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# Application of a Variational Principle to the Calculation of Low-Energy Electron Diffraction Intensities. II. The Generalized Formalism of Three-Dimensional Problems*

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A variational principle for the reflection coefficient is derived for elastic scattering from three-dimensional crystals. The crystal is assumed to possess perfect two-dimensional periodicity in the plane parallel to the crystal surface, but arbitrary variations of potential and lattice spacing in the perpendicular direction. As a result, this theory is valid for crystals with or without impurity layers. With linear trial functions, the reflection coefficient is uniquely given by the ratio of two determinants without any additional calculation of the wave field inside the crystal. Another variational principle is derived for the transmission coefficient of a plane wave transmitted through a three-dimensional crystal with a finite width. A modified Born approximation, which leads to the Born approximations, is obtained by inserting the incident and the adjoint plane waves in the variational equation without applying the variational principle. A general modified Born approximation is also obtained. For crystals having triperiodicity, the employment of Bloch waves as trial functions determines the reflection coefficient in terms of integrals over known functions and the perpendicular components of the wave numbers of the Bloch waves.

## I. INTRODUCTION

The fundamental theory of electron diffraction was first developed by Bethe,[1] who was able to give a qualitative explanation of the diffraction pattern by nonrelativistic elastic scattering from crystals with infinitely extended surfaces. Bethe assumed the crystal potential was equal to the periodic potential in the bulk up to the crystal surface. In his theory, the total wave field inside the crystal was represented by a superposition of Bloch waves with the same energy as that of the incident electrons and with their parallel (to the surface) components of the wave numbers differing from that of the incident plane wave by $2\pi$ times the two-dimensional reciprocal-lattice vectors. The Bloch waves were obtained by solving an energy secular equation derived from transforming the crystal potential into three-dimensional Fourier series. The reflection coefficient was calculated by matching the wave field inside the crystal to the incident and the diffracted plane waves on the crystal surface. He was able to deduce energy gaps and their corresponding large reflection coefficients by truncating the plane-wave expansion into two Fourier components (two-beam approximation). However, the strong scattering interaction involved in low-energy electron diffraction (LEED) causes slow convergence of the plane-wave expansion for Bloch waves; thus, the above two-beam model is not adequate in describing the diffraction pattern quantitatively. Boudreaux and Heine[2] developed a theory similar to Bethe's matching formalism by including evanescent solutions of the Schrödinger equation. They also pointed out the advantage of employing pseudopotentials in connection with the plane-wave expansion.

Hirabayashi and Takeishi's[3] treatment is an extension of von Laue's[4] theory for electron diffraction from a single layer of atoms. Their method transformed the potential into two-dimensional Fourier series. Because of the destruction of the perfect three-dimensional periodicity by the introduction of the crystal surface, it is appropriate to use the two-dimensional Fourier transformation. Von Laue's mixed representation was also applied by Marcus and Jepsen[5] to develop a transfer matrix method with a systematic computational procedure. Their technique requires the calculation of the eigenvectors, which are the discrete set of Bloch functions, of a transfer matrix.

The multiple scattering theory, which is based on Lax's[6] multiple scattering equations, was developed by McRae[7] and was able to yield a self-consistent description of the diffraction process for *s*-wave scatterers. Recently, McRae[8] developed a low-energy electron diffraction theory which is a general form of Darwin's[9] dynamical theory for x-ray diffraction. This layer-by-layer method obtains the reflection coefficient by diagonalizing a transfer matrix formed from the single-layer reflection and transmission coefficients which may be obtained by Kambe's[10,11] cellular method. The cellular method is another formalism which does not use Bloch functions explicitly. Kambe adopted the muffin-tin potential model and expanded the wave field inside the crystal into spherical harmonics. The mathematical procedure used by Korringa and Kohn and Rostoker[12] in their band theory of metals was applied by

Kambe to evaluate the integrals involved in the Green's function. The reflection coefficient was obtained by calculating the wave field on the surfaces of the inscribed spheres. However, the number of unknowns needed to be calculated becomes very large for a thick crystal.

In quantum mechanics, there exist variational methods[13] which are very fruitful when perturbation methods become tedious and complex to use. Usually a single physical quantity, in which we are interested, is given by a variational principle that leads to a stationary expression. Because of the stationary characteristic of the variational equation and its consequent insensitivity to the errors in the trial function, it is often possible to obtain very good estimates of the quantity with a relatively crude trial function. This is clearly a property of great significance during practical calculation. The accuracy of the result is increased by including more variational parameters in the trial function. Variational principles for the binding energy of atomic physics,[14] scattering phase shift and collision amplitude in nuclear physics,[15] and energy band theory[16] in solid state physics all have been proved quite successful.

In Paper I,[17] we have derived a variational principle for the reflection coefficient for elastic scattering from a one-dimensional crystal. For elastic scattering from periodic potentials, we found that all one-dimensional problems may be solved by employing a Bloch function with the wave number evaluated by a Hill's determinant.[18] The Kronig-Penney[19] model was investigated by using approximate trial functions, and the exact result was also obtained by our variational principle without having to calculate a complete solution of the Bloch function.

In this paper we propose a variational principle for the calculation of the reflectance for elastic scattering from three-dimensional crystals. The crystal is assumed to possess perfect two-dimensional periodicity in the plane parallel to the crystal surface but arbitrary variable scattering potential and lattice spacing in the normal direction. Consequently, this theory is valid for crystals with different composition in different atomic layers including possible surface contamination. If the Rayleigh-Ritz[20] technique is applied to the trial functions, the reflection coefficient is given uniquely by the ratio of two determinants, and an exact solution can be obtained with a sufficient number of terms in the trial functions. For a semi-infinite crystal, it is more convenient to use Bloch wave expansions. The reflection coefficient is also expressed by the ratio of two determinants.

## II. GREEN'S FUNCTION IN MIXED REPRESENTATION

The model's assumptions are essentially the same as those used in the theories mentioned above: (a) The nonrelativistic one-electron approximation is valid; (b) only elastic scattering is taken into consideration; (c) the crystal surfaces, which lie in the $y$-$z$ plane, extend to infinity; therefore, the crystal is considered to have perfect two-dimensional periodicity; (d) a monochromatic plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ comes from $x=-\infty$.

The three-dimensional nonrelativistic one-electron Schrödinger equation is

$$\nabla^2\psi(\vec{\mathrm{r}})+(k^2-V(\vec{\mathrm{r}}))\,\psi(\vec{\mathrm{r}})=0\;, \tag{2.1}$$

where the energy $k^2$ and the potential energy $V(\vec{\mathrm{r}})$ are in atomic units.[21]

The Schrödinger equation in the integral form is

$$\psi(\vec{\mathrm{r}})=\phi_0(\vec{\mathrm{r}})+\int G(\vec{\mathrm{r}},\vec{\mathrm{r}}')V(\vec{\mathrm{r}}')\psi(\vec{\mathrm{r}}')\,d\vec{\mathrm{r}}'\;, \tag{2.2}$$

where

$$\phi_0(\vec{\mathrm{r}})=e^{i\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}} \tag{2.3}$$

is the incident wave. The three-dimensional free-electron Green's function[22] $G(\vec{\mathrm{r}},\vec{\mathrm{r}}')$ is given by

$$G(\vec{\mathrm{r}},\vec{\mathrm{r}}')=-\frac{1}{(2\pi)^3}\int_C\frac{e^{i\vec{\mathrm{k}}'\cdot(\vec{\mathrm{r}}-\vec{\mathrm{r}}')}}{k'^2-k^2}\,d\vec{\mathrm{k}}'$$

$$=-\frac{1}{4\pi}\frac{e^{ik|\vec{\mathrm{r}}-\vec{\mathrm{r}}'|}}{|\vec{\mathrm{r}}-\vec{\mathrm{r}}'|}, \tag{2.4}$$

where $C$ is the contour along the real $k'$ axis passing above the singularity $k'=-k$ and below the singularity $k'=k$. The Green's function $G$ satisfies the equation

$$\nabla^2G(\vec{\mathrm{r}},\vec{\mathrm{r}}')+k^2G(\vec{\mathrm{r}},\vec{\mathrm{r}}')=\delta(\vec{\mathrm{r}}-\vec{\mathrm{r}}')\;. \tag{2.5}$$

Now we want to write the Green's function in a more convenient form by using the two-dimensional periodicity of the crystal. Both Fujiwara[23] and Kambe[24] have discussed the present problem. Kambe reduced the Schrödinger equation (2.1) into a set of coupled ordinary differential equations (von Laue's mixed representation) by expanding the wave function and the potential into two-dimensional Fourier series with the expansion coefficients as functions of one real space coordinate. The corresponding Green's function, similar to the one-dimensional problems, can be written in the mixed representation. He then recombined it to obtain the three-dimensional structural Green's function. Fujiwara applied an iteration method to calculate the higher-order Born approximations for the transmission coefficient by using the spectral representation of the Green's function (2.4) and then calculating the contour integrals.

The derivation we present below deals directly with the three-dimensional Green's function in the spectral form (2.4). By doing proper contour integrations which are simpler than Kambe's Fourier series expansion and recombination method, we have derived the same structural Green's function as his. Our approach is also different from Fujiwara's treatment in two respects: (a) We do not use the iterated solution which he could not prove convergent; instead, we consider the exact solution; (b) we include all the evanescent waves.

The model's assumption (c) is that the crystal has perfect two-dimensional periodicity in the plane parallel to the surface, i.e.,

$$V(\vec{r}+\vec{r}_{mn})=V(\vec{r}) \,, \qquad (2.6)$$

where $\vec{r}_{mn}=m\vec{a}_2+n\vec{a}_3$, with $m$ and $n$ integers, is a two-dimensional lattice vector. $\vec{a}_2$ and $\vec{a}_3$ are the two-dimensional primitive translation vectors. By applying Bloch's theorem[25] for a periodic lattice, the wave function inside the crystal should have two-dimensional periodicity. Thus

$$\psi(\vec{r}+\vec{r}_{mn})=e^{i\vec{k}_{\parallel}\cdot\vec{r}_{mn}}\psi(\vec{r}) \,, \qquad (2.7)$$

where $\vec{k}_{\parallel}$ is the parallel (to the surface) component of $\vec{k}$.

Substituting Eqs. (2.6) and (2.7) into the integral form of the Schrödinger equation (2.2), we obtain

$$\psi(\vec{r})=e^{i\vec{k}\cdot\vec{r}}+\sum_{m,n}\int G(\vec{r},\vec{r}\,'+\vec{r}_{mn})V(\vec{r}\,') \times e^{i\vec{k}_{\parallel}\cdot\vec{r}_{mn}}\psi(\vec{r}\,')d\vec{r}\,' \,, \qquad (2.8)$$

where the range of integration is reduced to a reference column,[26] i.e., a column with unit net surface area $A=|\vec{a}_2\times\vec{a}_3|$. The summation is over all $m$ and $n$.

This is different from the band-structure theory[12] where the range of integration of the integral equation (2.2) is reduced to one primitive cell by making use of the perfect three-dimensional periodic property of the crystal. Let us define the structural Green's function

$$\mathcal{G}(\vec{r},\vec{r}\,')=\sum_{m,n,}G(\vec{r},\vec{r}\,'+\vec{r}_{mn})e^{i\vec{k}_{\parallel}\cdot\vec{r}_{mn}} \,, \qquad (2.9)$$

which gives the effect at $\vec{r}$ due to waves scattered from $\vec{r}\,'$ and from all equivalent points in all other two-dimensional cells. The integral equation (2.8) can be written as

$$\psi(\vec{r})=e^{i\vec{k}\cdot\vec{r}}+\int\mathcal{G}(\vec{r},\vec{r}\,')V(\vec{r}\,')\psi(\vec{r}\,')d\vec{r}\,' \,, \qquad (2.10)$$

with the condition $(\nabla^2+k^2)\mathcal{G}(\vec{r},\vec{r}\,')=\delta(\vec{r}-\vec{r}\,')$, where $\vec{r}$ and $\vec{r}\,'$ are points in the reference column.

After doing the summation over $m$ and $n$, Eq. (2.9) becomes

$$\mathcal{G}(\vec{r},\vec{r}\,')=-\frac{1}{2\pi A}\sum_{\vec{v}}\int\frac{e^{i\vec{k}'\cdot(\vec{r}-\vec{r}\,')}}{k'^2-k^2}d\vec{k}' \times\delta(\vec{k}'_{\parallel}-\vec{k}_{\parallel}-2\pi\vec{v}) \,, \qquad (2.11)$$

where $\vec{k}'_{\parallel}$ is the parallel component of $\vec{k}'$ and $\vec{v}=m'\vec{b}_2+n'\vec{b}_3$, with $m'$ and $n'$ integers, is a two-dimensional reciprocal-lattice vector in the $y$-$z$ plane. Here $\vec{b}_2$ and $\vec{b}_3$ are the two-dimensional primitive translation reciprocal vectors satisfying

$$\vec{a}_i\cdot\vec{b}_j=\delta_{i,j}, \quad i,j=2,3 \,, \qquad (2.12)$$

where $\delta_{i,j}$ is the Kronecker $\delta$ function.

Since the structural Green's function $\mathcal{G}(\vec{r},\vec{r}\,')$ is a function of the difference $\vec{r}-\vec{r}\,'$, we can let $\vec{r}-\vec{r}\,'=\vec{R}$ and write $\mathcal{G}(\vec{r},\vec{r}\,')$ as $\mathcal{G}(\vec{R})$. We also define[27] $K_{\vec{v}}$ as

$$K_{\vec{v}}=[k^2-(\vec{k}_{\parallel}+2\pi\vec{v})^2]^{1/2} \,, \qquad (2.13)$$

which may be positive real or positive imaginary, as $k^2$ is larger or less than $(\vec{k}_{\parallel}+2\pi\vec{v})^2$, respectively.

The structural Green's function $\mathcal{G}$ of Eq. (2.11) can then be rewritten as

$$\mathcal{G}(\vec{R})=-\frac{1}{2\pi A}\sum_{\vec{v}}\int\frac{e^{ik'_{\perp}X}}{k'^2_{\perp}-K^2_{\vec{v}}}dk'_{\perp}\,e^{i(\vec{k}_{\parallel}+2\pi\vec{v})\circ\vec{R}_{\parallel}} \,, \qquad (2.14)$$

where $k'_{\perp}$ is the perpendicular component of $\vec{k}'$; $\vec{R}_{\parallel}$ and $X$ are the parallel and the perpendicular components of $\vec{R}$, respectively.

The singularities in the integrand of the above equation are at $k'_{\perp}=\pm K_{\vec{v}}$. The contribution to the integral from the infinitesimal neighborhood near $K_{\vec{v}}$ is determined by boundary conditions, i.e., we require that there is no incoming wave from $x\rightarrow+\infty$, and no exponentially increasing waves may exist as $x\rightarrow\pm\infty$. We choose the contour as shown in Fig. 1(a) for real $K_{\vec{v}}$. The main path of integration is along the real axis of $k'_{\perp}$. For $X>0$, the integral is evaluated by closing the contour with a semi-infinite circle $C$ in the positive imaginary $k'_{\perp}$ plane as shown in Fig. 1(b). The contribution to the integral from the path $C$ vanishes because of the small exponential term. The value of the integral is just $2\pi i$ times the residue of the integrand at the pole $+K_{\vec{v}}$.

$$-\frac{i}{2A}\sum_{\vec{v}(\mathrm{Re})}\frac{e^{iK_{\vec{v}}X}\,e^{i(\vec{k}_{\parallel}+2\pi\vec{v})\cdot\vec{R}_{\parallel}}}{K_{\vec{v}}} \,, \quad X>0 \qquad (2.15)$$

where Re means summation over all the $\vec{v}$ which gives real $K_{\vec{v}}$.

For $X<0$, we close the contour with a semi-infinite circle $C'$ in the negative imaginary $k'_{\perp}$ plane as shown in Fig. 1(c). The value of the integral is

$$-\frac{i}{2A}\sum_{\vec{v}(\mathrm{Re})}\frac{e^{-iK_{\vec{v}}X}\,e^{i(\vec{k}_{\parallel}+2\pi\vec{v})\cdot\vec{R}_{\parallel}}}{K_{\vec{v}}} \,, \quad X<0 \,. \qquad (2.16)$$

If $K_{\vec{v}}$ is imaginary, the singularities are on the imaginary axis of $k'_{\perp}$. The contour we choose is still along the real $k'_{\perp}$ axis as shown in Fig. 2(a). For $X>0$, we close the contour with a semi-infinite circle $C$ in the positive imaginary $k'_{\perp}$ plane as in

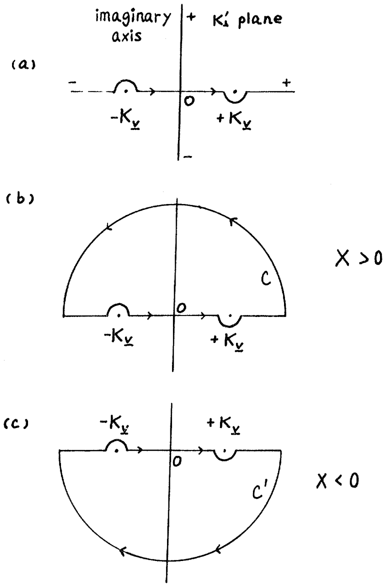

FIG. 1. Contours for the evaluation of the integral in Eq. (2.14) for real $K_{\vec{v}}$.

Fig. 2(b), and obtain

$$-\frac{1}{2A}\sum_{\vec{v}(\mathrm{Im})}\frac{1}{|K_{\vec{v}}|}\,e^{-|K_{\vec{v}}|X}\,e^{i(\vec{k}_{\parallel}+2\pi\vec{v})\cdot\vec{R}_{\parallel}},\quad X>0 \tag{2.17}$$

where Im means the summation is taken over all $\vec{v}$ with imaginary $K_{\vec{v}}$. For $X<0$, the contour is closed as shown in Fig. 2(c) yielding

$$-\frac{1}{2A}\sum_{\vec{v}(\mathrm{Im})}\frac{1}{|K_{\vec{v}}|}\,e^{|K_{\vec{v}}|X}\,e^{i(\vec{k}_{\parallel}+2\pi\vec{v})\cdot\vec{R}_{\parallel}},\quad X<0\ . \tag{2.18}$$

Equations (2.15)–(2.18) may be combined into one equation for the structural Green's function $\mathcal{G}$, with contributions from both real and imaginary $K_{\vec{v}}$:

$$\mathcal{G}(\vec{R})=-\frac{i}{2A}\sum_{\vec{v},\,K_{\vec{v}}\neq 0}\frac{1}{K_{\vec{v}}}\,e^{iK_{\vec{v}}|X|}\,e^{i(\vec{k}_{\parallel}+2\pi\vec{v})\cdot\vec{R}_{\parallel}}\ . \tag{2.19}$$

The summation is over all two-dimensional reciprocal-lattice vectors $\vec{v}$ except those which give $K_{\vec{v}}=0$. The case of $K_{\vec{v}}=0$ discussed by McRae[7] as the resonance case is not included in this formula. Equation (2.19) is identical to that obtained by Kambe.[24] When $X\neq 0$, the series is obviously convergent. Kambe[24] has applied Ewald's method to evaluate the above sum.[28]

Now we substitute the structural Green's function in the form of Eq. (2.19) into Eq. (2.10) yielding

$$\psi(\vec{r})=e^{i\vec{k}\cdot\vec{r}}-\frac{i}{2A}\sum_{\vec{v}}\frac{1}{K_{\vec{v}}}\int\exp(iK_{\vec{v}}|x-x'|)$$

$$\times\exp[i(\vec{k}_{\parallel}+2\pi\vec{v})\cdot(\vec{r}_{\parallel}-\vec{r}\,'_{\parallel})]\,V(\vec{r}\,')\,\psi(\vec{r}\,')\,d\vec{r}\,'\ . \tag{2.20}$$

By taking $x\rightarrow-\infty$ in Eq. (2.20), we obtain the wave function in the far left region from the crystal:

$$\psi(\vec{r})\rightarrow e^{i\vec{k}\cdot\vec{r}}+\sum_{\vec{v}(\mathrm{Re})}R_{\vec{v}}\,e^{i\vec{k}^{-}_{\vec{v}}\cdot\vec{r}}\quad, \tag{2.21}$$

where $\vec{k}^{-}_{\vec{v}}=[-K_{\vec{v}},\ (\vec{k}_{\parallel}+2\pi\vec{v})]$, which indicates the perpendicular and the parallel components explicitly, is the direction of the backward scattered wave $e^{i\vec{k}^{-}_{\vec{v}}\cdot\vec{r}}$. We note this verifies that the diffracted beams have the same reduced $\vec{k}_{\parallel}$.

The reflection coefficient is defined by

$$R_{\vec{v}}=-(i/2AK_{\vec{v}})\int e^{-i\vec{k}^{-}_{\vec{v}}\cdot\vec{r}\,'}\,V(\vec{r}\,')\,\psi(\vec{r}\,')\,d\vec{r}\,'\ . \tag{2.22}$$

Equation (2.21) includes the incident and the diffracted propagating plane waves which have the same energy and the same reduced parallel wave number. The evanescent waves near the surface damp out as $x\rightarrow-\infty$.

Similarly, the wave transmitted through a crystal with a finite width is obtained by taking $x\rightarrow+\infty$ in Eq. (2.20),

$$\psi(\vec{r})=\sum_{\vec{v}(\mathrm{Re})}T_{\vec{v}}\,e^{i\vec{k}^{+}_{\vec{v}}\cdot\vec{r}}\quad, \tag{2.23}$$

where $\vec{k}^{+}_{\vec{v}}=[K_{\vec{v}},\ (\vec{k}_{\parallel}+2\pi\vec{v})]$ is the direction of a forward scattered wave $e^{i\vec{k}^{+}_{\vec{v}}\cdot\vec{r}}$ and $T_{\vec{v}}$ is the transmission coefficient:

$$T_{\vec{v}}=\delta_{\vec{v},\vec{0}}-(i/2AK_{\vec{v}})\int e^{-i\vec{k}^{+}_{\vec{v}}\cdot\vec{r}\,'}\,V(\vec{r}\,')\,\psi(\vec{r}\,')\,d\vec{r}\,'\quad, \tag{2.24}$$

where $\delta_{\vec{v},\vec{0}}$ is a two-dimensional Kronecker δ func-

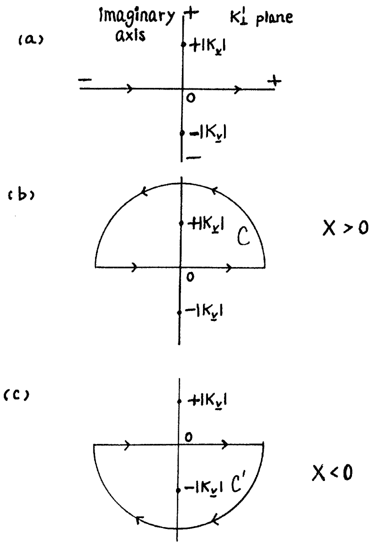

FIG. 2. Contours for the evaluation of the integral in Eq. (2.14) for imaginary $K_{\vec{v}}$.

tion.

Now we want to write the reflectance and the transmittance in terms of the reflection coefficient and in terms of the transmission coefficient, respectively. From quantum mechanics the probability current density vector[29] is defined as

$$\vec{J} = (\hbar/2im)[\psi^*(\vec{r})\vec{\nabla}\psi(\vec{r}) - \psi(\vec{r})\vec{\nabla}\psi^*(\vec{r})] \quad . \tag{2.25}$$

Thus the incident current density is

$$\vec{J}_{in} = (\hbar/m)\vec{k} \tag{2.26}$$

and the reflected current density in the direction of $\vec{k}_{\vec{v}}^{-}$ is

$$\vec{J}_{\vec{v}}^{-} = (\hbar/m)\vec{k}_{\vec{v}}^{-}\,|R_{\vec{v}}|^2 \quad . \tag{2.27}$$

The transmitted current density in the direction of $\vec{k}_{\vec{v}}^{+}$ is given by

$$\vec{J}_{\vec{v}}^{+} = (\hbar/m)\vec{k}_{\vec{v}}^{+}|\,T_{\vec{v}}|^2 \quad , \tag{2.28}$$

where we have used Eqs. (2.22) and (2.24) for the reflection and the transmission coefficients.

The law of conservation of current provides the following condition for the $R$'s and the $T$'s[5]:

$$\sum_{\vec{v}(\mathrm{Re})} \frac{K_{\vec{v}}}{k_\perp}\,|R_{\vec{v}}|^2 + \sum_{\vec{u}(\mathrm{Re})} \frac{K_{\vec{u}}}{k_\perp}\,|T_{\vec{u}}|^2 = 1 \quad . \tag{2.29}$$

The reflectance and the transmittance are defined as

$$|\vec{J}_{\vec{v}}^{\mp}|/|\vec{J}_{in}| \quad . \tag{2.30}$$

Therefore the reflectance in the direction of $\vec{k}_{\vec{v}}^{-}$ is $|R_{\vec{v}}|^2$, and the transmittance in the direction of $\vec{k}_{\vec{v}}^{+}$ is $|T_{\vec{v}}|^2$.

## III. DERIVATION OF VARIATIONAL PRINCIPLE

In this section we derive a variational principle for the calculation of three-dimensional LEED intensities. The variational principle for the transmission coefficient is also presented. The formulation below is similar to that of Morse and Feshbach[30] for three-dimensional scattering problems.

### A. Variational Principle for Reflection Coefficient

We start with the Schrödinger equation in integral form,

$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + \int \mathcal{G}(\vec{r},\vec{r}\,')\,V(\vec{r}\,')\,\psi(\vec{r}\,')\,d\vec{r}\,' \quad , \tag{3.1}$$

where $\mathcal{G}(\vec{r},\vec{r}\,')$ is in the form of Eq. (2.19) and the integral is taken over the reference column.

We define a quantity $A_{\vec{v}}$ associated with the scattering from $\vec{k}$ to $\vec{k}_{\vec{v}}^{-}$,

$$A_{\vec{v}} = i2A\,K_{\vec{v}}R_{\vec{v}}$$

$$= \int e^{-i\vec{k}_{\vec{v}}^{-}\cdot\vec{r}\,'}\,V(\vec{r}\,')\,\psi(\vec{r}\,')\,d\vec{r}\,' \quad . \tag{3.2}$$

In deriving the second expression we have used Eq. (2.22) for the reflection coefficient $R_{\vec{v}}$.

Since $A_{\vec{v}}$ and $R_{\vec{v}}$ are different only by a constant, the variational principle for $A_{\vec{v}}$ is equivalent to that for $R_{\vec{v}}$. We make the inhomogeneous Eq. (3.1) into a homogeneous equation in which $A_{\vec{v}}$ appears explicitly by making use of Eq. (3.2),

$$\psi(\vec{r}) = (1/A_{\vec{v}})\left(\int e^{-i\vec{k}_{\vec{v}}^{-}\cdot\vec{r}\,'}\,V(\vec{r}\,')\,\psi(\vec{r}\,')\,d\vec{r}\,'\right)e^{i\vec{k}\cdot\vec{r}}$$

$$+ \int \mathcal{G}(\vec{r},\vec{r}\,')\,V(\vec{r}\,')\,\psi(\vec{r}\,')\,d\vec{r}\,' \quad . \tag{3.3}$$

We then multiply both sides of Eq. (3.3) by $\tilde{\psi}(\vec{r})\,V(\vec{r})$ and integrate over the reference column. $\tilde{\psi}(\vec{r})$, the adjoint of $\psi(\vec{r})$, corresponds to a plane wave incident from $(-\vec{k}_{\vec{v}}^{-})$; the proof will be given later. We obtain

$$A_{\vec{v}} = \frac{\left[\int \tilde{\psi}(\vec{r})\,V(\vec{r})\,e^{i\vec{k}\cdot\vec{r}}\,d\vec{r}\right]\left[\int e^{-i\vec{k}_{\vec{v}}^{-}\cdot\vec{r}\,'}\,V(\vec{r}\,')\,\psi(\vec{r}\,')\,d\vec{r}\,'\right]}{\int \tilde{\psi}(\vec{r})\,V(\vec{r})\left[\psi(\vec{r}) - \int \mathcal{G}(\vec{r},\vec{r}\,')\,V(\vec{r}\,')\,\psi(\vec{r}\,')\,d\vec{r}\,'\right]d\vec{r}} \quad . \tag{3.4}$$

We first vary $A_{\vec{v}}$ with respect to $\tilde{\psi}$ and denote the variation of $A_{\vec{v}}$ with respect to $\tilde{\psi}$ by $\tilde{\delta}$:

$$\tilde{\delta}A_{\vec{v}} = \left[\int e^{-i\vec{k}_{\vec{v}}^{-}\cdot\vec{r}\,'}V(\vec{r}\,')\psi(\vec{r}\,')\,d\vec{r}\,'\right]\left\{\int d\vec{r}\,\delta\tilde{\psi}(\vec{r})V(\vec{r})\right.$$

$$\times\left[e^{i\vec{k}\cdot\vec{r}}\,\mathfrak{D} - \left(\psi(\vec{r}) - \int \mathcal{G}(\vec{r},\vec{r}\,')V(\vec{r}\,')\psi(\vec{r}\,')\,d\vec{r}\,'\right)\right.$$

$$\left.\left.\times\left(\int e^{i\vec{k}\cdot\vec{r}\,''}\,V(\vec{r}\,'')\tilde{\psi}(\vec{r}\,'')\,d\vec{r}\,''\right)\right]\right\}/\mathfrak{D}^2, \tag{3.5}$$

where $\mathfrak{D}$ is the denominator of Eq. (3.4).

If and only if $\psi(\vec{r})$ satisfies the Schrödinger equation (3.1), then Eq. (3.5) gives $\tilde{\delta}A_{\vec{v}}=0$, namely, $\partial A_{\vec{v}}/\partial\tilde{\psi}=0$. The properties of $\tilde{\psi}$ may be determined by varying $A_{\vec{v}}$ with respect to $\psi$. Let us denote the variation of $A_{\vec{v}}$ with respect to $\psi$ by $\bar{\delta}$,

$$\bar{\delta}A_{\vec{v}} = \left[\int e^{i\vec{k}\cdot\vec{r}\,'}V(\vec{r}\,')\tilde{\psi}(\vec{r}\,')\,d\vec{r}\,'\right]\left\{\int d\vec{r}\,\delta\psi(\vec{r})V(\vec{r})\right.$$

$$\times\left[e^{-i\vec{k}_{\vec{v}}^{-}\cdot\vec{r}}\,\mathfrak{D} - \left(\int e^{-i\vec{k}_{\vec{v}}^{-}\cdot\vec{r}\,''}\,V(\vec{r}\,'')\psi(\vec{r}\,'')\,d\vec{r}\,''\right)(\tilde{\psi}(\vec{r}))\right.$$

$$\left.\left.\times\int \mathcal{G}(\vec{r}\,',\vec{r})V(\vec{r}\,',\tilde{\psi}(\vec{r}\,')\,d\vec{r}\,')\right]\right\}/\mathfrak{D}^2 \,. \tag{3.6}$$

The interchange of $\mathcal{G}(\vec{r},\vec{r}\,')$ to $\mathcal{G}(\vec{r}\,',\vec{r})$ has been carried out. From Eq. (3.6), we see that $\bar{\delta}A_{\vec{v}}=0$, i.e., $\partial A_{\vec{v}}/\partial\psi=0$, if and only if $\tilde{\psi}(\vec{r})$ satisfies

$$\psi(\vec{r}) = \frac{\int\tilde{\psi}(\vec{r}\,')V(\vec{r}\,')\left[\psi(\vec{r}\,') - \int\mathcal{G}(\vec{r}\,',\vec{r}\,'')V(\vec{r}\,'')\psi(\vec{r}\,'')\,d\vec{r}\,''\right]d\vec{r}\,'}{\left[\int e^{-i\vec{k}_{\vec{v}}^{-}\cdot\vec{r}\,'}V(\vec{r}\,')\psi(\vec{r}\,')\,d\vec{r}\,'\right]}\,e^{-i\vec{k}_{\vec{v}}^{-}\cdot\vec{r}} + \int \mathcal{G}(\vec{r}\,',\vec{r})V(\vec{r}\,')\tilde{\psi}(\vec{r}\,')\,d\vec{r}\,' \quad . \tag{3.7}$$

Since $\mathcal{G}(\vec{r}\,', \vec{r})$ is equal to $\mathcal{G}_{-\vec{k}_{\vec{v}}^-}(\vec{r}, \vec{r}\,')$, which is the structural Green's function for $e^{-i\vec{k}_{\vec{v}}^-\cdot\vec{r}}$, $\tilde{\psi}(\vec{r})$ is also a solution of the Schrödinger equation with an incident wave in the form of $e^{-i\vec{k}_{\vec{v}}^-\cdot\vec{r}}$. Consequently, the variational principle is

$$\delta A_{\vec{v}} = 0, \tag{3.8}$$

when $\psi(\vec{r})$ and $\tilde{\psi}(\vec{r})$ are varied about the exact solutions. The notation $\delta$ means variation of $A_{\vec{v}}$ with respect to both $\psi$ and $\tilde{\psi}$. Thus the reflection coefficient $R_{\vec{v}}$ is the correct solution as well as an extremum when $\psi(\vec{r})$ and $\tilde{\psi}(\vec{r})$ are the exact solutions of the Schrödinger equation (2.1) with incident waves $e^{i\vec{k}\cdot\vec{r}}$ and $e^{-i\vec{k}_{\vec{v}}^-\cdot\vec{r}}$, respectively.

Physically, $\psi(\vec{r})$ is the wave field excited by the incident wave $e^{i\vec{k}\cdot\vec{r}}$, and $\tilde{\psi}(\vec{r})$ is the wave field excited by an incident plane wave with wave vector $(-\vec{k}_{\vec{v}}^-)$. If we indicate the incident and the diffracted directions in $A_{\vec{v}}$ explicitly by the notation $A(\vec{k}_{\vec{v}}^-|\vec{k})$, and $\psi(\vec{r})$ by $\phi(\vec{k})$, then $\tilde{\psi}(\vec{r}) = \phi(-\vec{k}_{\vec{v}}^-)$.

It follows from Eq. (3.4) that

$$A(\vec{k}_{\vec{v}}^-|\vec{k}) = A(-\vec{k}|-\vec{k}_{\vec{v}}^-), \tag{3.9}$$

which is a special case of the reciprocity theorem. Because of the two-dimensional periodic property of the crystal, this reciprocity theorem is different from that for scattering amplitude[30] where the scattering amplitude in the direction of $\vec{k}_s$ with the incident plane wave $e^{i\vec{k}\cdot\vec{r}}$ is equal to that in the direction of $-\vec{k}$ with an incident wave $e^{-i\vec{k}_s\cdot\vec{r}}$.

### B. Variational Principle for Transmission Coefficient

The derivation of the variational principle for the transmission coefficient of the transmitted wave through a crystal with a finite width is similar to that for the reflection coefficient. Using the same procedure as in Sec. III A, we obtain a variational equation for the transmission coefficient $T_{\vec{v}}$,

$$(T_{\vec{v}} - \delta_{\vec{v},\vec{0}})\, i\, 2AK_{\vec{v}} = \frac{[\int \tilde{\psi}_T(\vec{r})V(\vec{r})e^{i\vec{k}\cdot\vec{r}}d\vec{r}\,][\int e^{-i\vec{k}_{\vec{v}}^+\cdot\vec{r}\,'}V(\vec{r}\,')\psi(\vec{r}\,')\,d\vec{r}\,']}{\int d\vec{r}\,\tilde{\psi}_T(\vec{r})V(\vec{r})[\psi(\vec{r}) - \int \mathcal{G}(\vec{r},\vec{r}\,')V(\vec{r}\,')\psi(\vec{r}\,')\,d\vec{r}\,']}, \tag{3.10}$$

with the variational principle $\delta T_{\vec{v}} = 0$. The function $\tilde{\psi}_T(\vec{r})$, the adjoint of $\tilde{\psi}(\vec{r})$, corresponds to the incident plane wave $e^{-i\vec{k}_{\vec{v}}^+\cdot\vec{r}}$.

If we denote $T_{\vec{v}}$ by $T(\vec{k}_{\vec{v}}^+|\vec{k})$, the reciprocity theorem is

$$[T(\vec{k}_{\vec{v}}^+|\vec{k}) - \delta_{\vec{v},\vec{0}}]K_{\vec{v}} = [T(-\vec{k}|-\vec{k}_{\vec{v}}^+) - \delta_{\vec{0},\vec{v}}]k_\perp\,. \tag{3.11}$$

## IV. RAYLEIGH-RITZ TECHNIQUE

In order to determine the accuracy of the variational calculation, it is necessary to have a systematic procedure to improve the original trial function such as the Rayleigh-Ritz technique.[20] This method inserts a linear combination of a complete set of functions in the variational equation, and the set of linear expansion coefficients are considered as the variational parameters. The computational procedure involves first taking a few terms in the infinite series and performing the variational principle to obtain the best solution for the trial function assumed, then computing again with the variational method by increasing terms in the trial function until the value does not change with the addition of more terms. But care must be taken in applying the technique since the systematic omission of certain terms may cause false convergence.

We take a linear combination of $n$ given functions of a complete set as the trial function

$$\psi(\vec{r}) = \sum_{i=1}^{n} C_i(\vec{k})\phi_i(\vec{r}); \tag{4.1}$$

then

$$\tilde{\psi}(\vec{r}) = \sum_{i=1}^{n} \tilde{C}_i(-\vec{k}_{\vec{v}}^-)\tilde{\phi}_i(\vec{r}), \tag{4.2}$$

where $\phi_i$ and $\tilde{\phi}_i$ are known functions, and the complex expansion coefficients are taken as variational parameters.

Substituting Eqs. (4.1) and (4.2) into Eq. (3.4) yields

$$A_{\vec{v}} = \sum_{i,j=1}^{n} D_iE_jC_i\tilde{C}_j \Big/ \sum_{i,j=1}^{n} F_{i,j}C_i\tilde{C}_j\,, \tag{4.3}$$

where

$$\begin{aligned} D_i &= \int e^{-i\vec{k}_{\vec{v}}^-\cdot\vec{r}}V(\vec{r})\phi_i(\vec{r})\,d\vec{r}\,, \\ E_i &= \int e^{i\vec{k}\cdot\vec{r}}V(\vec{r})\tilde{\phi}_i(\vec{r})\,d\vec{r}\,, \\ F_{i,j} &= \int \tilde{\phi}_j(\vec{r})V(\vec{r}) \\ &\quad \times[\phi_i(\vec{r}) - \int \mathcal{G}(\vec{r},\vec{r}\,')V(\vec{r}\,')\phi_i(\vec{r}\,')\,d\vec{r}\,']\,d\vec{r}\,. \end{aligned} \tag{4.4}$$

Let us rewrite Eq. (4.3) as

$$\sum_{i,j=1}^{n}\left(F_{i,j} - \frac{1}{A_{\vec{v}}}D_iE_j\right)C_i\tilde{C}_j = 0\,. \tag{4.5}$$

The variational principle $\delta A_{\vec{v}} = 0$ yields

$$\frac{\partial A_{\vec{v}}}{\partial C_i} = \frac{\partial A_{\vec{v}}}{\partial \tilde{C}_i} = 0\,,\quad i = 1, 2, \ldots, n\,. \tag{4.6}$$

After performing the variational principle (4.6), a set of linear equations is obtained,

$$\begin{aligned} &\sum_{i=1}^{n}\left(F_{i,j} - \frac{1}{A_{\vec{v}}}D_iE_j\right)C_i = 0\,, \\ &\sum_{j=1}^{n}\left(F_{i,j} - \frac{1}{A_{\vec{v}}}D_iE_j\right)\tilde{C}_j = 0\,. \end{aligned} \tag{4.7}$$

The solution of this set of equations is possible only when the determinant of the coefficients of the $C_i$ and $\tilde{C}_i$ is set to zero:

$$\det|\Delta_{i,j}|=0\ , \tag{4.8}$$

where

$$\Delta_{i,j}=F_{i,j}-(1/A_{\vec{v}})D_iE_j\ . \tag{4.9}$$

For a given set of $\phi_i$'s and $\tilde{\phi}_i$'s, the only unknown in Eq. (4.8) is $A_{\vec{v}}$, which may be determined uniquely because Eq. (4.8) is linear in $A_{\vec{v}}$. The proof of the uniqueness is similar to that of Kohn's[31] proof for the collision determinant. We adopt his linear transformation here:

$$f_1=\sum_{i=1}^{n}C_iD_i,\quad f_i=C_i,\quad i\neq 1 \tag{4.10}$$

and

$$\tilde{f}_1=\sum_{i=1}^{n}\tilde{C}_iE_i,\quad \tilde{f}_i=\tilde{C}_i,\quad i\neq 1\ . \tag{4.11}$$

Then Eq. (4.5) becomes

$$\sum_{i,j=1}^{n}H_{i,j}f_i\tilde{f}_j-\frac{1}{A_{\vec{v}}}f_1\tilde{f}_1=0\ , \tag{4.12}$$

where

$$\begin{aligned}H_{1,1}&=\frac{F_{1,1}}{D_1E_1}\ ,\\ H_{1,j}&=\frac{F_{1,j}}{D_1}-\frac{F_{1,1}E_j}{D_1E_1}\ ,\\ &\qquad\qquad\qquad i,\ j\neq 1\\ H_{i,1}&=\frac{F_{i,1}}{E_1}-\frac{F_{1,1}D_i}{D_1E_1}\ ,\\ H_{i,j}&=F_{i,j}-\frac{D_iF_{1,j}}{D_1}-\frac{F_{i,1}E_j}{E_1}+\frac{F_{1,1}D_iE_j}{D_1E_1}\ .\end{aligned} \tag{4.13}$$

We then perform the variational principle $\delta A_{\vec{v}}=0$ with $f_i$ and $\tilde{f}_i$ as variational parameters. The compatibility determinant is set to zero,

$$|H_{i,j}-(1/A_{\vec{v}})\delta_{i1}\delta_{j1}|=0\ , \tag{4.14}$$

which is evidently linear in $A_{\vec{v}}$.

The solution for $A_{\vec{v}}$ may be written in the form of the ratio of two determinants,

$$A_{\vec{v}}=|M|\,/|\,H_{i,j}|\ , \tag{4.15}$$

where $|M|$ is the (1, 1) cofactor of $|H_{i,j}|$; in other words, $|M|=|H_{i,j}|_{i,j\neq 1}$. By adding $D_i$ times the first row of $|H_{i,j}|$ to the $i$th row, and $E_j$ times the resulting first column to the $j$th column, we find

$$|H_{i,j}|=(1/D_1E_1)|\,F_{i,j}|\ . \tag{4.16}$$

Thus the reflection coefficient is uniquely determined by

$$R_{\vec{v}}=\frac{-i}{2AK_{\vec{v}}}\,\frac{D_1E_1\,|H_{i,j}|_{i,j\neq 1}}{|F_{i,j}|}\ . \tag{4.17}$$

This is in contrast to the energy secular equation where the degree of the unknown energy is as high as the number of terms used in the trial function.

The exact reflection coefficient can be obtained if the wave functions converge fast.

## V. BORN APPROXIMATIONS AND MODIFIED BORN APPROXIMATIONS

The Born approximations may be obtained by putting the appropriate trial functions in the variational equation (3.4).

If we insert the incident wave $e^{i\vec{k}\cdot\vec{r}}$ for $\psi(\vec{r})$ and $e^{-i\vec{k}_{\vec{v}}\cdot\vec{r}}$ for $\tilde{\psi}(\vec{r})$ in Eq. (3.4), a modified Born approximation for the reflection coefficient is obtained without performing the variational principle for $A_{\vec{v}}$,

$$\begin{aligned}R_{\vec{v}}&=-\frac{-i}{2AK_{\vec{v}}}\,\frac{\left[\int e^{i\vec{k}\cdot\vec{r}}\,V(\vec{r})e^{-i\vec{k}_{\vec{v}}\cdot\vec{r}}\,d\vec{r}\right]^2}{\int d\vec{r}\,e^{-i\vec{k}_{\vec{v}}\cdot\vec{r}}\,V(\vec{r})\left[e^{i\vec{k}\cdot\vec{r}}-\int\mathcal{G}(\vec{r},\vec{r}\,')V(\vec{r}\,')e^{i\vec{k}\cdot\vec{r}\,'}d\vec{r}\,'\right]}\\ &\simeq-\frac{i}{2AK_{\vec{v}}}\left[\int e^{-i\vec{k}_{\vec{v}}\cdot\vec{r}}\,V(\vec{r})\,e^{i\vec{k}\cdot\vec{r}}+\int\int d\vec{r}\,e^{-i\vec{k}_{\vec{v}}\cdot\vec{r}}\,V(\vec{r})\mathcal{G}(\vec{r},\vec{r}\,')V(\vec{r}\,')e^{i\vec{k}\cdot\vec{r}\,'}d\vec{r}\,'+\cdots\right]\ .\end{aligned} \tag{5.1}$$

The first-order Born approximation can be deduced from Eq. (5.1) if the second term in the denominator is omitted. The second-order Born approximation may also be obtained from Eq. (5.1) by expanding the denominator and taking only the first two terms.

If the second term in the denominator of Eq. (5.1) is not small compared to the first term, the series will not converge, and it is better to use the formula without expanding the denominator.

The higher-order Born approximations can be deduced by using the iterated form of the wave functions as the trial functions. If we insert the $\psi(\vec{r})$ iterated once with the integral Schrödinger equation (2.10) and its corresponding $\tilde{\psi}(\vec{r})$, the third and the fourth Born approximations may be derived by expanding the denominator of the variational equation and taking the first two or three terms, respectively.

A more general form of Born approximation is derived by taking a linear combination of plane waves including a few evanescent waves as the trial functions,

$$\psi(\vec{r})=\sum_{i=1}^{n}C_i\,e^{i\vec{k}_{\vec{i}}^{+}\cdot\vec{r}},\quad \phi_i(\vec{r})=e^{i\vec{k}_{\vec{i}}^{+}\cdot\vec{r}}$$

and

$$\tilde{\psi}(\vec{r}) = \sum_{i=1}^{n} \tilde{C}_i e^{-i\vec{k}^{-}_{\vec{v}-\vec{i}}\cdot\vec{r}}\ ,\ \tilde{\phi}_i(\vec{r}) = e^{-i\vec{k}^{-}_{\vec{v}-\vec{i}}\cdot\vec{r}}\ , \tag{5.2}$$

where $i = 1$ to $n$ enumerates the two-dimensional reciprocal-lattice vectors in an arbitrary order.

Substituting Eq. (5.2) into Eqs. (4.4), (4.12), and (4.13), the reflection coefficient is given by

$$R_{\vec{v}} = -\frac{i}{2AK_{\vec{v}}}\frac{D_1 E_1 |H_{i,j}|_{i,j\neq 1}}{|F_{i,j}|}\ , \tag{5.3}$$

where

$$D_i = \int e^{i(\vec{k}^{+}_{\vec{i}} - \vec{k}^{-}_{\vec{v}})\cdot\vec{r}}\, V(\vec{r})\, d\vec{r}\ ,$$

$$E_i = \int e^{i(\vec{k} - \vec{k}^{-}_{\vec{v}-\vec{i}})\cdot\vec{r}}\, V(\vec{r})\, d\vec{r}\ , \tag{5.4}$$

$$F_{i,j} = \int e^{-i\vec{k}^{-}_{\vec{v}-\vec{j}}\cdot\vec{r}}\, V(\vec{r})$$

$$\times \left[e^{i\vec{k}^{+}_{\vec{i}}\cdot\vec{r}} - \int \mathcal{G}(\vec{r}, \vec{r}\,')V(\vec{r}\,')e^{i\vec{k}^{+}_{\vec{i}}\cdot\vec{r}\,'}\, d\vec{r}\,'\right] d\vec{r}\ ,$$

$$H_{i,j} = F_{i,j} - \frac{D_i F_{1,j}}{D_1} - \frac{F_{i,1} E_j}{E_1} + \frac{F_{1,1} D_i E_j}{D_1 E_1}\ ,\quad i, j \neq 1\ .$$

This general modified Born approximation is obtained after performing the variational principle for $A_{\vec{v}}$; therefore, it should be able to give better results than the modified Born approximation.

## VI. USE OF BLOCH THEOREM

The variational method described in Sec. III is a most general form for the calculation of LEED intensities from crystals with two-dimensional periodicity including only elastic scattering. No Bloch wave expansion is required for the trial functions; however, in the case of diffraction from a thick crystal, it is advantageous to employ Bloch waves. If we assume a perfect semi-infinite crystal, the total wave function inside the crystal may be represented by a superposition of Bloch waves excited by the incident wave $e^{i\vec{k}\cdot\vec{r}}$, i.e., Bloch waves with the same reduced $\vec{k}_{\parallel}$ and the same energy as those of the incident wave, but including only those which propagate or attenuate into the crystal. Similarly, the adjoint wave function $\tilde{\psi}(\vec{r})$ may be expanded into Bloch waves excited by $e^{-i\vec{k}^{-}_{\vec{v}}\cdot\vec{r}}$.

We take a finite number of those Bloch waves including all propagating waves and a few of the infinite evanescent waves as trial functions,

$$\psi(\vec{r}) = \sum_{g=1}^{n} C_g e^{i\vec{k}'_g\cdot\vec{r}}\, U_{\vec{k}'_g}(\vec{r})$$

and (6.1)

$$\tilde{\psi}(\vec{r}) = \sum_{g=1}^{n} \tilde{C}_g e^{i\tilde{\vec{k}}'_g\cdot\vec{r}}\, U_{\tilde{\vec{k}}'_g}(\vec{r})\ ,$$

where we have arranged $C_g$ and $\tilde{C}_g$ with $g = 1, 2, \ldots, n$ in decreasing order of importance in the construction of the wave functions. $U_{\vec{k}'_g}$ and $U_{\tilde{\vec{k}}'_g}$ are periodic functions; $\vec{k}'_g$ and $\tilde{\vec{k}}'_g$ are the wave numbers with their components indicated by $\vec{k}\,'_g = (k'_{g\perp}, \vec{k}_{\parallel} + 2\pi\vec{g})$ and $\tilde{\vec{k}}'_g = [\tilde{k}'_{g\perp}, -(\vec{k}_{\parallel} + 2\pi\vec{v}) + 2\pi\vec{g}]$. $\vec{g}$ is a two-dimensional reciprocal-lattice vector. The perpendicular components $k'_{g\perp}$ and $\tilde{k}'_{g\perp}$ may be complex for evanescent waves in the energy gaps or elsewhere.

Let us define

$$\Phi_g(\vec{r}) = C_g e^{i\vec{k}'_g\cdot\vec{r}}\, U_{\vec{k}'_g}(\vec{r})\ ,$$

$$\tilde{\Phi}_g(\vec{r}) = \tilde{C}_g e^{i\tilde{\vec{k}}'_g\cdot\vec{r}}\, U_{\tilde{\vec{k}}'_g}(\vec{r})\ . \tag{6.2}$$

The Bloch waves have the periodic properties such that

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

and (6.3)

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

where $d$ is the spacing between two identical layers as shown in Fig. 3.

By making use of the triperiodicity of the potential and the Bloch waves, and assigning an infinitesimal damping factor for $k'_{g\perp}$ and $\tilde{k}'_{g\perp}$, the range of integration of the integrals in the variational equation (3.4) is reduced to the reference column with width $d$ which we call the $d$-reference column,

$$A_{\vec{v}} = \sum_{g,h=1}^{n} D^g E^h \Big/ \sum_{g,h} F^{g,h}\ , \tag{6.4}$$

where

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

$$F^{g,h} = \frac{1}{1 - e^{i(k'_{g\perp} + \tilde{k}'_{h\perp})d}} \left\{ \int d\vec{r}\, \tilde{\Phi}_h(\vec{r})V(\vec{r}) \left( \Phi_g(\vec{r}) - \int \mathcal{G}(\vec{r}, \vec{r}\,')V(\vec{r}\,')\Phi_g(\vec{r}\,')\, d\vec{r}\,' \right) + \left[ \sum_{\vec{u}} \frac{i}{2AK_{\vec{u}}} \left( \frac{1}{e^{-i(K_{\vec{u}} + k'_{g\perp})d} - 1} \right.\right.\right. \tag{6.5}$$

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

with the integrals taken over the $d$-reference column.

Each of the Bloch waves $\Phi_g$ and $\tilde{\Phi}_g$ may be expanded into a complete set of functions with the expansion coefficients as variational parameters, e.g., the spherical harmonics expansion for muffin-tin potentials or the plane-wave expansion with pseudopotentials. We take $N$ of the complete set of functions in expanding the Bloch waves $\Phi_g$ and $\tilde{\Phi}_g$,

$$\Phi_g(\vec{r})=\sum_{i=1}^{N} C_i^g\,\phi_i^g(\vec{r})$$

and

$$\tilde{\Phi}_g(\vec{r})=\sum_{i=1}^{N}\tilde{C}_i^g\tilde{\phi}_i^g(\vec{r})\ . \tag{6.6}$$

Substituting Eq. (6.6) into Eqs. (6.4) and (6.5), making the transformation given by Eq. (4.10), then performing the variational principle $\delta A_{\vec{v}}=0$, the reflection coefficient is uniquely determined by

$$A_{\vec{v}}=\frac{D_1^1E_1^1\,|H_{i,j}^{g,h}|}{|F_{i,j}^{g,h}|}\ ,\ \begin{cases} i,g\neq 1,1\\ j,h\neq 1,1\end{cases}\text{for }|H_{i,j}^{g,h}| \tag{6.7}$$

where

$$D_i^g=\frac{1}{1-e^{i(K_{\vec{v}}^{-}+k'_{g\perp})d}}\int e^{-i\vec{k}_{\vec{v}}^{-}\cdot\vec{r}}\,V(\vec{r})\phi_i^g(\vec{r})\,d\vec{r}\ ,\quad E_i^g=\frac{1}{1-e^{i(k_\perp+\tilde{k}'_{g\perp})d}}\int e^{i\vec{k}\cdot\vec{r}}\,V(\vec{r})\tilde{\phi}_i^g(\vec{r})\,d\vec{r}\ ,$$

$$F_{i,j}^{g,h}=\frac{1}{1-e^{i(k'_{g\perp}+\tilde{k}'_{h\perp})d}}\Bigg[\int d\vec{r}\ \tilde{\phi}_j^h(\vec{r})\,V(\vec{r})\quad\left(\phi_i^g(\vec{r})-\int \mathcal{G}(\vec{r},\vec{r}\,')\,V(\vec{r}\,')\phi_i^g(\vec{r}\,')\,d\vec{r}\,'\right)$$

$$+\sum_{\vec{u}}\Bigg(\frac{i}{2AK_{\vec{u}}}\ \frac{1}{e^{-i(K_{\vec{u}}^{-}+k'_{g\perp})d}-1}\iint\tilde{\phi}_j^h(\vec{r})\,V(\vec{r})e^{i\vec{K}_{\vec{u}}^{-}\cdot(\vec{r}-\vec{r}\,')}V(\vec{r}\,')\phi_i^g(\vec{r}\,')\,d\vec{r}\,'\,d\vec{r}\quad+\frac{1}{e^{-i(K_{\vec{u}}^{+}+\tilde{k}'_{h\perp})d}-1} \tag{6.8}$$

$$\times\iint\tilde{\phi}_j^h(\vec{r})\,V(\vec{r})\,e^{i\vec{K}_{\vec{u}}^{+}\cdot(\vec{r}\cdot\vec{r}\,')}\,V(\vec{r}\,')\phi_i^g(\vec{r}\,')\,d\vec{r}\,'\,d\vec{r}\Bigg)\Bigg]\ ,$$

$$H_{i,j}^{g,h}=F_{i,j}^{g,h}-\frac{D_i^gF_{1,j}^{1,h}}{D_1^1}-\frac{F_{i,1}^{g,1}E_j^h}{E_1^1}+\frac{F_{1,1}^{1,1}D_i^gE_j^h}{D_1^1E_1^1}\ ,\ \begin{cases} g,i\neq 1,1\\ h,j\neq 1,1\end{cases}.$$

By employing Bloch waves, the range of integration of the integrals of Eq. (6.8) is reduced to a $d$-reference column. But all $k'_{g\perp}$ and $\tilde{k}'_{g\perp}$, which may be calculated from any energy band theory,[32] are required in evaluating the reflection coefficient. In principle, the eigenvalues $k'_{g\perp}$ and $\tilde{k}'_{g\perp}$ may be considered as nonlinear variational parameters. The terms under the summation of $\vec{u}$ in $F_{i,j}^{g,h}$ of Eq. (6.8) converge fast because of the exponential term $e^{-|K_{\vec{u}}|}$ for imaginary $K_{\vec{u}}$.

## VII. WAVE FUNCTIONS

The wave functions inside the crystal may be calculated from the set of linear equations (4.7), after $A_{\vec{v}}$ is evaluated from Eq. (4.8). For a general $\vec{k}$ of the incident wave, the coefficients $C_i$ in Eq. (4.1) are given by

$$\sum_{i=1}^{n}\left(F_{i,j}-\frac{1}{A_{\vec{v}}}D_i\,E_j\right)C_i=0. \tag{7.1}$$

We may set $C_1$ equal to unity and determine the remaining $(n-1)$ $C_i'$s by using any $(n-1)$ of Eq. (7.1). However, the wave function obtained by the variational method is usually less accurate than the reflection coefficient.

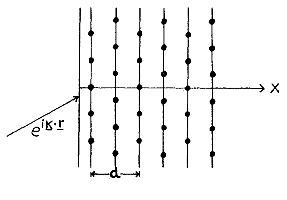

FIG. 3. Side view of a semi-infinite crystal with its structure repeating after every $d$. $e^{i\vec{k}\cdot\vec{r}}$ is the incident wave.

## VIII. DISCUSSION

The variational method described above for the reflection coefficient is similar to the variational principle for the scattering amplitude of particles in a force field.[30] However, they are different in two respects: (a) Instead of the force field in the collision problem, the scattering potential here is the crystal potential with perfect two-dimensional periodicity; (b) because of the two-dimensional periodicity, the diffracted waves are a discrete set of beams having the same reduced parallel wave vectors, while in particle scattering the angular distribution is continuous.

The variational equation (3.4) which leads to a stationary expression for the reflection coefficient involves two trial wave functions $\psi$ and $\tilde{\psi}$. Physically, $\psi$ and $\tilde{\psi}$ are the wave field and its adjoint wave field inside the crystal. By doing proper contour integrations with the right boundary conditions, the three-dimensional structural Green's function (2.9) was directly transformed into a mixed representation first derived by Kambe[24] using complex Fourier transformation and recombination method.

This theory is believed to be a most fundamental and direct method for the calculation of low-energy electron diffraction intensities. The reflection coefficient is given uniquely by Eq. (4.17) without any additional calculation of the expansion coefficients, nor is it necessary to perform the matching technique on the surface. The matching on the boundary is automatically carried out by using the integral form of the Schrödinger equation. Furthermore, the error in the reflection coefficient $R_{\vec{\nu}}$ resulting from a variational principle is of the second order compared to the error of the trial function (see Appendix A). Each element of the two determinants in Eq. (4.17) includes integrals of crystal potential and known functions over the reference column. The rank of the determinant $|H_{i,j}|$ with $i, j \neq 1$ in the numerator of Eq. (4.17) is one order less than that of the determinant $|F_{i,j}|$ in the denominator. The rank of $|F_{i,j}|$ is $n$, where $n$ is the number of terms included in the trial function.

This theory shares the advantage with Kambe's,[24] i.e., no Bloch wave expansion is necessary. However, with large numbers of atomic layers involved in the scattering process, it is more convenient to employ Bloch waves.

By using Bloch functions, the integrals appearing in the determinants of Eq. (6.7) for the reflection coefficient of a diffracted beam from a semi-infinite crystal is reduced to a reference column with width $d$, which is the spacing between two identical layers. The rank of the determinant $|F_{i,j}^{g,h}|$ of Eq. (6.7) is $nN$, where $n$ is the number of Bloch waves taken in the trial function and $N$ is the number of known functions into which each Bloch wave is expanded. For example, if we consider four Bloch waves and each Bloch wave is expanded into nine plane waves, the rank of $|F_{i,j}^{g,h}|$ is 36.

When this method is applied directly to LEED problems, elaborate work may be expected for the calculation of the integrals. If the crystal potential can be approximated by periodic spherically symmetric potentials, the problem is simplified to calculating some geometric structure constants as in the KKR band theory of metals[12] and also in Kambe's cellular[11] theory for low-energy electron diffraction. This application will be discussed in the succeeding paper.

On the other hand, this method may also provide a simplified picture for understanding the mechanism of low-energy electron diffraction from crystals by using simple approximate trial wave functions. Even the simple modified Born approximation can bring out interesting results as illustrated in the special case of the Kronig-Penney model in Paper I.[17] Numerical calculations for the three-dimensional modified Born approximation and the general modified Born approximation shall be worthwhile to carry out on a model potential.

This technique may also be extended to the case of a thick crystal consisting of impurity layers on a semi-infinite substrate. This case can be readily treated as the combination of a finite number of layers and a perfect semi-infinite crystal. Namely, the wave function in the impurity region is not expanded into Bloch waves, but the Bloch theorem is employed for the wave function in the substrate. This is discussed in detail in the succeeding paper which will deal with muffin-tin potentials.

When the inelastic scattering process is described by a complex potential, the variational principle presented above is also valid by substituting $V(\vec{r})$ with a complex potential and inserting evanescent waves for the trial functions.

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## APPENDIX A

If $\psi_t$ is a trial function

$$\psi_t(\vec{r}) = \psi(\vec{r}) + \epsilon\chi(\vec{r}) \quad , \tag{A1}$$

where $\epsilon$ is a small quantity and $\psi(\vec{r})$ is the exact wave function, then

$$\tilde{\psi}_t(\vec{r}) = \tilde{\psi}(\vec{r}) + \epsilon\tilde{\chi}(\vec{r}) \quad , \tag{A2}$$

where $\tilde{\psi}(\vec{r})$ is the exact adjoint wave function.

Substituting Eqs. (A1) and (A2) into the variational equation (3.4) yields an approximate reflection coefficient $R_{\vec{\nu}}^t$

$$R_{\vec{\nu}}^t = (-i/2AK_{\vec{\nu}})\{[\int e^{i\vec{k}\cdot\vec{r}}\, V(\vec{r})(\tilde{\psi}(\vec{r}) + \epsilon\tilde{\chi}(\vec{r}))d\vec{r}]\,[\int e^{-i\vec{k}_{\vec{\nu}}\cdot\vec{r}'}\, V(\vec{r}')(\psi(\vec{r}') + \epsilon\chi(\vec{r}'))d\vec{r}']\}/\{\int d\vec{r}\,[\tilde{\psi}(\vec{r})$$

$$+ \epsilon\tilde{\chi}(\vec{r})]\, V(\vec{r})\,[\psi(\vec{r}) + \epsilon\chi(\vec{r}) - \int \mathcal{G}(\vec{r}, \vec{r}')\, V(\vec{r}')(\psi(\vec{r}') + \epsilon\chi(\vec{r}'))d\vec{r}']\} \quad . \tag{A3}$$

The error in the reflection coefficient is

$$\Delta R_{\vec{\nu}} = R^t_{\vec{\nu}} - R$$

$$= \epsilon^2 (-i/2AK_{\vec{\nu}}) \{ [ \int \tilde{\chi}(\vec{r}\,') V(\vec{r}\,') e^{i\vec{k}\cdot\vec{r}\,'} d\vec{r}\,' ] [ \int e^{-i\vec{k}_{\vec{\nu}}\cdot\vec{r}} V(\vec{r}) \chi(\vec{r}) d\vec{r} ]$$

$$- [ \int e^{-i\vec{k}_{\vec{\nu}}\cdot\vec{r}\,'} V(\vec{r}\,') \psi(\vec{r}\,') d\vec{r}\,' ] [ \int \int d\vec{r}\, \tilde{\chi}(\vec{r}) V(\vec{r}) ( \chi(\vec{r}) - \int \mathcal{G}(\vec{r}, \vec{r}\,'') V(\vec{r}\,'') \chi(\vec{r}\,'') d\vec{r}\,'' ) ] \} / \mathfrak{D} = O(\epsilon^2) , \quad \text{(A4)}$$

where $\mathfrak{D}$ is the denominator of Eq. (A3).

The error in $R_{\vec{\nu}}$ is second order compared to the error in the wave functions.

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