only the diagonal element of the Green's function, which is the only one needed in the one-site approximation, but also any element. The procedures are illustrated by reference to an impurity in a "hydrogen metal." Finally, we have discussed the Koster-Slater method in terms of atomic orbitals.

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[†] Present address: Department of Materials Science, Stanford University, Stanford, Calif.

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Transition-Matrix Theory of Low-Energy Electron Diffraction

A. P. Shen
37 Wade Drive, Summit, New Jersey 07901

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A transition-matrix formulation is presented for calculating the scattering amplitude of an elastically scattered beam from a crystal with perfect two-dimensional periodicity in the surface plane. The scattering amplitude is expressed in the transition-matrix expansion for a general potential. When applied to the muffin-tin potential model, Beeby's multiple-scattering low-energy electron diffraction (LEED) theory, Kambe's modified Korringa-Kohn-Rostoker theory, Shen's application of the Shen-Krieger variational LEED theory, and the transition-matrix LEED theory can be transformed to give the identical exact solution of this problem. In analogy to the pseudopotential formalism in the energy-band theory, the scattering amplitude can be written in Born expansions for an effective potential which is, in general, weaker than the crystal potential for the nearly-free-electron model. It is shown that the infinity of the tangent of a phase shift can result in a resonance peak in the reflectance.

I. INTRODUCTION

The diffraction of low-energy electrons (LEED) is an important subject because of its potential as a method for studying the bulk and the surface structure of a crystal. A LEED experiment is performed by allowing a beam of low-energy electrons to interact with the crystal, which is formed by bringing together 10^{22} atoms in one cubic centimeter. It is not possible to solve this entire system of complicated interacting particles exactly by many-body quantum theory. Thus, a few assumptions are essential in the LEED theory. First, no relativistic effect need be taken into account since the energies of the incident electrons are very low ($\lesssim 100$ eV). (Relativistic effects may not be negligible in calculating LEED intensities for materials containing heavy atoms.) Second, the interaction of the incident electrons with the collection of ions and valence electrons is through an averaged crystal potential, i.e., a one-electron approximation is assumed. Third, lattice vibrations are neglected, i.e., the temperature effect is not taken into account. In addition to the above basic assumptions, a few more approximations have been assumed in most of the theoretical LEED work. Since the target crystal has a surface area of the size 10^{16} Å^2, the crystal is assumed to have an infinite surface plane. Consequently, the plane parallel to the crystal surface has perfect two-dimensional periodicity. Finally, the wave function of the incident electrons is assumed to be a monochromatic plane wave.

Recently, a number of theories[1–18] have been proposed for the calculation of LEED reflection intensities. The band-structure-matching formalism[1–9] consists of calculating the total wave function inside the crystal and then matching the wave functions and their derivatives inside and outside the crystal on the surface boundary to obtain the scattering amplitudes of the diffracted beams. The total wave function inside the crystal is written as a superposition of propagating and evanescent Bloch waves with the same energy and the same reduced parallel (to the surface) wave vector as those of the incident electrons, i.e., the parallel wave vectors are different by 2π times the two-dimensional reciprocal lattices lying in the surface plane. The wave function outside the crystal is represented by the sum of the incident and the diffracted plane waves with conservation of energy and reduced parallel wave vector. Usually, the Bloch wave of an infinite crystal is expanded into plane waves whose fast convergence is achieved by employing a pseudopotential[19,20] for the band-structure calculation. However, the pseudopotential theory[21] is basically a nearly-free-electron model (NFE) for the energy-band spectra and it is not applicable to all metals. Furthermore, the band-structure-matching method is difficult in practice to apply to crystals with surface contamination.

A few other theories[11–13,16] which do not require the use of Bloch waves have also been given. The common features of these theories are: (a) They all start from the integral representation of the Schrödinger equation, the Green's-function method, which matches the wave functions inside and outside the crystal automatically. (b) Physically, they are all based on the multiple-scattering theory. (c) All rest on the assumption that the potential is the sum of nonoverlapping spherically symmetric potentials. (d) The structural and the atomic properties are separated in the expression for the scattering amplitude. The structural properties are contained in the structure constants which are functions of the incident energy and the parallel wave vector and need to be calculated once for each type of lattice. The atomic properties are represented by the phase shifts of the spherically symmetric potentials. (e) These theories are most useful in studying crystals with a few layers of foreign atoms. However, when we discuss electron scattering from a semi-infinite crystal, it is found necessary to combine Bloch waves in the Green's-function method.[16–18]

In this paper, we shall apply Beeby and Edward's[22] multiple-scattering theory to investigate LEED problems. However, the formulation here uses reference columns as basic scattering units instead of atomic planes parallel to the surface as used in Beeby's[13] theory. The exact matrix expressions for the scattering amplitude have been given both for a general potential and for the muffin-tin-model potential.

In Secs. IV and V, we shall prove that, for muffin-tin potentials, Beeby's[13] LEED theory, Kambe's[12] modified Korringa-Kohn-Rostoker (KKR) theory, Shen's[16] application of the Shen-Krieger variational LEED theory, and the methods of this paper can all be transformed to give the identical result which is the exact solution of this problem.

In analogy to the pseudopotential formalism in the energy-band theory,[21] we are able to write the scattering amplitude in Born expansions for an effective potential which is, in general, weaker than the crystal potential for the NFE model. The relationship of this effective potential with a pseudopotential is discussed.

The experimental observation indicates sharp fluctuations in the reflection intensities.[23] McRae and Jennings[24] have explained this phenomenon as due to surface resonances. In Sec. VII, we shall show that the infinity in the tangent of a phase shift can result in a reflection intensity peak.

II. TRANSITION-MATRIX FORMULATION

The object of this section is to set up a formalism in which we can treat the LEED problem by using the transition-matrix expansion. The assumption we have made is that the crystal has perfect two-dimensional periodicity in the surface plane. In the direction perpendicular to the surface, the structural and the chemical compositions are arbitrary. Thus the crystal potential has the property

$$V(\vec{r}) = V(\vec{r} + \vec{l}_{\parallel}), \qquad (2.1)$$

where $\vec{l}_{\parallel} = n_1\vec{a}_1 + n_2\vec{a}_2$, with n_1 and n_2 integers, is a two-dimensional lattice vector lying in the plane parallel to the surface. The notations $\vec{a}_1$ and $\vec{a}_2$

are the primitive translation vectors which lie in the surface plane. The crystal potential $V(\vec{r})$ can then be written as the sum of the potentials $V_{\vec{l}_\parallel}(\vec{r})$ centered at each two-dimensional lattice site $\vec{l}_\parallel$:

$$V(\vec{r})=\sum_{\vec{l}_\parallel} V_{\vec{l}_\parallel}(\vec{r}-\vec{l}_\parallel). \tag{2.2}$$

The nonrelativistic one-electron total Hamiltonian is denoted by

$$H=H_0+V(\vec{r}) , \tag{2.3}$$

where H_0 is the kinetic-energy operator

$$H_0=-(\hbar^2/2m)\nabla^2 . \tag{2.4}$$

The stationary solution of the Hamiltonian H is denoted by $\psi(\vec{r})$ whose asymptotic behavior included only the incident wave $e^{i\vec{k}\cdot\vec{r}}$ and the diffracted outgoing waves. The incident plane wave $\phi_{\vec{k}}(\vec{r})=e^{i\vec{k}\cdot\vec{r}}$ has a propagating wave vector $\vec{k}$ and energy $E=\hbar^2k^2/2m$. The Schrödinger equation for $\psi(\vec{r})$ may be written as

$$H\psi(\vec{r})=E\psi(\vec{r}) . \tag{2.5}$$

The stationary solution is also the solution of a scattering integral equation[25]

$$|\psi\rangle=|\phi_{\vec{k}}\rangle+G_0V|\psi\rangle, \tag{2.6}$$

where we have denoted the corresponding vector of the wave function $\phi(\vec{r})=\langle\vec{r}\,|\phi\rangle$ as $|\phi\rangle$. The operator G_0 is the free-electron Green's-function operator of the system defined by[26]

$$G_0=\lim_{\epsilon\to0^+}\frac{1}{E-H_0+i\epsilon} , \quad \epsilon>0 . \tag{2.7}$$

The Green's function $G_0(\vec{r},\vec{r}\,')$ is defined as the matrix representation of the operator G_0[27] with units such that $\hbar^2/2m=1$:

$$\langle\vec{r}\,|G_0|\vec{r}\,'\rangle=-\frac{1}{4\pi}\frac{e^{ik|\vec{r}-\vec{r}\,'|}}{|\vec{r}-\vec{r}\,'|} . \tag{2.8}$$

The advantage of using operators is that they are usually easier in algebraic manipulation than their matrix representations. However, care must be taken when manipulating with singular operators. As a generalization of Eq. (2.7), associated with the Hamiltonian H for an energy E, a function G is defined[28]

$$G=\lim_{\epsilon\to0^+}\frac{1}{E-H+i\epsilon} , \quad \epsilon>0 \tag{2.9}$$

which is the Green's function of the whole system satisfying the relation[29]

$$\begin{aligned} G&=G_0+G_0VG ,\\ G&=G_0+GVG_0 . \end{aligned} \tag{2.10}$$

If we apply $V(1+GV)$ on both sides of Eq. (2.6) and make use of Eqs. (2.6) and (2.10), we obtain the following form for the vector $|\psi\rangle$:

$$|\psi\rangle=(1+G_0T)|\phi_{\vec{k}}\rangle , \tag{2.11}$$

where T is the transition-matrix operator associated with the electron scattering from the whole crystal defined formally by[30]

$$T=V+VGV , \tag{2.12}$$

with the following properties[30]:

$$\begin{aligned} T&=V+TG_0V ,\\ T&=V+VG_0T . \end{aligned} \tag{2.13}$$

Because of the perfect two-dimensional periodicity, the crystal may be described as being composed by identical reference columns. The reference column, first introduced by Kambe,[12] is a column whose cross section is equal to the surface net area $A=|\vec{a}_1\times\vec{a}_2|$ and whose length is equal to the width of the crystal. The transition matrix T associated with the scattering by the crystal thus can be written in terms of the transition matrix associated with scattering of electrons from a reference column by first iterating T with Eq. (2.13) and then substituting Eq. (2.2) to the resulting Born expansions for T[31]:

$$\begin{aligned} T=\sum_{\vec{l}_\parallel}\mathcal{T}_{\vec{l}_\parallel}+\sum_{\vec{l}_\parallel\neq\vec{l}_\parallel'}\mathcal{T}_{\vec{l}_\parallel}G_0\mathcal{T}_{\vec{l}_\parallel'}\\ +\sum_{\substack{\vec{l}_\parallel\neq\vec{l}_\parallel'\\ \vec{l}_\parallel'\neq\vec{l}_\parallel''}}\mathcal{T}_{\vec{l}_\parallel}G_0\mathcal{T}_{\vec{l}_\parallel'}G_0\mathcal{T}_{\vec{l}_\parallel''}+\cdots , \end{aligned} \tag{2.14}$$

where the transition matrix $\mathcal{T}_{\vec{l}_\parallel}$ associated with scattering from a reference column is defined by

$$\mathcal{T}_{\vec{l}_\parallel}=V_{\vec{l}_\parallel}+V_{\vec{l}_\parallel}GV_{\vec{l}_\parallel} , \tag{2.15a}$$

where G is the Green's function of the system with a reference column, and $\mathcal{T}_{\vec{l}_\parallel}$ satisfies the following properties:

$$\mathcal{T}_{\vec{l}_\parallel}=V_{\vec{l}_\parallel}+V_{\vec{l}_\parallel}G_0\mathcal{T}_{\vec{l}_\parallel}, \quad \mathcal{T}_{\vec{l}_\parallel}=V_{\vec{l}_\parallel}+\mathcal{T}_{\vec{l}_\parallel}G_0V_{\vec{l}_\parallel} . \tag{2.15b}$$

We note that the term $\vec{l}_\parallel=\vec{l}_\parallel''$ should be included in the third term of Eq. (2.14). Substituting Eq. (2.14) into Eq. (2.11), it follows that

$$|\psi\rangle=\Big(1+G_0\sum_{\vec{l}_\parallel}\mathcal{T}_{\vec{l}_\parallel}+G_0\sum_{\vec{l}_\parallel\neq\vec{l}_\parallel'}\mathcal{T}_{\vec{l}_\parallel}G_0\mathcal{T}_{\vec{l}_\parallel'}+\cdots\Big)|\phi_{\vec{k}}\rangle . \tag{2.16}$$

For identical reference columns, all the $\mathcal{T}_{\vec{l}_\parallel}$'s are equal and we can denote $\mathcal{T}_{\vec{l}_\parallel}$ by $\mathcal{T}$. By changing coordinates to the two-dimensional lattice sites $\vec{l}_\parallel$ and then summing over all $\vec{l}_\parallel$, we obtain

$$|\psi\rangle=(1+\mathcal{G}(\mathcal{T}+\mathcal{T}\mathcal{G}_r'\mathcal{T}+\cdots))|\phi_{\vec{k}}\rangle . \tag{2.17}$$

The integration in the above equation is taken over a reference column. The structural Green's function $\langle\vec{r}\,|\mathcal{G}|\vec{r}\,'\rangle$ is defined by[12,16]

$$\langle\vec{r}|\mathcal{G}|\vec{r}\,'\rangle$$
$$=\sum_{\vec{l}_\parallel}\langle\vec{r}|G_0|\vec{r}\,'+\vec{l}_\parallel\rangle e^{i\vec{k}_\parallel\cdot\vec{l}_\parallel}$$
$$=-\sum_{\substack{\vec{v}\\ K_{\vec{v}}\neq 0}}\frac{i}{2AK_{\vec{v}}}e^{i(\vec{k}_\parallel+2\pi\vec{v})\cdot(\vec{r}_\parallel-\vec{r}\,'_\parallel)}e^{iK_{\vec{v}}|x-x'|}\,, \quad (2.18)$$

where $\vec{v}=n_1'\vec{b}_1+n_2'\vec{b}_2$, with n_1' and n_2' as integers, is a two-dimensional reciprocal lattice vector in the plane parallel to the surface. $\vec{b}_1$ and $\vec{b}_2$ are the two-dimensional primitive translation reciprocal-lattice vectors with the following conditions:

$$\vec{b}_i\cdot\vec{a}_j=\delta_{ij}\,,\quad i,\ j=1,\ 2\,. \quad (2.19)$$

The symbol $K_{\vec{v}}$ is defined by

$$K_{\vec{v}}=[k^2-(\vec{k}_\parallel+2\pi\vec{v})^2]^{1/2}\,, \quad (2.20)$$

which may be positive real or imaginary depending on whether $k^2>(\vec{k}_\parallel+2\pi\vec{v})^2$ or $k^2<(\vec{k}_\parallel+2\pi\vec{v})^2$. We have denoted $X_\parallel$ and $X_\perp$ as the parallel and the perpendicular (to the surface) components of a vector $\vec{X}$, respectively. The incomplete structural Green's function is defined by

$$\langle\vec{r}|\mathcal{G}_r'|\vec{r}\,'\rangle=\langle\vec{r}|\mathcal{G}|\vec{r}\,'\rangle-\langle\vec{r}|G_0|\vec{r}\,'\rangle$$
$$=\sum_{\vec{l}_\parallel\neq 0}\langle\vec{r}|G_0|\vec{r}\,'+\vec{l}_\parallel\rangle e^{i\vec{k}_\parallel\cdot\vec{l}_\parallel}\,. \quad (2.21)$$

The structural Green's function $\mathcal{G}$ absorbs all the scattering from all the equivalent reference columns. The incomplete structural Green's function $\mathcal{G}_r'$ excludes the term $\vec{l}_\parallel=0$. This omission is fundamental to the theory which uses an expansion in terms of the transition matrix instead of the expansion of the potential V.

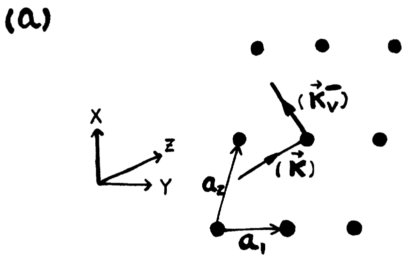
The wave field in the vacuum region far from the crystal is obtained by letting $z\to-\infty$ in Eq. (2.17):

$$|\psi\rangle=|\phi_{\vec{k}}\rangle+\sum_{\vec{v}}R_{\vec{v}}|\phi_{\vec{k}_{\vec{v}}^-}\rangle\,, \quad (2.22)$$

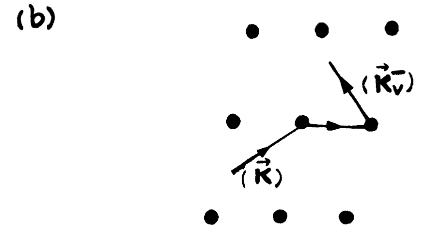
which is the sum of the incident plane wave $e^{i\vec{k}\cdot\vec{r}}$ and all the allowed propagating reflected beams $\phi_{\vec{k}_{\vec{v}}^-}=e^{i\vec{k}_{\vec{v}}^-\cdot\vec{r}}$ in the direction of $\vec{k}_{\vec{v}}^-$ whose components are $(\vec{k}_\parallel+2\pi\vec{v},\ -K_{\vec{v}})$. Each reflected wave has its parallel wave vector different from the incident parallel wave vector $\vec{k}_\parallel$ by 2π times a reciprocal lattice vector $\vec{v}$. This is the consequence of the perfect two-dimensional periodicity in the surface plane. The scattering amplitude is defined by

$$R_{\vec{v}}=\frac{-i}{2AK_{\vec{v}}}\langle\phi_{\vec{k}_{\vec{v}}^-}|\mathcal{T}+\mathcal{T}\mathcal{G}_r'\mathcal{T}+\mathcal{T}\mathcal{G}_r'\mathcal{T}\mathcal{G}_r'\mathcal{T}+\cdots|\phi_{\vec{k}}\rangle\,. \quad (2.23)$$

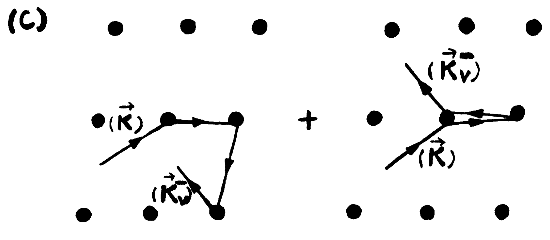
This is the general formula for the scattering amplitude as a power series of the transition matrix $\mathcal{T}$ associated with the entire scattering properties of electrons scattered from a reference column. The various terms in the above equation can be interpreted easily by multiple scattering between reference columns. The first term is the first-order transition amplitude of an electron scattered from the state $e^{i\vec{k}\cdot\vec{r}}$ to the state $e^{i\vec{k}_{\vec{v}}\cdot\vec{r}}$ by simple scattering from the reference columns. The scattering amplitude of an electron scattered by a reference column is shown by Fig. 1(a). The second term represents the total transition amplitude of an electron via double scattering between the reference columns. The mechanism associated with the second-order scattering is shown by Fig. 1(b). Figure 1(b) represents the scattering process that an incident electron is first scattered by a reference column, then the scattered electron propagates to



SINGLE SCATTERING



DOUBLE SCATTERING



TRIPLE SCATTERING

FIG. 1. Diagrams representing the scattering processes associated with the first three terms in Eq. (2.23) in which reference columns are considered as basic scattering units. The diagram shows the front view of the crystal. The dots represent the two-dimensional lattice sites and the solid arrow indicates the direction of the electron propagation. $\vec{a}_1$ and $\vec{a}_2$ are the primitive translation vectors in the surface plane. $(\vec{k})$ and $(\vec{k}_{\vec{v}}^-)$ represent the incident and the diffracted beams, respectively.

another reference column which scatters the electron to the final state $e^{i\vec{k}_{\vec{v}}\cdot\vec{r}}$ outside the crystal. Similarly, each nth-order term represents the transition amplitude of the electron after n sucessive scatterings by the reference columns. The third-order term is represented by Fig. 1(c), which shows two types of triple scatterings between the reference columns.

By manipulating the operators, the perturbation terms in Eq. (2.23) can be summed formally to give the scattering amplitude in a compact matrix inversion form:

$$R_{\vec{v}} = -\frac{i}{2AK_{\vec{v}}}\langle\phi_{\vec{k}_{\vec{v}}}|(\mathcal{T}^{-1}-\mathcal{G}_r')^{-1}|\phi_{\vec{k}}\rangle\,, \qquad (2.24)$$

provided the matrix $\mathcal{T}$ and $\mathcal{G}_r'$ are well behaved. As long as the potential is integrable to obtain $\mathcal{T}$, the scattering amplitude of a diffracted beam in the direction of $\vec{k}_{\vec{v}}$ can be computed by either Eq. (2.23) or Eq. (2.24). We note that besides the perfect two-dimensional periodicity of the crystal, there are no other restrictions imposed on the potential.

III. APPLICATION TO COMPLEX-ATOMIC MULTIPLE LAYERS

In Sec. II, the scattering amplitude is given in terms of the transition matrix associated with the scattering of an electron scattered from a reference column. For LEED, the incident electrons usually penetrate at least a few layers of the crystal; thus, the first task of this problem is to compute the reference column transition matrix $\mathcal{T}$. Kambe[12] has pointed out that for complex-atomic layers, the reference column can be chosen such that the walls of the reference column do not pass through the center of any ion. For a crystal with a finite number of atomic layers, we can label the N ions assigned in the reference column, i.e., the ions whose centers are in the reference column, by the number $\mu = 1, 2, \ldots, N$. The center of the μth ion is located at $\vec{c}_\mu$. Thus, the crystal potential in the reference column can be written as

$$V(\vec{r}) = \sum_\mu V_\mu(\vec{r}-\vec{c}_\mu). \qquad (3.1)$$

Since the potential is not restricted to the muffin-tin model, $V_\mu(r)$ is the potential in the μth polyhedron, which is a primitive cell for monoatomic layers or a Wigner-Seitz-like polyhedron for complex-atomic layers. The reference-column transition matrix $\mathcal{T}$ may be written in terms of the single-center transition matrix t_μ associated with the scattering of an electron scattered by the potential V_μ:

$$\mathcal{T} = \sum_\mu t_\mu + \sum_{\mu\neq\nu} t_\mu G_0 t_\nu + \sum_{\substack{\mu\neq\xi\\ \xi\neq\nu}} t_\mu G_0 t_\xi G_0 t_\nu + \cdots\,, \qquad (3.2)$$

where $\mu, \nu, \xi = 1, 2, \ldots, N$ and the single-center transition matrix t_μ is defined by

$$t_\mu = V_\mu + V_\mu G V_\mu\,, \qquad (3.3a)$$

where G is the Green's function of the system with a single scattering center V_μ, and t_μ satisfies the following conditions:

$$t_\mu = V_\mu + V_\mu G_0 t_\mu\,,$$
$$t_\mu = V_\mu + t_\mu G_0 V_\mu\,. \qquad (3.3b)$$

Equation (3.2) may readily be obtained by substituting Eq. (3.1) into Eq. (2.15) and making use of Eq. (3.3). The calculation of the single-center transition matrix t_μ may be carried out by applying the methods used in collision theories [for example, see M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964), pp. 221–357] for both noncentral and central forces. The latter will be discussed in Sec. IV.

The reference-column transition matrix $\mathcal{T}$ can be computed by using the multiple-scattering series of Eq. (3.2).

The reflection coefficient $R_{\vec{v}}$ can be expressed in terms of the single-center transition matrix t_μ by substituting Eq. (3.2) into Eq. (2.23):

$$\begin{aligned}R_{\vec{v}} = \left(-\frac{i}{2AK_{\vec{v}}}\right)\langle\phi_{\vec{k}_{\vec{v}}}|\Big[\Big(\sum_\mu t_\mu + \sum_{\mu\neq\nu} t_\mu G_0 t_\nu + \cdots\Big)\\ + \Big(\sum_\mu t_\mu + \sum_{\mu\neq\nu} t_\mu G_0 t_\nu + \cdots\Big)\mathcal{G}_r'\Big(\sum_\mu t_\mu + \sum_{\mu\neq\nu} t_\mu G_0 t_\nu + \cdots\Big)\\ + \Big(\sum_\mu t_\mu + \sum_{\mu\neq\nu} t_\mu G_0 t_\nu + \cdots\Big)\mathcal{G}_r'\Big(\sum_\mu t_\mu + \sum_{\mu\neq\nu} t_\mu G_0 t_\nu + \cdots\Big)\\ \times\mathcal{G}_r'\Big(\sum_\mu t_\mu + \sum_{\mu\neq\nu} t_\mu G_0 t_\nu + \cdots\Big) + \cdots\Big]|\phi_{\vec{k}}\rangle\,. \qquad (3.4)\end{aligned}$$

By changing coordinates to the centers of the ions associated in the reference column, i.e., we define the coordinate in the μth polyhedron as $\vec{r}_\mu = \vec{r} - \vec{c}_\mu$, Eq. (3.4) thus becomes

$$\begin{aligned}R_{\vec{v}} = \left(-\frac{i}{2AK_{\vec{v}}}\right)\sum_{\mu,\nu}\langle\phi^{\mu}_{\vec{k}_{\vec{v}}}|\Big(t_\mu\delta_{\mu\nu} + t_\mu\mathcal{G}'^{\mu\nu}t_\nu\\ + \sum_\xi t_\mu\mathcal{G}'^{\mu\xi}t_\xi\mathcal{G}'^{\xi\nu}t_\nu + \cdots\Big)|\phi^{\nu}_{\vec{k}}\rangle\,, \qquad (3.5)\end{aligned}$$

where $\mathcal{G}'^{\mu\nu}$ is defined by

$$\begin{aligned}\langle\vec{r}_\mu|\mathcal{G}'^{\mu\nu}|\vec{r}_\nu'\rangle\\ = \langle\vec{r}_\mu + \vec{c}_\mu|\mathcal{G}^{\mu\nu}|\vec{r}_\nu' + \vec{c}_\nu\rangle - \langle\vec{r}_\mu + \vec{c}_\mu|G_0|\vec{r}_\nu' + \vec{c}_\nu\rangle\delta_{\mu\nu}\\ = \langle\vec{r}|\mathcal{G}|\vec{r}\,'\rangle - \langle\vec{r}|G_0|\vec{r}\,'\rangle\delta_{\mu\nu} \qquad (3.6)\end{aligned}$$

and $|\phi^\mu\rangle$ is defined by

$$\langle\vec{r}_\mu|\phi^\mu\rangle = \langle\vec{r}_\mu + \vec{c}_\mu|\phi\rangle\,. \qquad (3.7)$$

Similar to the discussion given in Sec. II, the various terms of Eq. (3.5) can be interpreted by multiple scattering between different single-scattering forces centered at the centers of the ions. The nth term of Eq. (3.5) represents the nth-order transition amplitude of an incident electron with the wave function $e^{i\vec{k}\cdot\vec{r}}$ scattered to the state $e^{i\vec{k}_{\mp}\cdot\vec{r}}$ in vacuum via n successive scatterings between different single-scattering centers.

IV. APPLICATION TO MUFFIN-TIN POTENTIALS

In this section we apply the transition-matrix formulation to muffin-tin potentials. Since we shall obtain the exact reflection coefficient, it does not make any difference whether we use the expansion in the reference-column transition matrix $\mathcal{T}$ shown by Eq. (2.23) or Eq. (3.4) or we use the expansion in single-center transition matrix t_μ shown by Eq. (3.5). In the muffin-tin potential model, each atom lies at the center of a nonoverlapping sphere within which the potential is spherically symmetric. In the region between the spheres, the potential is a constant. Thus, the potential $V_\mu(\vec{r})$ of Eq. (3.1) satisfies the following conditions:

$$V_\mu(\vec{r}) = V_\mu(r) \text{ is spherically symmetric for } r < r_\mu^c , \qquad V_\mu(\vec{r}) = 0 \quad \text{for } r \geq r_\mu^c , \tag{4.1}$$

where r_μ^c is the radius of the μth potential sphere. For a spherically symmetric potential, the single-center transition matrix t_μ can be expanded into spherical harmonics and it is diagonal in the angular momentum representation:

$$\langle \vec{r}_\mu | t_\mu | \vec{r}_\mu' \rangle = \sum_{L,L'} \langle \vec{r}_\mu | \mathcal{Y}_L \rangle \langle r_\mu | t_l^\mu | r_\mu' \rangle \langle \mathcal{Y}_{L'} | \vec{r}_\mu' \rangle \delta_{LL'} , \tag{4.2}$$

where $\langle \vec{r}_\mu | \mathcal{Y}_L \rangle$ is the spherical harmonics defined by

$$\langle \vec{r}_\mu | \mathcal{Y}_L \rangle = \left[\left(\frac{2l+1}{4\pi} \right) \left(\frac{(l-|m|)!}{(l+|m|)!} \right) \right]^{1/2} P_l^{|m|}(\cos\theta_\mu) e^{im\phi_\mu} , \tag{4.3}$$

with r_μ, θ_μ, and ϕ_μ as the spherical components of $\vec{r}_\mu$ and L indicating the pair of indices l, m. The function $P_l^{|m|}$ is an associated Legendre polynomial.[32] The normalization condition of the spherical harmonics is

$$\langle \mathcal{Y}_{L'} | \mathcal{Y}_L \rangle = \delta_{LL'} . \tag{4.4}$$

The incomplete structural Green's function $\mathcal{G}'^{\mu\nu}$ may be expanded into spherical harmonics[12]:

$$\langle \vec{r}_\mu | \mathcal{G}'^{\mu\nu} | \vec{r}_\nu' \rangle = \sum_{L,L'} \langle \vec{r}_\mu | Lk \rangle \mathcal{G}'^{\mu\nu}_{LL'} \langle L'k | \vec{r}_\nu' \rangle , \tag{4.5}$$

where $\langle \vec{r}_\mu | Lk \rangle$ is defined by

$$\langle \vec{r}_\mu | Lk \rangle = \langle \vec{r}_\mu | \mathcal{Y}_L \rangle \langle r_\mu | j_l k \rangle , \tag{4.6}$$

with $\langle r_\mu | j_l k \rangle$ a spherical Bessel function of argument $r_\mu k$.[33]

The coefficient $\mathcal{G}'^{\mu\nu}_{LL'}$ can be shown as[12]

$$\mathcal{G}'^{\mu\nu}_{LL'} = A^{\mu\nu}_{LL'} + ik\delta_{LL'}\delta_{\mu\nu} . \tag{4.7}$$

The imaginary part comes from the imaginary part of the Green's function $\langle \vec{r}_\mu | G_0 | \vec{r}_\mu' \rangle$ which is diagonal in the angular momentum representation.

$$\langle \vec{r}_\mu | G_0 | \vec{r}_\mu' \rangle = k \sum_{L,L'} \langle \vec{r}_\mu | Lk \rangle \left(\frac{\langle r_\mu' | n_l k \rangle}{\langle r_\mu | j_l k \rangle} - i \right) \delta_{LL'} \langle L'k | \vec{r}_\mu' \rangle , \qquad r_\mu < r_\mu' < r_\mu^c \tag{4.8}$$

where $\langle r_\mu | n_l k \rangle$ is a spherical Neumann function of argument $r_\mu k$.[33] The structure constant $A^{\mu\nu}_{LL'}$ is characteristic of the incident energy, the parallel wave vector $\vec{k}_\parallel$, and the lattice structure, but independent of the potential and the lattice constant.

The plane wave can also be expanded into spherical harmonics[12]:

$$\langle \vec{r}_\mu | \phi^\mu_{\vec{k}} \rangle = \sum_L 4\pi i^l \langle \vec{r}_\mu | Lk \rangle \langle \mathcal{Y}_L | \vec{k} \rangle e^{i\vec{k}\cdot\vec{c}_\mu} \tag{4.9a}$$

and

$$\langle \phi^\mu_{\vec{k}_{\mp}} | \vec{r}_\mu \rangle = \sum_L 4\pi i^{-l} \langle \vec{k}_{\mp} | \mathcal{Y}_L \rangle \langle Lk | \vec{r}_\mu \rangle e^{-i\vec{k}_{\mp}\cdot\vec{c}_\mu} . \tag{4.9b}$$

By substituting Eqs. (4.2), (4.5), and (4.9) into Eq. (3.5), and by integrating over the surface of all the spheres assigned in the reference column, we obtain an exact scattering amplitude in perturbation series:

$$R_{\mp} = -\frac{i}{2AK_{\mp}} \sum_{\substack{L,L' \\ \mu,\nu}} (4\pi)^2 i^{l'-l} \langle \vec{k}_{\mp} | \mathcal{Y}_L \rangle e^{-i\vec{k}_{\mp}\cdot\vec{c}_\mu} \times \left(\langle k | t_l^\mu \rangle \delta_{LL'} \delta_{\mu\nu} + \langle k | t_l^\mu \rangle \mathcal{G}'^{\mu\nu}_{LL'} \langle k | t_{l'}^\nu \rangle + \cdots \right) \times \langle \mathcal{Y}_{L'} | \vec{k} \rangle e^{i\vec{k}\cdot\vec{c}_\nu} , \tag{4.10}$$

where $\langle k | t_l^\mu \rangle$ is the diagonal element of the transition matrix t_μ in the angular momentum representation[34];

$$\langle k | t_l^\mu \rangle = \langle j_l k | t_l^\mu | j_l k \rangle = \langle Lk | t_\mu | Lk \rangle = -\frac{1}{k} \sin\eta_l^\mu \, e^{i\eta_l^\mu} , \tag{4.11}$$

where η_l^μ is the lth phase shift of the μth muffin tin.

The geometric series in Eq. (4.10) can be summed formally to obtain

$$R_{\mp} = -\frac{i}{2AK_{\mp}} \sum_{\substack{L,L' \\ \mu,\nu}} (4\pi)^2 i^{l'-l} e^{-i\vec{k}_{\mp}\cdot\vec{c}_\mu} \langle \vec{k}_{\mp} | \mathcal{Y}_L \rangle \times \{ (t^{-1} - \mathcal{G}')^{-1} \}^{\mu\nu}_{LL'} \langle \mathcal{Y}_{L'} | \vec{k} \rangle e^{i\vec{k}\cdot\vec{c}_\nu} . \tag{4.12}$$

With the aid of Eq. (4.11), the matrix $(t^{-1} - \mathcal{G}')$ can be written as

$$\underline{\mathrm{F}} = (t^{-1} - \mathcal{G}') = -\,(A^{\mu\nu}_{LL'} + k\cot\eta^{\mu}_{l}\,\delta_{LL'}\,\delta_{\mu\nu}) \;. \qquad (4.13)$$

If we define a column matrix $\underline{\mathrm{D}}$ with the element

$$D^{\mu}_{L} = 4\pi\, e^{i\vec{k}\cdot\vec{c}_{\mu}}\, i^{l}\langle \mathcal{Y}_{L}|\vec{k}\rangle \qquad (4.14)$$

and a row matrix $\underline{\mathrm{E}}$ with the element

$$E^{\mu}_{L} = 4\pi\, e^{-i\vec{k}_{\vec{v}}^{-}\cdot\vec{c}_{\mu}}\,(i)^{-l}\langle \vec{k}_{\vec{v}}^{-}|\mathcal{Y}_{L}\rangle \;, \qquad (4.15)$$

then by making use of Eqs. (4.13)–(4.15), Eq. (4.12) can be rewritten as

$$R_{\vec{v}} = -\,\frac{i}{2AK_{\vec{v}}}\,\underline{\mathrm{E}}\,\underline{\mathrm{F}}^{-1}\underline{\mathrm{D}} \;. \qquad (4.16)$$

If we rearrange terms in Eq. (4.10), we can easily obtain

$$\begin{aligned} R_{\vec{v}} = \left(-\frac{i(4\pi)^2}{2AK_{\vec{v}}}\right) \sum_{L,L'} i^{l'-l}\langle \vec{k}_{\vec{v}}^{-}|\mathcal{Y}_{L}\rangle \Big(& \sum_{\mu} e^{i(\vec{k}-\vec{k}_{\vec{v}}^{-})\cdot\vec{c}_{\mu}}\,\tau^{\mu}_{LL'} \\ & + \sum_{\mu\neq\nu} e^{-i\vec{k}_{\vec{v}}^{-}\cdot\vec{c}_{\mu}}\,\tau^{\mu}_{LL_1}\,\mathcal{G}^{\mu\nu}_{L_1L_2}\,\tau^{\nu}_{L_2L'}\,e^{i\vec{k}\cdot\vec{c}_{\nu}} \\ & + \sum_{\substack{\mu\neq\xi\\ \xi\neq\nu}} e^{-i\vec{k}_{\vec{v}}^{-}\cdot\vec{c}_{\mu}}\,\tau^{\mu}_{LL_1}\,\mathcal{G}^{\mu\xi}_{L_1L_2}\,\tau^{\xi}_{L_2L_3}\,\mathcal{G}^{\xi\nu}_{L_3L_4}\,\tau^{\nu}_{L_4L'}\,e^{i\vec{k}\cdot\vec{c}_{\nu}} + \cdots \Big) \\ & \times \langle \mathcal{Y}_{L'}|\vec{k}\rangle \;, \end{aligned} \qquad (4.17)$$

where $\tau^{\mu}_{LL'}$ is the element of the matrix τ_{μ} (the nomenclature is the same as that used by Beeby[13]) in angular momentum representation:

$$\tau^{\mu}_{LL'} = \{\tau_{\mu}\}_{LL'} = \{(t^{-1} - \mathcal{G}')^{-1}\}^{\mu\mu}_{LL'} \;. \qquad (4.18)$$

The matrix τ_{μ} represents the total scattering operator for an electron scattered from a single monoatomic subplane μ with the perfect two-dimensional periodicity.

Equation (4.17) is equivalent to that obtained by Beeby[13] except that of the factor $1/K_{\vec{v}}$. This difference arises from the assumption of Beeby's theory that the target crystal is small compared to the distance to the observation point. The asymptotic wave function in his theory is, therefore, a spherical wave. Without making this approximation, our method has found the diffracted beams in the vacuum are propagating and exponentially decaying plane waves by assuming the perfect two-dimensional periodicity. Thus, our method not only provides an exact solution but also can be extended readily to the calculation of the exponentially decaying waves near the crystal surface.

V. DIRECT ALGEBRAIC APPROACH

In Sec. IV, we have expressed the reflection coefficient in the explicit matrix form of Eq. (4.16) by formally summing up the infinite perturbation series of Eq. (4.10). However, the convergence of the perturbation series is not proved. In this section we shall obtain the same exact result by a direct algebraic derivation which justifies the validity of the formal summation.

Also in this section we shall show that under the same assumptions, the results given in Sec. IV is identical to those obtained by Kambe[12] and by Shen.[16] Since the crystal possesses perfect two-dimensional periodicity in the surface plane, the Bloch theorem[35] requires the corresponding two-dimensional periodicity for the wave function in the crystal:

$$\langle \vec{r} + \vec{l}_{\parallel}|\psi\rangle = e^{i\vec{k}_{\parallel}\cdot\vec{l}_{\parallel}}\langle \vec{r}|\psi\rangle \;. \qquad (5.1)$$

Substituting Eq. (5.1) into Eq. (2.6) and summing over all the two-dimensional lattice vectors $\vec{l}_{\parallel}$, we obtain

$$|\psi\rangle = |\phi^{+}_{\vec{k}}\rangle + \mathcal{G}\,V|\psi\rangle \;. \qquad (5.2)$$

By taking $z \to -\infty$ in Eq. (5.2), we again obtain the wave function in the far left region from the crystal as expressed in Eq. (2.22):

$$|\psi\rangle = |\phi^{+}_{\vec{k}}\rangle + \sum_{\vec{v}} R_{\vec{v}}\, e^{i\vec{k}_{\vec{v}}\cdot\vec{r}} \;, \qquad (5.3)$$

where the scattering amplitude is now expressed in terms of the potential,

$$R_{\vec{v}} = \langle \phi^{-}_{\vec{k}_{\vec{v}}}|V|\psi\rangle(-i/2AK_{\vec{v}}) \;. \qquad (5.4)$$

The integration is over a reference column. We then combine Eqs. (5.2) and (5.4) to make $R_{\vec{v}}$ appear explicitly in Eq. (5.2):

$$|\psi\rangle = |\phi^{+}_{\vec{k}}\rangle\,\frac{-i/2AK_{\vec{v}}}{R_{\vec{v}}}\,\langle \phi^{-}_{\vec{k}_{\vec{v}}}|V|\psi\rangle + \mathcal{G}\,V|\psi\rangle \;. \qquad (5.5)$$

By using the properties of Eqs. (3.1) and (4.1), we can change coordinates and rearrange terms to obtain

$$\begin{aligned} (1 - G_0 V_{\mu})|\psi^{\mu}\rangle = \sum_{\nu=1}^{N} \Big\{ & |\phi^{\mu}_{\vec{k}}\rangle\,\frac{(-i)}{R_{\vec{v}}\,2AK_{\vec{v}}} \\ & \times \langle \phi^{\nu}_{\vec{k}_{\vec{v}}^{-}}| + \mathcal{G}'^{\mu\nu} \Big\}\, V_{\nu}|\psi^{\nu}\rangle \;. \end{aligned} \qquad (5.6)$$

We operate the single-center transition matrix t_{μ} defined by Eq. (3.3) on both sides of Eq. (5.6); thus it follows that

$$V_{\mu}|\psi^{\mu}\rangle = \sum_{\nu=1}^{N} \Big\{ t_{\mu}|\phi^{\mu}_{\vec{k}}\rangle\,\frac{(-i)}{R_{\vec{v}}\,2AK_{\vec{v}}}$$

$$\times \langle \phi_{\vec{k}_{\mathbf{g}}^{-}}^{\nu} | + t_\mu \mathcal{G}'^{\mu\nu} \Big\} V_\nu | \psi^\nu \rangle \;. \qquad (5.7)$$

With the aid of Eqs. (4.2), (4.5), and (4.9), we obtain a set of linear equations:

$$V_\mu | \psi^\mu \rangle = \sum_{\nu=1}^{N} \sum_{L,L'} t_\mu | Lk \rangle \left(\frac{-i(4\pi)^2 i^{l-l'}}{2R_{\mathbf{g}} A K_{\mathbf{g}}} \langle \mathcal{Y}_L | \vec{k} \rangle \langle \vec{k}_{\mathbf{g}}^{-} | \mathcal{Y}_{L'} \rangle e^{i(\vec{k}\cdot\vec{c}_\mu - \vec{k}_{\mathbf{g}}^{-}\cdot\vec{c}_\nu)} + \mathcal{G}'^{\mu\nu}_{LL'} \right) \langle L'k | V_\nu | \psi^\nu \rangle \;. \qquad (5.8)$$

We then operate $\langle Lk | \vec{r}_\mu \rangle$ on both sides of the above equation and it becomes

$$\sum_{L',\nu} \left[\delta_{\mu\nu} \delta_{LL'} - \left(\langle Lk | t_\mu | Lk \rangle \frac{-i(4\pi)^2 i^{l-l'}}{2AK_{\mathbf{g}} R_{\mathbf{g}}} e^{i(\vec{k}\cdot\vec{c}_\mu - \vec{k}_{\mathbf{g}}^{-}\cdot\vec{c}_\nu)} \langle \mathcal{Y}_L | \vec{k} \rangle \langle \vec{k}_{\mathbf{g}}^{-} | \mathcal{Y}_{L'} \rangle + \mathcal{G}'^{\mu\nu}_{LL'} \right) \right] \langle L'k | V_\nu | \psi^\nu \rangle = 0 \;. \qquad (5.9)$$

In order to have nontrivial solutions for the set of linear equations, the determinant of the coefficient of $\langle L'k | V_\nu | \psi^\nu \rangle$ must vanish:

$$\det \left| \left(\langle Lk | t_\mu | Lk \rangle^{-1} \delta_{\mu\nu} \delta_{LL'} - \mathcal{G}'^{\mu\nu}_{LL'} \right) - \frac{(-i)(4\pi)^2 i^{l-l'}}{2AK_{\mathbf{g}} R_{\mathbf{g}}} \langle \mathcal{Y}_L | \vec{k} \rangle \langle \vec{k}_{\mathbf{g}}^{-} | \mathcal{Y}_{L'} \rangle e^{i(\vec{k}\cdot\vec{c}_\mu - \vec{k}_{\mathbf{g}}^{-}\cdot\vec{c}_\mu)} \right| = 0 \;. \qquad (5.10)$$

The matrix element of the first term is identical to that which appears in the denominator of Eq. (4.16). Equation (5.10) may be written in the following form with the aid of Eqs. (4.13), (4.14), and (4.15):

$$\det \left| F_{LL'}^{\mu\nu} - \frac{(-i)}{2AK_{\mathbf{g}} R_{\mathbf{g}}} D_L^\mu E_{L'}^\nu \right| = 0 \;. \qquad (5.11)$$

This is identical to that obtained by Shen's[16] application of the Shen-Krieger variational principle. In the Appendix we shall show that the same determinantal equation can be obtained by Kambe's LEED theory.

Now if we go back to Eq. (5.9) and write $\langle Lk | V_\mu | \psi^\mu \rangle$ as C_L^μ which is an element of the column matrix $\underline{C}$, Eq. (5.9) then becomes

$$\underline{F}\,\underline{C} = - \frac{i}{2AK_{\mathbf{g}} R_{\mathbf{g}}} \beta \underline{D} \;, \qquad (5.12)$$

where

$$\beta = \underline{E}\,\underline{C} \;. \qquad (5.13)$$

If we suppose the matrix F has an inversion $\underline{F}^{-1}$, we can operate $\underline{F}^{-1}$ on Eq. (5.13) and then operate $\underline{E}$ on the resulting equation to obtain[36]

$$R_{\mathbf{g}} = \frac{-i}{2AK_{\mathbf{g}}} \underline{E}\,\underline{F}^{-1} \underline{D} \;, \qquad (5.14)$$

which is identical to Eq. (4.16).

This completes the proof that for a finite number of layers with muffin-tin potentials, Beeby's multiple-scattering LEED theory,[13] Kambe's modified KKR LEED theory,[12] Shen's application of the Shen-Krieger variational method,[16] and the methods presented in this paper all give the same exact solution and can be transformed into one another.

VI. NEARLY-FREE-ELECTRON CASE

The band structures of many metals and semiconductors are nearly-free-electron band structures. This free-electron-like nature suggests the possibility of using perturbation theory for the calculation of the energy-band spectrum and leads to the introduction of the pseudopotential theory.[37] By constructing a pseudopotential which is weak due to the effect of adding a negative potential to the true crystal potential, the same band structure can be obtained. In this section we shall show that corresponding to the pseudopotential theory for the band structure calculation, the scattering amplitude $R_{\mathbf{g}}$ of LEED may be written in Born expansions for an effective potential which is weak compared to the crystal potential.

By substituting Eq. (3.6) into Eq. (3.5) and by regrouping terms in the resulting equation, it follows that

$$R_{\mathbf{g}} = - \frac{i}{2AK_{\mathbf{g}}} \sum_{\mu,\nu} \{ \langle \phi_{\vec{k}_{\mathbf{g}}^{-}}^{\mu} | \Gamma_\mu \delta_{\mu\nu} + \Gamma_\mu \mathcal{G}^{\mu\nu} \Gamma_\nu + \cdots | \phi_{\vec{k}}^{\nu} \rangle \} \;, \qquad (6.1)$$

where the operator Γ_μ is defined by[38]

$$\Gamma_\mu = (t_\mu^{-1} + G_0)^{-1} \;. \qquad (6.2)$$

For spherically symmetric potentials, the explicit plane-wave representation of t_μ^{-1} and G_0 are given by Eqs. (4.8) and (4.11), respectively. Since both t_μ^{-1} and G_0 are diagonal in the angular momentum representation, Γ_μ is also diagonal in the angular momentum representation. We can expand Γ_μ in spherical harmonics:

$$\langle \vec{r} | \Gamma_\mu | \vec{r}\,' \rangle = \sum_L \langle r | \Gamma_l^\mu | r' \rangle \langle \hat{r} | \mathcal{Y}_L \rangle \langle \mathcal{Y}_L | \hat{r}' \rangle \;. \qquad (6.3)$$

The diagonal element of Γ_μ in angular momentum representation is defined by

$$\Gamma^{\mu}_{LL'} = \langle j_l k | \Gamma^{\mu}_{l} | j_l k \rangle \delta_{LL'} = \langle k | \Gamma^{\mu}_{l} \rangle \delta_{LL'} = -(1/k) \tan\eta'^{\mu}_{l} \delta_{LL'} , \tag{6.4}$$

where the cotangent of the modified phase shift η'^{μ}_{l} is defined by[39]

$$\cot\eta'^{\mu}_{l} = \cot\eta^{\mu}_{l} - \frac{\langle r^{\mu}_{l} | n_l k\rangle}{\langle r^{\mu}_{l} | j_l k\rangle} = \frac{\langle r^{\mu}_{l} | j_l k \rangle - \langle r^{\mu}_{l} | n_l k\rangle \tan\eta^{\mu}_{l}}{\tan\eta^{\mu}_{l} \langle r^{\mu}_{l} | j_l k \rangle} \tag{6.5}$$

with r^{μ}_{l} chosen between the interval $(0, r^{c}_{\mu})$.

Now if we define a function $|\psi_e\rangle$ by

$$\langle \vec{r} | \psi_e \rangle = \langle \vec{r} | \phi_k \rangle + \langle \vec{r} | \mathcal{G} \Gamma | \psi_e \rangle , \tag{6.6}$$

where Γ is an effective potential for a reference column,

$$\Gamma = \sum_{\mu} \Gamma_\mu , \tag{6.7}$$

then $|\psi_e\rangle$ is a solution of the Schrödinger equation

$$H_e \psi_e = E \psi_e , \tag{6.8}$$

where the effective Hamiltonian is defined by

$$H_e = H_0 + \sum_{\vec{l}_{\parallel}} \Gamma(\vec{r} - \vec{l}_{\parallel}) . \tag{6.9}$$

With the aid of Eq. (6.6), Eq. (6.1) may be written as

$$R_{\vec{g}} = -\frac{i}{2AK_{\vec{g}}} \langle \phi_{\vec{k}_{\vec{g}}^{-}} | \Gamma | \psi_e \rangle . \tag{6.10}$$

If we compare the above equation with Eq. (5.4), we see that the scattering amplitude $R_{\vec{g}}$ is now expressed in terms of the effective potential Γ and the effective wave function $|\psi_e\rangle$. Thus Eq. (6.1) is in Born expansions for an effective potential Γ.

By making use of Eqs. (6.3) and (6.4), it follows immediately from Eq. (6.1) that

$$R_{\vec{g}} = -\frac{i}{2AK_{\vec{g}}} (4\pi)^2 \sum_{\substack{L,L' \\ \mu,\nu}} e^{-\vec{k}_{\vec{g}}^{-} \cdot \vec{c}_\mu} i^{-l} \langle \vec{k}_{\vec{g}}^{-} | \mathcal{Y}_L \rangle \times (\Gamma^{\mu}_{LL} \delta_{\mu\nu} \delta_{LL'} + \Gamma^{\mu}_{LL} \mathcal{G}^{\mu\nu}_{LL'} \Gamma^{\nu}_{L'L'} + \cdots) \times i^{l'} \langle \mathcal{Y}_{L'} | \vec{k} \rangle e^{i\vec{k} \cdot \vec{c}_\nu} , \tag{6.11}$$

where

$$\mathcal{G}^{\mu\nu}_{LL'} = A^{\mu\nu}_{LL'} + k \frac{\langle r^{\mu}_{l} | n_l k \rangle}{\langle r^{\mu}_{l} | j_l k \rangle} \delta_{LL'} \delta_{\mu\nu} .$$

We note that r^{μ}_{l} is chosen according to the r^{μ}_{l} in Eq. (6.5).

The ratio $\langle r^{\mu}_{l} | n_l k \rangle / \langle r^{\mu}_{l} | j_l k \rangle$ becomes very large after l is larger than 2 or 3.[38] Thus, $\tan\eta'^{\mu}_{l}$ is small for l larger than 2 or 3, no matter what value η^{μ}_{l} is. This may be a very powerful factor for fast convergence of the Born expansions in Eq. (6.11).

In the case where $\tan\eta^{\mu}_{l}$ is small through the energy range considered for LEED problems, $\tan\eta'^{\mu}_{l}$ remains small except when $\langle r^{\mu}_{l} | j_l k \rangle - \langle r^{\mu}_{l} | n_l k \rangle \tan\eta^{\mu}_{l}$ is very small. However, by adjusting the value of r^{μ}_{l}, $\langle r^{\mu}_{l} | j_l k \rangle - \langle r^{\mu}_{l} | n_l k \rangle \tan\eta^{\mu}_{l}$ can be avoided to be near zero.[39] Thus,

$$\tan\eta'^{\mu}_{l} \simeq \tan\eta^{\mu}_{l} \simeq \sin\eta^{\mu}_{l} . \tag{6.12}$$

For small $\tan\eta^{\mu}_{l}$, the phase shift may be obtained by the Born approximation[40]

$$\tan\eta^{\mu}_{l} = -k \langle j_l k | U^{\mu}_{l} | j_l k \rangle , \tag{6.13}$$

where $\langle r_\mu | U^{\mu}_{l} | r'_\mu \rangle$ is the spherical component l of a pseudopotential[40];

$$\langle r_\mu | U^{\mu}_{l} | r'_\mu \rangle = \frac{\langle r_\mu | V_\mu \rangle}{r_\mu r'_\mu} \delta(r_\mu - r'_\mu) - \sum_{\alpha} \langle r | V | \chi^{\mu}_{l\alpha} \rangle \langle \chi^{\mu}_{l\alpha} | r' \rangle , \tag{6.14}$$

with $|\chi^{\mu}_{l\alpha}\rangle$ the radial wave functions of the μth atomic core state of momentum l. The sum is over all core states α.

If we take only the first-order terms in Eq. (6.11) and substitute Eq. (6.13) for $\tan\eta^{\mu}_{l}$, we shall obtain

$$R_{\vec{g}} = -\frac{i}{2AK_{\vec{g}}} (4\pi) \sum_{\mu,l} e^{-i\vec{k}_{\vec{g}}^{-} \cdot \vec{c}_\mu} (2l+1) P_l(\vec{k} \cdot \vec{k}_{\vec{g}}^{-} / k^2) \times \langle j_l k | U^{\mu}_{l} | j_l k \rangle e^{i\vec{k} \cdot \vec{c}_\mu} = \sum_{\mu} e^{i(\vec{k} - \vec{k}_{\vec{g}}^{-}) \cdot \vec{c}_\mu} \langle \phi^{\mu}_{\vec{k}_{\vec{g}}^{-}} | U_\mu | \phi^{\mu}_{\vec{k}} \rangle \left(-\frac{i}{2AK_{\vec{g}}} \right) , \tag{6.15}$$

where P_l is a Legendre polynomial and $\langle \vec{r}_\mu | U_\mu | \vec{r}_\mu{}' \rangle$ is a pseudopotential defined by[40]

$$\langle \vec{r}_\mu | U_\mu | \vec{r}'_\mu \rangle = \langle \vec{r}_\mu | V_\mu \rangle \delta \langle \vec{r}_\mu - \vec{r}'_\mu \rangle - \sum_{L,\alpha} \langle \vec{r}_\mu | V_\mu | \chi^{\mu}_{L\alpha} \rangle \langle \chi^{\mu}_{L\alpha} | \vec{r}'_\mu \rangle , \tag{6.16}$$

whose spherical components are $\langle r_\mu | U^{\mu}_{l} | r'_\mu \rangle$ and the sum is over all core states $|\chi^{\mu}_{L\alpha}\rangle$, which is defined by

$$\langle \vec{r}_\mu | \chi^{\mu}_{L\alpha} \rangle = \langle r_\mu | \chi^{\mu}_{l\alpha} \rangle \langle \vec{r}_\mu | \mathcal{Y}_L \rangle . \tag{6.17}$$

Equation (6.15) is the first-order Born approximation for a pseudopotential. We note that it is accurate only to the first order in $\tan\eta^{\mu}_{l} \ll 1$. To this order, $\tan\eta^{\mu}_{l} \simeq \sin\eta^{\mu}_{l}$, Eq. (6.15) is also equivalent to that obtained by taking the first-order terms in Eq. (4.10):

$$R_{\vec{v}}=\left(\frac{i(4\pi)}{2AK_{\vec{v}}k}\right)\sum_{\mu,l}e^{i(\vec{k}-\vec{k}_{\vec{v}}^{-})\cdot\vec{c}_{\mu}}(2l+1)$$
$$\times P_l(\vec{k}\cdot\vec{k}_{\vec{v}}^{-}/k^2)\sin\eta_l^{\mu}\,e^{i\eta_l^{\mu}}\,,\qquad(6.18)$$

which is just the pseudokinematic theory.[12]

McRae[11] and Watts[10] have shown that the Born approximation does not predict the secondary Bragg peaks arising from multiple scatterings between identical atomic planes. For the investigation of secondary Bragg peaks, it may be necessary to include higher-order terms in Eq. (6.11).

VII. RESONANCE CASE

In the case where $\tan\eta_l^{\mu}$ passes through an infinity in the incident electron energy range for LEED, Γ_{LL}^{μ} also has a corresponding infinity at the resonance energy despite the adjustment of r_l^{μ}.[39] It follows from Eq. (6.11) that the singularity in the matrix element Γ_{LL}^{μ} leads to a peak in the reflectance. It seems that Eq. (5.14) is a more suitable formula for calculating the LEED intensities in this case since the matrix involves the small value of $\cot\eta_l^{\mu}$ at the resonance energy. The consequences of the resonance on the scattering amplitude can be estimated only by detailed investigation. However, for illustration purposes, we consider the simple case of a pseudokinematic theory with resonances. For simplicity we assume the crystal is monoatomic and there is only one resonance in the energy range discussed here. Thus the phase shift can be written as[39]

$$\tan\eta_l\cong\tan\eta_l''+\frac{W}{E_0-E}\,\delta_{l\lambda}\,,\qquad(7.1)$$

where E_0 is the resonance energy and $\tan\eta_l''$ is a small value defined by

$$\tan\eta_l''=-k\langle j_l k|\,U_l\,|j_l k\rangle\,.\qquad(7.2)$$

W is the width of the resonance and is defined by

$$W=k\langle j_\lambda k|\,V\,|\Phi_\lambda\rangle\,,\qquad(7.3)$$

where $|\Phi_\lambda\rangle$ is the resonant function satisfying

$$\left(-\frac{1}{r^2}\,\nabla r^2\nabla+V+\frac{\lambda(\lambda+1)}{r^2}-E_0\right)|\Phi_\lambda\rangle=0,\qquad(7.4)$$

with the following boundary conditions:

$$\langle r|\nabla|\ln\Phi_\lambda\rangle_{r=r^c}=\langle r|\nabla|\ln(n_l k)\rangle|_{r=r^c}\,.\qquad(7.5)$$

The symbol ∇ means d/dr.

The second term in Eq. (7.1) is also very small except when the incident energy is near the resonant energy E_0.

By substituting Eq. (7.1) into Eq. (6.18), we obtain

$$R_{\vec{v}}=\frac{i}{2AK_{\vec{v}}k}\,(4\pi)\Bigg\{\sum_{\mu,l}e^{i(\vec{k}-\vec{k}_{\vec{v}}^{-})\cdot\vec{c}_{\mu}}\,(2l+1)\,P_l\,(\vec{k}\cdot\vec{k}_{\vec{v}}^{-}/k^2)$$
$$\times\sin\eta_l''\,e^{i\eta_l''}-\sum_{\mu}e^{i(\vec{k}-\vec{k}_{\vec{v}}^{-})\cdot\vec{c}_{\mu}}\,(2\lambda+1)\,P_\lambda\,(\vec{k}\cdot\vec{k}_{\vec{v}}^{-}/k^2)$$
$$\times W/(E-E_0+iW)\Bigg\}\,,\qquad(7.6)$$

which is the pseudokinematic theory with a resonance. Near the resonant energy E_0 there is a peak in the reflectance.

VIII. DISCUSSION

The method outlined in this paper provides a general and fundamental theory for the calculation of LEED intensities. The scattering amplitude of the diffracted beam in the direction of $\vec{k}_{\vec{v}}^{-}$ is expressed in power series of the reference-column transition matrix $\mathcal{T}$ by Eq. (2.23). The method of considering reference columns as basic scattering units is probably advantageous in dealing with systems which favor strong scattering in the reference columns but relatively weak scattering between the reference columns. One possible example of these systems is the system of normally incident electrons on a crystal with closely packed atoms in the normal direction to the surface.

The calculation of the reference-column transition matrix $\mathcal{T}$ by using Eq. (3.2) may turn out to be complicated. However, the possibility of obtaining approximate solutions for $\mathcal{T}$ should be studied further.

The exact reflection coefficient is also expressed in the single-center transition matrix t_μ by Eq. (3.5). Since the crystal is not restricted to the muffin-tin model, Eqs. (2.23) and (3.5) may be applied to overlapping ionic potentials. The method proposed here also shares the advantage with other multiple-scattering theories,[12,13,16] i.e., no Bloch-wave expansion is required. As a result, this method is extremely useful in studying crystals with impurity layers. Furthermore, the perturbation expression is capable of giving a clearer physical picture for the electron scattering processes. The other advantage of this transition-matrix formalism is that no wave function and energy band need be calculated.

Equation (4.16) is the expression for the scattering amplitude in a compact matrix form for the case of muffin-tin potentials. The elements of the matrix $\underline{F}$ are expressed in terms of the structure constants $A_{LL'}^{\mu\nu}$ and the tangent of the phase shifts $\tan\eta_l^{\mu}$. The structure constants, which are functions of the incident energy E and the parallel wave vector $\vec{k}_{\parallel}$, are characteristic of the lattice structure but independent of the potential and the lattice constants. They need to be calculated once for each type of lattice structure and they may be calculated according to Kambe's transformations.[12] Since the phase shifts appear in the tangential form, the scattering amplitude does not change as η_l^μ is reduced by modulo 2π. This has the same cancellation effect as a repulsive potential added to the crystal potential to form the pseudopotential in cancelling the oscillations for the wave function far from the core. The phase shifts can easily be calculated by numerical integration or by WKB method.[41] The dimension of the matrix $\underline{F}$ depends on the number of atoms assigned in the reference column and on the number of $\tan\eta_l^\mu$ which are nonzero. If there are N atoms assigned in the reference column and $l_\mu + 1$ phase shifts need to be considered, the dimension of the matrix $\underline{F}$ is $N(l_\mu+1)^2$. However, the symmetry of the incident wave vector $\vec{k}$ and the crystal structure can reduce the dimension of the matrix considerably.[12,16]

Since the calculation for the structure constants requires much computational time, it is desirable to find a way to obtain the approximate structure constants by a method which is analogous to that for the approximate structure constants used in energy-band calculations.[40]

Equation (6.11) expresses the scattering amplitude in Born expansions for an effective potential which is weak when $\tan\eta_l^\mu$'s are small and favors fast convergence. This is an analogy to the pseudopotential formulation for the energy-band calculation. Since the representation in phase shifts can eliminate the difficulty of calculating the pseudopotential from core states, this method is simpler than the pseudopotential energy-band-matching formalism.[19,20]

In the case when there are virtual resonances in $\tan\eta_l^\mu$, Eq. (4.16) seems more suitable for use. One kind of the surface resonance[24] is identified by Eq. (7.6) as arising from the virtual resonance in $\tan\eta_l^\mu$.

APPENDIX: DERIVATION OF EQ. (5.11) BY KAMBE'S MODIFIED KKR METHOD

We start with Eq. (5.5) for the wave function with the scattering amplitude $R_{\mp\vec{v}}$ appearing explicitly:

$$|\psi\rangle = |\phi_{\vec{k}}\rangle \frac{-i}{2AK_{\mp\vec{v}}R_{\mp\vec{v}}} \langle\phi_{\vec{k}_{\mp\vec{v}}}^{-}|V|\psi\rangle + \mathcal{G}\,V|\psi\rangle . \qquad \text{(A1)}$$

This is a self-consistent solution for $|\psi\rangle$.

With the aid of the Schrödinger equation given by Eq. (2.5) and by applying the Green's theorem,[42] the volume integration in Eq. (A1) may be transformed into surface integrations[12]:

$$|\psi\rangle = |\phi_{\vec{k}}\rangle \frac{-i}{2AK_{\mp\vec{v}}R_{\mp\vec{v}}} \Big((\langle\phi_{\vec{k}_{\mp\vec{v}}}^{-}|\partial_{r'}\psi\rangle - \langle\partial_{r'}\phi_{\vec{k}_{\mp\vec{v}}}^{-}|\psi\rangle)$$

$$+ (\mathcal{G}|\partial_{r'}\psi\rangle - \partial_{r'}\mathcal{G}|\psi\rangle)\Big) , \qquad \text{(A2)}$$

where the symbol ∂_r denotes $\partial/\partial r$, and the surface integration is taken over all the surfaces of the muffin-tin potentials assigned in the reference column.

By changing coordinates to the centers of the atoms assigned in the reference column, Eq. (A2) may be rewritten as

$$|\psi^\mu\rangle = \sum_\nu |\phi_{\vec{k}}^\mu\rangle \frac{-i}{2AK_{\mp\vec{v}}R_{\mp\vec{v}}} \Big((\langle\phi_{\vec{k}_{\mp\vec{v}}}^{\nu -}|\partial_{r_\nu}\psi^\nu\rangle$$

$$- \langle\partial_{r_\nu}\phi_{\vec{k}_{\mp\vec{v}}}^{\nu -}|\psi^\nu\rangle)_{r_\nu=r_\nu^c} + (\mathcal{G}^{\mu\nu}|\partial_{r_\nu}\psi^\nu\rangle$$

$$- \partial_{r_\nu}\mathcal{G}^{\mu\nu}|\psi^\nu\rangle)_{r_\nu=r_\nu^c}\Big) . \qquad \text{(A3)}$$

For muffin-tin potentials, both the wave function $|\psi^\mu\rangle$ and the structural Green's function $\mathcal{G}^{\mu\nu}$ may be expanded into spherical harmonics[12]:

$$|\psi^\mu\rangle = \sum_L \gamma_L^\mu \langle r_\mu|R_l^\mu\rangle\langle\vec{r}_\mu|\mathcal{Y}_L\rangle , \qquad \text{(A4)}$$

where γ_L^μ is the expansion coefficient, and

$$\mathcal{G}^{\mu\nu} = \sum_{L,L'} \langle\vec{r}_\mu|\mathcal{Y}_L\rangle\big(\langle r_\mu|j_l k\rangle A_{LL'}^{\mu\nu}$$

$$+ k\langle r_\mu|n_l k\rangle\delta_{LL'}\delta_{\mu\nu}\big)\langle j_{l'}k|r_\nu'\rangle\langle\mathcal{Y}_{L'}|\vec{r}_\nu'\rangle . \qquad \text{(A5)}$$

Substituting Eqs. (4.9), (A4), and (A5) into Eq. (A3) and carrying out the surface integrations to evaluate $\gamma_L^\mu\langle r_\mu^c|R_l^\mu\rangle$, we obtain

$$\sum_{L',\nu}\Big\{\delta_{LL'}\delta_{\mu\nu} - \frac{(-i)(4\pi)^2}{2AK_{\mp\vec{v}}R_{\mp\vec{v}}} i^{l-l'} e^{i(\vec{k}\cdot\vec{c}_\mu - \vec{k}_{\mp\vec{v}}\cdot\vec{c}_\nu)}$$

$$\times\langle\mathcal{Y}_L|\vec{k}\rangle\langle\vec{k}_{\mp\vec{v}}|\mathcal{Y}_{L'}\rangle\langle r_\mu^c|j_l k\rangle[j_{l'}, R_{l'}]$$

$$- (\langle r_\mu^c|j_l k\rangle A_{LL'}^{\mu\nu} + k\langle r_\mu^c|n_l k\rangle\delta_{LL'}\delta_{\mu\nu})$$

$$\times[j_{l'}, R_{l'}]\Big\}\gamma_{l'}^\nu\langle r_\nu^c|R_{l'}^\nu\rangle = 0 , \qquad \text{(A6)}$$

where $[f, g]$ is the Wronskian defined by

$$[f, g] = (f\nabla_\mu g - g\nabla_\mu f)_{r_\mu = r_\mu^c} . \qquad \text{(A7)}$$

The phase shift of the partial wave l in the μth muffin-tin potential is defined by[43]

$$\tan\eta_l^\mu = [j_l, R_l]/[n_l, R_l] . \qquad \text{(A8)}$$

With the aid of Eq. (A8), Eq. (A6) becomes

$$\sum_{L',\nu}\Big(F_{LL'}^{\mu\nu} - \frac{-i}{2AK_{\mp\vec{v}}R_{\mp\vec{v}}} D_L^\mu E_{L'}^\nu\Big)$$

$$\times\frac{\tan\eta_{l'}^\nu k^{-1}}{\langle r_\nu^c|j_{l'}k\rangle - \langle r_\nu^c|n_{l'}k\rangle\tan\eta_{l'}^\nu}\gamma_{L'}^\nu\langle r_\nu^c|R_{l'}^\nu\rangle = 0 . \qquad \text{(A9)}$$

In order to have nontrivial solutions for the coefficients $\gamma_L^\mu \langle r_\mu | R_l^\mu \rangle$, the determinant of the coefficients should vanish:

$$\det\left|\left(F_{LL'}^{\mu\nu} - \frac{-i}{2AK_{\mp}R_{\mp}} D_L^\mu E_{L'}^\nu\right) \frac{k^{-1}\tan\eta_{l'}^\nu}{\langle r_\nu^c | j_{l'} k\rangle - \langle r_\nu^c | n_{l'} k\rangle \tan\eta_{l'}^\nu}\right| = 0 \,. \qquad \text{(A10)}$$

After factoring out

$$k^{-1}\tan\eta_{l'}^\nu / (\langle r_\nu^c | j_{l'} k\rangle - \langle r_\nu^c | n_{l'} k\rangle \tan\eta_{l'}^\nu) \,,$$

Eq. (A10) becomes

$$\det\left| F_{LL'}^{\mu\nu} - \frac{-i}{2AK_{\mp}R_{\mp}} D_L^\mu E_{L'}^\nu \right| = 0 \,, \qquad \text{(A11)}$$

which is identical to Eq. (5.11).

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Equivalence of van der Waals Forces between Solids and the Surface-Plasmon Interaction

E. Gerlach
Battelle Institut, e.V., Frankfurt, Main, Germany

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It is shown that the well-known Lifshitz formula for the retarded van der Waals attraction between two solid half-spaces can be obtained from the zero-point energy of the interacting surface plasmons.

INTRODUCTION

Recently it was shown[1] that a nonretarded van der Waals attraction between solid half-spaces (separated by a gap) can be obtained from the interaction of the surface excitations on either side of