

Ist das Semistabilitätsgebiet so schmal, daß

$$\Delta S_N : \Delta V_N = 0 : 0,$$

so kann man die l'Hospital-Regel anwenden, wenn man S_N und V_N als Funktion von T, \bar{P} betrachtet und wenn $\partial S/\partial T$ usw. einen endlichen Sprung bei Durchgang durch die Lambda-Umwandlung machen; so kommt

$$\frac{d\bar{P}}{dT} = \frac{(\partial/\partial T) \Delta S_N}{(\partial/\partial T) \Delta V_N} = \frac{(\partial/\partial \bar{P}) \Delta S_N}{(\partial/\partial \bar{P}) \Delta V_N}$$

(Ehrenfest-Relationen).

Macht aber $(\partial S/\partial T)_P$ keinen endlichen Sprung auf der Lambda-Linie, sondern hat eine Unendlichkeits-

stelle ähnlich wie $-\log |T - T_\lambda|$, so ist die Ehrenfest-Relation nicht mehr anwendbar. Man hat aber immer noch die Möglichkeit $\partial S_N/\partial T$ und $\partial V_N/\partial T$ in der Nähe der Umwandlungslinie zu vergleichen und statt

$$\Delta(\partial/\partial T) S_N = \Delta(\partial/\partial T) V_N \cdot d\bar{P}/dT$$

und

$$\Delta(\partial/\partial T) V_N = \Delta(\partial/\partial \bar{P}) V_N \cdot d\bar{P}/dT$$

die Beziehungen zu prüfen

$$\frac{\partial}{\partial T} S_N = \frac{d\bar{P}}{dT} \cdot \frac{\partial}{\partial T} V_N + c_1, \quad \frac{\partial}{\partial T} V_N = \frac{d\bar{P}}{dT} \frac{\partial}{\partial \bar{P}} V_N + c_2$$

(Pippard-Relationen).

Theory of Low-Energy Electron Diffraction

II. Cellular Method for Complex Monolayers and Multilayers

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The method of calculating the intensities of waves in low-energy electron diffraction (LEED) which was applied in Part I to monatomic layers is generalized and applied to complex monolayers and multilayers. Using the "muffin-tin" model, which is widely used in the band theory of metals, the wave function is expanded in spherical harmonics on the surfaces of the set of atomic spheres which build a two-dimensional unit of the structure. The expansion coefficients are determined from the condition that the wave function should satisfy the integral equation of the problem on each of the surfaces of the atomic spheres.

The method is interpreted physically in terms of the multiple scattering by the system of atoms. Corresponding to the expansion of the wave function on the atomic spheres the waves falling on and scattered by the atoms are decomposed into "partial waves". In this picture the theory is shown to be essentially equivalent to the dynamical theory of Ewald and also to the LEED theory of McRae. The pseudokinematical theory of Hoerni is derived if the multiple scattering is completely neglected.

The method can be modified, particularly for higher electron energies, to the form which introduces the "scattering matrix" of atomic layers and finally to the form which makes use of Bloch functions and thus becomes equivalent to the usual dynamical theory of X-ray and electron diffraction.

In Part I¹ of the present paper (referred to as I) the cellular method, that is, a calculation using Green's function constructed in a two-dimensional Wigner-Seitz cell (KAMBE², referred to as GI), was applied to low-energy electron diffraction (LEED) by "simple" monatomic layers, which contain only one atom per unit cell. In the present Part II the theory is generalized to the case of "complex" layers, which have more than one atom per unit cell. The atoms in the unit cell may be of different kinds, and their centers need not be situated in a

plane. The present theory applies also to multilayers, i. e. an assembly of many atomic layers stacked together. Each layer may be simple or complex. All the layers, which may be different in structure, should have, however, common periods in two dimensions, so that the whole structure has a two-dimensional periodicity. This assumption is essential for applying the results of the general theory developed in GI. The common periods need not be identical with the periods of the constituent layers, but may be common multiples of them.

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¹ K. KAMBE, Z. Naturforsch. **22 a**, 322 [1967].

² K. KAMBE, Z. Naturforsch. **22 a**, 422 [1967].



The mathematical procedure in Part I was analogous to the method of KOHN and ROSTOKER³ who investigated simple three-dimensional lattices in the band theory of metals. Their method was extended by SEGALL⁴ to complex three-dimensional lattices. We follow Segall's method in the present paper.

This part contains in §§ 1–5 the mathematical development of the theory. Its physical interpretation and the relation to other theories will be discussed in §§ 6–8. Particularly, in § 8 the relation of the present approach to the methods making use of Bloch functions (e. g. Bethe's dynamical theory⁵) is considered. These methods are more suitable for application if a large number of equivalent layers of a crystal are involved, that means, at higher energies. In the case of LEED the depth of penetration is usually so small that a calculation by the present method may be feasible.

§ 1. Integral Equation

In I it has been shown that by means of the muffin-tin model the problem can be reduced to the solution of an integral equation on the surface of a sphere. We use here also the muffin-tin model.

Since we assume now that one unit cell contains more than one atom, and since different kinds of atoms may have different radii, it is of little use to introduce a two-dimensional Wigner-Seitz cell as in I. We go back to the conventional two-dimensional unit cell, which has been considered in GI and named "column of reference". According to the structure of the layers it may happen that the side planes of the column cut the atomic spheres into a

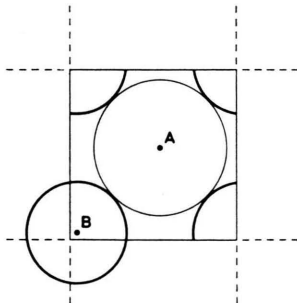


Fig. 1. Column of reference (upper view) with the atoms "assigned" to it. Atom A not cut; Atom B cut into segments.

few segments. An example is shown in Fig. 1. It is, however, always possible to choose the two-dimensional unit cell in such a way that the walls of the column of reference do not cut through any atomic center. Then all those atoms whose centers are situated inside the column of reference are called to be "assigned" to the column of reference. The set of atoms assigned to the column builds the two-dimensional unit of the layer (Fig. 2).

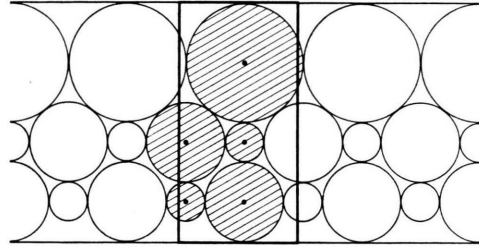


Fig. 2. Column of reference (side view). The atoms "assigned" to the column are indicated by shading.

We have in the column the integral equation [cf. I, Eq. (8)]

$$\psi(\mathbf{r}) = \psi^{(0)}(\mathbf{r}) + \int_{\text{column}} G(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi(\mathbf{r}') d\tau', \quad (1.1)$$

where the potential $V(\mathbf{r})$ is considered to be a sum of atomic potentials

$$V(\mathbf{r}) = \sum_n \sum_i V_i(|\mathbf{r} - \mathbf{c}_i - \mathbf{a}_{nt}|), \quad (1.2)$$

where n is the index of two-dimensional unit cells, i the index of atoms assigned to one unit cell, \mathbf{c}_i the position of the center of the i -th atom in the column of reference, \mathbf{a}_{nt} the n -th lattice vector, and $V_i(r)$ the potential of the i -th atom, which is assumed to be spherically symmetric and exactly zero outside the radius r_i of the atomic sphere. Thus

$$V_i(r) = 0 \quad \text{if} \quad r > r_i. \quad (1.3)$$

In the same way as in I, § 2, we can modify the Eq. (1.1), if the point \mathbf{r} lies outside the spheres, into the form

$$\psi(\mathbf{r}) = \psi^{(0)}(\mathbf{r}) + \sum_{\text{segments}} \int \left(G \frac{\partial \psi}{\partial \mathbf{r}'} - \frac{\partial G}{\partial \mathbf{r}'} \psi \right) d\mathbf{s}', \quad (1.4)$$

where the surface integrals are taken on the surfaces of all the segments contained in the column^{5a}. Ob-

³ W. KOHN and N. ROSTOKER, Phys. Rev. **94**, 1111 [1954].

⁴ B. SEGALL, Phys. Rev. **105**, 108 [1957].

⁵ H. BETHE, Ann. Phys. (4) **87**, 55 [1928].

^{5a} $\partial/\partial \mathbf{r}'$ is the derivative taken normal to the surface with respect to \mathbf{r}' .

serving the periodicity of the solution [I, Eq. (7)]

$$\psi(\mathbf{r} + \mathbf{a}_{nt}) = \exp\{i \mathbf{K}_{0t} \cdot \mathbf{a}_{nt}\} \psi(\mathbf{r}) \quad (1.5)$$

and of Green's function [GI, Eq. (35 a, b)]

$$G(\mathbf{r}, \mathbf{r}' + \mathbf{a}_{nt}) = \exp\{-i \mathbf{K}_{0t} \cdot \mathbf{a}_{nt}\} G(\mathbf{r}, \mathbf{r}'), \quad (1.6)$$

we find easily that the sum of the surface integrals on the segments of one atom can be replaced by the surface integral on the atomic sphere assigned to the column of reference (Fig. 1). We obtain

$$\psi = \psi^{(0)} + \sum_j \int_{\text{sphere } j} \left(G \frac{\partial \psi}{\partial \nu'} - \frac{\partial G}{\partial \nu'} \psi \right) ds'. \quad (1.7)$$

The surface integrals are now to be taken over all

the atomic spheres which are assigned to the column of reference⁶.

Following SEGALL⁴ we write

$$\mathbf{r} = \bar{\mathbf{r}} + \mathbf{c}_i, \quad \mathbf{r}' = \bar{\mathbf{r}}' + \mathbf{c}_j, \quad (1.8)$$

and

$$G(\mathbf{r}, \mathbf{r}') = G(\bar{\mathbf{r}} - \bar{\mathbf{r}}' + \mathbf{c}_i - \mathbf{c}_j) = \mathcal{G}^{(ij)}(\bar{\mathbf{r}}, \bar{\mathbf{r}}'). \quad (1.9)$$

In (1.7) \mathbf{r}' is situated on the j -th sphere. We write then $\bar{\mathbf{r}}' = \mathbf{r}_j'$. One obtains in the limit of \mathbf{r} approaching the i -th sphere from outside, that is, in the limit $\mathbf{r} \rightarrow \mathbf{r}_i$,

$$\psi(\mathbf{r}_i + \mathbf{c}_i) = \psi^{(0)}(\mathbf{r}_i + \mathbf{c}_i) + \sum_j \int \left[\mathcal{G}^{(ij)}(\mathbf{r}_i, \mathbf{r}_j') \left(\frac{\partial}{\partial \mathbf{r}'} \psi(\bar{\mathbf{r}}' + \mathbf{c}_j) \right)_{\bar{\mathbf{r}}' = \mathbf{r}_j'} - \left(\frac{\partial}{\partial \mathbf{r}'} \mathcal{G}^{(ij)}(\mathbf{r}_i, \bar{\mathbf{r}}') \right)_{\bar{\mathbf{r}}' = \mathbf{r}_j'} \psi(\mathbf{r}_j' + \mathbf{c}_j) \right] ds_j'. \quad (1.10)$$

This is a system of integral equations, the number of which is equal to the number of atoms assigned to the column.

§ 2. Expansion in Spherical Harmonics

As in I we expand ψ and $\psi^{(0)}$ in spherical harmonics. This should be done now on each of the atomic spheres assigned to the column. We write

$$\psi(\mathbf{r}_i + \mathbf{c}_i) = \sum_{lm} C_{lm}^{(i)} R_l^{(i)}(r_i) Y_{lm}(\vartheta_i, \varphi_i), \quad (2.1)$$

$$\psi^{(0)}(\mathbf{r}_i + \mathbf{c}_i) = \exp\{i \mathbf{K}_0 \cdot \mathbf{c}_i\} \sum_{lm} 4\pi i^l Y_{lm}^*(\vartheta_{K_0}, \varphi_{K_0}) j_l(\kappa r_i) Y_{lm}(\vartheta_i, \varphi_i), \quad (2.2)$$

where \mathbf{K}_0 is the wave vector of the incident wave.

For $i=j$ the Green's function can be expanded into the form [I, Eq. (14)]

$$\mathcal{G}^{(ii)}(\mathbf{r}_i, \mathbf{r}_i') = \sum_{lm} \sum_{l'm'} [\delta_{ll'} \delta_{mm'} \kappa n_l(\kappa r_i) j_l(\kappa r_i) + A_{lm'l'm'}^{(ii)} j_l(\kappa r_i) j_{l'}(\kappa r_i)] Y_{lm}(\vartheta_i, \varphi_i) Y_{l'm'}^*(\vartheta_i', \varphi_i'), \quad (2.3)$$

where the "structure constants" $A_{lm'l'm'}^{(ii)}$, having here the index (ii) , are identical to the expression $A_{lm'l'm'}$ of I, Eq. (14) and therefore independent of i .

For $i \neq j$ we have always $\mathbf{r}_i + \mathbf{c}_i \neq \mathbf{r}_j' + \mathbf{c}_j$ under the condition that all the spheres don't touch one another. This means $\mathbf{r} \neq \mathbf{r}'$ in $G(\mathbf{r}, \mathbf{r}')$, so that the Green's function $\mathcal{G}^{(ij)}(\mathbf{r}_i, \mathbf{r}_j')$ has no singularity. It can be expressed in the form [SEGALL⁴, Eq. (24)]

$$\mathcal{G}^{(ij)}(\mathbf{r}_i, \mathbf{r}_j') = \sum_{lm} \sum_{l'm'} A_{lm'l'm'}^{(ij)} j_l(\kappa r_i) j_{l'}(\kappa r_j) Y_{lm}(\vartheta_i, \varphi_i) Y_{l'm'}^*(\vartheta_j', \varphi_j'), \quad (i \neq j). \quad (2.4)$$

On substitution of (2.1) – (2.4) into (1.10) we obtain

$$\begin{aligned} 4\pi i^l Y_{lm}^*(\vartheta_{K_0}, \varphi_{K_0}) j_l(\kappa r_i) \exp\{i \mathbf{K}_0 \cdot \mathbf{c}_i\} \\ = C_{lm}^{(i)} R_l^{(i)}(r_i) + \sum_{j \neq i} \sum_{l'm'} [\delta_{ij} \delta_{ll'} \delta_{mm'} r_i^2 \kappa n_l(\kappa r_i) j_l(\kappa r_i) + r_j^2 A_{lm'l'm'}^{(ij)} j_l(\kappa r_i) j_{l'}(\kappa r_j)] \\ \times \left[\frac{1}{j_{l'}(\kappa r)} \frac{dj_{l'}}{dr} - \frac{1}{R_{l'}^{(j)}(r)} \frac{dR_{l'}^{(j)}}{dr} \right]_{r=r_j} C_{l'm'}^{(j)} R_{l'}^{(j)}(r_j). \end{aligned} \quad (2.5)$$

We write

$$X_{lm}^{(i)} = C_{lm}^{(i)} R_l^{(i)}(r_i) \quad (2.6)$$

⁶ It is to be noted that we arrive at (1.7) equally well if we have constructed a Wigner-Seitz cell for the complex structure, which would just enclose the atoms assigned to the column.

and introduce the phase shifts of partial waves for the i -th atom $\eta_l^{(i)}$ by putting [cf. I, Footnote ^{13a}; KOHN-ROSTOKER ³, Eq. (A 3.2)]

$$\left[\frac{dR_l^{(i)}}{dr} / R_l^{(i)} \right]_{r=r_i} = \left[\left(\frac{dj_l}{dr} - \frac{dn_l}{dr} \tan \eta_l^{(i)} \right) / (j_l - n_l \tan \eta_l^{(i)}) \right]_{r=r_i}. \quad (2.7)$$

Then we have

$$\beta_{lm}^{(i)} = X_{lm}^{(i)} + \sum_{j'l'm'} \alpha_{lm'l'm'}^{(ij)} X_{l'm'}^{(j)}, \quad (2.8)$$

where

$$\beta_{lm}^{(i)} = 4\pi i^l Y_{lm}^* (\vartheta_{K_0}, \varphi_{K_0}) j_l(\kappa r_i) \exp\{i \mathbf{K}_0 \cdot \mathbf{c}_i\}, \quad (2.9)$$

and

$$\alpha_{lm'l'm'}^{(ij)} = [\delta_{ij} \delta_{ll'} \delta_{mm'} n_l(\kappa r_i) + \kappa^{-1} j_l(\kappa r_i) A_{lm'l'm'}^{(ij)}] \frac{\tan \eta_{l'}^{(j)}}{j_{l'}(\kappa r_j) - n_{l'}(\kappa r_j) \tan \eta_{l'}^{(j)}}. \quad (2.10)$$

These expressions are not quite convenient for practical calculation because the quantity

$$\tan \eta_{l'}^{(j)} / [j_{l'}(\kappa r_j) - n_{l'}(\kappa r_j) \tan \eta_{l'}^{(j)}]$$

may become accidentally infinitely large depending on the values of $\eta_{l'}^{(j)}$ and κr_j . To avoid this we put

$$x_{lm}^{(i)} = X_{lm}^{(i)} / \{ \sqrt{4\pi} i^l [j_l(\kappa r_i) \cos \hat{\eta}_l^{(i)} - n_l(\kappa r_i) \sin \hat{\eta}_l^{(i)}] \}, \quad (2.11)$$

where $\hat{\eta}_l^{(i)}$ is obtained from $\eta_l^{(i)}$ by reducing the phase angle $2\eta_l^{(i)}$ to its principal value $2\hat{\eta}_l^{(i)}$, which is confined to the range $(-\pi, \pi)$. Then we have in place of (2.8)

$$\sqrt{4\pi} Y_{lm}^* (\vartheta_{K_0}, \varphi_{K_0}) \exp\{i \mathbf{K}_0 \cdot \mathbf{c}_i\} = x_{lm}^{(i)} \cos \hat{\eta}_l^{(i)} + \sum_{j'l'm'} \frac{A_{lm'l'm'}^{(ij)}}{\kappa^{l-l'}} (\sin \hat{\eta}_{l'}^{(j)}) x_{l'm'}^{(j)}. \quad (2.12)$$

This form does not contain a quantity which becomes accidentally infinitely large depending on the values of $\eta_{l'}^{(j)}$ and κr_j . In fact it does not contain r_i at all. We will see in § 4 that the final expressions of the intensities of the diffracted waves also do not contain r_i .

§ 3. Calculation of the Structure Constants

For the calculation of the structure constants $A_{lm'l'm'}^{(ij)}$ in the case $i \neq j$ we distinguish between two cases. If the point \mathbf{r} lies on the sphere i and the point \mathbf{r}' lies on the sphere j we have in the first case always $z - z' \neq 0$. In the second case $z - z'$ can be zero. The geometrical implication is seen in Fig. 3. The latter case includes the important situation that the centers of a pair of atoms have the same z -coordinate in a complex monolayer. In the first case the expression of the structure constant is much simpler than in the second case.

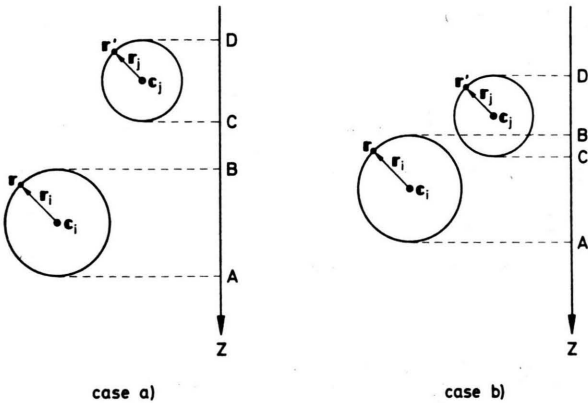


Fig. 3. Two cases of atom pairs for which the expressions of the structure constants are different. Case a), always $z - z' \neq 0$. The ranges of the z -coordinates of \mathbf{r} and \mathbf{r}' , AB and CD, do not overlap. Case b), not always $z - z' \neq 0$. AB and CD overlap.

Case a), always $z - z' \neq 0$

This case is realized for the pairs of atoms which belong to different atomic layers which are not direct neighbours. In this case we can use the expression of $G(\mathbf{r}, \mathbf{r}')$ given by I, Eq. (20)

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{A} \sum_p \frac{1}{i 2 \Gamma_p} \exp\{i \Gamma_p |z - z'| + i \mathbf{K}_{pt} \cdot (\mathbf{r}_t - \mathbf{r}_t')\}. \quad (3.1)$$

We have the relation

$$\begin{aligned} \Gamma_p &= +\sqrt{\kappa^2 - |\mathbf{K}_{pt}|^2} & \text{if } \kappa^2 > |\mathbf{K}_{pt}|^2, \\ \Gamma_p &= +i\sqrt{|\mathbf{K}_{pt}|^2 - \kappa^2} & \text{if } \kappa^2 < |\mathbf{K}_{pt}|^2. \end{aligned} \quad (3.2)$$

$$\text{Writing now } \mathbf{c}_{ij} = \mathbf{c}_i - \mathbf{c}_j, \quad (3.3)$$

we obtain, for example, in the case where always $z > z'$

$$\mathcal{G}^{(ij)}(\mathbf{r}_i, \mathbf{r}_j') = \frac{1}{A} \sum_p \frac{1}{i 2 \Gamma_p} \exp\{i \mathbf{K}_p^+ \cdot (\mathbf{r}_i - \mathbf{r}_j' + \mathbf{c}_{ij})\}, \quad (3.4)$$

where \mathbf{K}_p^+ is the vector which has the tangential component \mathbf{K}_{pt} and the normal component Γ_p . The series (3.4) is absolutely and uniformly convergent (with respect to \mathbf{r}_i and \mathbf{r}_j') owing to the assumption $z - z' \neq 0$ (cf. GI, § 3). Therefore, from (2.4) we have

$$\begin{aligned} A_{lm'l'm'}^{(ij)} &= [j_l(\kappa r_i) j_{l'}(\kappa r_j)]^{-1} \int d\Omega_i \int d\Omega_j' Y_{lm}^*(\vartheta_i, \varphi_i) Y_{l'm'}(\vartheta_j', \varphi_j') \mathcal{G}^{(ij)}(\mathbf{r}_i, \mathbf{r}_j') \\ &= \frac{1}{A} \sum_p \frac{1}{i 2 \Gamma_p} \exp\{i \mathbf{K}_p^+ \cdot \mathbf{c}_{ij}\} [j_l(\kappa r_i)]^{-1} \int d\Omega_j' Y_{lm}^*(\vartheta_i, \varphi_i) \exp\{i \mathbf{K}_p^+ \cdot \mathbf{r}_i\} \\ &\quad \times [j_{l'}(\kappa r_j)]^{-1} \int d\Omega_j' Y_{l'm'}(\vartheta_j', \varphi_j') \exp\{-i \mathbf{K}_p^+ \cdot \mathbf{r}_j'\}. \end{aligned} \quad (3.5)$$

From the expansion formula of plane waves [cf. (2.2)] we have

$$\exp\{i \mathbf{K}_p^+ \cdot \mathbf{r}_i\} = 4\pi \sum_l j_l(\kappa r_i) Y_{lm}^*(\vartheta_{K_p}^+, \varphi_{K_p}) Y_{lm}(\vartheta_i, \varphi_i), \quad (3.6)$$

where $\mathbf{K}_p^+ = (\kappa, \vartheta_{K_p}^+, \varphi_{K_p})$. Putting (3.6) into (3.5) we obtain

$$A_{lm'l'm'}^{(ij)} = \frac{(4\pi)^2}{A} i^{l-l'} \sum_p \frac{1}{2i\Gamma_p} \exp\{i \mathbf{K}_p^+ \cdot \mathbf{c}_{ij}\} Y_{l,-m}(\vartheta_{K_p}^+, \varphi_{K_p}) Y_{l'm'}(\vartheta_{K_p}^+, \varphi_{K_p}). \quad (3.7)$$

Similarly for $z < z'$ we obtain

$$A_{lm'l'm'}^{(ij)} = \frac{(4\pi)^2}{A} i^{l-l'} \sum_p \frac{1}{2i\Gamma_p} \exp\{i \mathbf{K}_p^- \cdot \mathbf{c}_{ij}\} Y_{l,-m}(\vartheta_{K_p}^-, \varphi_{K_p}) Y_{l'm'}(\vartheta_{K_p}^-, \varphi_{K_p}), \quad (3.8)$$

where \mathbf{K}_p^- is the vector which has the tangential component \mathbf{K}_{pt} and the normal component $-\Gamma_p$. Its angular coordinates are given by $\vartheta_{K_p}^-$ and φ_{K_p} .

We note that (3.7) and (3.8) include the terms for which Γ_p is imaginary. The definitions of the spherical harmonics $Y_{lm}(\vartheta_{K_p}^\pm, \varphi_{K_p})$ for these terms are described in Appendix 1. Particularly it is to be noted that $Y_{l,-m}$ in (3.7) and (3.8) cannot be replaced by Y_{lm}^* .

Case b), not always $z - z' \neq 0$

In this case we should use I, Eq. (25) for Green's function. For this purpose, following SEGALL⁴, we expand Green's function at first in spherical harmonics of a variable

$$\bar{\mathbf{R}} = \bar{\mathbf{r}} - \bar{\mathbf{r}}' \quad (3.9)$$

$$\text{in the form} \quad \mathcal{G}^{(ij)}(\bar{\mathbf{R}}) = \sum_{LM} D_{LM}^{(ij)} j_L(\bar{R}) Y_{LM}(\bar{\Theta}, \bar{\Phi}), \quad (3.10)$$

where $\bar{\mathbf{R}} = (\bar{R}, \bar{\Theta}, \bar{\Phi})$. Then we have the relation

$$A_{lm'l'm'}^{(ij)} = 4\pi i^{l-l'} \sum_L i^{-L} C_{L,m-m';lm;l'm'} D_{L,m-m'}^{(ij)}, \quad (3.11)$$

$$\text{where} \quad C_{LM;lm;l'm'} = \int Y_{LM}(\vartheta, \varphi) Y_{lm}^*(\vartheta, \varphi) Y_{l'm'}(\vartheta, \varphi) d\Omega, \quad (3.12)$$

$$\text{and} \quad |l-l'| \leq L \leq l+l'. \quad (3.13)$$

$$\text{Following HAM and SEGALL}^7 \text{ [Eq. (7.11)] we write} \quad D_{LM}^{(ij)} = D_{LM}^{(ij)(1)} + D_{LM}^{(ij)(2)}. \quad (3.14)$$

In Appendix 2 it is shown that⁸

$$\begin{aligned} D_{LM}^{(ij)(1)} &= -\frac{1}{A\kappa} i^{|M|+1} 2^{-L} [(2L+1)(L+|M|)! (L-|M|)!]^{\frac{1}{2}} \sum_p \exp\{i \mathbf{K}_{pt} \cdot \mathbf{c}_{ijt} - i M \varphi_{K_p}\} \\ &\quad \times \sum_{n=0}^{L-|M|} \frac{1}{n!} \left(\frac{\Gamma_p}{\kappa}\right)^{2n-1} A_{np} \sum_{s=n}^{\min(2n, L-|M|)} \binom{n}{2n-s} \frac{(-\kappa c_{ijz})^{2n-s} (K_{pt}/\kappa)^{L-s}}{\left(\frac{L-|M|-s}{2}\right)! \left(\frac{L+|M|-s}{2}\right)!}, \end{aligned} \quad (3.15)$$

⁷ F. S. HAM and B. SEGALL, Phys. Rev. **124**, 1786 [1961].

⁸ Cf. Appendix 4. b).

where \mathbf{c}_{ijt} and c_{ijz} are the tangential and normal components of \mathbf{c}_{ij} , respectively, and

$$A_{np} = \int_{\exp\{-i\pi\} \Gamma_p^2 \omega/2}^{\infty} \eta^{-\frac{1}{2}-n} \exp \left\{ -\eta + \left(\frac{\Gamma_p c_{ijz}}{2} \right)^2 \frac{1}{\eta} \right\} d\eta. \quad (3.16)$$

The summation over s in (3.15) should be taken either for even or for odd values of s according as $L - |M|$ is even or odd, and it should run in the range $n \leq s \leq \min(2n, L - |M|)$, where $\min(2n, L - |M|)$ designates the smaller number of $2n$ and $L - |M|$. The integral (3.16) is somewhat more complicated than the incomplete gamma functions, which we could use in I. It is closely related to the integral contained in (3.20) below and its evaluation will be discussed in Appendix 3 of the present paper.

If $c_{ijz} = 0$ we have obviously

$$D_{LM}^{(ij)(1)} = - \frac{1}{A \kappa} i^{|M|+1} 2^{-L} [(2L+1)(L+|M|)!(L-|M|)!]^{\frac{1}{2}} \sum_p \exp\{i \mathbf{K}_{pt} \cdot \mathbf{c}_{ijt} - i M \varphi_{Kp}\} \\ \times \sum_{n=0}^{(L-|M|)/2} \frac{1}{n!} \left(\frac{\Gamma_p/\kappa}{L+|M|-2n} \right)^{2n-1} \left(\frac{K_{pt}/\kappa}{L-|M|-2n} \right)^{L-2n} \Gamma\left(\frac{1}{2} - n, e^{-i\pi} \Gamma_p^2 \omega/2\right). \quad (3.17)$$

This form is identical to I, Eq. (40)⁸ except the factor $\exp\{i \mathbf{K}_{pt} \cdot \mathbf{c}_{ijt}\}$.

If $K_{pt} = 0$ we have

$$D_{LM}^{(ij)(1)} = 0 \quad (3.18)$$

if $M \neq 0$, or if $M = 0$ and L odd. If $M = 0$ and L is even the summation over n in (3.15) should be replaced by

$$\sum_{n=L/2}^L \frac{1}{n!} \left(\frac{\Gamma_p}{\kappa} \right)^{2n-1} A_{np} \binom{n}{2n-L} (-\kappa c_{ijz})^{2n-L}. \quad (3.19)$$

$D_{LM}^{(ij)(2)}$ can be obtained by a method similar as used in I (cf. Appendix 2 of the present paper):

$$D_{LM}^{(ij)(2)} = - \frac{\kappa}{\sqrt{4\pi}} \sum_n \exp\{-i \mathbf{K}_{0t} \cdot \mathbf{a}_{nt}\} (-\kappa |\mathbf{a}_{nt} + \mathbf{c}_{ij}|)^L Y_{LM}^* (\vartheta_{\mathbf{a}_{nt} + \mathbf{c}_{ij}}, \varphi_{\mathbf{a}_{nt} + \mathbf{c}_{ij}}) \\ \times \int_0^{\kappa^2 \omega/2} u^{-\frac{3}{2}-L} \exp \left\{ u - \left(\frac{\kappa |\mathbf{a}_{nt} + \mathbf{c}_{ij}|}{2} \right)^2 \frac{1}{u} \right\} du, \quad (3.20)$$

where $\vartheta_{\mathbf{a}_{nt} + \mathbf{c}_{ij}}$, $\varphi_{\mathbf{a}_{nt} + \mathbf{c}_{ij}}$ are the angular coordinates of the vector $\mathbf{a}_{nt} + \mathbf{c}_{ij}$. We note that in the series (3.20) the term for which $|\mathbf{a}_{nt}| = 0$ is, in contrast to I, Eq. (46 b), not excluded. We need not investigate this term separately because we assume here that $|\mathbf{c}_{ij}| \neq 0$. The integral in (3.20) has the same form as I_L in I, Appendix 2, and its evaluation is discussed there.

We note that many structure constants are closely connected with each other. For example, the values of the structure constants are equal for all pairs of atoms if the values of \mathbf{c}_{ij} are equal. We have no such symmetry as Eq. (A-2) of SEGALL's paper⁴ against the exchange of indices ilm and $j'l'm'$, but the two structure constants related by this exchange are connected in such a way that they can be obtained in one process of calculation.

§ 4. Amplitudes of Scattered Waves

By a consideration similar as I, § 5 we obtain from (1.7) for the amplitudes of reflected waves⁹

$$R_p = \frac{2\pi}{i \Gamma_p A} \sum_i r_i^2 \exp\{-i \mathbf{K}_p^- \cdot \mathbf{c}_i\} \sum_l (-i)^l j_l(\kappa r_i) \left[\frac{1}{R_l^{(i)}} \frac{dR_l^{(i)}}{dr} - \frac{1}{j_l} \frac{dj_l}{dr} \right]_{r=r_i} \sum_m Y_{lm}(\vartheta_{\mathbf{K}_p}, \varphi_{\mathbf{K}_p}) X_{lm}^{(i)} \quad (4.1)$$

$$\text{or} \quad R_p = \frac{i 2\pi}{A \kappa \Gamma_p} \sum_i \exp\{-i \mathbf{K}_p^- \cdot \mathbf{c}_i\} \sum_l (-i)^l \frac{\tan \eta_l^{(i)}}{j_l(\kappa r_i) - n_l(\kappa r_i) \tan \eta_l^{(i)}} \sum_m Y_{lm}(\vartheta_{\mathbf{K}_p}, \varphi_{\mathbf{K}_p}) X_{lm}^{(i)} \quad (4.2)$$

⁹ Cf. Appendix 4. a).

and for transmitted waves⁹

$$T_p = \delta_{p0} + \frac{2\pi}{i\Gamma_p A} \sum_i r_i^2 \exp\{-i\mathbf{K}_p^+ \cdot \mathbf{c}_i\} \sum_l (-i)^l j_l(\kappa r_i) \left[\frac{1}{R_l^{(i)}} \frac{dR_l^{(i)}}{dr} - \frac{1}{j_l} \frac{dj_l}{dr} \right]_{r=r_i} \sum_m Y_{lm}(\vartheta_{K_p}^+, \varphi_{K_p}) X_{lm}^{(i)} \quad (4.3)$$

$$\text{or } T_p = \delta_{p0} + \frac{i2\pi}{A\kappa\Gamma_p} \sum_i \exp\{-i\mathbf{K}_p^+ \cdot \mathbf{c}_i\} \sum_l (-i)^l \frac{\tan \eta_l^{(i)}}{j_l(\kappa r_i) - n_l(\kappa r_i) \tan \eta_l^{(i)}} \sum_m Y_{lm}(\vartheta_{K_p}^+, \varphi_{K_p}) X_{lm}^{(i)}. \quad (4.4)$$

These amplitudes are, as in I, physically significant only in the case of real Γ_p , because if Γ_p is imaginary they are the amplitudes of evanescent waves, which decay exponentially with the distance from the crystal surfaces.

Using (2.11) we can write

$$R_p = \frac{i2\pi}{A\kappa\Gamma_p} \sum_i \exp\{-i\mathbf{K}_p^- \cdot \mathbf{c}_i\} \sum_{lm} \sin \hat{\eta}_l^{(i)} \sqrt{4\pi} Y_{lm}(\vartheta_{K_p}^-, \varphi_{K_p}) x_{lm}^{(i)}, \quad (4.5)$$

$$T_p = \delta_{p0} + \frac{i2\pi}{A\kappa\Gamma_p} \sum_i \exp\{-i\mathbf{K}_p^+ \cdot \mathbf{c}_i\} \sum_{lm} \sin \hat{\eta}_l^{(i)} \sqrt{4\pi} Y_{lm}(\vartheta_{K_p}^+, \varphi_{K_p}) x_{lm}^{(i)}. \quad (4.6)$$

We note again that these expressions do not contain the atomic radii r_i (cf. § 2).

§ 5. Number of Unknowns and Symmetry Consideration

The number of the unknowns $X_{lm}^{(i)}$ is determined from the number of atoms assigned to the column and the number of partial waves necessary for each atom. The number of partial waves is determined from the number of $\tan \eta_l^{(i)}$'s which are not negligibly small compared to 1. For low-energy electrons this number is small (<10). This is one of the most important points which makes the present method applicable only for low-energy electrons and not for high-energy electrons, since for high-energy electrons we need a large number of partial waves for each atom.

The number of unknowns increases very rapidly with the increase of the number of partial waves. For example, if we have only one atom in the unit cell (monatomic layer) the number of unknowns is given by $N_l = (l_{\max} + 1)^2$ and the number of coefficients $\alpha_{lm'l'm'}^{(ii)}$ in (2.8) is given by $N_l(N_l + 1)/2$. This is, typically, ca. 8000 for $l_{\max} = 10$.

The number of unknowns and coefficients can be reduced considerably if we have a geometrical symmetry of the system: wave and lattice.

In the band theory^{3,7} linear combinations of spherical harmonics with common l are constructed with the help of the group theory and only those combinations which are compatible with the symmetry of the system are taken into account. In the present theory the reduction can be found quickly in an intuitive way.

If the primary wave falls on the layer perpendicularly to the surface, that is, if $|\mathbf{K}_{0t}| = 0$, and if the layer has an n -fold rotation axis which is perpendicular to the layer and goes through some of the atom-centers in the cell, then for such atoms the unknowns $X_{lm}^{(i)}$ for which m is not a multiple (positive and negative, zero included) of n disappear. The symmetry of these components is not compatible with the symmetry required for the wave function on the surface of such atomic spheres.

If the layer has a mirror plane lying perpendicular to the layer and going through the center of some atoms in the unit cell, and if the direction of the primary wave is parallel to this mirror plane, then the component $X_{lm}^{(i)}$ for these atoms is equal to the component $X_{l,-m}^{(i)}$ when we take $\varphi_i = 0$ in the direction of the mirror plane. This means that the wave function on these atomic spheres can only contain the function

$$[Y_{lm}(\vartheta_i, \varphi_i) + Y_{l,-m}(\vartheta_i, \varphi_i)]/2 = N_{lm} P_l^{|m|}(\cos \vartheta_i) \cos(m \varphi_i) \quad (5.1)$$

as a component, the other component

$$[Y_{lm}(\vartheta_i, \varphi_i) - Y_{l,-m}(\vartheta_i, \varphi_i)]/(2i) = N_{lm} P_l^{|m|}(\cos \vartheta_i) \sin(m \varphi_i) \quad (5.2)$$

disappearing completely because this component has no mirror symmetry.

§ 6. Relation to the Pseudokinematical Theory

Since in crystals the atomic potentials may be strongly overlapping, it is, rigorously speaking, impossible to separate the scattering by a crystal into

single processes of scattering by atoms. Every volume element in the crystal takes part equally in the multiple scattering. Hence, according to the usual dynamical theory of electron diffraction (BETHE⁵) the crystal is regarded as a continuum with periodically varying potential and the wave equation is solved in this potential field. The muffin-tin model may be a rather rough approximation of the potential in crystals, but its advantage is that we can again separate the scattering by the crystal into single processes of scattering by atoms. The multiple scattering by the system of atoms is, as a matter of fact, separated in this model into two kinds of processes, namely, the multiple scattering inside single atoms¹⁰ and the series of scattering processes which occur *successively* at different atoms. The possibility of this separation is also assumed in the pseudokinematical theory (HOERNI¹¹, see particularly Fig. 1 of his first paper). In HOERNI's theory the successive processes are totally neglected, whereas they are fully taken into account in the present theory. This will be explained more closely in § 7. The concept of multiple scattering appears to be confined usually to the successive processes, so that any difference between the results of the pseudokinematical theory and the present theory may be regarded as the effect of "multiple scattering" in the usual sense.

Although the pseudokinematical theory may not be satisfactory for LEED, it is worth while to compare it with the present theory to explore the effect of multiple scattering. We apply here the pseudokinematical theory to the muffin-tin model.

For the scattering by a single atom we apply the usual form of Green's function

$$G_a(\mathbf{r}, \mathbf{r}') = -\exp\{i\kappa R\}/(4\pi R). \quad (6.1)$$

For $r > r'$ we have the expansion formula (MORSE-FESHBACH¹², p. 1466)

$$G_a(\mathbf{r}, \mathbf{r}') = -i \sum_{lm} \kappa h_l^{(1)}(\kappa r) j_l(\kappa r') Y_{lm}(\vartheta, \varphi) Y_{lm}^*(\vartheta', \varphi'), \quad (6.2)$$

where $h_l^{(1)}(\kappa r)$ is the spherical Hankel function of the first kind:

$$h_l^{(1)}(\kappa r) = j_l(\kappa r) + i n_l(\kappa r).$$

The integral equation for the scattering by a muffin-tin atom i is given by

$$\psi = \psi^{(0)} + \int_{\text{sphere } i} \left(G_a \frac{\partial \psi}{\partial \nu'} - \frac{\partial G_a}{\partial \nu'} \psi \right) ds', \quad (6.3)$$

The second term

$$\psi_s^{(i)} = \int_{\text{sphere } i} \left(G_a \frac{\partial \psi}{\partial \nu'} - \frac{\partial G_a}{\partial \nu'} \psi \right) ds' \quad (6.4)$$

is obviously the wave scattered by the atom i . Substituting (6.2) into (6.3) and expanding on the surface of the sphere in spherical harmonics, we obtain

$$X_{lm}^{(i)} = \beta_{lm}^{(i)} + \Delta_l^{(i)} X_{lm}^{(i)}, \quad (6.5)$$

$$\text{where } \Delta_l^{(i)} = \frac{i h_l^{(1)}(\kappa r_i) \tan \eta_l^{(i)}}{j_l(\kappa r_i) - n_l(\kappa r_i) \tan \eta_l^{(i)}}. \quad (6.6)$$

Hence from (2.9)

$$\begin{aligned} X_{lm}^{(i)} &= \beta_{lm}^{(i)} / (1 - \Delta_l^{(i)}) \\ &= \exp\{i \mathbf{K}_0 \cdot \mathbf{c}_i\} 4\pi i^l Y_{lm}^*(\vartheta_{K_0}, \varphi_{K_0}) \\ &\quad \times \frac{1}{2} [h_l^{(1)}(\kappa r_i) \exp\{i 2 \eta_l^{(i)}\} + h_l^{(2)}(\kappa r_i)], \end{aligned} \quad (6.7)$$

where $h_l^{(2)}(\kappa r_i)$ is the spherical Hankel function of the second kind:

$$h_l^{(2)}(\kappa r_i) = j_l(\kappa r_i) - i n_l(\kappa r_i).$$

The pseudokinematical theory assumes that the scattered wave from the assembly of atoms is a simple superposition of the scattered waves from single atoms. This superposition is given obviously by (1.7) if we substitute for ψ on the right-hand side the values which are obtained for each atom separately as a solution of (6.3). This means that we put $X_{lm}^{(i)}$ given by (6.7) into (4.2) and (4.4). Using the addition formula

$$\begin{aligned} P_l(\cos \Theta_{p0}^\pm) &= \frac{4\pi}{2l+1} \sum_m Y_{lm}(\vartheta_{K_p}^\pm, \varphi_{K_p}) Y_{lm}^*(\vartheta_{K_0}, \varphi_{K_0}), \end{aligned} \quad (6.8)$$

where Θ_{p0}^\pm are the angles between \mathbf{K}_p^\pm and \mathbf{K}_0 , we obtain

$$R_p = \frac{i 2\pi}{A \Gamma_p} \sum_i \exp\{-i(\mathbf{K}_p - \mathbf{K}_0) \cdot \mathbf{c}_i\} f^{(i)}(\Theta_{p0}^-), \quad (6.9)$$

$$T_p = \delta_{p0} + \frac{i 2\pi}{A \Gamma_p} \sum_i \exp\{-i(\mathbf{K}_p - \mathbf{K}_0) \cdot \mathbf{c}_i\} f^{(i)}(\Theta_{p0}^+), \quad (6.10)$$

¹⁰ We mean by "the multiple scattering inside an atom" every deviation of the atomic scattering amplitude from the first Born approximation. In fact, the deviation can always be understood as the multiple scattering by volume elements of the atom. This problem is practically solved by the usual partial-wave method.

¹¹ J. A. HOERNI, Phys. Rev. **102**, 1530, 1534 [1956].

¹² P. M. MORSE and H. FESHBACH, Methods of Theoretical Physics, 2 Vols., McGraw-Hill, New York 1953.

where

$$f^{(i)}(\Theta_{p0}^{\pm}) = \frac{1}{i 2 \pi} \sum_l (2l+1) (\exp\{i 2 \eta_l^{(i)}\} - 1) P_l(\cos \Theta_{p0}^{\pm}) \quad (6.11)$$

is the exact atomic scattering amplitude for the i -th atom (sphere).

If we replace $f^{(i)}(\Theta_{p0}^{\pm})$ in (6.9) and (6.10) by the first Born scattering amplitude $f_B^{(i)}(\Theta_{p0}^{\pm})$ we obtain the expressions of the usual *kinematical theory*.

For comparison with (6.9) and (6.10) the results of the present theory, (4.5) and (4.6), may be written in the form

$$R_p = \frac{i 2 \pi}{A \Gamma_p} \sum_i \exp\{-i(\mathbf{K}_p^- - \mathbf{K}_0) \cdot \mathbf{c}_i\} f_M^{(i)}(\mathbf{K}_p^-, \mathbf{K}_0), \quad (6.12)$$

$$T_p = \delta_{p0} + \frac{i 2 \pi}{A \Gamma_p} \sum_i \exp\{-i(\mathbf{K}_p^+ - \mathbf{K}_0) \cdot \mathbf{c}_i\} f_M^{(i)}(\mathbf{K}_p^+, \mathbf{K}_0), \quad (6.13)$$

where

$$f_M^{(i)}(\mathbf{K}_p^{\pm}, \mathbf{K}_0) = \frac{1}{i 2 \pi} \sum_l (2l+1) (\exp\{i 2 \eta_l^{(i)}\} - 1) \frac{4 \pi}{2l+1} \sum_m Y_{lm}(\vartheta_{K_p}^{\pm}, \varphi_{K_p}) Y_{lm}^*(\vartheta_{K_0}, \varphi_{K_0}) y_{lm}^{(i)} \quad (6.14)$$

where

$$y_{lm}^{(i)} = x_{lm}^{(i)} / [\sqrt{4 \pi} Y_{lm}^*(\vartheta_{K_0}, \varphi_{K_0}) \exp\{i \mathbf{K}_0 \cdot \mathbf{c}_i\} \exp\{i \eta_l^{(i)}\}]. \quad (6.15)$$

$f_M^{(i)}$ may be called the effective atomic scattering amplitude in the multiple-scattering approach. The value of $x_{lm}^{(i)}$ should be determined by the system (2.12). The difference between the kinematical theory, the pseudokinematical theory, and the present multiple-scattering theory may be detected in the difference between the quantities $f_B^{(i)}$, $f^{(i)}$, and $f_M^{(i)}$. Obviously the pseudokinematical form (6.11) can be obtained from (6.14) if we put $y_{lm}^{(i)} = 1$. Thus, the effect of the multiple scattering may be expressed also by the deviation of the value of $y_{lm}^{(i)}$ given by (6.15) from the value 1.

§ 7. Multiple Scattering and Partial Waves

The physical interpretation of the present approach may best be given in terms of the multiple-scattering picture. A general theory of multiple-scattering by large system of scatterers was given by LAX¹³ and applied by McRAE¹⁴ to LEED. The present theory is essentially equivalent to McRAE's one, and the relation between the two theories can be clarified also in the multiple-scattering picture.

The scattering by a single muffin-tin atom is represented by the integral equation (6.3). It shows that the wave function on the surface and outside

the atomic sphere is composed of two parts: the primary plane wave $\psi^{(0)}$ and the scattered wave $\psi_s^{(i)}$. In the pseudokinematical theory we neglect the multiple scattering so that we use (6.3) although the atom i is surrounded by other atoms. Now we note that (6.3) *should hold on the surface of the sphere i also when the primary $\psi^{(0)}$ is not a plane wave*. If we take into account the multiple scattering the primary wave for the atom i should be made up of the plane wave $\psi^{(0)}$ and the scattered waves from *all other atoms* $\psi_s^{(j')}$ ($j' \neq i$). We should have instead of (6.3)

$$\psi = \psi^{(i)} + \psi_s^{(i)}, \quad (7.1)$$

where the "primary" $\psi^{(i)}$, which is called „anregendes Feld“ by EWALD¹⁵ and the effective field by LAX¹³ and McRAE¹⁴, is given by

$$\psi^{(i)} = \psi^{(0)} + \sum_{j' \neq i} \psi_s^{(j')}. \quad (7.2)$$

If we substitute (7.2) into (7.1) we obtain

$$\psi = \psi^{(0)} + \sum_{j'} \psi_s^{(j')}. \quad (7.3)$$

The summation is taken over *all* atoms and this equation is actually the integral equation for the system of atoms, which can be derived from first principles and is essentially equivalent to (1.7)

¹³ M. LAX, Rev. Mod. Phys. **23**, 287 [1951]; Phys. Rev. **85**, 621 [1952].

¹⁴ E. G. McRAE, J. Chem. Phys. **45**, 3258 [1966]; Surface Sci. **8**, 14 [1967].

¹⁵ P. P. EWALD, Rev. Mod. Phys. **37**, 46 [1965].

[if we overlook for the moment the difficulty of convergence in the summation over an infinite number of atoms].

If $\psi^{(i)}$ in (7.1) is assumed to be known we can solve the equation for ψ and calculate $\psi_s^{(i)}$. This process may be represented by the *functional*¹⁶

$$\psi_s^{(i)} = F^{(i)}(\psi^{(i)}). \quad (7.4)$$

This relation represents with (7.2) the "self-consistency", which means that the scattered waves $\psi_s^{(i)}$ should be determined in such a way that the effective field $\psi^{(i)}$ constructed from $\psi^{(0)}$ and $\psi_s^{(j')}(j' \neq i)$ would satisfy (7.4) for all atoms of the system at the same time.

We find at this stage that the present theory is a generalization of Ewald's dynamical theory of X-ray diffraction by crystals (EWALD¹⁵, see also JAMES¹⁷). Ewald regards atoms as point dipoles so that the scattered wave¹⁸ $\psi_s^{(i)}$ is given as a function of the value of $\psi^{(i)}$ at the position of the dipole i . Thus, introduction of the quantity $\psi^{(i)}$ is essential for Ewald's model, whereas it plays no role in the present theory because the scattered wave $\psi_s^{(i)}$ is given directly by (6.4), which includes ψ and not $\psi^{(i)}$. The expression (7.4) is more accessible for physical interpretation than (6.4) because the cause of exciting the scattered wave is $\psi^{(i)}$ and not ψ . In this sense the right-hand side of (6.4) includes the cause and the result at the same time. Mathematically, however, the form (6.4) is more direct and more convenient for analysis than (7.4)¹⁹.

Modification of (7.3) into the form (1.7) for reducing the number of atoms from infinity to a finite number is only a matter of convenience, although the main mathematical difficulty lies in this process. Expansion of (1.7) in spherical harmonics brings also some complication, so that it may be worth while to recapitulate the multiple-scattering picture in the expanded form.

We consider again the scattering by an atom. This is represented in the expanded form by (6.5), which implies with (6.4) that the scattered wave outside the atomic sphere ($\bar{r} \geq r_i$) is given by

$$\psi_s^{(i)}(\bar{\mathbf{r}} + \mathbf{c}_i) = \sum_{lm} \Delta_l^{(i)} X_{lm}^{(i)} \frac{h_l^{(1)}(\kappa \bar{r})}{h_l^{(1)}(\kappa r_i)} Y_{lm}(\bar{\vartheta}, \bar{\varphi}). \quad (7.5)$$

$\psi_s^{(i)}$ is represented as a sum of *partial waves*, which have the characteristic angular distribution determined by $Y_{lm}(\bar{\vartheta}, \bar{\varphi})$. With the radial change $h_l^{(1)}(\kappa \bar{r})$ each of the partial waves is a solution of the wave equation in the vacuum outside the sphere. Thus, the quantities $\Delta_l^{(i)} X_{lm}^{(i)}$ give the amplitudes of partial waves of $\psi_s^{(i)}$. Similarly ψ and $\psi^{(i)}$ can be represented as a sum of partial waves around the atom i .

In the pseudokinematical theory $\psi_s^{(i)}$ is excited by $\psi^{(0)}$, the primary plane wave, so that $\beta_{lm}^{(i)}$ in (6.5) is given by (2.9). In the multiple scattering theory according to the above consideration $\psi_s^{(i)}$ should be excited by $\psi^{(i)}$ given by (7.2). This is actually found to be the case in (2.8), which may be rewritten as

$$X_{lm}^{(i)} = \beta_{lm}^{(i)} + \sum_{j'l'm'} F_{lm'l'm'}^{(ij)} \Delta_{l'}^{(j)} X_{l'm'}^{(j)} + \Delta_l^{(i)} X_{lm}^{(i)}, \quad (7.6)$$

where from (2.10) and (6.6)

$$F_{lm'l'm'}^{(ij)} = [-\delta_{ij} \delta_{ll'} \delta_{mm'} + i \kappa^{-1} A_{lm'l'm'}^{(ij)}] \frac{j_l(\kappa r_i)}{h_l^{(1)}(\kappa r_j)}. \quad (7.7)$$

A comparison with (7.1) shows that the quantity

$$\xi_{lm}^{(i)} = \beta_{lm}^{(i)} + \sum_{j'l'm'} F_{lm'l'm'}^{(ij)} \Delta_{l'}^{(j)} X_{l'm'}^{(j)}, \quad (7.8)$$

is the amplitude of the lm -th partial wave of $\psi^{(i)}$. It consists of $\beta_{lm}^{(i)}$ coming from the plane wave $\psi^{(0)}$ and the sum over the contributions of $\psi_s^{(j')}(j' \neq i)$ ²⁰; each partial wave of $\psi_s^{(j')}$ having the amplitude $\Delta_{l'}^{(j')} X_{l'm'}^{(j')}$ contributes to $\xi_{lm}^{(i)}$ with the proportionality factor $F_{lm'l'm'}^{(ij)}$ (Fig. 4). It is clear that $F_{lm'l'm'}^{(ij)}$ is the lm -th expansion coefficient of the $l'm'$ -th partial

¹⁶ Substitution of (7.4) into (7.3) and (7.2) gives the functional equations

$$\begin{aligned} \psi &= \psi^{(0)} + \sum_{j'} F^{(j')} \langle \psi^{(j')} \rangle, \\ \psi^{(i)} &= \psi^{(0)} + \sum_{j' \neq i} F^{(j')} \langle \psi^{(j')} \rangle. \end{aligned}$$

These are the basic equations of LAX¹³ and McRAE¹⁴ and are obviously direct consequences of the integral equation (7.3).

¹⁷ R. W. JAMES, *The Optical Principles of the Diffraction of X-rays*, G. Bell, London 1948.

¹⁸ In Ewald's model¹⁵ $\psi_s^{(i)}$ has only the component $X_{00}^{(i)}$ [cf. (7.5)].

¹⁹ A third alternative form, of course, is to divide ψ and $\psi^{(i)}$ into the parts "going into" and "coming out of" the atoms and to introduce S matrices or T matrices. (Cf. J. L. BEEBY, *J. Phys. C (Proc. Phys. Soc.)*, Ser. 2, **1**, 82 [1968]; K. HIRABAYASHI, *J. Phys. Soc. Japan* **24**, 846 [1968]).

²⁰ The summation with respect to j in (7.6) and (7.8) is taken only over the atoms assigned to the column of reference. It can be proved that the term $j=i$ does not contain the contribution from the atom i itself, but only from the atoms equivalent to the atom i by the lattice periodicity.

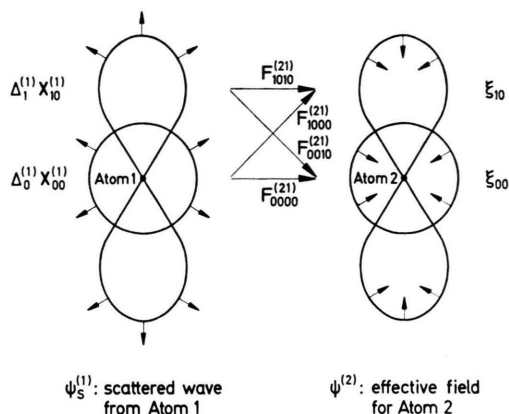


Fig. 4. The partial waves of the scattered wave from the atom 1 and of the effective field for the atom 2. The atoms are indicated only by the positions of their centers. Only the two components 00 and 10 are shown. The characteristic angular distributions of their amplitudes are indicated by contours. The quantities $\Delta_1^{(1)} X_{10}^{(1)}$ etc. put to contours are the amplitudes of the partial waves, and the quantities $F_{1010}^{(21)}$ etc. put to arrows are the proportionality factors with which the amplitudes of the scattered-wave components are multiplied as a contribution to the effective-field components.

wave of $\psi_s^{(i)}$ in spherical harmonics on the surface of the atomic sphere i . As a matter of fact $F_{lm'l'm'}^{(ij)}$ contains the lattice sum over all atoms in the layer which are equivalent to the atom j [with respect to the lattice translation \mathbf{a}_{nt}] so that it has the complicated form (7.7). It is to be noted that $F_{lm'l'm'}^{(ij)}$ is again a kind of structure constants, being independent of the scattering property of atoms, which are contained only in the quantity $\Delta_l^{(i)}$.

By solving the system (2.8), or (7.6), we obtain the "self-consistent" solution for the wave function ψ in terms of $X_{lm}^{(i)}$, or for the scattered waves $\psi_s^{(i)}$ in terms of $\Delta_l^{(i)} X_{lm}^{(i)}$.

wave function	ψ	$X_{lm}^{(i)}$
primary field	$\psi^{(0)}$	$\beta_{lm}^{(i)}$
effective field for the i -th atom	$\psi^{(i)}$	$\xi_{lm}^{(i)}$
scattered wave from the i -th atom	$\psi_s^{(i)}$	$\Delta_l^{(i)} X_{lm}^{(i)}$

Table 1. Waves in the multiple scattering theory and their expansion coefficients.

The various kinds of waves introduced above and their expansion coefficients on the i -th sphere are tabulated in Table 1.

§ 8. Use of Bloch Functions

The most important feature of the present approach, which is common to McRAE's¹⁴, may be that *it does not use Bloch functions*. This is the point which makes the present approach quite different from the usual dynamical theory of X-ray^{15, 17, 21} and electron diffraction⁵ and also from the band theory of metals²².

The solution should have indeed the Bloch-type translational property (1.5) *parallel* to the layer due to the symmetry of the problem (see GI), but it need not have the same kind of property in the perpendicular direction. Since in LEED the number of atomic layers which take part in the scattering process is small, the use of Bloch functions brings no essential advantage. On the other hand, owing to this discarding of Bloch functions the present method is particularly suitable for the study of structure of surfaces which are expected to be quite different from the structure of netplanes inside the crystal. This is almost always the case in the application of LEED to surface chemistry.

The use of Bloch functions becomes significant when the electron energy becomes relatively high, say, 1 keV or higher. If the direction of the incident wave is not nearly parallel to the surface, the depth of penetration of the incident electrons may be, say, 100 atomic layers or more. We describe here briefly how in such cases we may introduce Bloch functions into our theory.

Since we have a large number of equivalent layers except a few surface layers it is advantageous to calculate at first the "scattering matrix" of each layer. This can be done in the model which is essentially equivalent to that of DARWIN's dynamical theory²⁴ of X-ray diffraction^{24a}. A basic assumption

²¹ M. v. LAUE, Röntgenstrahlinterferenzen, Akademische Verlagsgesellschaft, Frankfurt/M. 1960.

²² A comprehensive survey of the methods of the Band theory can be found in ZIMAN²³. Following the convention of the Band theory we define here Bloch function as a function which has the Bloch-type translational property in all three dimensions. It need not be represented, as in the usual dynamical theory⁵, by a superposition of plane waves. In the Band theory Bloch functions are often constructed in other ways, particularly in the muffin-tin model (see ZIMAN²³).

²³ J. M. ZIMAN, Principles of the Theory of Solids, Cambridge University Press 1964.

²⁴ C. G. DARWIN, Phil. Mag. **27**, 315, 675 [1914].

^{24a} Note added in proof: A detailed account of the application of Darwin's method to LEED has been given by E. G. McRAE (1968, to be published in Surface Science). The "scattering matrix" is called by him, certainly more properly, the "transfer matrix".

of this method is that the z -projections of the atoms from different layers do not overlap [the case (a) of Fig. 3]. This assumption may be good, for example, for the (111) net-planes of f.c.c. lattices since this overlapping of the z -projections is relatively small. Between equivalent layers there are layers of vacuum, which are called here the "gaps" (see Fig. 5). In these gaps the solution of the Schrödinger equation with the periodicity condition (1.5) can be always represented by a superposition of plane waves $\exp\{i\mathbf{K}_p^\pm \cdot \mathbf{r}\}$, where \mathbf{K}_p^\pm are defined in § 3^{24b}. It is easy to modify the theory of §§ 1–4 to obtain the "scattering matrix" of the n -th atomic layer, which is defined here as the transformation matrix from the set of plane-wave amplitudes $\varphi_{p(n-1)}^\pm$ in the $(n-1)$ -th gap (lying above the n -th atomic layer) to the set $\varphi_{p(n)}^\pm$. The scattering matrix of the whole system of atomic layers can be obtained as the product of the scattering matrices of the atomic layers²⁵.

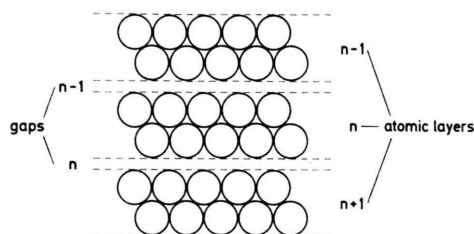


Fig. 5. Equivalent atomic layers and the gaps between them.

If we have a large number of equivalent layers it is advantageous to *diagonalize* the scattering matrix by calculating its eigenvalues and eigenvectors^{25a}. If we write the i -th eigenvalue in the form

$$\lambda_i = \exp\{i k_{zi} d\}, \quad (8.1)$$

where d is the spacing of the equivalent layers, and k_{zi} is in general a complex number, and assume that the plane-wave amplitudes $\varphi_{p(n-1)}^\pm$ are equal to the i -th eigenvector, then we have

$$\varphi_{p(n)}^\pm = \exp\{i k_{zi} d\} \varphi_{p(n-1)}^\pm. \quad (8.2)$$

This means that there exists a solution of the Schrödinger equation which satisfies the condition

$$\psi(x, y, z + d) = \exp\{i k_{zi} d\} \psi(x, y, z). \quad (8.3)$$

Since we assume *a priori* that the condition (1.5) is satisfied, this solution is nothing but a *Bloch function* (see footnote²²). For this Bloch function the energy κ^2 and the tangential component \mathbf{K}_{0t} are given and the eigenvalues of the normal component k_{zi} , which may be complex numbers, are to be calculated. This is just the Bloch function which appears in the standard dynamical theory of BETHE⁵. Bethe uses the plane-wave expansion for obtaining the Bloch functions. BOUDREAU and HEINE²⁹, who developed a similar theory as Bethe's, pointed out the advantage of the use of pseudopotentials in connection with the plane-wave expansion. The procedure just sketched above is an alternative method^{25b}. The original Korringa-Kohn-Rostoker method as well as APW, OPW etc. (see ZIMAN²³) may be also applied to calculate the Bloch functions.

The scattering matrix of the whole system of atomic layers can be obtained by building the product of the scattering matrices of the atomic layers. If all the layers are equivalent and we know the eigenvalues and eigenvectors this product can be easily calculated. Alternatively, we may calculate Bloch functions by using any of the above-mentioned methods and construct the scattering matrix of the whole system. This has been shown by NIEHRS³⁰ and FUJIMOTO³¹ for high-energy electrons. If we have extra surface layers we should multiply their scattering matrices with the above product. The solution of the scattering problem by the whole system is then easily obtained by considering the conditions of out-going waves in the upper and lower vacuum (cf. I, § 1). If we neglect the surface layers this method is exactly the same as that of the usual dynamical theory of X-ray and electron diffraction (DARWIN²⁴, EWALD¹⁵, VON LAUE²¹, BETHE⁵ etc.). We note that DARWIN²⁴, who considered the atomic layers as extremely thin plates with given

^{24b} These include the waves with imaginary Γ_p .

²⁵ The method is in this connection equivalent to the "multi-slice method" of COWLEY and MOODIE²⁶, HOWIE and WHELAN²⁷, and BOERSCH, JESCHKE and RAITH²⁸, but more exact within the validity of the chosen model.

^{25a} We assume here that the scattering matrix is diagonalizable.

^{25b} Another alternative method has been given by P. M. MARCUS and D. W. JEPSEN, Phys. Rev. Letters **20**, 925 [1968].

²⁶ J. M. COWLEY and A. F. MOODIE, Acta Cryst. **10**, 609 [1957]; **12**, 353, 360 [1959].

²⁷ A. HOWIE and M. J. WHELAN, Proc. Roy. Soc. London A **263**, 217 [1961].

²⁸ H. BOERSCH, G. JESCHKE, and H. RAITH, Z. Phys. **181**, 436 [1964].

²⁹ D. S. BOUDREAU and V. HEINE, Surface Sci. **8**, 426 [1967].

³⁰ H. NIEHRS, Z. Naturforsch. **14a**, 504 [1959].

³¹ F. FUJIMOTO, J. Phys. Soc. Japan **14**, 1558 [1959].

scattering matrices, and EWALD¹⁵, who considered lattices of point scatterers, practically used also Bloch functions in our sense (see footnote ²²).

§ 9. Conclusions

The method of Korringa and Kohn-Rostoker in the band theory of metals has been applied, in its generalized form by Segall, to the scattering problem by complex two-dimensional lattices of atoms. The method is a straightforward generalization of that applied to monatomic layers in Part I. The problem is reduced to a system of linear algebraic equations for determination of the expansion coefficients of the wave function on the surfaces of atomic spheres. The coefficients of the equations contain the "structure constants", which depend only on the structure and not on the kind of atoms, and the phase-shift data of the atoms.

The calculation of the structure constants is somewhat more complicated than in the case of monatomic layers, but a much simpler form can be derived for a pair of atoms which belong to different atomic layers if their *z*-projections don't overlap.

The number of the expansion coefficients can be reduced considerably if the incident wave lies in a certain symmetric direction with respect to the layer. Many coefficients prove to disappear owing to the symmetry.

The corresponding formulae of the pseudokinematical theory, in which the multiple scattering is completely neglected, are given also in an expanded form in spherical harmonics for the purpose of comparison with the present theory.

The method is interpreted physically in terms of multiple scattering, first in the general form and then in the form expanded in spherical harmonics. In both forms the wave function is separated, with respect to each atom of the system, into the "effective field" $\psi^{(i)}$, the sum of the waves which fall on the atom, and the scattered wave. The condition of the "self-consistency" between these waves leads to the integral equation used in the present theory. In this form the theory is shown to be equivalent to the dynamical theory of Ewald and also to the LEED theory of McRae.

It is emphasized that the particular feature of the present method is that it does not use Bloch functions and is particularly suitable for the study of surface layers.

In the case that many equivalent atomic layers should be taken into account, as is the case at higher electron energies, it proves to be advantageous to modify the method to the calculation of the "scattering matrices" of layers. For this purpose it is necessary to assume that there are "gaps" between the atomic layers. In the gaps the wave function can be represented as a set of discrete plane waves, and the scattering matrices give the relation between the sets of waves above and below the atomic layers.

For the purpose of calculating the product of the scattering matrices for many equivalent layers the scattering matrix is diagonalized. It is shown that this process is equivalent to the calculation of Bloch functions, and in this sense the method becomes equivalent to the standard dynamical theory of X-ray and electron diffraction.

The author wishes to thank Prof. Dr. K. MOLIÈRE for his encouragement and valuable suggestions.

Appendix 1: Spherical Harmonics with Imaginary Arguments

If in (3.1) $|\mathbf{K}_{pt}| > \kappa$, the vector \mathbf{K}_p^+ in (3.6) has an imaginary normal component I_p according to (3.2). In this case the expression (3.6) requires a particular analytical investigation.

The formula (WATSON³², p. 368; footnotes ³²⁻³⁴ see p. 1294)

$$\exp\{i z \cos \Theta\} = \left(\frac{\pi}{2z}\right)^{\frac{1}{2}} \sum_{n=0}^{\infty} (2n+1) i^n J_{n+\frac{1}{2}}(z) P_n(\cos \Theta) \quad (\text{A } 1.1)$$

is valid for arbitrary *complex* values of $\cos \Theta$. This can be seen at once from Gegenbauer's derivation of the formula (WATSON³², p. 368–369). On the other hand, we have the addition formula (WHITTAKER-WATSON³³, p. 326)

$$P_n(\cos \Theta) = P_n(x) P_n(x') + 2 \sum_{m=1}^n (-1)^m \frac{(n-m)!}{(n+m)!} P_n^m(x) P_n^m(x') \cos(m\omega), \quad (\text{A } 1.2)$$

where

$$\cos \Theta = x x' - (x^2 - 1)^{1/2} (x'^2 - 1)^{1/2} \cos \omega, \quad (\text{A } 1.3)$$

and $P_n^m(x)$ are associated Legendre functions with a complex argument in Hobson's definition. This formula is valid for arbitrary *complex* values of x , x' and $\cos \omega$. Thus, putting

$$z = \kappa r_i, \quad x = \pm i | \Gamma_p | / \kappa, \quad x' = \cos \vartheta_i, \quad \omega = \varphi_i - \varphi_{Kp} + (\pm \pi - \pi) / 2 \quad (\text{A } 1.4)$$

and substituting (A 1.2) into (A 1.1), we obtain in place of (3.6)

$$\begin{aligned} & \exp \{ i (K_{pt} r_i \sin \vartheta_i \cos (\varphi_i - \varphi_{Kp}) \pm i | \Gamma_p | r_i \cos \vartheta_i) \} \\ &= \sum_{lm} 4 \pi i^l j_l(\kappa r_i) N_{lm}^2(\mp i)^{|m|} P_l^{|m|}(\pm i | \Gamma_p | / \kappa) P_l^{|m|}(\cos \vartheta_i) \exp \{ i m (\varphi_i - \varphi_{Kp}) \} \end{aligned} \quad (\text{A } 1.5)$$

where $P_l^{|m|}(\cos \vartheta_i)$ is the usual Ferrers' associated Legendre function (WHITTAKER-WATSON³³, p. 323) and

$$N_{lm} = \left[\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{\frac{1}{2}}. \quad (\text{A } 1.6)$$

Similarly for $\exp \{ -i \mathbf{K}_p^\pm \cdot \mathbf{r} \}$ we obtain

$$\begin{aligned} & \exp \{ -i (K_{pt} r_i \sin \vartheta_i \cos (\varphi_i - \varphi_{Kp}) \pm i | \Gamma_p | r_i \cos \vartheta_i) \} \\ &= \sum_{lm} 4 \pi i^l j_l(\kappa r_i) N_{lm}^2(\mp i)^{|m|} P_l^{|m|}(\pm i | \Gamma_p | / \kappa) P_l^{|m|}(\cos \vartheta_i) \exp \{ -i m (\varphi_i - \varphi_{Kp}) \}. \end{aligned} \quad (\text{A } 1.7)$$

Hence the formulae (3.7) and (3.8) are valid if we *define* the spherical harmonics for imaginary Γ_p as

$$Y_{lm}(\vartheta_{Kp}^\pm, \varphi_{Kp}) = N_{lm}(\mp i)^{|m|} P_l^{|m|}(\pm i | \Gamma_p | / \kappa) \exp \{ i m \varphi_{Kp} \}. \quad (\text{A } 1.8)$$

We note that $Y_{l, -m}$ is not equal to Y_{lm}^* in these cases.

Appendix 2: Calculation of Structure Constants

It follows from I, Eq. (25) that

$$D_{LM}^{(ij)(1)} = - \frac{1}{2\pi A} \left(\frac{\pi}{2} \right)^{\frac{1}{2}} \sum_p \exp \{ i \mathbf{K}_{pt} \cdot \mathbf{c}_{ijt} \} \lim_{\bar{R} \rightarrow 0} \{ I_{LMp}^{(1)}(\bar{R}) / j_L(\kappa \bar{R}) \}, \quad (\text{A } 2.1)$$

$$\text{and} \quad D_{LM}^{(ij)(2)} = - \frac{1}{4\pi^2} \left(\frac{\pi}{2} \right)^{\frac{1}{2}} \sum_n \exp \{ -i \mathbf{K}_{0t} \cdot \mathbf{a}_{nt} \} \lim_{\bar{R} \rightarrow 0} \{ I_{LMn}^{(2)}(\bar{R}) / j_L(\kappa \bar{R}) \}, \quad (\text{A } 2.2)$$

$$\begin{aligned} \text{where} \quad I_{LMp}^{(1)}(\bar{R}) &= \int_0^{2\pi} d\bar{\Phi} \int_0^\pi \sin \bar{\Theta} d\bar{\Theta} Y_{LM}^*(\bar{\Theta}, \bar{\Phi}) \exp \{ i \mathbf{K}_{pt} \cdot \bar{\mathbf{R}}_t \} \\ &\quad \times \int_\omega^{\infty \exp \{ i \varphi_p \}} \zeta^{-\frac{1}{2}} \exp \{ \frac{1}{2} [I_p^2 \zeta - (\bar{Z} + c_{ijz})^2 / \zeta] \} d\zeta, \end{aligned} \quad (\text{A } 2.3)$$

$$\begin{aligned} \text{and} \quad I_{LMn}^{(2)}(\bar{R}) &= \int_0^{2\pi} d\bar{\Phi} \int_0^\pi \sin \bar{\Theta} d\bar{\Theta} Y_{LM}^*(\bar{\Theta}, \bar{\Phi}) \\ &\quad \times \int_{1/\omega}^{\infty} \zeta^{-\frac{1}{2}} \exp \{ -\frac{1}{2} (|\bar{\mathbf{R}} + \mathbf{c}_{ij} + \mathbf{a}_{nt}|^2 \zeta - \kappa^2 / \zeta) \} d\zeta, \end{aligned} \quad (\text{A } 2.4)$$

where $\bar{\mathbf{R}}_t$ and \bar{Z} are respectively the tangential and normal components of $\bar{\mathbf{R}}$.

The integral with respect to ζ in (A 2.3) can be expanded into a power series

$$\begin{aligned} & \int_\omega^{\infty \exp \{ i \varphi_p \}} \zeta^{-\frac{1}{2}} \exp \{ \frac{1}{2} [I_p^2 \zeta - (\bar{Z} + c_{ijz})^2 / \zeta] \} d\zeta \\ &= \sum_n \frac{1}{n!} [-\frac{1}{2} (2 c_{ij} \bar{Z} + \bar{Z}^2)]^n \int_\omega^{\infty \exp \{ i \varphi_p \}} \zeta^{-\frac{1}{2}-n} \exp \{ \frac{1}{2} [I_p^2 \zeta - c_{ijz}^2 / \zeta] \} d\zeta. \end{aligned} \quad (\text{A } 2.5)$$

Integration with respect to $\bar{\Phi}$ gives a form similar as I, Eq. (A 2)³⁴. We have then the integral with respect to $\bar{\Theta}$

$$\int_0^\pi \sin \bar{\Theta} d\bar{\Theta} P_L^{|M|}(\cos \bar{\Theta}) J_{|M|}(K_{pt} \bar{R} \sin \bar{\Theta}) (2 \bar{R} c_{ijz} \cos \bar{\Theta} + \bar{R}^2 \cos^2 \bar{\Theta})^n. \quad (\text{A } 2.6)$$

As in I, Appendix 1 the Bessel function can be expanded into a power series of $\sin \bar{\Theta}$. The last factor can be expanded by the binomial formula. We find that for each term of this binomial expansion only one term from the power series of the Bessel function must be taken into account. This is due to the fact that we need only the lowest non-vanishing power of \bar{R} in $I_{LMp}^{(1)}(\bar{R})$ for the purpose of putting into (A 2.1) and taking the limit $\bar{R} \rightarrow 0$. The lowest power proves to be \bar{R}^L . On collecting such terms for each n and putting into (A 2.1), we obtain (3.15).

Appendix 3: Calculation of the Integral Δ_{np}

For the integral Δ_{np} given by (3.16) we put

$$x = e^{-i\pi} I_p^2 \omega / 2, \quad z^2 = I_p^2 c_{ij} z^2, \quad (\text{A } 3.1)$$

and write

$$\Delta_n = \int_x^\infty \eta^{-\frac{1}{2}-n} \exp\{-\eta + z^2/(4\eta)\} d\eta. \quad (\text{A } 3.2)$$

Δ_n satisfies the recurrence formula

$$(z/2)^2 \Delta_{n+1} = (\frac{1}{2} - n) \Delta_n + \Delta_{n-1} - x^{\frac{1}{2}-n} \exp\{-x + z^2/(4x)\}, \quad (\text{A } 3.3)$$

which can be derived from (A 3.2) by integration by parts.

Introducing the complex error function $w(z)$ given in I (A 8), we can write for $n=0$ and $n=1$

$$\Delta_0 = \frac{\sqrt{\pi}}{2} \exp\left\{-x + \frac{z^2}{4x}\right\} \left[w\left(-\frac{z}{2\sqrt{x}} + i\sqrt{x}\right) + w\left(\frac{z}{2\sqrt{x}} + i\sqrt{x}\right) \right], \quad (\text{A } 3.4)$$

$$\Delta_1 = \frac{\sqrt{\pi}}{i2} \frac{2}{z} \exp\left\{-x + \frac{z^2}{4x}\right\} \left[w\left(-\frac{z}{2\sqrt{x}} + i\sqrt{x}\right) - w\left(\frac{z}{2\sqrt{x}} + i\sqrt{x}\right) \right]. \quad (\text{A } 3.5)$$

We can derive these formulae from (A 3.2) following Ewald's analysis (EWALD³⁵, Anhang). It is to be noted that from (A 3.1) either x or z^2 is negative according as I_p^2 is positive or negative. If x is negative we define

$$\sqrt{x} = -i\sqrt{|x|}, \quad z > 0, \quad (\text{A } 3.6)$$

and if z^2 is negative we define

$$z = i|z|, \quad x > 0. \quad (\text{A } 3.7)$$

Appendix 4: Errata of Part I

a) In Eqs. (53), (54) and (55) the spherical harmonics Y_{lm} should read respectively $Y_{lm}(\vartheta_{K_p}^\pm, \varphi_{K_p})$, $Y_{lm}(\vartheta_{K_p}^-, \varphi_{K_p})$ and $Y_{lm}(\vartheta_{K_p}^+, \varphi_{K_p})$.

The text under Eq. (53) should read:

"where $\kappa (= |\mathbf{K}_p^\pm|)$, $\vartheta_{K_p}^\pm$, φ_{K_p} are the polar coordinates of the vectors \mathbf{K}_p^\pm , which have the tangential components \mathbf{K}_{pt} and the normal components $\pm \Gamma_p$. From (24) \mathbf{K}_p^\pm have ...".

b) In Eq. (40) the factor $(-1)^L$ should be omitted.

In Eqs. (A 2) and (A 3) the argument of the Bessel function $-K_{pt} R \sin \Theta$ should read $K_{pt} R \sin \Theta$.

In Eq. (A 6) the factor $(-K_{pt} R/2)^{L-2n}$ should read $(K_{pt} R/2)^{L-2n}$.

In the Table on p. 330 the factor $-1/(A\kappa)$ in the third equation should read $1/(A\kappa)$. In the same equation the factor $\sqrt{6}$ should read $\sqrt{6}/2$ ^{35a}.

c) In Eq. (A 9) $\Gamma(1/2, \kappa)$ should read $\Gamma(1/2, x)$.

³² G. N. WATSON, Theory of Bessel Functions, Cambridge University Press 1944 (2nd ed.).

³³ E. T. WHITTAKER and G. N. WATSON, A Course of Modern Analysis, Cambridge University Press 1927 (2nd ed.).

³⁴ Cf. Appendix 4. b).

³⁵ P. P. EWALD, Ann. Phys. (4) **64**, 253 [1921].

^{35a} The author is indebted to Dr. P. J. JENNINGS (Bell Telephone Laboratories) for pointing out this error.