\sum_n^{|\boldsymbol{a}_{nt}|\neq 0}\exp\{-i\,\boldsymbol{K}_{0t}\cdot\boldsymbol{a}_{nt}\}\int_{1/\omega}^{\infty}\zeta^{-\frac{1}{2}}\exp\left\{-\frac{1}{2}\left(|\boldsymbol{R}+\boldsymbol{a}_{nt}|^2\,\zeta - \frac{\varkappa^2}{\zeta}\right)\right\}\mathrm{d}\zeta \\ &-\frac{1}{4\pi^2}\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\int_{1/\omega}^{\infty}\zeta^{-\frac{1}{2}}\exp\left\{-\frac{1}{2}\left(R^2\,\zeta - \frac{\varkappa^2}{\zeta}\right)\right\}\mathrm{d}\zeta, \end{aligned} \tag{25}$$

where
$$\boldsymbol{R} = \boldsymbol{r} - \boldsymbol{r}', \qquad R = |\boldsymbol{R}|, \qquad \boldsymbol{R}_t = \boldsymbol{r}_t - \boldsymbol{r}_t', \qquad Z = z - z'. \tag{26}$$

The integrals are contour integrals. ω is an arbitrary complex number satisfying the condition $\Re\mathrm{e}(\omega) > 0$, $|\omega| < \infty$. We choose here ω to be real $(\omega > 0)$. φ_p is given by

$$\varphi_p = \pi - 2\arg\Gamma_p \tag{27}$$

and equal to π or 0 according as $\Gamma_p^2 > 0$ or $\Gamma_p^2 < 0$ according to (24).

[13a] We assume, for all l, $R_l(r_i) = \mathrm{const}\,(j_l(\varkappa r_i) - n_l(\varkappa r_i)\tan\eta_l) \neq 0$.

It is advantageous to expand the GREEN's function in the form (KOHN–ROSTOKER [3])

$$G(\boldsymbol{R}) = -\frac{\cos(\varkappa R)}{4\pi R} + \sum_{LM} D_{LM}\, j_L(\varkappa R)\, Y_{LM}(\Theta, \Phi), \tag{28}$$

where R, Θ, Φ are the polar coordinates of $\boldsymbol{R}$. The structure constants $A_{lm\,l'm'}$ can be derived from D_{LM} as

$$A_{lm\,l'm'} = 4\pi\, i^{l-l'} \sum_{L} i^{-L}\, D_{L,\,m-m'}\, C_{L,\,m-m';\,lm;\,l'm'}, \tag{29}$$

where

$$C_{LM;\,lm;\,l'm'} = \int_0^{2\pi} \mathrm{d}\varphi \int_0^{\pi} \sin\vartheta\, \mathrm{d}\vartheta\, Y_{LM}(\vartheta, \varphi)\, Y^*_{lm}(\vartheta, \varphi)\, Y_{l'm'}(\vartheta, \varphi), \tag{30}$$

and

$$|l - l'| \leqq L \leqq l + l'. \tag{31}$$

The two series appearing in (25) are uniformly convergent with respect to $\boldsymbol{R}$ so that they can be term-wise integrated when we calculate D_{LM} from [HAM and SEGALL [5], Eqs. (7.7) – (7.10)]

$$D_{LM} = \lim_{R\to 0} \frac{1}{j_L(\varkappa R)} \int_0^{2\pi} \mathrm{d}\Phi \int_0^{\pi} \sin\Theta\, \mathrm{d}\Theta\, Y^*_{LM}(\Theta, \Phi) \left[G(\boldsymbol{R}) + \frac{\cos(\varkappa R)}{4\pi R} \right]. \tag{32}$$

Following HAM and SEGALL [5] we write

$$D_{LM} = D^{(1)}_{LM} + D^{(2)}_{LM} + D^{(3)}_{00}\, \delta_{L0} \tag{33}$$

where

$$D^{(1)}_{LM} = -\frac{1}{2\pi A} \left(\frac{\pi}{2}\right)^{\frac{1}{2}} \sum_{p} \lim_{R\to 0} \frac{1}{j_L(\varkappa R)}\, I^{(1)}_{LM_p}(R), \tag{34}$$

$$D^{(2)}_{LM} = -\frac{1}{4\pi^2} \left(\frac{\pi}{2}\right)^{\frac{1}{2}} \sum_{n}^{|\boldsymbol{a}_{nt}|\neq 0} \exp\{-i\,\boldsymbol{K}_{0t}\cdot\boldsymbol{a}_{nt}\} \lim_{R\to 0} \frac{1}{j_L(\varkappa R)}\, I^{(2)}_{LM_n}(R), \tag{35}$$

and

$$D^{(3)}_{00} = \lim_{R\to 0} \frac{\sqrt{4\pi}}{j_0(\varkappa R)} \left[\frac{\cos(\varkappa R)}{4\pi R} - \frac{1}{4\pi^2} \left(\frac{\pi}{2}\right)^{\frac{1}{2}} \int_{1/\omega}^{\infty} \zeta^{-\frac{1}{2}} \exp\left\{ -\frac{1}{2} \left(R^2\zeta - \frac{\varkappa^2}{\zeta} \right) \right\} \mathrm{d}\zeta \right]. \tag{36}$$

Here we have introduced the expressions

$$I^{(1)}_{LM_p}(R) = \int_0^{2\pi} \mathrm{d}\Phi \int_0^{\pi} \sin\Theta\, \mathrm{d}\Theta\, Y^*_{LM}(\Theta, \Phi) \sum_{\omega}^{\infty \exp\{i\varphi_p\}} \exp\{i\,\boldsymbol{K}_{pt}\cdot\boldsymbol{R}_t\} \int_{\omega} \zeta^{-\frac{1}{2}} \exp\left\{ \frac{1}{2} \left(\Gamma_p{}^2\zeta - \frac{Z^2}{\zeta} \right) \right\} \mathrm{d}\zeta \tag{37}$$

and

$$I^{(2)}_{LM_n}(R) = \int_0^{2\pi} \mathrm{d}\Phi \int_0^{\pi} \sin\Theta\, \mathrm{d}\Theta\, Y^*_{LM}(\Theta, \Phi) \int_{1/\omega}^{\infty} \zeta^{-\frac{1}{2}} \exp\left\{ -\frac{1}{2} \left(|\boldsymbol{R} + \boldsymbol{a}_{nt}|^2 \zeta - \frac{\varkappa^2}{\zeta} \right) \right\} \mathrm{d}\zeta. \tag{38}$$

In (37) and (38) the exponential decrease of the integrand for the integration over ζ guarantees that the order of integration can be inverted.

In the **Appendix 1** it is shown that if $L - |M|$ is odd

$$D^{(1)}_{LM} = 0, \tag{39}$$

and if $L - |M|$ is even

$$\begin{aligned} D^{(1)}_{LM} = {} & -\frac{1}{A\varkappa} \frac{(-1)^L\, i^{|M|+1}}{2^L} \left[(2L+1)\,(L+|M|)!\;\; (L-|M|)! \right]^{\frac{1}{2}} \\ & \times \sum_{p} \exp(-i\,M\,\varphi_{Kp}) \sum_{n=0}^{(L-|M|)/2} \frac{(K_{pt}/\varkappa)^{L-2n}\, (\Gamma_p/\varkappa)^{2n-1}}{n!\,[\tfrac{1}{2}(L-|M|-2n)]!\,[\tfrac{1}{2}(L+|M|-2n)]!} \\ & \times \Gamma\left((1-2n)/2,\; e^{-\pi i}\,\alpha\,\Gamma_p{}^2/\varkappa^2\right), \end{aligned} \tag{40}$$

where K_{pt} and φ_{Kp} are the polar coordinates of $\boldsymbol{K}_{pt}$, which is always perpendicular to the z-axis, and

$$\alpha = \varkappa^2\,\omega/2. \tag{41}$$

Examples of $D^{(1)}_{LM}$ given by (40) for $L = 0$, 1, 2 are tabulated at the end of the paper.

The incomplete gamma functions $\Gamma((1-2n)/2, e^{-\pi i}\,\alpha\,\Gamma_p^2/\varkappa^2)$ can be derived successively for $n=1,2,\ldots$ by the recurrence formula (ERDÉLYI [14] Vol. 2, p. 134)

$$b\,\Gamma(b,x) = \Gamma(b+1,x) - x^b\,e^{-x} \tag{42}$$

from the value for $n=0$,

$$\Gamma(\tfrac{1}{2},x) = \left(\sqrt{\pi} - 2\int_0^{\sqrt{x}} e^{-t^2}\,\mathrm{d}t\right) \qquad \text{if} \quad \arg x = 0 \tag{43}$$

or

$$\Gamma(\tfrac{1}{2},x) = \left(\sqrt{\pi} + 2\,i\int_0^{\sqrt{-x}} e^{t^2}\,\mathrm{d}t\right) \qquad \text{if} \quad \arg x = -\pi\,. \tag{44}$$

The error integrals can be taken from tables or evaluated directly by numerical quadrature (cf. Appendix 2).

In (38) we apply the expansions formula of plane waves [cf. Eq. (13)]

$$\exp\{-\zeta\,\boldsymbol{a}_{nt}\cdot\boldsymbol{R}\} = \exp\{i(i\,\zeta\,\boldsymbol{a}_{nt})\cdot\boldsymbol{R}\} = 4\pi\sum_{LM} i^L\,j_L(i\,\zeta\,a_{nt}R)\;Y^*_{LM}(\vartheta_{a_{nt}},\varphi_{a_{nt}})\;Y_{LM}(\Theta,\Phi), \tag{45}$$

where a_{nt}, $\vartheta_{a\,nt}$ $(=\pi/2)$, $\varphi_{a\,nt}$ are the polar coordinates of $\boldsymbol{a}_{nt}$.

We obtain from (38) and (35), if $L-|M|$ is odd,

$$D^{(2)}_{LM} = 0\,, \tag{46 a}$$

and if $L-|M|$ is even

$$D^{(2)}_{LM} = -\frac{\varkappa}{4\pi}\,\frac{(-1)^L\,(-1)^{(L-|M|)/2}}{2^{2L}\left(\frac{L-|M|}{2}\right)!\left(\frac{L+|M|}{2}\right)!}\,[(2L+1)\,(L-|M|)\,!\,(L+|M|)\,!]^{\frac{1}{2}}$$

$$\times\sum_n^{|\boldsymbol{a}_{nt}|\neq 0}\exp\{-i(\boldsymbol{K}_{0t}\cdot\boldsymbol{a}_{nt}+M\,\varphi_{a_{nt}})\}\;(\varkappa\,a_{nt})^L\int_0^{\infty} u^{-\frac{3}{2}-L}\exp\left\{u-\frac{\varkappa^2\,a_{nt}^2}{4\,u}\right\}\mathrm{d}u\,. \tag{46 b}$$

The integral can be evaluated without difficulty by numerical quadrature (cf. Appendix 2).

To calculate $D^{(3)}_{00}$ we expand the integral of (36) in a series of incomplete gamma functions as (A 1). These can be expressed as a sum of a gamma function and a power series of their argument [ERDÉLYI et al. [14] Vol. 2, p. 135, Eq. (5)]. We find that the first gamma function cancels $-\cos(\varkappa R)/(4\pi R)$ in (36). The first terms of the power series are independent of R and give (cf. MORSE [4] and HAM and SEGALL [5])

$$D^{(3)}_{00} = -\frac{\varkappa}{4\pi}\sum_{n=0}^{\infty}\frac{\alpha^{n-\frac{1}{2}}}{n!\,(n-\frac{1}{2})}\,. \tag{47}$$

This can be modified to the form (ERDÉLYI et al. [14], Vol. 2, p. 133 ff.)

$$D^{(3)}_{00} = -\frac{\varkappa}{4\pi}\,i\,\gamma(-\tfrac{1}{2}, e^{i\pi}\alpha) = -\frac{\varkappa}{2\pi}\left[2\int_0^{\sqrt{\alpha}} e^{t^2}\,\mathrm{d}t - \frac{e^{\alpha}}{\sqrt{\alpha}}\right] \tag{48}$$

(cf. Appendix 2).

§ 5. Amplitudes of Scattered Waves

To obtain the amplitudes of the waves coming out from the layer we need the values of the solution on the surfaces. These are given by (12) where the point $\boldsymbol{r}$ lies either on the upper surface or on the lower surface. Since always $|z-z'|\neq 0$ in these cases, the expression (20) becomes significant (cf. GI [7]). It can be put in (12) and termwise integrated. We obtain on the upper surface $z=z_{\mathrm{I}}$

$$\psi(\boldsymbol{r}_t, z_{\mathrm{I}}) = \psi^{(0)}(\boldsymbol{r}_t, z_{\mathrm{I}}) + \frac{1}{A}\sum_p\frac{1}{2\,i\,\Gamma_p}\exp\{-i\,\Gamma_p\,z_{\mathrm{I}} + i\,\boldsymbol{K}_{pt}\cdot\boldsymbol{r}_t\}$$

$$\times\int\left[\exp\{i\,\Gamma_p\,z' - i\,\boldsymbol{K}_{pt}\cdot\boldsymbol{r}_t'\}\,\frac{\partial\psi}{\partial r'} - \psi\,\frac{\partial}{\partial r'}\exp\{\,i\,\Gamma_p\,z' - i\,\boldsymbol{K}_{pt}\cdot\boldsymbol{r}_t'\}\right]\mathrm{d}s', \tag{49}$$

[14] A. ERDÉLYI et al., Higher Transcendental Functions, 3 Vols., McGraw-Hill, New York 1953.

and on the lower surface $z = z_{II}$

$$\psi(\boldsymbol{r}_t, z_{II}) = \psi^{(0)}(\boldsymbol{r}_t, z_{II}) + \frac{1}{A}\sum_p \frac{1}{2\,i\,\Gamma_p} \exp\{i\,\Gamma_p z_{II} + i\,\boldsymbol{K}_{pt}\cdot\boldsymbol{r}_t\} \times \int\left[\exp\{-i\,\Gamma_p z' - i\,\boldsymbol{K}_{pt}\cdot\boldsymbol{r}_t'\}\frac{\partial\psi}{\partial r'} - \psi'\frac{\partial}{\partial r'}\exp\{-i\,\Gamma_p z' - i\,\boldsymbol{K}_{pt}\cdot\boldsymbol{r}_t'\}\right]ds'. \quad (50)$$

It follows obviously that, if Γ_p is real,

$$R_p = \frac{1}{2\,i\,\Gamma_p A}\int\left[\exp\{i\,\Gamma_p z' - i\,\boldsymbol{K}_{pt}\cdot\boldsymbol{r}_t'\}\frac{\partial\psi}{\partial r'} - \psi'\frac{\partial}{\partial r'}\exp\{i\,\Gamma_p z' - i\,\boldsymbol{K}_{pt}\cdot\boldsymbol{r}_t'\}\right]ds' \quad (51)$$

are the amplitudes of the "reflected" waves coming out from the upper surface, and

$$T_p = \delta_{p0} + \frac{1}{2\,i\,\Gamma_p A}\int\left[\exp\{-i\,\Gamma_p z' - i\,\boldsymbol{K}_{pt}\cdot\boldsymbol{r}_t'\}\frac{\partial\psi}{\partial r'} - \psi'\frac{\partial}{\partial r'}\exp\{-i\,\Gamma_p z' - i\,\boldsymbol{K}_{pt}\cdot\boldsymbol{r}_t'\}\right]ds' \quad (52)$$

are the amplitudes of the "transmitted" waves coming out from the lower surface. On expanding again the plane waves in spherical harmonics we obtain

$$\exp\{\pm i\,\Gamma_p z' - i\,\boldsymbol{K}_{pt}\cdot\boldsymbol{r}_t'\} = 4\pi\sum_{lm}(-i)^l j_l(\varkappa r')\,Y_{lm}(\mp\vartheta_{Kp}, \varphi_{Kp})\,Y_{lm}^*(\vartheta', \varphi'), \quad (53)$$

where $\varkappa(=|\boldsymbol{K}_p|)$, ϑ_{Kp}, φ_{Kp} are the polar coordinates of the vector $\boldsymbol{K}_p$, which has the tangential component $\boldsymbol{K}_{pt}$ and the normal component Γ_p. From (24) $\boldsymbol{K}_p$ has always the magnitude $\varkappa$. Putting (53) into (51) and (52) we get

$$R_p = \frac{2\pi r_i^2}{i\,\Gamma_p A}\sum_l(-i)^l j_l(\varkappa r_i)\left[\frac{1}{R_l}\frac{dR_l}{dr} - \frac{1}{j_l}\frac{dj_l}{dr}\right]_{r=r_i}\sum_m Y_{lm}(-\vartheta_{Kp}, \varphi_{Kp})\,X_{lm} \quad (54)$$

and

$$T_p = \delta_{p0} + \frac{2\pi r_i^2}{i\,\Gamma_p A}\sum_l(-i)^l j_l(\varkappa r_i)\left[\frac{1}{R_l}\frac{dR_l}{dr} - \frac{1}{j_l}\frac{dj_l}{dr}\right]_{r=r_i}\sum_m Y_{lm}(\vartheta_{Kp}, \varphi_{Kp})\,X_{lm}. \quad (55)$$

We note that the exact positions of the surfaces and the walls do not influence these results at all. We note also that we need here, as for (15), only those X_{lm}'s for which the difference between $(dR_l/dr)/R_l$ and $(dj_l/dr)/j_l$ is appreciable.

§ 6. s-Wave Scatterers

As a particular case we consider *s*-wave scatterers. This case has been investigated in detail by Mc Rae [10, 15]. For *s*-wave scatterers all phase shifts η_l vanish except η_0. This can be realized if the atom potential is a delta function. The choice of the atom radius r_i is then quite arbitrary so long as the atomic spheres do not overlap.

The coefficients $\alpha_{lm\,l'm'}$ given by (18) reduce to

$$\alpha_{lm\,l'm'} = r_i^2\,\delta_{l'0}\,\delta_{m'0}\,[\delta_{l0}\,\delta_{m0}\,\varkappa\,n_0\,j_0 + A_{lm00}\,j_l\,j_0]\,\varepsilon_0, \quad (56)$$

where for brevity the argument $\varkappa r_i$ of spherical Bessel functions is omitted, and

$$\varepsilon_0 = \left(\frac{1}{j_0}\frac{dj_0}{dr} - \frac{1}{R_0}\frac{dR_0}{dr}\right)_{r=r_i}. \quad (57)$$

[15] We appreciate very much that Dr. E. G. McRae (Bell Telephone Lab.) has given us an insight into this work before publication.

or in accordance with Eq. (19)

$$\varepsilon_0 = \frac{1}{\varkappa\,r_i^2\,j_0}\frac{\tan\eta_0}{j_0 - n_0\tan\eta_0}. \quad (58)$$

The relation (56) gives particularly

$$\alpha_{0000} = r_i^2\,j_0\,\varepsilon_0(\varkappa\,n_0 + A_{0000}\,j_0). \quad (59)$$

We obtain from Eqs. (29) – (31)

$$A_{0000} = \sqrt{4\pi}\,D_{00}, \quad (60)$$

from (15) $$X_{00} = \frac{\beta_{00}}{1+\alpha_{0000}}, \quad (61)$$

from (17) $$\beta_{00} = \sqrt{4\pi}\,j_0, \quad (62)$$

and from (54) and (55)

$$R_p = -\frac{\sqrt{\pi}\,r_i^2}{i\,\Gamma_p A}\varepsilon_0\,j_0\,X_{00}, \quad (63)$$

$$T_p = \delta_{p0} - \frac{\sqrt{\pi}\,r_i^2}{i\,\Gamma_p A}\varepsilon_0\,j_0\,X_{00}. \quad (64)$$

We find easily that

$$R_p = -\frac{2\pi}{i\,\Gamma_p A}\frac{\tan\eta_0}{\varkappa + \sqrt{4\pi}\,D_{00}\tan\eta_0}, \quad (65)$$

$$T_p = \delta_{p0} + R_p. \quad (66)$$

We see that these quantities are independent of the choice of the atom radius r_i. The equality of R_p and T_p for $p \neq 0$ follows from the isotropy of s-wave scattering.

A comparison of the above formulae with Mc RAE's ones [10] shows that both are completely identical. The quantity $S'(0,0)$ in his theory corresponds to $-(i\varkappa + \sqrt{4\pi}\, D_{00})$ in our expression.

§ 7. Discussion

We see that most part of the numerical work will be required for the calculation of the structure constants. We expect however that the series (40) and (46) can be made satisfactorily rapidly convergent by choosing a suitable value of α, and that only a small number of constants $\alpha_{lm\,l'm'}$ needs to be calculated owing to the rapid approach of $(\mathrm{d}R_l/\mathrm{d}r)/R_l$ to $(\mathrm{d}j_l/\mathrm{d}r)/j_l$ as mentioned in § 3.

It is to be noted that the system (15) is *inhomogeneous*, so that solution of this system causes no essential difficulty once we have the values of $R_l(r_i)$, $(\mathrm{d}R_l/\mathrm{d}r)_{r=r_i}$, and $A_{lm\,l'm'}$.

The author wishes to thank Prof. Dr. K. MOLIÈRE for his encouragement to this work.

Appendix 1. Calculation of the Integral (37)

The ζ-integration in (37) can be expanded into a power series of Z^2 as

$$\int_{\omega}^{\infty \exp\{i\varphi_p\}} \zeta^{-\frac{1}{2}} \exp\left\{\frac{1}{2}\left(\Gamma_p{}^2\,\zeta - \frac{Z^2}{\zeta}\right)\right\} \mathrm{d}\zeta = \sum_n \frac{1}{n!}\left(-\frac{Z^2}{2}\right)^n \left(e^{-\pi i}\,\frac{\Gamma_p{}^2}{2}\right)^{n-\frac{1}{2}} \Gamma\left(\frac{1}{2} - n,\, e^{-\pi i}\,\frac{\omega}{2}\,\Gamma_p{}^2\right). \quad \text{(A 1)}$$

We put (A 1) into (37) and express $\boldsymbol{R}_t$ and Z by the polar coordinates. Then integration by Φ gives (MORSE–FESHBACH [13], Vol. 2, p. 1371)

$$\int_0^{2\pi} \mathrm{d}\Phi \exp\{-i\,M\,\Phi + i\,K_{pt}\,R\sin\Theta\cos(\varphi_{K_p} - \Phi)\} = 2\pi\, i^{|M|} \exp\{-i\,M\,\varphi_{K_p}\}\, J_{|M|}(-K_{pt}\,R\sin\Theta). \quad \text{(A 2)}$$

Integration by Θ has then the form

$$\int_0^{\pi} \sin\Theta\,\mathrm{d}\Theta\, P_L{}^{|M|}\,(\cos\Theta)\, J_{|M|}(-K_{pt}\,R\sin\Theta)\,(\cos\Theta)^{2n}, \quad \text{(A 3)}$$

where the factor $(\cos\Theta)^{2n}$ comes from Z^{2n} of (A 1). We find at once that the integral vanishes if $L-|M|$ is odd. Thus

$$I^{(1)}_{LM_p}(R) = 0 \qquad \text{for all } p \text{ if } L-|M| \text{ is odd.} \quad \text{(A 4)}$$

If $L-|M|$ is even we expand the BESSEL function in (A 3) into a power series of its argument and find, after termwise integration, that the lowest power of R is R^{L-2n}. Hence the lowest power of R in $I^{(1)}_{LM_p}(R)$ is R^L. The summation over n coming from (A 1) must be taken only from 0 to $(L-|M|)/2$ because the higher terms give higher powers of R than R^L. Observing that (MORSE-FESHBACH [13], Vol. 2, p. 1573)

$$j_L(\varkappa R) \underset{R\to 0}{\rightarrow} \frac{2^{L+1}(L+1)!}{(2L+2)!}\,(\varkappa R)^L, \quad \text{(A 5)}$$

we find that, for $L-|M|$ even,

$$\begin{aligned} D^{(1)}_{LM} = &-\frac{1}{2\pi A}\left(\frac{\pi}{2}\right)^{\frac{1}{2}} \sum_p \frac{(2L+2)!}{2^{L+1}(L+1)!\,\varkappa^L R^L} N_{LM}\, 2\pi\, i^{|M|} \exp\{-i\,M\,\varphi_{K_p}\} \\ &\times \sum_{n=0}^{(L-|M|)/2} \frac{1}{n!}\left(-\frac{R^2}{2}\right)^n \left(e^{-\pi i}\,\frac{\Gamma_p{}^2}{2}\right)^{n-\frac{1}{2}} \Gamma\left(\frac{1}{2} - n,\, e^{-\pi i}\,\frac{\Gamma_p{}^2}{2}\,\omega\right) \\ &\times \frac{(-1)^{\frac{1}{2}(L-|M|-2n)}\left(-\frac{K_{pt}\,R}{2}\right)^{L-2n}}{\left(\frac{L-|M|-2n}{2}\right)!\left(\frac{L+|M|-2n}{2}\right)!} \times \frac{2^L\,L!\,(L-|M|)!}{(2L)!}\,(-1)^{\frac{1}{2}(L-|M|-2n)}\,\frac{1}{2\pi N_{LM}{}^2}, \end{aligned} \quad \text{(A 6)}$$

where N_{LM} is the normalizing factor of spherical harmonics (3)

$$N_{LM} = \left[\frac{2L+1}{4\pi}\frac{(L-|M|)!}{(L+|M|)!}\right]^{\frac{1}{2}}. \tag{A 7}$$

It follows then (40).

Appendix 2. Evaluation of the Integrals

The integrals in Eqs. (43), (44), (46 b) and (48) can be derived from the complex error function with a complex argument

$$w(z) = \exp\{-z^2\}[1 + (2i/\sqrt{\pi}) \int_0^z \exp\{t^2\}\, dt], \tag{A 8}$$

which is tabulated [16].

We find at once from Eqs. (43) and (44)

$$\Gamma(1/2, \varkappa) = \sqrt{\pi}\, e^{-x}\, w(\sqrt{|x|}\exp\{i(\arg x + \pi)/2\}), \tag{A 9}$$

and from (48)

$$D_{00}^{(3)} = -\frac{\varkappa e^{\alpha}}{2\sqrt{\pi}}\left\{i[e^{-\alpha} - w(\sqrt{\alpha})] - \frac{1}{\sqrt{\pi\alpha}}\right\}. \tag{A 10}$$

The integral in Eq. (46 b),

$$I_L = \int_0^{\alpha} u^{-L-1/2} \exp\{u - [\varkappa^2 a_{nt}^2/(4u)]\}\, du \tag{A 11}$$

satisfies a recurrence formula

$$(\varkappa a_{nt}/2)^2 I_{L+1} = [(2L+1)/2]\, I_L - I_{L-1} + \alpha^{-L-1/2} \exp\{\alpha - [\varkappa^2 a_{nt}^2/(4\alpha)]\} \tag{A 12}$$

which can be derived easily by partial integration. One starts from $L=0$, where I_0 and I_{-1} can be expressed by means of $w(z)$ as

$$I_0 = \sqrt{\pi}\left(\frac{\varkappa a_{nt}}{2}\right)^{-1} \exp\{\alpha - [\varkappa^2 a_{nt}^2/(4\alpha)]\}\, \Re\mathfrak{e}\{w(\sqrt{\alpha} + i[\varkappa a_{nt}/(2\sqrt{\alpha})])\} \tag{A 13}$$

and

$$I_{-1} = \sqrt{\pi} \exp\{\alpha - [\varkappa^2 a_{nt}^2/(4\alpha)]\}\, \Im\mathfrak{m}\{w(\sqrt{\alpha} + i[\varkappa a_{nt}/(2\sqrt{\alpha})])\}. \tag{A 14}$$

We can derive these formulae from Eq. (A 11) following Ewald's analysis (Ewald [6], Anhang) and using the properties of $w(z)$ [16].

$$\begin{aligned}
D_{00}^{(1)} &= -\frac{1}{A\varkappa}\sum_p i\,\frac{\varkappa}{\Gamma_p}\,\Gamma(\tfrac{1}{2}, e^{-\pi i}\alpha\,\Gamma_p^2/\varkappa^2)\\
D_{10}^{(1)} &= 0\\
D_{1,\pm1}^{(1)} &= -\frac{1}{A\varkappa}\sum_p \exp\{\mp i\,\varphi_{Kp}\}\,\sqrt{6}\,\frac{K_p t}{\Gamma_p}\,\Gamma(\tfrac{1}{2}, e^{-\pi i}\alpha\,\Gamma_p^2/\varkappa^2)\\
D_{20}^{(1)} &= -\frac{1}{A\varkappa}\sum_p i\,\frac{\sqrt{5}}{2}\left[\frac{K_p t^2}{\varkappa\,\Gamma_p}\,\Gamma\left(\frac{1}{2}, e^{-\pi i}\alpha\frac{\Gamma_p^2}{\varkappa^2}\right) + \frac{\Gamma_p}{\varkappa}\,\Gamma\left(-\frac{1}{2}, e^{-\pi i}\alpha\frac{\Gamma_p^2}{\varkappa^2}\right)\right]\\
D_{2,\pm1}^{(1)} &= 0\\
D_{2,\pm2}^{(1)} &= -\frac{1}{A\varkappa}\sum_p \exp\{\mp i\,2\,\varphi_{Kp}\}\left(-i\,\sqrt{\frac{15}{2}}\right)\frac{K_p t^2}{2\varkappa\,\Gamma_p}\,\Gamma\left(\frac{1}{2}, e^{-\pi i}\alpha\frac{\Gamma_p^2}{\varkappa^2}\right)
\end{aligned}$$

Table. Structure constants $D_{LM}^{(1)}$ for $L=0, 1, 2$

[16] V. N. Faddeeva and N. M. Terent'ev, Tables of Values of the Function $w(z) = \exp\{-z^2\}[1 + (2i/\sqrt{\pi}) \int_0^z \exp\{t^2\}\, dt]$ for Complex Argument, Pergamon Press, New York 1961. — B. D. Fried and S. D. Conte, The Plasma Dispersion Function, Academic Press, New York 1961. — M. Abramowitz and I. E. Stegun, Handbook of Mathematical Functions, Dover Publication, New York 1965.