Application of a Variational Principle to the Calculation of Low-Energy Electron Diffraction Intensities. III. Application to Muffin-Tin Potentials*

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The variational principle derived in the previous paper is applied to the muffin-tin potential model. For electron scattering from a crystal with a finite number of layers, the exact reflection coefficient is expressed as the ratio of two determinants; the elements of the determinants are formed in terms of the phase shifts and the structure constants, which are dependent on the energy, the parallel component of the wave vector of the incident electrons, and the lattice geometry. For s-wave and p-wave scatterers of a monoatomic layer, analytic evaluation of the reflection coefficients is possible. For s-wave scatterers, our result is identical to those obtained by Kambe and by McRae. For p-wave scatterers, our result is again identical to that predicted by Kambe's equations. For scattering from a semi-infinite crystal, a discrete set of Bloch waves is inserted in the variational equation and the reflection coefficient is written in terms of the structure constants, the phase shifts, and the perpendicular components of the wave vectors of the Bloch waves. The results are valid for crystals with perfect two-dimensional periodicity in the plane parallel to the crystal surface, but have arbitrarily variable scattering potential and lattice spacing in the perpendicular direction.

I. INTRODUCTION

In the preceding paper, we have proposed a variational principle, which leads to a stationary expression for the reflection coefficient of elastic scattering. The crystal is assumed to possess perfect two-dimensional periodicity in the plane parallel to the surface and arbitrary variations of crystal geometry and chemical composition in the perpendicular direction. With linear trial functions, the reflection coefficient is given by the ratio of two determinants whose elements involve integrals of known functions and the crystal potential.

A Green's-function method has been developed by Korringa, and Kohn and Rostoker[1,2] (KKR theory) for the calculation of the energy band structure of metals. They employed a muffin-tin-potential model and the spherical harmonics expansion of a Bloch wave. The muffin-tin potential is defined by confining each atom in an inscribed sphere within which the potential is spherically symmetric, and in the interstitial regions the potential is constant. Because of the perfect triperiodicity of the crystal, the summation over all lattice points is absorbed in a structural Green's function. The advantage of the KKR theory is the separation of the lattice geometric and the atomic scattering properties. The atomic potential appears through the logarithmic derivative of the radial function at the surface of the inscribed sphere. The main computational efforts are on the structure constants, which are characteristics of the crystal geometry. Once tab-

ulated for a given lattice type, the structure constants need not be calculated again.

In the present work, we apply the variational principle derived in the preceding paper to muffin-tin potentials. The mathematical procedure for evaluating the integrals in the variational equation is similar to that in the KKR band theory.[1,2]

For the crystal with a finite number of layers, the wave field inside the crystal is expanded into spherical harmonics. The exact reflection coefficient is expressed as the ratio of two determinants; the elements of the determinants are formed in terms of structure constants and the phase shifts. The structure constants, which are the same as those in Kambe's[3,4] theory, are dependent on the energy, the parallel component of the incident wave vector, and the lattice geometry. The method shares the advantage with the KKR band theory[1,2] and Kambe's LEED theory,[3,4] i.e., the structural and the atomic properties are segregated and can be evaluated separately. Furthermore, since no Bloch wave expansion for the wave field inside the crystal is required, this method is valid for crystals with possible impurity surface layers. For s-wave and p-wave scatterers of a monoatomic layer, analytic evaluation of the reflection coefficient is possible. For s-wave scatterers, our result is identical to those obtained by Kambe[3] and by McRae.[5] For p-wave scatterers, our result is again identical to that predicted by Kambe's equations.[3]

However, in the case of electron scattering from a semi-infinite crystal, it is more convenient to

employ Bloch waves. By inserting a discrete set of Bloch waves in the variational equation, the reflection coefficient is expressed in terms of the structure constants, the phase shifts, and the perpendicular components of the wave vectors of the Bloch waves. We first investigate the electron scattering from a perfect semi-infinite crystal. The case of a semi-infinite crystal with a few foreign atomic layers on the surface is described as the combination of the methods for a finite number of layers and a perfect semi-infinite substrate. This variational method together with the Bloch theorem eliminates the difficulty of evaluating a large number of structure constants for a semi-infinite crystal and thus represents an advantage over Kambe's[4] cellular method.

II. APPLICATION TO A MONOATOMIC LAYER

We first apply the variational principle derived in the preceding paper to the simplest possible case, i.e., electron diffraction from a crystal consisting of a single monoatomic layer. The monolayer is assumed to have two infinite surface planes which are parallel to each other and lie in the y-z plane. Each atom is confined in a sphere that does not overlap neighboring spheres. The potential is spherically symmetric inside the sphere about the center of the atom and null in the space between the spheres. The effective periodic potential of the monoatomic layer is defined as

$$V(\vec{r}) = \sum_{m,n} V_e(|\vec{r} - \vec{r}_{mn}|), \quad m,n = 0, \pm 1, \pm 2, \ldots$$

$$(2.1)$$

where the origin of the coordinate system is at the center of an arbitrary atom and $\vec{r}_{mn} = m\vec{a}_2 + n\vec{a}_3$. $\vec{a}_2$ and $\vec{a}_3$ are the two-dimensional primitive translation vectors in the y-z plane, and $\vec{r}_{mn}$ is a two-dimensional lattice vector. $V_e(|\vec{r} - \vec{r}_{mn}|)$ is the potential in the primitive cell centered at $\vec{r}_{mn}$, and its values are

$$V_e(r) = \text{spherically symmetric}, \quad r < r_a$$

$$V_e(r) = 0, \qquad\qquad r \geq r_a \qquad (2.2)$$

where r_a is the radius of the sphere.

The boundary condition is that the incident plane wave $e^{i\vec{K}\cdot\vec{r}}$ comes from $x = -\infty$. In the preceding paper, we have shown that the wave function in the vacuum as $x \to -\infty$ is given by

$$\psi(\vec{r}) \to e^{i\vec{K}\cdot\vec{r}} + \sum_{\vec{v}(Re)} R_{\vec{v}} e^{i\vec{K}_{\vec{v}}^- \cdot \vec{r}}, \qquad (2.3)$$

where $R_{\vec{v}}$ is the reflection coefficient of the diffracted plane wave in the direction of $\vec{K}_{\vec{v}}^-$. The parallel component (to the crystal surface) of $\vec{K}_{\vec{v}}^-$ is different from the incident parallel wave vector $\vec{K}_{\parallel}$ by 2π times the two-dimensional reciprocal-lattice vector $\vec{v}$, and the perpendicular component of $\vec{K}_{\vec{v}}^-$ is $-K_{\vec{v}}$, where $K_{\vec{v}} = [k^2 - (\vec{K}_{\parallel} + 2\pi\vec{v})^2]^{1/2}$. Let us denote the components of $\vec{K}_{\vec{v}}^-$ explicitly by $[-K_{\vec{v}}, (\vec{K}_{\parallel} + 2\pi\vec{v})]$. The symbol Re appearing under the summation means the summation is taken over all the two-dimensional reciprocal-lattice vectors which give real $K_{\vec{v}}$.

The quantity $A_{\vec{v}}$ is defined as

$$A_{\vec{v}} = i2AK_{\vec{v}}R_{\vec{v}}, \qquad (2.4)$$

where A is a unit two-dimensional area in the surface plane, i.e., $A = |\vec{a}_2 \times \vec{a}_3|$. The variational equation, which gives a stationary expression for the reflection coefficient $R_{\vec{v}}$, is given in the preceding paper by

$$A_{\vec{v}} = i2AK_{\vec{v}}R_{\vec{v}}$$

$$= \frac{[\int e^{i\vec{K}\cdot\vec{r}} V(\vec{r}) \psi(\vec{r}) d\vec{r}][\int e^{-i\vec{K}_{\vec{v}}^-\cdot\vec{r}'} V(\vec{r}')\psi(\vec{r}') d\vec{r}']}{\int \psi(\vec{r}) V(\vec{r}) [\psi(\vec{r}) - \int 9(\vec{r},\vec{r}') V(\vec{r}') \psi(\vec{r}') d\vec{r}'] d\vec{r}},$$

$$(2.5)$$

with the variational principle $\delta A_{\vec{v}} = 0$. The range of integration of the integrals in the above equation is over a column with unit surface area A, i.e., the reference column. The structural Green's function $9(\vec{r}, \vec{r}')$ is derived in the preceding paper as

$$9(\vec{r},\vec{r}') = \sum_{\vec{u}, K_{\vec{u}} \neq 0} \left(-\frac{i}{2AK_{\vec{u}}} \exp[i(\vec{K}_{\parallel} + 2\pi\vec{u}) \cdot (\vec{r}_{\parallel} - \vec{r}_{\parallel}')] \exp(iK_{\vec{u}}|x - x'|) \right), \qquad (2.6)$$

satisfying the Schrödinger equation

$$(\nabla^2 + k^2) 9(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}'), \qquad (2.7)$$

where $\vec{r}$ and $\vec{r}'$ are in the reference column, and k^2 is the incident electron energy in atomic units.[6] For the monoatomic layer with the effective potential defined by Eq. (2.2), we need to integrate over a sphere of radius r_a, since the interstitial region

is vacuum.

The limiting procedure of Kohn and Rostoker[1] should be used in this problem because of the singularity of the Green's function $9(\vec{r}, \vec{r}')$ at $\vec{r} = \vec{r}'$. We set the range of integration as

$$0 \leq r < r_a - 2\epsilon, \quad 0 \leq r' < r_a - \epsilon, \qquad (2.8)$$

where ϵ is a small quantity. Thus

$$A_{\tilde{\Psi}} = \lim_{\epsilon \to 0} \frac{[\int_{r<r_a} e^{i\vec{k}\cdot\vec{r}} V(\vec{r})\psi(\vec{r})\,d\vec{r}][\int_{r'<r_a} e^{-i\vec{k}_{\tilde{\Psi}}\cdot\vec{r}'} V(\vec{r}')\psi(\vec{r}')\,d\vec{r}']}{\int_{r<r_a-2\epsilon} d\vec{r}\,\tilde{\psi}(\vec{r})\,V(\vec{r})[\psi(\vec{r}) - \int_{r'<r_a-\epsilon} \mathcal{G}(\vec{r},\vec{r}')V(\vec{r}')\psi(\vec{r}')\,d\vec{r}']} \quad . \tag{2.9}$$

The exact wave functions $\psi(\vec{r})$ and $\tilde{\psi}(\vec{r})$ are the solutions of the same Schrödinger equation

$$[\nabla^2 + k^2 - V(\vec{r})]\,\phi(\vec{r}) = 0 , \tag{2.10}$$

but they satisfy different boundary conditions; i.e., $\psi(\vec{r})$ corresponds to the incident plane wave $e^{i\vec{k}\cdot\vec{r}}$, while $\tilde{\psi}(\vec{r})$ corresponds to an incident wave $e^{-i\vec{k}_{\tilde{\Psi}}\cdot\vec{r}}$.

The plane waves $e^{i\vec{k}\cdot\vec{r}}$ and $e^{-i\vec{k}_{\tilde{\Psi}}\cdot\vec{r}}$ satisfy the same Schrödinger equation for free space,

$$(\nabla^2 + k^2)\phi_0(\vec{r}) = 0 . \tag{2.11}$$

By using Green's theorem[7] together with Eqs. (2.8), (2.10), and (2.11), we can transform the volume integrations in Eq. (2.9) into surface integrations,

$$A_{\tilde{\Psi}} = \lim_{\epsilon \to 0} \frac{\{\int_{r=r_a} ds\,[e^{i\vec{k}\cdot\vec{r}},\tilde{\psi}(\vec{r})]\}\{\int_{r'=r_a} ds'\,[e^{-i\vec{k}_{\tilde{\Psi}}\cdot\vec{r}'},\psi(\vec{r}')]\}}{\int_{r=r_a-2\epsilon} ds \int_{r'=r_a-\epsilon} ds'\,[\tilde{\psi}(\vec{r}),\,[\mathcal{G}(\vec{r},\vec{r}'),\,\psi(\vec{r}')]_{r'=r_a-\epsilon}]_{r=r_a-2\epsilon}} , \tag{2.12}$$

where we have defined

$$[f,g] = \left(f(\vec{r})\,\frac{\partial g(\vec{r})}{\partial r} - g(\vec{r})\,\frac{\partial f(\vec{r})}{\partial r}\right)_{r=r_a} \tag{2.13}$$

as the Wronskian of f and g evaluated at $r = r_a$, if not specified explicitly.

The exact wave functions $\psi(\vec{r})$ and $\tilde{\psi}(\vec{r})$ can be expressed by a linear combination of the complete set of spherical harmonics. It is natural to truncate the wave functions into a finite series of spherical harmonics as the trial functions,

$$\psi(\vec{r}) = \sum_{l=0}^{ln} \sum_{m=-l}^{l} C_{lm} Y_{lm}(\theta,\phi) R_l(r) \tag{2.14}$$

and

$$\tilde{\psi}(\vec{r}) = \sum_{l=0}^{ln} \sum_{m=-l}^{l} \tilde{C}_{lm} Y_{lm}^*(\theta,\phi) R_l(r) , \tag{2.15}$$

where (r, θ, ϕ) are the spherical coordinates of $\vec{r}$, and C_{lm} and $\tilde{C}_{lm}$ are complex expansion coefficients. The radial function $R_l(r)$ is the solution of the following equation[8]:

$$\left(-\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{l(l+1)}{r^2} + V(\vec{r}) - k^2\right)R_l(r) = 0 , \tag{2.16}$$

with the conditions

$$R_l(0) = \text{finite},$$
$$R_l(r_a) = \text{const}\times[j_l(kr_a) - \tan\eta_l\,n_l(kr_a)] , \tag{2.17}$$

where η_l is the lth phase shift of the atom. The spherical and the Neumann Bessel functions are defined as[9]

$$j_l(x) = (\pi/2x)^{1/2} J_{l+1/2}(x) ,$$

$$n_l(x) = (-1)^{l+1}(\pi/2x)^{1/2} J_{-l-1/2}(x), \tag{2.18}$$

where $J_{l+1/2}(x)$ is the Bessel function of the first kind.

The spherical harmonics $Y_{lm}(\theta,\phi)$ are defined as

$$Y_{lm}(\theta,\phi) = \left[\left(\frac{2l+1}{4\pi}\right)\left(\frac{(l-|m|)!}{(l+|m|)!}\right)\right]^{1/2}$$
$$\times P_l^{|m|}(\cos\theta)\,e^{im\phi} , \tag{2.19}$$

with the normalization condition

$$\int_0^{2\pi} d\phi \int_{-1}^{1} Y_{lm}(\theta,\phi)\,Y_{l'm'}^*(\theta,\phi)\,d(\cos\theta)$$
$$= \delta_{ll'}\,\delta_{mm'} . \tag{2.20}$$

The plane-wave functions $e^{i\vec{k}\cdot\vec{r}}$ and $e^{-i\vec{k}_{\tilde{\Psi}}\cdot\vec{r}}$ may also be expanded into spherical harmonics,[10]

$$e^{i\vec{k}\cdot\vec{r}} = \sum_{l,m} 4\pi i^l\,Y_{lm}(\theta,\phi)\,Y_{lm}^*(\theta_{\vec{k}},\phi_{\vec{k}})\,j_l(kr) ,$$
$$\tag{2.21}$$

$$e^{-i\vec{k}_{\tilde{\Psi}}\cdot\vec{r}} = \sum_{l,m} 4\pi(-i)^l\,Y_{lm}^*(\theta,\phi)\,Y_{lm}(\theta_{\vec{k}_{\tilde{\Psi}}},\phi_{\vec{k}_{\tilde{\Psi}}})\,j_l(kr) ,$$

where θ, ϕ; $\theta_{\vec{k}}, \phi_{\vec{k}}$; and $\theta_{\vec{k}_{\tilde{\Psi}}}, \phi_{\vec{k}_{\tilde{\Psi}}}$ are the angular coordinates of $\vec{r}$, $\vec{k}$, and $\vec{k}_{\tilde{\Psi}}$, respectively.

Following the procedure of Kohn and Rostoker[1] in the band theory of metals and applied by Kambe[3] in LEED theory, we can write the Green's function as

$$\mathcal{G}(\vec{r},\vec{r}') = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} [A_{lm;l'm'}\,j_l(kr)j_{l'}(kr')$$
$$+ \delta_{ll'}\,\delta_{mm'}\,kj_l(kr)n_l(kr')]\,Y_{lm}(\theta,\phi)\,Y_{l'm'}^*(\theta',\phi'),$$
$$r < r' < r_a \tag{2.22}$$

where (r', θ', ϕ') are the spherical coordinates of

$\vec{r}'$, and the structure constants $A_{lm;l'm'}$, which are functions of k^2 and $\vec{k}_{\parallel}$, are characteristic for the lattice structure. The structure constants are the same as those in Kambe's[3] theory.

We substitute Eqs. (2.14), (2.15), (2.21), and (2.22) into Eq. (2.12) and integrate over θ, ϕ and θ', ϕ'. Finally, the limit $\epsilon \to 0$ is taken and $A_{\vec{q}}$ is given by

$$A_{\vec{q}} = \frac{(4\pi)^2 \sum_{l,m} \sum_{l',m'} C_{lm} \tilde{C}_{l'm'} i^{l'-l} Y_{lm}(\theta_{\vec{k}_{\vec{q}}}^-, \phi_{\vec{k}_{\vec{q}}}^-) Y_{l'm'}^*(\theta_{\vec{k}'}\phi_{\vec{k}})[j_l, R_l][j_{l'}, R_{l'}]}{-\sum_{l,m}\sum_{l',m'} C_{lm}\tilde{C}_{l'm'}\{A_{l'm';lm}[j_l, R_l] + k\delta_{ll'}\delta_{mm'}[n_l, R_l]\}[j_{l'}, R_{l'}]} \quad (2.23)$$

As an immediate consequence of the above equation, the lth partial wave in the trial functions does not contribute to the reflection coefficient $R_{\vec{q}}$, if the Wronskian $[R_l, j_l]$ is zero.

After the variational principle $\delta A_{\vec{q}} = 0$, which yields $\partial A_{\vec{q}}/\partial C_{lm} = \partial A_{\vec{q}}/\partial \tilde{C}_{lm} = 0$, is performed on Eq. (2.23), a set of linear equations is obtained:

$$\sum_{l,m} \Delta_{lm;l'm'} C_{lm} = 0 , \quad (2.24)$$

$$\sum_{l',m'} \Delta_{lm;l'm'} \tilde{C}_{l'm'} = 0 ,$$

where

$$\Delta_{lm;l'm'} = \{[(4\pi)^2/A_{\vec{q}}] i^{l'-l} Y_{l'm'}^*(\theta_{\vec{k}}, \phi_{\vec{k}}) Y_{lm}(\theta_{\vec{k}_{\vec{q}}}^-, \phi_{\vec{k}_{\vec{q}}}^-)$$

$$+ A_{l'm';lm} + k\delta_{ll'}\delta_{mm'}\cot\eta_l\}[j_l, R_l][j_{l'}, R_{l'}] , \quad (2.25)$$

and the tangent of the phase shift η_l is written as[1]

$$\tan\eta_l = [R_l, j_l]/[R_l, n_l] . \quad (2.26)$$

The condition that the set of linear equations (2.24) has nontrivial solution is that the determinant of $\Delta_{lm;l'm'}$ equals zero. The determinant appears to have a common factor $[R_l, j_l]$ in the (l, m) row and a common factor $[R_{l'}, j_{l'}]$ in the (l', m') column where $m = -l$ to l and $m' = -l'$ to l'. If $[R_l, j_l]$ is zero, namely, the phase shift η_l is modulo π, all determinants $\Delta_{lm;l'm'}$ arising from trial functions containing the lth partial wave are zero. However, we know this partial wave does not contribute to the reflection coefficient, so that these terms should be excluded in the determinant. We divide the (l, m) row with $m = -l$ to l by $[R_l, j_l]$ and the (l', m') column with $m' = -l'$ to l' by $[R_{l'}, j_{l'}]$ before equating the determinant to zero. Thus

$$\det\{[(4\pi)^2/A_{\vec{q}}] i^{l'-l} Y_{l'm'}^*(\theta_{\vec{k}}, \phi_{\vec{k}}) Y_{lm}(\theta_{\vec{k}_{\vec{q}}}^-, \phi_{\vec{k}_{\vec{q}}}^-)$$

$$+ A_{l'm';lm} + k\delta_{ll'}\delta_{mm'}\cot\eta_l\} = 0 . \quad (2.27)$$

Equation (2.27) is linear in $A_{\vec{q}}$ as shown in the preceding paper, and $A_{\vec{q}}$ is determined uniquely in terms of the phase shifts and the structure constants. After applying the transformation derived in the preceding paper, $A_{\vec{q}}$ may be expressed ex-

plicitly in determinental form,

$$A_{\vec{q}} = i2AK_{\vec{q}}R_{\vec{q}} = \frac{4\pi|H_{lm;l'm'}|_{l,l'\neq 0}}{|F_{lm;l'm'}|} ,$$

$$l, l' = 0, 1, \ldots, l_n \quad (2.28)$$

where

$$H_{lm;l'm'} = F_{lm;l'm'} - \frac{D_{lm}F_{00;l'm'}}{D_{00}}$$

$$- \frac{F_{lm;00}E_{l'm'}}{E_{00}} + \frac{F_{00;00}E_{l'm'}D_{lm}}{D_{00}E_{00}}$$

for l and $l' \neq 0$, and

$$F_{lm;l'm'} = -(A_{l'm';lm} + k\delta_{ll'}\delta_{mm'}\cot\eta_l) ,$$

$$D_{lm} = 4\pi i^{-l} Y_{lm}(\theta_{\vec{k}_{\vec{q}}}^-, \phi_{\vec{k}_{\vec{q}}}^-) , \quad (2.29)$$

$$E_{lm} = 4\pi i^l Y_{lm}^*(\theta_{\vec{k}}, \phi_{\vec{k}}) .$$

We observe that r_a does not appear in the reflection coefficient. We will evaluate analytically the reflection coefficients for two special cases.

A. s-Wave Scatterers

For s-wave scatterers, all phase shifts η_l vanish except η_0. It follows from Eq. (2.25) that all the $\Delta_{lm;l'm'}$ vanish except $\Delta_{00;00}$. The reflection coefficient is obtained without performing the variational principle $\delta A_{\vec{q}} = 0$. Thus the reflection coefficient $R_{\vec{q}}$ of a reflected beam in the direction of $\vec{k}_{\vec{q}}^-$ is given by

$$R_{\vec{q}} = \frac{2\pi i}{AK_{\vec{q}}} \frac{\tan\eta_0}{A_{00;00}\tan\eta_0 + k} , \quad (2.30)$$

which is identical to that obtained by Kambe,[3] and by McRae.[5]

B. p-Wave Scatterers

For p-wave scatterers, all phase shifts vanish except η_0 and η_1. We assume that the wave and the lattice have certain symmetry such that the wave field inside the crystal does not contain the spherical harmonics with $m = \pm 1$, e.g., the incident wave falls perpendicularly on a layer of square lattice.

From Eq. (2.28) we obtain

$$R_{\vec{q}} = \frac{2\pi i}{AK_{\vec{q}}} \; [A_{10;10} + i3^{1/2}(A_{10;00}\cos\theta_{\vec{K}_{\vec{q}}^-} - A_{00;10}) + 3(A_{00;00} + k\cot\eta_0)\cos\theta_{\vec{K}_{\vec{q}}^-} + k(\cot\eta_1 + 3\cot\eta_0\cos\theta_{\vec{K}_{\vec{q}}^-})]/$$

$$[(A_{00;00}A_{10;10} - A_{00;10}A_{10;10}) + k(A_{00;00}\cot\eta_1 + A_{10;10}\cot\eta_0) + k^2\cot\eta_0\cot\eta_1] \; . \quad (2.31)$$

In Appendix A, we have evaluated the reflection coefficient for p-wave scatterers by solving the set of equations given by Kambe.[3] The two results are identical, but the derivation here is much simpler.

The reflection coefficient $R_{\vec{q}}$ given by Eq. (2.28) can give an exact solution, if the number of nonzero $\tan\eta_i$ is finite.

III. APPLICATION TO COMPLEX MULTIPLE LAYERS

The method used to calculate the reflection coefficient for a monoatomic layer may be generalized to the case of complex-atomic multiple layers. The crystal has perfect two-dimensional periodicity, otherwise arbitrary variations in structure and composition. The crystals may have different atoms in each layer, and the space between layers is not necessarily the same. Hence, this variational method which we will derive is especially useful for the case of a crystal with impurity layers.

As Kambe[4] has pointed out, the side planes of the reference column may cut the atomic spheres into a few segments, but it is possible to choose a reference column such that the side planes of the reference column do not pass through the center of any atom. All the atoms with their centers inside the reference column are called by Kambe[4] as assigned to the column of reference. We assume that there are N atoms assigned in the reference column, in which atoms are stacked together to form layers or a complex-atomic layer. The potential about each of these atoms is nonzero only in the spheres which are nonoverlapping and centered at the centers of the atoms. We label the N atoms in an arbitrary but convenient order.

The effective potential is the sum of the atomic potentials

$$V(\vec{r}) = \sum_{i=1}^{N} \sum_{m,n} V_i(|\vec{r} - \vec{c}_i - \vec{r}_{mn}|),$$

$$m, n = 0, \pm 1, \pm 2, \ldots \quad (3.1)$$

where $\vec{c}_i$ is the position of the center of the ith sphere assigned in the reference column. The summation is over all N atoms assigned in the reference column and all two-dimensional lattice vectors $\vec{r}_{mn}$. The potential in the ith sphere is given by

$$V_i(r) = \text{spherically symmetric}, \quad r < r_i$$
$$V_i(r) = 0, \quad r \geq r_i \quad (3.2)$$

where r_i is the radius of the ith sphere.

The variational equation for $A_{\vec{q}}$ is given by Eq. (2.5),

$$A_{\vec{q}} = \{[\int_{\text{segments}} e^{i\vec{K}\cdot\vec{r}} V(\vec{r})\tilde{\psi}(\vec{r})d\vec{r}][\int_{\text{segments}} e^{-i\vec{K}_{\vec{q}}\cdot\vec{r}'} V(\vec{r}')\psi(\vec{r}')d\vec{r}']\}/$$

$$\{\int_{\text{segments}} d\vec{r}\,\tilde{\psi}(\vec{r})V(\vec{r})[\psi(\vec{r}) - \int_{\text{segments}} \mathcal{G}(\vec{r},\vec{r}')V(\vec{r}')\psi(\vec{r}')d\vec{r}']\} \; , \quad (3.3)$$

where the integrals are over the volume of all the segments in the reference column. Since the crystal has perfect two-dimensional periodicity, the wave functions also have the following two-dimensional periodicity:

$$\psi(\vec{r} + \vec{r}_{mn}) = e^{i\vec{K}_{\parallel}\cdot\vec{r}_{mn}}\psi(\vec{r})$$

and $\quad (3.4)$

$$\tilde{\psi}(\vec{r} + \vec{r}_{mn}) = e^{-i\vec{K}_{\parallel}\cdot\vec{r}_{mn}}\tilde{\psi}(\vec{r}) \; .$$

Since the structural Green's function $\mathcal{G}(\vec{r}, \vec{r}')$ is a function of $(\vec{r} - \vec{r}')$, we have

$$\mathcal{G}(\vec{r} + \vec{r}_{mn}, \vec{r}' + \vec{r}_{mn}) = \mathcal{G}(\vec{r}, \vec{r}') \; . \quad (3.5)$$

We find in our case that the integrals over all the segments in the reference column can also be replaced by integrals over all the spheres assigned in the reference column.[4] Following Segall,[2] we change the coordinate system to the center of the ith sphere assigned in the reference column,

$$\vec{r} = \vec{r}_i + \vec{c}_i \; , \quad \vec{r}' = \vec{r}_i' + \vec{c}_i \; , \quad (3.6)$$

where $\vec{r}_i$ and $\vec{r}_i'$ are coordinates with respect to the center of the ith sphere.

The wave functions $\psi_i(\vec{r}_i)$ and $\tilde{\psi}_i(\vec{r}_i)$ in the ith sphere are defined as

$$\psi_i(\vec{r}_i) = \psi(\vec{r}) = \psi(\vec{r}_i + \vec{c}_i) \; ,$$

$$\tilde{\psi}_i(\vec{r}_i) = \tilde{\psi}(\vec{r}) = \tilde{\psi}(\vec{r}_i + \vec{c}_i) \ . \qquad (3.7)$$

Using the same derivation as in Sec. II, the

volume integrations can be transformed into surface integrations. Thus

$$A_{\vec{v}} = \frac{\sum_{i,j=1}^{N} e^{i\vec{K}\cdot\vec{c}_j}\, e^{-i\vec{K}_{\vec{v}}^{-}\cdot\vec{c}_i}\{\int [e^{i\vec{K}\cdot\vec{r}_j},\ \tilde{\psi}_j]_{r_j}\, dS_j\}\{\int [e^{-i\vec{K}_{\vec{v}}^{-}\cdot\vec{r}_i},\ \psi_i]_{r_i}\, dS'_i\}}{\sum_{i,j=1}^{N} \int\int [\tilde{\psi}_j, [\mathcal{G}^{j,i}, \psi_i]_{r_i}]_{r_j} dS'_i dS_j} \ , \qquad (3.8)$$

where r_i is the radius of the ith sphere, and the structural Green's function $\mathcal{G}^{ij}$ is defined as

$$\mathcal{G}^{ij}(\vec{r}_i, \vec{r}'_j) = \mathcal{G}(\vec{r}_i + \vec{c}_i, \vec{r}'_j + \vec{c}_j) = \mathcal{G}(\vec{r}, \vec{r}') \ , \qquad (3.9)$$

where $\vec{r}$ is a point in the ith sphere and $\vec{r}'$ is a point in the jth sphere. When $i=j$, the structural Green's function $\mathcal{G}^{ij}$ has a singularity at $\vec{r}_i = \vec{r}'_i$, and the limiting procedure for the monoatomic layer should also be employed here. If $i \neq j$, there is no singularity in the Green's function for non-overlapping spheres. $\mathcal{G}^{ij}$ can be expanded in spherical harmonics[2,4]:

$$\mathcal{G}^{ij'}(\vec{r}_i, \vec{r}'_j) = \sum_{l,m}\sum_{l',m'} [A^{i;j}_{lm;l'm'}\, j_l(k|\vec{r}_i|)j_{l'}(k|\vec{r}'_j|)$$

$$+ k\delta_{ij}\delta_{ll'}\delta_{mm'}n_{l'}(k|\vec{r}'_j|)j_l(k|\vec{r}_i|)]$$

$$Y_{lm}(\theta_i, \phi_i)Y^*_{l'm'}(\theta'_j, \phi'_j),$$

$$r_i < r'_i \text{ for } i = j \ . \qquad (3.10)$$

The wave functions $\psi_i(\vec{r}_i)$ and $\tilde{\psi}_i(\vec{r}_i)$ may be expanded in spherical harmonics about the center of the ith sphere, and we take a subset of the complete set of spherical harmonics as the trial wave functions,

$$\psi_i(\vec{r}_i) = \sum_{l=0}^{l=l_{n_i}}\sum_{m=-l}^{l} C^i_{lm} R^i_l(|\vec{r}_i|)Y_{lm}(\theta_i, \phi_i) \ , $$
$$\qquad (3.11)$$
$$\hat{\psi}_i(\vec{r}_i) = \sum_{l=0}^{l=l_{n_i}}\sum_{m=-l}^{l} \tilde{C}^i_{lm} R^i_l(|\vec{r}_i|)Y^*_{lm}(\theta_i, \phi_i) \ , $$

where $(|\vec{r}_i|, \theta_i, \phi_i)$ are the spherical coordinates of $\vec{r}_i$ with respect to the center of the ith sphere.

Inserting the trial functions (3.11) and the structural Green's function (3.10) into Eq. (3.8), integrating over θ_i, ϕ_i and θ'_j, ϕ'_j then applying the variational principle $\delta A_{\vec{v}} = 0$, and finally setting the compatibility determinant equal to zero, we obtain a unique solution for the reflection coefficient $R_{\vec{v}}$,

$$R_{\vec{v}} = -\frac{2\pi i e^{i(\vec{K}-\vec{K}_{\vec{v}}^{-})\cdot\vec{c}_1}}{AK_{\vec{v}}^{-}}\frac{|H^{i;j}_{lm;l'm'}| \ \begin{matrix} i, l\neq 1,0 \\ j, l'\neq 1,0 \end{matrix}}{|F^{i;j}_{lm;l'm'}|} \ , \qquad (3.12)$$

where

$$H^{i;j}_{lm;l'm'} = F^{i;j}_{lm;l'm'} - \frac{D^i_{lm} F^{1;j}_{00;l'm'}}{D^1_{00}} - \frac{F^{i;1}_{lm;00}E^j_{l'm'}}{E^1_{00}}$$

$$+ \frac{F^{1;1}_{00;00}D^i_{lm}E^j_{l'm'}}{D^1_{00}E^1_{00}} \ , \qquad \begin{cases} i, l\neq 1,0 \\ j, l'\neq 1,0 \end{cases}$$

and

$$F^{i;j}_{lm;l'm'} = -(A^{j;i}_{l'm';lm} + k\delta_{ij}\delta_{ll'}\delta_{mm'}\cot\eta^i_l) \ , \qquad (3.13)$$

$$D^i_{lm} = 4\pi i^{-l} e^{-i\vec{K}_{\vec{v}}^{-}\cdot\vec{c}_i}Y_{lm}(\theta_{\vec{K}_{\vec{v}}^{-}}, \phi_{\vec{K}_{\vec{v}}^{-}}) \ ,$$

$$E^i_{lm} = 4\pi i^l e^{i\vec{K}\cdot\vec{c}_i}Y^*_{lm}(\theta_{\vec{K}}, \phi_{\vec{K}}) \ .$$

The tangent of the phase shift η^i_l associated with the ith atom assigned in the reference column is defined as

$$\tan\eta^i_l = [j_l, R^i_l]_{r_i}/[n_l, R^i_l]_{r_i} \ . \qquad (3.14)$$

The structure constants $A^{i;j}_{lm;l'm'}$ are the same as those in Kambe's[3,4] theory. Ham and Segall[11] used Ewald's[12] method including summations in both the coordinate and the reciprocal spaces to calculate the structure constants in KKR band theory. Kambe[3,4] applied their method to evaluate the structure constants $A^{i;j}_{lm;l'm'}$ for low-energy electron diffraction theory. For the sake of completeness, we include his results in Appendix B. The structure constants $A^{i;i}_{lm;l'm'}$ are in the same expression as $A_{lm;l'm'}$ of a monoatomic layer.

IV. APPLICATION TO A SEMI-INFINITE CRYSTAL

For the case of electron scattering from a semi-infinite crystal, the problem in principle may be solved in the same way as that for multiple atomic layers. The number of layers should be taken such that the reflection coefficient of the diffracted beam does not change when more layers are taken into consideration. However, the problem becomes very complicated because of the necessity to calculate a large number of structure constants. This difficulty may be avoided by employing the Bloch theorem.

A. Perfect Semi-Infinite Crystal

For a perfect semi-infinite crystal, we make use of the Bloch theorem as follows. By assuming the crystal has perfect three-dimensional periodicity, the total wave function inside the crystal is the linear combination of a set of Bloch waves, which include propagating waves and an infinite number

of evanescent waves, with the same energy and the same reduced $\vec{k}_\parallel$ as those of the incident plane wave. The Bloch wave is in the following form:

$$\psi_g(\vec{r}) = U_{\vec{k}'_g}(\vec{r}) e^{i\vec{k}'_g \cdot \vec{r}}, \tag{4.1}$$

where $U_{\vec{k}'_g}(\vec{r})$ is a periodic function, and $\vec{k}'_g$ is the wave vector of the Bloch wave and is written explicitly by $(k'_{g\perp}, \vec{k}_\parallel + 2\pi\vec{g})$. The parallel component of $\vec{k}'_g$ is different from $\vec{k}_\parallel$ by 2π times the two-dimensional reciprocal-lattice vector $\vec{g}$ and the perpendicular component $k'_{g\perp}$ may be complex for an evanescent wave in the gap or elsewhere.

Similarly, $\tilde{\psi}(\vec{r})$ is the superposition of the discrete set of Bloch waves in the following form:

$$\tilde{\psi}_g(\vec{r}) = U_{\tilde{k}'_g}(\vec{r}) e^{i\tilde{k}'_g \cdot \vec{r}}, \tag{4.2}$$

where $U_{\tilde{k}'_g}(\vec{r})$ is a periodic function and the wave number $\tilde{k}'_g$ is denoted by $[\tilde{k}'_{g\perp}, -(\vec{k}_\parallel + 2\pi\vec{v}) + 2\pi\vec{g}]$.

Because of the three-dimensional periodicity assumed in the crystal, the Bloch waves at different layers have the relations

$$\psi_g(x+d, \vec{r}_\parallel) = e^{ik'_{g\perp}d} \psi_g(\vec{r})$$

and (4.3)

$$\tilde{\psi}_g(x+d, \vec{r}_\parallel) = e^{i\tilde{k}'_{g\perp}d} \tilde{\psi}_g(\vec{r}),$$

where d is the spacing between two identical layers. We take a superposition of a finite number of Bloch waves including all propagating waves and a few of

the infinite evanescent waves as the trial functions. Thus

$$\psi(\vec{r}) = \sum_{g=1}^{n} C_g \psi_g(\vec{r})$$

and (4.4)

$$\tilde{\psi}(\vec{r}) = \sum_{g=1}^{n} \tilde{C}_g \tilde{\psi}_g(\vec{r}),$$

where $g = 1$ to n enumerate the two-dimensional reciprocal-lattice vector $\vec{g}$ in an arbitrary order. C_g and $\tilde{C}_g$ are the expansion coefficients; ψ_g and $\tilde{\psi}_g$ are Bloch waves defined by Eq. (4.3). We represent the wave propagating in the direction of $\vec{k}'_g$ (evanescent wave if $k'_{g\perp}$ is complex) by Φ_g and the corresponding adjoint wave by $\tilde{\Phi}_g$,

$$\Phi_g(\vec{r}) = C_g \psi_g(\vec{r}), \quad \tilde{\Phi}_g(\vec{r}) = \tilde{C}_g \tilde{\psi}_g(\vec{r}). \tag{4.5}$$

Thus the trial wave can be written by

$$\psi(\vec{r}) = \sum_{g=1}^{n} \Phi_g(\vec{r}), \quad \tilde{\psi}(\vec{r}) = \sum_{g=1}^{n} \tilde{\Phi}_g(\vec{r}). \tag{4.6}$$

In Sec. VI of the preceding paper, we derived a variational expression for $A_{\vec{v}}$ by employing Bloch waves. The variational equation for $A_{\vec{v}}$ is given by

$$A_{\vec{v}} = \sum_{g,h=1}^{n} D^g E^h \Big/ \sum_{g,h=1}^{n} F^{g,h}, \tag{4.7}$$

where

$$D^g = \frac{1}{1 - e^{i(K_{\vec{v}} + k'_{g\perp})d}} \int e^{-i\vec{k}_{\vec{v}} \cdot \vec{r}} V(\vec{r}) \Phi_g(\vec{r}) \, d\vec{r}, \quad E^g = \frac{1}{1 - e^{i(k_\perp + \tilde{k}'_{g\perp})d}} \int e^{i\vec{k} \cdot \vec{r}} V(\vec{r}) \tilde{\Phi}_g(\vec{r}) \, d\vec{r},$$

$$F^{g,h} = \frac{1}{1 - e^{i(k'_{g\perp} + \tilde{k}'_{h\perp})d}} \left[\int d\vec{r} \, \tilde{\Phi}_h(\vec{r}) V(\vec{r}) \left(\Phi_g(\vec{r}) - \int \mathcal{G}(\vec{r}, \vec{r}') V(\vec{r}') \Phi_g(\vec{r}') \, d\vec{r}' \right) - \sum_{\vec{u}} \frac{i}{2AK_{\vec{u}}} \left(\frac{+1}{1 - e^{-i(K_{\vec{u}} + k'_{g\perp})d}} \right. \tag{4.8}$$

$$\times \iint \tilde{\Phi}_h(\vec{r}) V(\vec{r}) e^{i\vec{k}_{\vec{u}}^+ \cdot (\vec{r} - \vec{r}')} V(\vec{r}') \Phi_g(\vec{r}') \, d\vec{r}' d\vec{r} + \frac{1}{1 - e^{-i(K_{\vec{u}} + \tilde{k}_{h\perp})d}} \iint \tilde{\Phi}_h(\vec{r}) V(\vec{r}) e^{i\vec{k}_{\vec{u}}^- \cdot (\vec{r} - \vec{r}')} V(\vec{r}') \Phi_g(\vec{r}') \, d\vec{r}' d\vec{r} \right) \Bigg],$$

where $\vec{k}_{\vec{u}}^+$ is defined by $(K_{\vec{u}}, \vec{k}_\parallel + 2\pi\vec{u})$ and the summation is taken over all the two-dimensional reciprocal-lattice vectors. The range of integration is over the reference column with a width d; we call it the d-reference column.

We consider the general case of crystals with complex-atomic layers, since the case for monoatomic layers can be considered as a special case of the complex-atomic layers. The crystal has identical structure and composition after every distance d, but otherwise the layers may be different in both scattering potential and lattice spacing. The crystal potential in the width d is defined by Eqs.

(3.1) and (3.2), and it repeats with d. We assume there are N atoms assigned in the d-reference column and each atom is confined in a nonoverlapping sphere with radius r_i. The integrals are taken over the N spheres assigned in the d-reference column.

Similarly to the derivation presented in Sec. II, the volume integrations may be transformed into surface integrations. The transformation of coordinate system given by Eq. (3.6) should also be carried out here. Thus Eqs. (4.7) and (4.8) become

$$A_{\vec{v}} = \sum_{g,h=1}^{n} \sum_{i,j=1}^{N} D^{g,i} E^{h,j} \Big/ \sum_{g,h=1}^{n} \sum_{i,j=1}^{N} F^{gi,hj} \tag{4.9}$$

and

$$D^{g,i} = \frac{e^{-i\vec{k}'_{\vec{q}}\cdot\vec{c}_i}}{1 - e^{i(K_{\vec{q}}+k'_{g\perp})d}} \int [e^{-i\vec{k}_{\vec{q}}\cdot\vec{r}}, \Phi^i_g]_{r_i}\, dS_i\,, \qquad E^{g,i} = \frac{e^{i\vec{k}\cdot\vec{c}_i}}{1 - e^{i(k_\perp+\tilde{k}'_{g\perp})d}} \int [e^{i\vec{k}\cdot\vec{r}}, \tilde{\Phi}^i_g]_{r_i}\, dS_i\,,$$

$$F^{gi,hj} = \frac{1}{1 - e^{i(k'_{g\perp}+\tilde{k}'_{h\perp})d}} \left[\iint [\tilde{\Phi}^j_h[\mathcal{G}^{ji}, \Phi^i_g]_{r_i}]_{r_j}\, dS'_i\, dS_j + \sum_{\vec{q}} \frac{i}{2AK_{\vec{q}}} \right. \tag{4.10}$$

$$\left. \times \left(\frac{e^{i\vec{k}^+_{\vec{q}}\cdot(\vec{c}_j-\vec{c}_i)}}{e^{-i(K_{\vec{q}}+k'_{g\perp})d}-1} \iint [e^{i\vec{k}^+_{\vec{q}}\cdot\vec{r}}, \tilde{\Phi}^j_h]_{r_j}[e^{-i\vec{k}^+_{\vec{q}}\cdot\vec{r}'}, \Phi^i_g]_{r_i}\, dS'_i\, dS_j + \frac{e^{i\vec{k}^+_{\vec{q}}\cdot(\vec{c}_j-\vec{c}_i)}}{e^{-i(K_{\vec{q}}+\tilde{k}'_{h\perp})d}-1} \iint [e^{i\vec{k}^+_{\vec{q}}\cdot\vec{r}}, \tilde{\Phi}^j_h]_{r_j}[e^{-i\vec{k}^+_{\vec{q}}\cdot\vec{r}'},\Phi^i_g]_{r_i}\, dS'_i\, dS_j \right) \right],$$

where $\Phi^i_g(\vec{r}_i)$ and $\tilde{\Phi}^i_g(\vec{r}_i)$ are the Bloch waves in the ith inscribed sphere. The summation in Eq. (4.9) is taken over all the atoms assigned in the d-reference column and over the Bloch waves in expanding the trial functions.

The Bloch waves Φ^i_g and $\tilde{\Phi}^i_g$ may be expanded into spherical harmonics, and we take a finite number of the spherical harmonics as trial functions:

$$\Phi^i_g(\vec{r}_i) = \sum_{l=0}^{l=l_{n_i}} \sum_{m=-l}^{l} C^{g,i}_{l,m} Y_{lm}(\theta_i, \phi_i) R^i_l(|\vec{r}_i|), \tag{4.11}$$

$$\tilde{\Phi}^i_g(\vec{r}_i) = \sum_{l=0}^{l=l_{n_i}} \sum_{m=-l}^{l} \tilde{C}^{g,i}_{l,m} Y^*_{lm}(\theta_i, \phi_i) R^i_l(|\vec{r}_i|).$$

As in Eq. (2.21), the wave functions $e^{\pm i\vec{k}^\pm_{\vec{q}}\cdot\vec{r}_i}$ may be expanded into spherical harmonics.

$$e^{i\vec{k}^\pm_{\vec{q}}\cdot\vec{r}_i} = 4\pi \sum_{l,m} i^l Y_{l,-m}(\theta_{\vec{k}^\pm_{\vec{q}}}, \phi_{\vec{k}_\parallel+2\pi\vec{q}})$$

$$\times Y_{lm}(\theta, \phi) j_l(k|\vec{r}_i|),$$

$$e^{-i\vec{k}^\pm_{\vec{q}}\cdot\vec{r}_i} = 4\pi \sum_{l,m} i^{-l} Y_{lm}(\theta_{\vec{k}^\pm_{\vec{q}}}, \phi_{\vec{k}_\parallel+2\pi\vec{q}}) \tag{4.12}$$

$$\times Y^*_{lm}(\theta, \phi) j_l(k|\vec{r}_i|),$$

where $\phi_{\vec{k}_\parallel+2\pi\vec{q}}$ is the polar angular coordinate of the vector $\vec{k}_\parallel + 2\pi\vec{q}$ and $\theta_{\vec{k}^\pm_{\vec{q}}}$ is defined by $\theta_{\vec{k}^\pm_{\vec{q}}} = \cos^{-1}(\pm K_{\vec{q}}/k)$.

When $K_{\vec{q}}$ is imaginary, the spherical harmonics[4] $Y_{lm}(\theta_{\vec{k}^\pm_{\vec{q}}}, \phi_{\vec{k}_\parallel+2\pi\vec{q}})$ have complex arguments and are defined by

$$Y_{lm}(\theta_{\vec{k}^\pm_{\vec{q}}}, \phi_{\vec{k}_\parallel+2\pi\vec{q}}) = \left[\left(\frac{2l+1}{4\pi}\right) \left(\frac{(l-|m|)!}{(l+|m|)!}\right) \right]^{1/2}$$

$$\times (\pm i)^{-|m|} e^{im\phi_{\vec{k}_\parallel+2\pi\vec{q}}} p^{|m|}_l(\pm i|K_{\vec{q}}|/k), \tag{4.13}$$

where $p^{|m|}_l(x)$ is Hobson's associated Legendre function.[13]

Inserting Eqs. (3.10), (4.11), and (4.12) into Eqs. (4.9) and (4.10) and carrying out the variational

principle $\delta A_{\vec{q}} = 0$ yields

$$R_{\vec{q}} = \frac{2\pi i}{AK_{\vec{q}}} \frac{-e^{i(\vec{k}-\vec{k}^+_{\vec{q}})\cdot\vec{c}_1}}{(1 - e^{i(k_\perp+\tilde{k}'_{1\perp})d})(1 - e^{i(K_{\vec{q}}+k'_{1\perp})d})} \frac{|H_{g,t}|_{g,t\neq1}}{|F_{g,t}|}, \tag{4.14}$$

where

$$H_{g,t} = F_{g,t} - \frac{D_g F_{1,t}}{D_1} - \frac{F_{g,1} E_t}{E_1} + \frac{F_{1,1} D_g E_t}{D_1 E_1},$$

$$g, t \neq 1$$

$$F_{q,t} = \frac{1}{1 - e^{i(k'_{g\perp}+\tilde{k}'_{h\perp})d}} \left[-(A^{j;i}_{l'm';lm} + k\delta_{ij}\delta_{ll'}\delta_{mm'}\cot\eta^i_l) \right.$$

$$+ \sum_{\vec{q}} \frac{(4\pi)^2 i^{l'+1-l}}{2AK_{\vec{q}}} \left(\frac{e^{i\vec{k}^+_{\vec{q}}\cdot(\vec{c}_j-\vec{c}_i)}}{e^{-i(K_{\vec{q}}+\tilde{k}'_{h\perp})d}-1} Y_{lm}(\theta_{\vec{k}^+_{\vec{q}}}, \phi_{\vec{k}_\parallel+2\pi\vec{q}}) \right.$$

$$\times Y_{l'-m'}(\theta_{\vec{k}^+_{\vec{q}}}, \phi_{\vec{k}_\parallel+2\pi\vec{q}}) + \frac{e^{i\vec{k}^-_{\vec{q}}\cdot(\vec{c}_j-\vec{c}_i)}}{e^{-i(K_{\vec{q}}+k'_{g\perp})d}-1}$$

$$\left. \left. \times Y_{lm}(\theta_{\vec{k}^-_{\vec{q}}}, \phi_{\vec{k}_\parallel+2\pi\vec{q}}) Y_{l',-m'}(\theta_{\vec{k}^-_{\vec{q}}}, \phi_{\vec{k}_\parallel+2\pi\vec{q}}) \right) \right],$$

$$D_q = \frac{4\pi i^{-l}}{1 - e^{i(K_{\vec{q}}+k'_{g\perp})d}} Y_{lm}(\theta_{\vec{k}^-_{\vec{q}}}, \phi_{\vec{k}_{\vec{q}}}) e^{-i\vec{k}^-_{\vec{q}}\cdot\vec{c}_i},$$

$$E_q = \frac{4\pi i^l}{1 - e^{i(k_\perp+\tilde{k}'_{g\perp})d}} Y^*_{lm}(\theta_{\vec{k}}, \phi_{\vec{k}}) e^{i\vec{k}\cdot\vec{c}_i}.$$

We have ordered $C^{g,i}_{l,m}$ and $\tilde{C}^{g,i}_{l,m}$ in the order of decreasing importance in the construction of the wave functions and relabeled them as C_q and $\tilde{C}_q$, where $q = 1, 2, \ldots, n_s$ indicates a certain combination of g, i, l, and m. The terms in the determinants $|F_{q,t}|$ and $|H_{q,t}|_{q,t\neq1}$ are functions of the structure constants, the phase shifts, and the perpendicular components of the wave vectors of the Bloch waves. The structure constants $A^{i;j}_{lm;l'm'}$ are the same as those for the layers in d. The perpendicular wave vectors $k'_{g\perp}$ and $\tilde{k}'_{g\perp}$ may be considered as nonlinear variational parameters in principle or computed from any band theory.

B. Semi-Infinite Crystal With Surface Contamination

The extension to a contaminated semi-infinite crystal is straightforward. We assume the crystal is composed of a selvedge consisting of a few impurity layers, and a semi-infinite substrate whose geometric and atomic structures repeat after a distance d in the perpendicular direction. The crystal should have perfect two-dimensional periodicity in the plane parallel to the surface.

The case is a combination of those for a finite number of layers (the selvedge) and the perfect semi-infinite crystal (the substrate). Thus we can expand the wave field in the selvedge into spherical harmonics and the wave field in the substrate as a superposition of Bloch waves with each Bloch wave expanded in spherical harmonics. We label the atoms assigned in the impure reference column by $im = 1,\ 2,\ \ldots,\ n_{im}$, and those assigned in the d-reference column of the substrate by $s = 1,\ 2,\ \ldots,\ n_s$. Inserting the combination of selvedge and substrate wave functions into the variational equation (2.5) and carrying out the same procedure as discussed in Sec. III yields

$$R_{\vec{v}} = \frac{2\pi e^{i(\vec{k}-\vec{k}_{\vec{v}})\cdot\vec{c}_1}}{iAK_{\vec{v}}} \frac{|H_{q,t}|_{q,t\neq1}}{|F_{q,t}|}, \qquad (4.16)$$

where

$$H_{q,t} = F_{q,t} - \frac{D_q F_{1,t}}{D_1} - \frac{F_{q,1}E_t}{E_1} + \frac{F_{1,1}D_q E_t}{E_1 D_1},$$
$$q,\ t \neq 1, 1. \qquad (4.17)$$

The notations D_q, E_q, and $E_{q,t}$ are defined by different functions according to whether they are defined in the selvedge or in the substrate. When $q,\ t = 1,\ 2,\ \ldots,\ n_{im}$, representing a certain combination of im, l, and m in the selvedge, D_q, E_q, and $F_{q,t}$ are defined by

$$F_{q,t} = -\left(A^{im';\,im}_{l'm';\,lm} + k\delta_{im;im'}\,\delta_{ll'}\,\delta_{mm'}\,\cot\eta_l^{im}\right),$$

$$D_q = 4\pi i^{-l}\, Y_{lm}(\theta_{\vec{k}_{\vec{v}}},\ \phi_{\vec{k}_{\vec{v}}})e^{-i\vec{k}_{\vec{v}}\cdot\vec{c}_{im}}, \qquad (4.18)$$

$$E_q = 4\pi i^{l}\, Y^*_{lm}(\theta_{\vec{k}},\ \phi_{\vec{k}})e^{i\vec{k}\cdot\vec{c}_{im}},$$

where $\vec{c}_{im}$ is the position of the center of the imth sphere assigned in the reference column.

When $q,\ t = n_{im}+1,\ n_{im}+2,\ldots,\ n_{im}+n_s$, representing a certain combination of s, $\vec{g}$, l, and m in the substrate, D_q, E_q, and $F_{q,t}$ are defined by

$$F_{q,t} = \frac{1}{1-e^{i(k'_{g\perp}+\tilde{k}'_{h\perp})d}}\left[-\left(A^{s';\,s}_{l'm';\,lm} + k\delta_{ss'}\,\delta_{ll'}\,\delta_{mm'}\,\cot\eta_l^{s}\right) + \sum_{\vec{u}}\frac{(4\pi)^2 i^{l'+1-l}}{2AK_{\vec{u}}}\right.$$

$$\times \left(\frac{e^{i\vec{k}^+_{\vec{u}}\cdot(\vec{c}_{s'}-\vec{c}_s)}}{e^{-i(K_{\vec{u}}+\tilde{k}'_{h\perp})d}-1}\, Y_{lm}(\theta_{\vec{k}^+_{\vec{u}}},\ \phi_{\vec{k}_{\parallel}+2\pi\vec{u}})\, Y_{l',-m'}(\theta_{\vec{k}^+_{\vec{u}}},\ \phi_{\vec{k}_{\parallel}+2\pi\vec{u}}) + \frac{e^{i\vec{k}^-_{\vec{u}}\cdot(\vec{c}_{s'}-\vec{c}_s)}}{e^{-i(K_{\vec{u}}+k'_{g\perp})d}-1}\, Y_{lm}(\theta_{\vec{k}^-_{\vec{u}}},\ \phi_{\vec{k}_{\parallel}+2\pi\vec{u}})\, Y_{l',-m'}(\theta_{\vec{k}^+_{\vec{u}}},\ \phi_{\vec{k}_{\parallel}+2\pi\vec{u}})\right)\right],$$

$$D_q = \frac{4\pi i^{-l}}{1-e^{i(K_{\vec{v}}+k'_{g\perp})d}}\, Y_{lm}(\theta_{\vec{k}_{\vec{v}}},\ \phi_{\vec{k}_{\vec{v}}})e^{-i\vec{k}_{\vec{v}}\cdot\vec{c}_s}, \quad E_q = \frac{4\pi i^{l}}{1-e^{i(k_{\perp}+k'_{g\perp})d}}Y^*_{lm}(\theta_{\vec{k}},\ \phi_{\vec{k}})e^{i\vec{k}\cdot\vec{c}_s}, \qquad (4.19)$$

where $\vec{c}_s$ is the position of the center of the sth atom assigned in the d-reference column in the substrate. The eigenvalues $k'_{g\perp}$ and $\tilde{k}'_{g\perp}$ are the perpendicular components of the wave vectors of the Bloch waves used in expanding the wave functions in the substrate.

When $q = 1,\ 2,\ \ldots,\ n_{im}$ and $t = n_{im}+1,\ n_{im}+2,\ \ldots,\ n_{im}\pm n_s$, $F_{q,t}$ is defined by

$$F_{q,t} = -\sum_{\vec{u}}\frac{(4\pi)^2 i^{l'+1-l}}{2AK_{\vec{u}}}\frac{e^{i\vec{k}^+_{\vec{u}}\cdot(\vec{c}_s-\vec{c}_{im})}}{1-e^{i(K_{\vec{u}}+\tilde{k}'_{h\perp})d}}$$

$$\times Y_{lm}(\theta_{\vec{k}^+_{\vec{u}}},\ \phi_{\vec{k}_{\parallel}+2\pi\vec{u}})Y_{l',-m'}(\theta_{\vec{k}^+_{\vec{u}}},\ \phi_{\vec{k}_{\parallel}+2\pi\vec{u}}).$$

$$(4.20)$$

When $q = n_{im}+1,\ n_{im}+2,\ \ldots,\ n_{im}+n_s$ and $t = 1,\ 2,\ \ldots,\ n_{im}$, $F_{q,t}$ is defined by

$$F_{q,t} = -\sum_{\vec{u}}\frac{(4\pi)^2 i^{l'+1-l}}{2AK_{\vec{u}}}\frac{e^{i\vec{k}^+_{\vec{u}}\cdot(\vec{c}_{im}-\vec{c}_s)}}{1-e^{i(K_{\vec{u}}+k'_{g\perp})d}}$$

$$\times Y_{lm}(\theta_{\vec{k}^+_{\vec{u}}},\ \phi_{\vec{k}_{\parallel}+2\pi\vec{u}})Y_{l',-m'}(\theta_{\vec{k}^+_{\vec{u}}},\ \phi_{\vec{k}_{\parallel}+2\pi\vec{u}}).$$

$$(4.21)$$

The structure constants in this case are the same as those for a crystal of width d with surface impurity layers.

V. SYMMETRY OF STRUCTURE CONSTANTS AND WAVE FUNCTION

The number of independent structure constants that need to be calculated can be reduced considerably if the incident wave and the lattice geometry have certain symmetry.

If the parallel component of the incident wave

vector $\vec{k}_{\shortparallel} = 2\pi \vec{u}$, where $\vec{u}$ is an arbitrary two-di-
mensional reciprocal-lattice vector including the
case $\vec{u} = 0$, it follows from Eq. (2.6) that

$$\mathcal{G}\,(\vec{r} - \vec{r}') = \mathcal{G}\,(\vec{r}' - \vec{r}). \qquad (5.1)$$

The symmetry property of Eq. (5.1) yields the
relationship for the structure constants:

$$A^{i;j}_{l\,m;\,l'\,m'} = A^{j;i}_{l'(-m');\,l(-m)}\,. \qquad (5.2)$$

If $\vec{k}_{\shortparallel}$ is invariant under a certain symmetry op-
erator S of the two-dimensional lattice (the plane
parallel to the crystal surface), we obtain

$$\psi(x,\,S\vec{r}_{\shortparallel}\,) = \psi(\vec{r})\,. \qquad (5.3)$$

For example, if the lattice has n-fold rotational
symmetry about an axis which is perpendicular to
the surface through the center of the ith atom with
normal incident wave, the wave field $\psi^i(\vec{r}_i)$ inside
the ith sphere may be expanded into spherical
harmonics with $m =$ multiples of n.

VI. DISCUSSION

If the crystal potential is given by Eq. (3.2) to
a sufficiently good approximation, the methods de-
scribed above are believed to provide a self-consis-
tent and convenient way for calculating LEED in-
tensities. The reflection coefficients are uniquely
given by Eqs. (3.12) and (4.16) as the ratio of two
determinants. The atomic scattering, the geo-
metrical crystal structure, and the interlayer
scattering properties are separated in the elements
of the determinants. The atomic potential appears
through the phase shifts η^i_j which are functions of
the incident energy k^2. The phase shifts, which
can be computed from Eq. (2.16), should be cal-
culated by using the scattering potential in the
solid, which is different from the free atomic scat-
tering potential because of the overlapping of the
charge densities of the atoms in the solid. The
structural properties appear through the structure
constants $A^{i;j}_{l m;\,l'\,m'}$ which are functions of $\vec{k}_{\shortparallel}$ and k^2.
Most computational efforts will be on the structure
constants. However, the structure constants need
to be calculated for each type of lattice once and
for all. If the incident wave and the lattice geom-
etry have certain symmetry, the number of
structure constants that have to be computed can
be reduced greatly. The interlayer scattering is
expressed through the perpendicular components
of the wave vectors $k'_{g\perp}$ and $\bar{k}'_{g\perp}$ which can be ob-
tained from conventional energy-band-spectrum
calculation. The possibility of using approximate
$k'_{g\perp}$ and $\bar{k}'_{g\perp}$ in Eq. (4.10) to obtain an accurate reflec-
tion coefficient needs to be studied further.

For a finite number of layers, the diffraction
pattern is obtained with the knowledge of the atomic
scattering properties of each atom. For a semi-

infinite crystal with or without surface impure
layers, the reflection coefficient is obtained if the
phase shifts and the eigenvalues $k'_{g\perp}$ and $\bar{k}'_{g\perp}$ are
given. All the necessary information of the poten-
tial in Eq. (3.2) is given if the phase shifts η^i_l of
all the partial waves associated with each atom are
known. Therefore, the potential need not appear
explicitly in the reflection coefficient. Further-
more, the phase shifts also give the scattering
cross section of each atom, hence, the diffraction
pattern. When a large number of layers are
stacked together to form three-dimensional solids,
multiple scattering between layers in the bulk is
described by the energy band spectrum.

It follows from Eqs. (3.13) and (4.15) that all
multiples of 2π in the phase shifts do not contribute
to the reflection coefficient. If we write $\eta^i_l = 2m\pi
+ \delta^i_l$, only the remainder δ^i_l counts where $0 \leqslant \delta^i_l
\leqslant 2\pi$. Thus a deep potential which may give a large
phase shift does not necessarily generate strong
scattering when compared to a shallow potential.
When δ^i_l is around $m\pi$, i.e., the atomic scattering
cross section is small, there is small contribution
to the reflection coefficient in Eqs. (3.12) and
(4.16). The strong reflection corresponds to large
scattering cross section, namely, the remainder
of the phase shift δ^i_l is around $\frac{1}{2}\pi$ or $\frac{3}{2}\pi$. The sum-
mation over all the angular momenta l complicates
the above picture, therefore without detailed cal-
culation it is not clear how the diffraction pattern
would be affected.

The exact reflection coefficient can be obtained
by Eq. (3.12) provided the number of $\delta^i_l \neq 0$ modulo
π and the number of atomic layers are finite. By
expanding the wave field into spherical harmonics,
all the evanescent waves are automatically in-
cluded. This is in contrast to Bethe's plane wave
and matching formalism where the exact solution
usually cannot be obtained because of the require-
ment of the truncation of the plane waves for ex-
panding the Bloch wave and the truncation of the
infinite evanescent Bloch waves. The determinant
$|H^{i;j}_{l m;\,l'\,m'}|$ $(i,\; l \neq 1,\; 0;\, j,\, l' \neq 1,\; 0)$ of the numerator
in Eq. (3.12) is obtained by crossing out the first
row and the first column of the determinant
$|H^{i;j}_{l m;\,l'\,m'}|$. Hence, the rank of $|H^{i;j}_{l m;\,l'\,m'}|$ with i,
$l \neq 1$, 0 and j, $l' \neq 1$, 0 is always one order less than
that of the determinant $|F^{i;j}_{l m;\,l'\,m'}|$. The rank of
$|F^{i;j}_{l m;\,l'\,m'}|$, which depends on the number of the
spherical harmonics in expanding the wave field
inside the crystal and also on the number of atoms
assigned in the reference column, is $\sum_{i=1}^{N} (l_{n_i} + 1)^2$.
We have included all the spherical harmonics up to
$l = l_{n_i}$ for the wave field in the ith inscribed sphere.
If the lattice geometry and the incident wave have
certain symmetry, the rank of the determinant
can be reduced considerably. For example, if we
consider a square monoatomic layer with no sym-

metry for $\vec{k}_{\parallel}$ and the number of phase shifts need be taken is 10, the rank of $|F^{i;j}_{lm;\,l'm'}|$ is 100. However, if $\vec{k}_{\parallel} = 0$, the rank is reduced to 16. Equation (4.16) provides a method for calculating the reflectance from a semi-infinite crystal. By employing Bloch waves for the crystal except for a few surface layers, the difficulty of computing a large number of structure constants is eliminated but all the eigenvalues $k'_{g\perp}$ and $\tilde{k}'_{g\perp}$ are required. However, the perpendicular components of the wave vectors $k'_{g\perp}$ and $\tilde{k}'_{g\perp}$ can be obtained more easily than the Bloch waves since eigenvalues can in general be obtained more accurately than eigenvectors. The rank of the determinant $|F_{q,t}|$ in Eq. (4.16) is $n_{im} + n_s$.

From Eq. (3.2), the interstitial space is assumed to be vacuum and consequently the surface step potential is not taken into consideration. The main restriction of the methods described above is that they are valid for crystals whose potentials can be approximated by the muffin-tin form. However, for most solids of interest, the muffin-tin model is a sufficiently good approximation, especially for metals.

We emphasize the ability of this variational method in studying crystals with a few layers of foreign atoms on the surface, e.g., adsorption of gases on a metal surface. The convergence of this method is expected to be rapid for very low-energy (≤ 100 eV) incident electrons on solids composed of light atoms because the number of phase shifts required and the number of atomic layers involved in the scattering process are small. This variational phase-shift method provides a unified and direct method for the calculation of LEED intensities from both clean and contaminated crystals with no additional calculation of the wave field inside the crystal.

APPENDIX A: EVALUATION OF THE REFLECTION COEFFICIENT $R_{\vec{v}}$ FROM A MONOATOMIC LAYER OF p-WAVE SCATTERERS BY SOLVING KAMBE'S EQUATIONS

From Kambe's[3] LEED theory, we have

$$\beta_{lm} = \chi_{lm} + \sum_{l'm'} \alpha_{lm;\,l'm'} \chi_{l'm'} , \qquad (A1)$$

where

$$\beta_{lm} = 4\pi i^l Y^*_{lm}(\theta_{\vec{k}}, \phi_{\vec{k}}) j_l(kr_a)$$

and $\qquad (A2)$

$$\alpha_{lm;\,l'm'} = [\delta_{ll'}\delta_{mm'} n_l(kr_a) + k^{-1} A_{lm;\,l'm'} j_l(kr_a)]$$

$$\times \frac{\tan\eta_{l'}}{j_{l'}(kr_a) - n_{l'}(kr_a)\tan\eta_{l'}} .$$

We solve the set of linear equations (A1) for χ_{00} and χ_{10}:

$$\chi_{00} = \frac{\beta_{00}(1 + \alpha_{10;10}) - \beta_{10}\,\alpha_{00;10}}{(1 + \alpha_{00;00})(1 + \alpha_{10;10}) - \alpha_{00;10}\,\alpha_{10;00}}$$

and $\qquad (A3)$

$$\chi_{10} = \frac{\beta_{10}(1 + \alpha_{00;00}) - \beta_{00}\,\alpha_{10;00}}{(1 + \alpha_{00;00})(1 + \alpha_{10;10}) - \alpha_{00;10}\,\alpha_{10;00}} .$$

The reflection coefficient $R_{\vec{v}}$ is given by Kambe[3] as

$$R_{\vec{v}} = -\frac{2\pi r_a^2}{K_{\vec{v}} A} \sum_{l=0}^{1} (-i)^l j_l(kr_a)$$

$$\times \left(\frac{1}{R_l}\frac{dR_l}{dr} - \frac{1}{j_l}\frac{dj_l}{dr}\right)_{r=r_a} Y_{10}(\theta_{\vec{k}_{\vec{v}}}, \phi_{\vec{k}_{\vec{v}}})\chi_{10} .$$

$$(A4)$$

Substituting Eqs. (A2) and (A3) into Eq. (A4) yields

$$R_{\vec{v}} = \frac{2\pi i}{A K_{\vec{v}}} \left[A_{10;10} + i\,3^{1/2}(A_{10;00}\cos\theta_{\vec{k}_{\vec{v}}} - A_{00;10}) + 3(A_{00;00} + k\cot\eta_0)\cos\theta_{\vec{k}_{\vec{v}}} + k(\cot\eta_1 + 3\cot\eta_0\cos\theta_{\vec{k}_{\vec{v}}})\right] /$$

$$[(A_{00;00}A_{10;10} - A_{00;10}A_{10;00}) + k(A_{00;00}\cot\eta_1 + A_{10;10}\cot\eta_0) + k^2\cot\eta_0\cot\eta_1] . \qquad (A5)$$

APPENDIX B: CALCULATION OF THE STRUCTURE CONSTANTS

The structure constants $A^{i;j}_{lm;\,l'm'}$ have been calculated by Kambe.[3,4] For $i = j$, the structure constant $A^{i;i}_{lm;\,l'm'}$ is identical to the expression for the monoatomic single-layer structure constant $A_{lm;\,l'm'}$, hence it is independent of i.

1. $i = j$

For $i = j$, the structure constants $A_{lm;\,l'm'}$ are calculated in terms of the incomplete γ functions[13]:

$$A_{lm;\,l'm'} = 4\pi i^{l-l'} \sum_L i^{-L} D_{L,\,m-m'}\, C_{L,\,m-m';\,lm;\,l'm'} , \qquad (B1)$$

where

$$C_{LM;\,lm;\,l'm'}$$

$$= \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\, Y_{LM}(\theta, \phi)\, Y^*_{lm}(\theta, \phi)\, Y_{l'm'}(\theta, \phi) ,$$

$$|l - l'| \leq L \leq l + l' \qquad (B2)$$

$$D_{LM} = D_{LM}^{(1)} + D_{LM}^{(2)} + D_{00}^{(3)} \delta_{L0} \; . \qquad (B3)$$

When $L - |M|$ is odd, both $D_{LM}^{(1)}$ and $D_{LM}^{(2)}$ vanish:

$$D_{LM}^{(1)} = D_{LM}^{(2)} = 0 \; . \qquad (B4)$$

If $L - |M|$ is even, we have

$$D_{LM}^{(1)} = -\frac{1}{Ak} \frac{i^{|M|+1}}{2^L} \left[(2L+1)(L+|M|)!(L-|M|)! \right]^{1/2} \sum_{\vec{u}} \exp(-iM\phi_{(\vec{k}_\parallel + 2\pi\vec{u})})$$

$$\times \sum_{n=0}^{(L-|M|)/2} \frac{[|\vec{k}_\parallel + 2\pi\vec{u}|/k]^{L-2n} (K_{\vec{u}}/k)^{2n-1}}{n! \left[\frac{1}{2}(L-|M|-2n)\right]! \left[\frac{1}{2}(L+|M|-2n)\right]!} \; \Gamma\left(\frac{1}{2}(1-2n), \; e^{-\pi i} \, \alpha \, \frac{K_{\vec{u}}^2}{k^2}\right)$$

and

$$\qquad (B5)$$

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

$$\times \sum_{m,n}^{|\vec{r}_{mn}| \neq 0} \exp[-i(\vec{k}_\parallel \cdot \vec{r}_{mn} + M\phi_{\vec{r}_{mn}})] (k|\vec{r}_{mn}|)^L \int_0^\alpha t^{-3/2-L} \exp\left(t - \frac{k^2|\vec{r}_{mn}|^2}{4t}\right) dt \; ,$$

where $\phi_{(\vec{k}_\parallel + 2\pi\vec{u})}$ is the angular polar coordinate of $(\vec{k}_\parallel + 2\pi\vec{u})$ lying in the y-z plane. $\Gamma(b, x)$ is the incomplete γ function[14] and $\alpha = k^2\omega/2$, where ω is an arbitrary complex number satisfying $\mathrm{Re}(\omega) > 0$ and $|\omega| < \infty$.

$D_{00}^{(3)}$ is given by

$$D_{00}^{(3)} = -\frac{k}{2\pi} \left(2 \int_0^{\sqrt{\alpha}} e^{t^2} dt - \frac{e^\alpha}{\sqrt{\alpha}}\right) \; . \qquad (B6)$$

2. $i \neq j$

For $i \neq j$, the discussion is separated for two cases. If the point $\vec{r}$ lies on the surface of the ith sphere and the point $\vec{r}'$ lies on the surface of the jth sphere, the first possible case is that $x - x'$ is always not zero; the second case is that $x - x'$ can be zero.

If $x - x'$ is always not equal to zero, the structure constants $A_{lm; l'm'}^{i;j}$ are given by

$$A_{lm; l'm'}^{i;j} = \frac{(4\pi)^2}{A} i^{l-l'} \sum_{\vec{u}} \frac{1}{2i K_{\vec{u}}}$$

$$\times \exp[i\vec{k}_{\vec{u}}^+ \cdot (\vec{c}_i - \vec{c}_j)] Y_{l,-m}(\theta_{\vec{k}_{\vec{u}}^+}, \phi_{(\vec{k}_\parallel + 2\pi\vec{u})})$$

$$\times Y_{l'm'}(\theta_{\vec{k}_{\vec{u}}^+}, \phi_{(\vec{k}_\parallel + 2\pi\vec{u})}) \; , \quad x > x'$$

$$A_{lm; l'm'}^{i;j} = \frac{(4\pi)^2}{A} i^{l-l'} \sum_{\vec{u}} \frac{1}{2i K_{\vec{u}}}$$

$$\times \exp[i\vec{k}_{\vec{u}}^- \cdot (\vec{c}_i - \vec{c}_j)] Y_{l,-m}(\theta_{\vec{k}_{\vec{u}}^-}, \phi_{(\vec{k}_\parallel + 2\pi\vec{u})})$$

$$\times Y_{l'm'}(\theta_{\vec{k}_{\vec{u}}^-}, \phi_{(\vec{k}_\parallel + 2\pi\vec{u})}) \; , \quad x < x' \; . \qquad (B7)$$

We note that the spherical harmonics $Y_{lm}(\theta_{\vec{k}_{\vec{u}}^-}, \phi_{(\vec{k}_\parallel + 2\pi\vec{u})})$ and $Y_{l'm'}(\theta_{\vec{k}_{\vec{u}}^-}, \phi_{(\vec{k}_\parallel + 2\pi\vec{u})})$ may have complex argument.

If $x - x'$ can be zero, the structure constant $A_{lm; l'm'}^{i;j}$ is given by the following expressions:

$$A_{lm; l'm'}^{i;j} = 4\pi i^{l-l'} \sum_L i^{-L} C_{L, m-m'; lm; l'm'} D_{L, m-m'}^{ij} \; , \qquad (B8)$$

where

$$C_{LM; lm; l'm'} = \int Y_{LM}(\theta, \phi) Y_{lm}^*(\theta, \phi) Y_{l'm'}(\theta, \phi) d\Omega \; , \qquad (B9)$$

with

$$|l - l'| \leq L \leq l + l' \qquad (B10)$$

and

$$D_{LM}^{ij} = D_{LM}^{ij(1)} + D_{LM}^{ij(2)} \; .$$

The notation $D_{LM}^{ij(1)}$ is given by

$$D_{LM}^{ij(1)} = -\frac{1}{Ak} i^{|M|+1} 2^{-L} \left[(2L+1)(L+|M|)!(L-|M|)! \right]^{1/2} \sum_{\vec{u}} \exp[i(\vec{k}_\parallel + 2\pi\vec{u}) \cdot (\vec{c}_i - \vec{c}_j)_\parallel - iM\phi_{(\vec{k}_\parallel + 2\pi\vec{u})}]$$

$$\times \sum_{n=0}^{L-|M|} \frac{1}{n!} \left(\frac{K_{\vec{u}}}{k}\right)^{2n-1} \Delta_{n\vec{u}} \sum_{s=n}^{\min(2n, L-|M|)} \binom{n}{2n-s} \frac{[+k(\vec{c}_i - \vec{c}_j)_\perp]^{2n-s} [(\vec{k}_\parallel + 2\pi\vec{u})/k]^{L-s}}{[\frac{1}{2}(L-|M|-S)]! [\frac{1}{2}(L+|M|-S)]!} \; , \qquad (B11)$$

where $(\vec{c}_i - \vec{c}_j)_\parallel$ and $(\vec{c}_i - \vec{c}_j)_\perp$ are the parallel and the normal components of $\vec{c}_i - \vec{c}_j$, respectively; min($2n$, $L - |M|$) means the smaller number of $2n$ and $L - |M|$. The symbol $\Delta_{n\vec{u}}$ is defined as

$$\Delta_{n\vec{u}} = \int_{\exp(-i\pi)K_{\vec{u}}^2\omega/2}^{\infty} t^{-1/2-n} \exp\left[-t + \left(\frac{K_{\vec{u}}(\vec{c}_i - \vec{c}_j)_\perp}{2} \right)^2 \frac{1}{t} \right] dt \ . \tag{B12}$$

$D_{LM}^{ij(2)}$ is given by

$$D_{LM}^{ij(2)} = -\frac{2^{-L} k}{\sqrt{(4\pi)}} \sum_{m,n} \exp[-i(\vec{k}_\parallel \cdot \vec{r}_{mn})] (-k|\vec{r}_{mn} + \vec{c}_i - \vec{c}_j|)^L$$

$$\times Y_{LM}^* (\theta_{\vec{r}_{mn}+\vec{c}_i-\vec{c}_j}, \phi_{\vec{r}_{mn}+\vec{c}_i-\vec{c}_j}) \int_0^{k^2\omega/2} t^{-3/2-L} \exp\left[t - \left(\frac{k|\vec{r}_{mn}+\vec{c}_i-\vec{c}_j|}{2} \right)^2 \frac{1}{t} \right] dt \ , \tag{B13}$$

where $\theta_{(\vec{r}_{mn}+\vec{c}_i-\vec{c}_j)}$ and $\phi_{(\vec{r}_{mn}+\vec{c}_i-\vec{c}_j)}$ are the angular coordinates of the vector $(\vec{r}_{mn}+\vec{c}_i-\vec{c}_j)$.

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