

Multiple-scattering approach to angle-resolved photoemission

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(Received 10 October 1977)

A Green's-function formulation of angle-resolved ultraviolet photoemission spectroscopy is presented for surfaces with overlayer adsorbed systems. Multiple scatterings of the initial state are included through the use of cluster wave functions solved from a self-consistent $X\alpha$ scattered-wave method. The final-state process is expressed in terms of a scattering T matrix which propagates the final-state electron through surface layers of the crystal lattice, in the presence of inelastic damping. It is found that major angular asymmetries in the photoemission intensity profiles arise from multiple scatterings off neighboring ion cores. Our formulation, in the limit of taking a single wave function from a single ion-core, reduces to the photoemission theory of a core level.

I. INTRODUCTION

Angle-resolved ultraviolet photoemission spectroscopy (ARUPS) has increasingly been recognized as a useful tool for studying surfaces of clean and overlayer adsorbed systems.¹⁻¹⁹ Recent advances in experimental instrumentation and the use of the synchrotron radiation source result in the acquisition of much experimental spectra as functions of photon energy, photon polarization, incident angle, electron exit angle, electron exit plane, etc. These data contain potential information of the direction and symmetry of surface bonds as well as the location of chemisorption sites.^{13,20}

In order to interpret the data, it is now established that multiple-scattering effects, especially by the immediate neighbor atoms, are extremely important.¹¹ Both the initial-state wave function and final-state wave function result from strong interactions of an electron with a number of atomic potentials. In this paper, we present a dynamical theory of angle-resolved UPS based on the multiple-scattering (Green's-function) approach. For the treatment of the initial state, we solve for the self-consistent cluster wave function using the $X\alpha$ scattered-wave method ($X\alpha$ SW).²¹ The final-state process is written in terms of a multiple-scattering T matrix which propagates the photoexcited electron through the surface layer of the system. Due to strong inelastic damping of the final-energy electron, only a few (5-10) surface layers are penetrated. Our approach, in the limit of taking a single atomic wave function from a single ion core, reduces to the core-emission theories previously reported.^{14,15,22}

We note that the formulation contains a number of approximations. Among these, the most important ones are as follows. (i) The effect of the positively charged hole is not treated properly. The extent to which the hole can be included is

through the use of transition-state wave functions in calculating excitation matrix elements. A check of phase shifts and excitation matrix elements computed from ground-state and transition-state potential showed only minor differences. It seems that in solids, major angular asymmetries in the photoemission intensity spectra arise from multiple scattering by the neighboring atoms. (ii) Since we use initial-state wave functions of a cluster of atoms, we neglect the \vec{k}_{\parallel} dispersion of the initial state. Our formulation, however, is general and can include \vec{k}_{\parallel} -dependent initial-state wave functions. The selection of cluster wave functions as the initial state is by choice. We judge that a proper description of the initial-state surface wave function requires an accurate and self-consistent treatment of potential and charge distribution of the adsorbate and neighboring atoms in the local region surrounding the adsorbed atom or molecule. In this respect, the $X\alpha$ scattered-wave scheme seems to produce adequate results.^{23,24} Furthermore, experimental measurements of the adsorbate-derived levels for S, O, and CO show very mild dependences on \vec{k}_{\parallel} .^{3,4,7,25} (iii) In the treatment of final-state multiple-scattering processes, differences in scattering factors of the "host" ion cores, i.e., ion cores from which the photoelectron is excited, are neglected. Judging from the differences in scattering factors of transition-state and ground-state potential, we estimate that for solids such as $c(2 \times 2)$ O and S-Ni(001) systems, this difference would produce unimportant angular effects on the photoemission spectra. (iv) Finally, the muffin-tin form is used for the crystal potential. To summarize, the basis of our approach relies on the importance of multiple scattering. We argue that once multiple-scattering effects are properly included for initial and final-state wave functions, major features in the photoemission intensity spectra can be accounted for.

II. DEFINITION OF GREEN'S FUNCTION AND T MATRIX FOR PHOTOEMISSION

In a one-electron description, the wave function of the photoelectron at the observation point \vec{R} is

$$\psi(\vec{R}) = \int d^3r G(\vec{R} - \vec{r}) H_I \psi_i(\vec{r}), \quad (1)$$

where the interaction Hamiltonian is

$$H_I = -\frac{e}{2mc} \vec{A} \cdot \vec{P} - \frac{e}{2mc} \vec{P} \cdot \vec{A} + \frac{e^2}{2mc^2} \vec{A}^2 + e\phi. \quad (2)$$

Neglecting the \vec{A}^2 term and in a homogeneous medium with no net charge, a gauge function exists so that $\vec{\nabla} \cdot \vec{A} = 0$ and $\phi = 0$. The interaction Hamiltonian in the dipole approximation is

$$H_I = -\frac{e}{mc} \vec{A} \cdot \vec{P}. \quad (3)$$

In Eq. (1), $\psi_i(\vec{r})$ is the initial-state wave function.

In terms of the free-electron propagator G_0 and the T matrix of the entire system (substrate plus overlayer), G can be written as

$$G = G_0 + G_0 T G_0, \quad (4)$$

where²⁶

$$G_0(\vec{r}_1 - \vec{r}_2) = \left(\frac{2m}{\hbar^2}\right) \frac{1}{(2\pi)^3} \int d^3k \frac{e^{i\vec{k} \cdot (\vec{r}_1 - \vec{r}_2)}}{\vec{k}_0^2 - \vec{k}^2}. \quad (5)$$

In Eq. (5), \vec{k}_0^2 is the complex "energy" of an electron in a medium with absorption $\Sigma(E)$. The dispersion relation

$$\vec{k}_0^2 = \frac{2m}{\hbar^2} [E - \Sigma(E)] \quad (6)$$

holds inside the solid.

If the system is divided into nonoverlapping regions α and the scattering by each region α is described by t_α , then T in Eq. (4) can be written as

$$T = \sum_{\text{all } \alpha} t_\alpha + \sum_{\text{all } \alpha} T'_\alpha G_0 t_\alpha, \quad (7)$$

where T'_α is the matrix to describe the remaining scattering process after the electron has been scattered by the region α . T'_α can be written as

$$T'_\alpha = \sum_{\alpha' \neq \alpha} t_{\alpha'} + \sum_{\substack{\alpha', \alpha'' \\ \alpha' \neq \alpha'' \\ \alpha' \neq \alpha}} t_{\alpha'} G_0 t_{\alpha''} + \dots \quad (8)$$

or

$$T'_\alpha = \sum_{\alpha' \neq \alpha} t_{\alpha'} + \sum_{\alpha' \neq \alpha} T_{\alpha'} G_0 t_{\alpha'}. \quad (9)$$

Combining Eqs. (1), (4), and (9), the outgoing photoelectron can be expressed as

$$\begin{aligned} \psi(\vec{R}) = & G_0 |\phi\rangle + \sum_{\alpha} G_0 t_{\alpha} G_0 |\phi\rangle \\ & + \sum_{\alpha} G_0 T'_\alpha G_0 t_{\alpha} G_0 |\phi\rangle, \end{aligned} \quad (10)$$

where

$$|\phi\rangle = -\frac{e}{mc} \vec{A} \cdot \vec{P} |\psi_i\rangle$$

is the excited-state wave function. In Eq. (10), the first term represents the direct-excitation term with no scattering, the second term is the single scattering by t_α , the scattering can be due to the adsorbate or substrate; the last term includes all higher-order scattering events.

III. GRADIENT $V(\vec{r})$ FORM OF THE INTERACTION HAMILTONIAN

In Eq. (1), G is the final-state one-electron propagator describing the motion of the excited electron in the potential due to the substrate and the adsorbate. Suppose the entire system is represented by the Hamiltonian

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V$$

and the eigenvalues of the initial and final state are ϵ_i and ϵ_f , then

$$H |\psi_i\rangle = \epsilon_i |\psi_i\rangle \quad (11)$$

and

$$H(\vec{r}) G(\vec{R} - \vec{r}) = \epsilon_f G(\vec{R} - \vec{r}) - \delta(\vec{R} - \vec{r}). \quad (12)$$

Using the fact that the initial wave function $\psi_i(\vec{r})$ vanishes at the observation point \vec{R} , and also assuming that G is calculated from the same Hamiltonian as the initial state, it is shown in Appendix A that the forms

$$\left(-\frac{e}{mc}\right) \vec{A} \cdot \vec{P}$$

and

$$\left(-i\hbar \frac{e}{mc} \frac{1}{\epsilon_f - \epsilon_i}\right) \vec{A} \cdot \vec{\nabla} V$$

are equivalent. In fact, all three forms of the interaction Hamiltonian

$$H_I = \left(-\frac{e}{mc}\right) \vec{A} \cdot \vec{P} \quad (13)$$

$$= \left(-\frac{e(\epsilon_f - \epsilon_i)}{\hbar c}\right) \vec{A} \cdot \vec{r} \quad (14)$$

$$= \left(-i\hbar \frac{e}{mc} \frac{1}{\epsilon_f - \epsilon_i}\right) \vec{A} \cdot \vec{\nabla} V, \quad (15)$$

are equivalent as long as the conditions set forth

in Appendix A are satisfied. In practice, the initial and final wave functions are usually calculated from slightly different Hamiltonians and Eqs. (13), (14), and (15) do not produce identical results. In subsequent calculations using muffin-tin-type potential, out of efficiency, we shall use Eq. (15) for H_f .

IV. ROLE OF MUFFIN-TIN POTENTIAL IN FINAL-STATE CALCULATION

In the following, we shall use muffin-tin-type potentials. With this approximation, it is shown in Appendix B that the photoelectron wave function at the observation point \vec{R} can be written as

$$\begin{aligned} \psi(\vec{R}) = & G_0|\phi\rangle + \left(\frac{2m}{\hbar^2}\right) ik_0 \sum_{\alpha} \sum_L (-i)^{-l} h_l^{(1)}(k_0|\vec{R}-\vec{R}_\alpha|) Y_L(\vec{R}-\vec{R}_\alpha) M_L^\alpha \\ & + \left(\frac{2m}{\hbar^2}\right) ik_0 \sum_{\alpha} \sum_L \sum_{L'} (-i)^{-l'} h_{l'}^{(1)}(k_0|\vec{R}-\vec{R}_\alpha|) Y_{L'}(\vec{R}-\vec{R}_\alpha) \left(\sum_{i,j=0}^{\infty} T^{ij} G^{j\alpha(\alpha)}\right)_{L'L} M_L^\alpha, \end{aligned} \quad (16)$$

where \vec{R}_α is the location for the center of the α th muffin-tin sphere; $k_0 = |\vec{k}_f|$ is the magnitude of the photoelectron momentum; $h_l^{(1)}$ are the spherical hankel functions of the first kind; Y_L are the spherical harmonics with $L = (l, m)$; T^{ij} and $G^{j\alpha(\alpha)}$ are the multilayer scattering matrices and the structural propagator defined in Appendix B. The index $q(\alpha)$ represents the q th layer in which the

α th sphere lies.

In the derivation of Eq. (16), we have assumed that the scattering ion cores have two-dimensional translation symmetry. In other words, the perturbation introduced by the fact that the potential at the photoemission site is different from that of other sites in the layer due to the hole is neglected. In Eq. (16), the matrix elements M_L^α are explicitly

$$M_L^\alpha = -(-i)^l \int d^3r [e^{i\delta_l^\alpha} R_l^f(|\vec{r}-\vec{R}_\alpha|) - j_l(k_0|\vec{r}-\vec{R}_\alpha|)] Y_L^*(\vec{r}-\vec{R}_\alpha) (-i\hbar) \frac{e}{mc} \frac{1}{\epsilon_f - \epsilon_i} \vec{A} \cdot \vec{\nabla} V(\vec{r}) \psi_i(\vec{r}). \quad (17)$$

In the above equation, δ_l^α is the l th phase shift of the α th sphere at the final energy ϵ_f . j_l is the spherical Bessel function. R_l^f is the normalized radial part of the solution to Schrödinger's equation inside the α th sphere with energy ϵ_f . Physically, the function inside the first bracket in Eq. (17) represents the wave function scattered by the spherical potential of the α th sphere alone. We shall now write Eq. (16) in an integral form. This is done so that we can eventually use plane-wave boundary conditions. Using the integral form

$$h_l^{(1)}(k_0|\vec{r}-\vec{R}_\alpha|) Y_L(\vec{r}-\vec{R}_\alpha) = \frac{(i)^{l-1}}{2\pi^2 k_0} \int d^3k \frac{e^{i\vec{k}\cdot\vec{r}} e^{-i\vec{k}\cdot\vec{R}_\alpha}}{k_0^2 - k^2} Y_L(\vec{k}), \quad (18)$$

we write Eq. (16) as

$$\psi(\vec{R}) = G_0|\phi\rangle - \left(\frac{2m}{\hbar^2}\right) \left(\frac{1}{2\pi^2}\right) \int \frac{d^3k e^{i\vec{k}\cdot\vec{R}}}{k_0^2 - k^2} \sum_\alpha e^{-i\vec{k}\cdot\vec{R}_\alpha} \left(\sum_L Y_L(\vec{k}) M_L^\alpha + \sum_{L,L'} Y_{L'}(\vec{k}) \sum_{i,j=0}^{\infty} (T^{ij} G^{j\alpha(\alpha)})_{L'L} M_L^\alpha \right) \quad (19)$$

$$= G_0|\phi\rangle - \left(\frac{2m}{\hbar^2}\right) \frac{1}{(2\pi^2)} \int \frac{d^3k e^{i\vec{k}\cdot\vec{R}}}{k_0^2 - k^2} A(\vec{k}). \quad (20)$$

Before studying the scattering amplitude $A(\vec{k})$, we first look at the matrix elements M_L^α in more detail.

V. MATRIX ELEMENTS M_L^α AND ROLE OF THE MUFFIN-TIN POTENTIAL IN THE INITIAL STATE

In Eq. (19), the only place where the initial-state wave function ψ_i comes in is through matrix ele-

ments M_L^α . In order to evaluate M_L^α , we first give an explicit form for ψ_i . Since we have assumed the muffin-tin-potential model, $\psi_i(\vec{r})$ has the following form

$$\psi_i(\vec{r}) = \sum_B \Theta(b_B - r_B) f_B(\vec{r}_B) + \delta_{\vec{r}, \vec{R}_I} f_{II}(\vec{r}), \quad (21)$$

where $\Theta(x)$ is the usual step function: $\Theta(x) = 1$ if x

≥ 0 and $\Theta(x) = 0$ otherwise; b_β is the radius of the β th muffin-tin sphere; $\vec{r}_\beta = \vec{r} - \vec{R}_\beta$ is the position vector relative to the β th sphere center; $\delta_{\vec{r}, \text{II}}$ is the Kronecker function in the sense that $\delta_{\vec{r}, \text{II}} = 1$ if \vec{r} is in the intersphere region II and equal to zero otherwise. The initial state in the intersphere region is described by $f_{\text{II}}(\vec{r})$, while inside sphere β it is described by

$$f_\beta(\vec{r}_\beta) = \sum_L C_L^\beta \bar{R}_L^\beta(r_\beta) \bar{Y}_L(\vec{r}_\beta).$$

$$M_L^\alpha = -(-i)^l (-i\hbar) \left(\frac{e}{mc} \right) \frac{1}{\epsilon_f - \epsilon_i} \sum_{\alpha \mathbf{1} \gamma} \int_{\gamma^*} d^3 r_\gamma [e^{i\theta_i} R_i^\alpha(r_\alpha) - j_i(k_0 r_\alpha)] Y_L^*(\vec{r}_\alpha) \vec{A} \cdot \vec{\nabla} V(r_\gamma) \left[\sum_{\beta \in C} \Theta(b_\beta - r_\beta) f_\beta(\vec{r}_\beta) \right].$$

In the above equation, γ^* indicates that the integral over sphere γ has to include the surface contribution due to the discontinuity of the potential across the muffin-tin-sphere surface. This surface term would be discussed in more detail in Sec. VIII.

Noting that $\Theta(b_\beta - r_\beta) = 0$ if \vec{r} is not inside sphere β , we have

$$M_L^\alpha = D \sum_{\beta \in C} \int_{\beta^*} d^3 r_\beta [e^{i\theta_i} R_i^\alpha(r_\alpha) - j_i(k_0 r_\alpha)] \times Y_L^*(\vec{r}_\alpha) \vec{A} \cdot \vec{\nabla} V(r_\beta) f_\beta(\vec{r}_\beta), \quad (22)$$

where

$$D = -(-i)^l (-i\hbar) \left(\frac{e}{mc} \right) \frac{1}{\epsilon_f - \epsilon_i}. \quad (23)$$

It is shown in Appendix C that for $\beta \neq \alpha$, we have the following expansion theorem

$$[e^{i\theta_i} R_i^\alpha(r_\alpha) - j_i(k_0 r_\alpha)] Y_L^*(\vec{r}_\alpha) = t_i^\alpha(k_0) \sum_{L_1} G_{LL_1}^{\alpha\beta}(k_0) j_{L_1}(k_0 r_\beta) Y_{L_1}^*(\vec{r}_\beta), \quad (24)$$

where

$$t_i^\alpha(k_0) = -\frac{\hbar^2}{2m} \frac{1}{k_0} e^{i\theta_i} \sin \delta_i^\alpha; \quad (25)$$

and

$$G_{LL_1}^{\alpha\beta}(k_0) = -4\pi i \left(\frac{2m}{\hbar^2} \right) k_0 \times \sum_{L'} i'^\alpha(LL_1L') h_{L'}^{(1)}(k_0 R_{\alpha\beta}) Y_{L'}(\vec{R}_{\alpha\beta}). \quad (26)$$

Here we use the real spherical harmonics because it is commonly employed in the initial-state calculations. Since we are considering the photoemission from an adsorbate-induced initial state, C_L^β is nonzero only for β belonging to the cluster from which we calculate the initial state. Thus the summation in Eq. (21) is over spheres in the cluster only.

Substituting Eq. (21) into Eq. (17) and using the fact that $\vec{\nabla} V = 0$ in the intersphere region, we obtain

In Eq. (26), $a(LL_1L')$ are the Clebsch-Gordan coefficients defined by

$$a(LL_1L') = \int Y_L^*(\vec{r}) Y_{L_1}(\vec{r}) Y_{L'}^*(\vec{r}) d\Omega, \quad (27)$$

and

$$\vec{R}_{\alpha\beta} = \vec{R}_\alpha - \vec{R}_\beta. \quad (28)$$

With the above expansion theorem, Eq. (22) becomes, after separating the summation into two parts

$$M_L^\alpha = m_L^\alpha + \sum_{\beta \neq \alpha} \sum_{L_1} t_i^\alpha G_{LL_1}^{\alpha\beta} S_{L_1}^\beta, \quad (29)$$

where

$$m_L^\alpha = D \int_{\alpha^*} d^3 r_\alpha [e^{i\theta_i} R_i^\alpha(r_\alpha) - j_i(k_0 r_\alpha)] \times Y_L^*(\vec{r}_\alpha) \vec{A} \cdot \vec{\nabla} V(r_\alpha) f_\alpha(\vec{r}_\alpha) \quad (30)$$

and

$$S_{L_1}^\beta = D \int_{\beta^*} d^3 r_\beta j_{L_1}(k_0 r_\beta) Y_{L_1}^*(\vec{r}_\beta) \vec{A} \cdot \vec{\nabla} V(r_\beta) f_\beta(\vec{r}_\beta). \quad (31)$$

Substituting Eq. (29) into Eq. (19), we obtain for the scattering amplitude $A(\vec{k})$

$$\begin{aligned}
A(\vec{k}) &= \sum_{\text{all } \alpha} \sum_{\mathcal{L}} Y_{\mathcal{L}}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}_{\alpha}} m_{\mathcal{L}}^{\alpha} + \sum_{\text{all } \alpha} \sum_{\mathcal{L}} Y_{\mathcal{L}}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}_{\alpha}} \sum_{\beta \neq \alpha} \sum_{\mathcal{L}_1} t^{\alpha} G_{\mathcal{L}\mathcal{L}_1}^{\alpha\beta} S_{\mathcal{L}_1}^{\beta} \\
&+ \sum_{\text{all } \alpha} \sum_{\mathcal{L}} \sum_{\mathcal{L}'} Y_{\mathcal{L}'}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}_{\alpha}} \left(\sum_{i,j=0}^{\infty} T^{ij} G^{jq(\alpha)} \right) \sum_{\mathcal{L}'} m_{\mathcal{L}'}^{\alpha} \\
&+ \sum_{\text{all } \alpha} \sum_{\mathcal{L}} \sum_{\mathcal{L}'} Y_{\mathcal{L}'}(\vec{k}) e^{-i\vec{k} \cdot \vec{R}_{\alpha}} \left(\sum_{i,j=0}^{\infty} T^{ij} G^{jq(\alpha)} \right) \sum_{\mathcal{L}\mathcal{L}'} \sum_{\beta \neq \alpha} \sum_{\mathcal{L}_1} t^{\alpha} G_{\mathcal{L}\mathcal{L}_1}^{\alpha\beta} S_{\mathcal{L}_1}^{\beta}. \tag{32}
\end{aligned}$$

In the last term of the above equation, note that G^{jq} is the multilayer structural factor with j, q denoting the j th and q th layer, while $G^{\alpha\beta}$ is the three-dimensional structural factor with α and β denoting the α th and β th atomic sites.

Employing the matrix representation Y for $\{Y_{\mathcal{L}}\}$ and G for $\{G_{\mathcal{L}\mathcal{L}_1}\}$, etc., we have

$$\begin{aligned}
A(\vec{k}) &= Y(\vec{k}) \left[\sum_{\text{all } \alpha} e^{-i\vec{k} \cdot \vec{R}_{\alpha}} m_{\alpha} + \sum_{\text{all } \alpha} e^{-i\vec{k} \cdot \vec{R}_{\alpha}} \sum_{\beta \neq \alpha} t^{\alpha} G^{\alpha\beta} S^{\beta} \right. \\
&\left. + \sum_{\text{all } \alpha} e^{-i\vec{k} \cdot \vec{R}_{\alpha}} \left(\sum_{i,j=0}^{\infty} T^{ij} G^{jq(\alpha)} \right) m_{\alpha} + \sum_{\text{all } \alpha} e^{-i\vec{k} \cdot \vec{R}_{\alpha}} \left(\sum_{i,j=0}^{\infty} T^{ij} G^{jq(\alpha)} \right) \sum_{\beta \neq \alpha} t^{\alpha} G^{\alpha\beta} S^{\beta} \right]. \tag{33}
\end{aligned}$$

In Eq. (33), we note that $m_{\mathcal{L}}^{\alpha}$ and $S_{\mathcal{L}}^{\alpha}$ are nonvanishing only for α belonging to the cluster. Then Eq. (33) reduces to

$$\begin{aligned}
A(\vec{k}) &= Y(\vec{k}) \left[\sum_{\alpha \in \mathcal{C}} e^{-i\vec{k} \cdot \vec{R}_{\alpha}} m_{\alpha} + \sum_{\text{all } \alpha} e^{-i\vec{k} \cdot \vec{R}_{\alpha}} \sum_{\substack{\beta \in \mathcal{C} \\ \beta \neq \alpha}} t^{\alpha} G^{\alpha\beta} S^{\beta} + \sum_{\alpha \in \mathcal{C}} e^{-i\vec{k} \cdot \vec{R}_{\alpha}} \left(\sum_{i,j=0}^{\infty} T^{ij} G^{jq(\alpha)} \right) m_{\alpha} \right. \\
&\left. + \sum_{\text{all } \alpha} e^{-i\vec{k} \cdot \vec{R}_{\alpha}} \left(\sum_{i,j=0}^{\infty} T^{ij} G^{jq(\alpha)} \right) \sum_{\substack{\beta \in \mathcal{C} \\ \beta \neq \alpha}} t^{\alpha} G^{\alpha\beta} S^{\beta} \right] \\
&= Y(\vec{k})(A1 + A2 + A3 + A4). \tag{34}
\end{aligned}$$

In the following, we change the summations over different atomic indices ($\sum_{\alpha} \sum_{\beta}$, etc.) into summations over layer indices (\sum_q , etc.). Doing this, we can express $\psi(\vec{R})$ in terms of the multilayer scattering matrix and structural factors.

VI. CHANGING SUMMATIONS OVER ATOMIC INDICES TO LAYER INDICES

In Eq. (34), the summations are over different atoms belonging to the cluster $\sum_{\alpha \in \mathcal{C}}$. In the following, we separate this sum into two parts: the first sum is over different atoms in a given layer q : ($\sum_{\alpha(a) \in \mathcal{C}}$), and then the sum is taken over all layers ($K\mathcal{C}$) that contain atoms of the cluster

($\sum_{q \in K\mathcal{C}}$). The terms A1, A2, A3, and A4 in Eq. (34) are now considered separately

$$A1 = \sum_{q \in K\mathcal{C}} \lambda^q, \tag{35}$$

where

$$\lambda^q = \sum_{\substack{\alpha(a) \\ \alpha \in \mathcal{C}}} e^{-i\vec{k} \cdot \vec{R}_{\alpha}} m_{\alpha}. \tag{36}$$

Similarly, A3 in Eq. (34) becomes

$$A3 = \sum_{q \in K\mathcal{C}} \left(\sum_{i,j=0}^{\infty} T^{ij} G^{jq} \right) \lambda^q. \tag{37}$$

As for A2, we have

$$A2 = \sum_{\beta \in \mathcal{C}} e^{-i\vec{k} \cdot \vec{R}_{\beta}} \left[t^{q_1} \sum_{\alpha(a_1(\beta))} e^{-i\vec{k} \cdot \vec{R}_{\alpha}} G^{\alpha\beta} + \sum_{\substack{q=0 \\ q \neq a_1(\beta)}}^{\infty} t^q \left(\sum_{\alpha(a)} e^{-i\vec{k} \cdot \vec{R}_{\alpha}} G^{\alpha\beta} \right) \right] S^{\beta}. \tag{38}$$

In Eq. (38), we have separated the sum inside the bracket into two parts: one is over the different atoms (except β itself) in the layer $q_1(\beta)$ where β lies, the other is over other planes $q \neq q_1(\beta)$. In each layer we sum over all the atoms contained in the layer. Then by definition (Appendix C), we have

$$\sum_{\alpha(q_1(\beta))} e^{-i\vec{k} \cdot \vec{R}_{\alpha\beta}} G^{\alpha\beta} = G^{q_1(\beta)q_1(\beta)}, \quad (39)$$

and

$$\sum_{\alpha(q)} e^{-i\vec{k} \cdot \vec{R}_{\alpha\beta}} G^{\alpha\beta} = G^{qq_1(\beta)}, \quad (40)$$

which are the multilayer structural constants. Note also that we have used the subplane concept where all ion cores in a subplane are of the same kind. Thus, we can put $t^{\alpha(q)} = t^q$. Then the term A2 becomes

$$\begin{aligned} A2 &= \sum_{\beta \in C} e^{-i\vec{k} \cdot \vec{R}_{\beta}} \sum_{q=0}^{\infty} t^q G^{qq_1(\beta)} S^{\beta} \\ &= \sum_{q_1 \in KC} \left(\sum_{q=0}^{\infty} t^q G^{qq_1} \right) \eta^{q_1}, \end{aligned} \quad (41)$$

where

$$\eta^{q_1} = \sum_{\substack{\beta(q_1) \\ \beta \in C}} e^{-i\vec{k} \cdot \vec{R}_{\beta}} S^{\beta}. \quad (42)$$

Similarly, A4 can be written as

$$A4 = \sum_{q_1 \in KC} \sum_{q=0}^{\infty} \left(\sum_{i,j=0}^{\infty} T^{ij} G^{jq} \right) t^q G^{qq_1} \eta^{q_1}. \quad (43)$$

Adding the four terms A1, A2, A3, and A4 together, we have

$$\begin{aligned} A(\vec{k}) &= Y(\vec{k}) \left[\sum_{q_1 \in KC} \left(1 + \sum_{i,j=0}^{\infty} T^{ij} G^{jq_1} \right) \lambda^{q_1} \right. \\ &\quad \left. + \sum_{q_1 \in KC} \sum_{q=0}^{\infty} \left(1 + \sum_{i,j=0}^{\infty} T^{ij} G^{jq} \right) \right. \\ &\quad \left. \times t^q G^{qq_1} \eta^{q_1} \right]. \end{aligned} \quad (44)$$

We can further expand

$$\begin{aligned} 1 + \sum_{i,j=0}^{\infty} T^{ij} G^{jq} &= 1 + \sum_{\substack{i,j=0 \\ j \neq q}}^{\infty} T^{ij} G^{jq} \\ &\quad + \sum_{\substack{i,j=0 \\ j=q}}^{\infty} T^{ij} G^{jq} \tau^q G^{qq} + \tau^q G^{qq} \\ &= \left(1 + \sum_{\substack{i,j=0 \\ i \neq q}}^{\infty} T^{ij} G^{jq} \right) (1 + \tau^q G^{qq}), \end{aligned} \quad (45)$$

where τ^q is the layer scattering matrix constant

$$\tau^q = (1 - t^q G^{qq})^{-1} t^q. \quad (46)$$

Then, it can be shown that Eq. (44) becomes

$$\begin{aligned} A(\vec{k}) &= Y(\vec{k}) \sum_{q_1 \in KC} \left[\left(1 + \sum_{\substack{i,j=0 \\ j \neq q_1}}^{\infty} T^{ij} G^{jq_1} \right) (1 + \tau^{q_1} G^{q_1 q_1}) (\lambda^{q_1} + t^{q_1} G^{q_1 q_1} \eta^{q_1}) \right. \\ &\quad \left. + \sum_{\substack{q=0 \\ q \neq q_1}}^{\infty} \left(1 + \sum_{\substack{i,j=0 \\ j \neq q}}^{\infty} T^{ij} G^{jq} \right) (1 + \tau^q G^{qq}) t^q G^{qq_1} \eta^{q_1} \right]. \end{aligned} \quad (47)$$

Noting that

$$1 + \tau^q G^{qq} = (1 - t^q G^{qq})^{-1} = (1 - X^q)^{-1}, \quad (48)$$

where

$$X^q = t^q G^{qq} \quad (49)$$

and

$$(1 + \tau^q G^{qq}) t^q = (1 - X^q)^{-1} t^q = \tau^q, \quad (50)$$

then Eq. (47) becomes

$$A(\vec{k}) = Y(\vec{k}) \sum_{q_1 \in KC} \left[\left(1 + \sum_{\substack{i,j=0 \\ j \neq q_1}}^{\infty} T^{ij} G^{jq_1} \right) (1 - X^{q_1})^{-1} (\lambda^{q_1} + t^{q_1} G^{q_1 q_1} \eta^{q_1}) + \sum_{\substack{q=0 \\ q \neq q_1}}^{\infty} \left(1 + \sum_{\substack{i,j=0 \\ j \neq q}}^{\infty} T^{ij} G^{jq} \right) \tau^q G^{qq_1} \eta^{q_1} \right]. \quad (51)$$

Picking up the nonscattering term in Eq. (20), we have

$$\begin{aligned}
G_0|\phi\rangle &= \int d^3r G_0(\vec{R}-\vec{r})(-i\hbar)\left(\frac{e}{mc}\right)\frac{1}{\epsilon_f-\epsilon_i}\vec{A}\cdot\vec{\nabla}V(\vec{r})\psi_i(\vec{r}) \\
&= \sum_{\alpha\in\mathcal{C}}\int_{\alpha^+} d^3r G_0(\vec{R}-\vec{R}_\alpha-(\vec{r}-\vec{R}_\alpha))(-i\hbar)\left(\frac{e}{mc}\right)\frac{1}{\epsilon_f-\epsilon_i}\vec{A}\cdot\vec{\nabla}V(\vec{r}_\alpha)f_\alpha(\vec{r}_\alpha) \\
&= \sum_{\alpha\in\mathcal{C}}\left(\frac{2m}{\hbar^2}\right)\int_{\alpha^+} d^3r_\alpha \sum_L Y_L(\vec{R}-\vec{R}_\alpha)(-ik_0)h_i^{(1)}(k_0|\vec{R}-\vec{R}_\alpha|) \\
&\quad \times Y_L^*(\vec{r}_\alpha)j_l(k_0r_\alpha)(-i\hbar)\left(\frac{e}{mc}\right)\frac{1}{\epsilon_f-\epsilon_i}\vec{A}\cdot\vec{\nabla}V(r_\alpha)f_\alpha(\vec{r}_\alpha).
\end{aligned} \tag{52}$$

Using the integral form of Eq. (18), we have

$$\begin{aligned}
G_0|\phi\rangle &= -\left(\frac{2m}{\hbar^2}\right)\left(\frac{1}{2\pi^2}\right)\int\frac{d^3k e^{i\vec{k}\cdot\vec{R}}}{k_0^2-k^2} \\
&\quad \times \left[\sum_{\alpha\in\mathcal{C}}\sum_L Y_L(\vec{k})e^{-i\vec{k}\cdot\vec{R}_\alpha}(-i)^l(i\hbar)\left(\frac{e}{mc}\right)\frac{1}{\epsilon_f-\epsilon_i}\int_{\alpha^+} d^3r_\alpha j_l(k_0r_\alpha)Y_L^*(\vec{r}_\alpha)\vec{A}\cdot\vec{\nabla}V(r_\alpha)f_\alpha(\vec{r}_\alpha)\right] \\
&= -\left(\frac{2m}{\hbar^2}\right)\left(\frac{1}{2\pi^2}\right)\int\frac{d^3k e^{i\vec{k}\cdot\vec{R}}}{k_0^2-k^2} Y(\vec{k})\sum_{\alpha\in\mathcal{K}\mathcal{C}}\eta^\alpha.
\end{aligned} \tag{53}$$

Putting Eqs. (53) and (51), into Eq. (20), we have

$$\begin{aligned}
\psi(\vec{R}) &= -\left(\frac{2m}{\hbar^2}\right)\left(\frac{1}{2\pi^2}\right)\int\frac{d^3k e^{i\vec{k}\cdot\vec{R}}}{k_0^2-k^2} Y(\vec{k})\sum_{\alpha_1\in\mathcal{K}\mathcal{C}}\left[\eta^{\alpha_1}+\sum_{\substack{q=0 \\ \alpha\neq\alpha_1}}^{\infty}\left(1+\sum_{\substack{i,j=0 \\ j\neq\alpha}}^{\infty}T^{ij}G^{jq}\right)\tau^\alpha G^{\alpha\alpha_1}\eta^{\alpha_1}\right. \\
&\quad \left.+\left(1+\sum_{\substack{i,j=0 \\ j\neq\alpha_1}}^{\infty}T^{ij}G^{jq}\right)(1-X^{\alpha_1})^{-1}(\lambda^{\alpha_1}+t^{\alpha_1}G^{\alpha_1\alpha_1}\eta^{\alpha_1})\right] \\
&= -\left(\frac{2m}{\hbar^2}\right)\left(\frac{1}{2\pi^2}\right)\int\frac{d^3k e^{i\vec{k}\cdot\vec{R}}}{k_0^2-k^2} B(\vec{k}).
\end{aligned} \tag{54}$$

$$\tag{55}$$

The first two terms of $B(\vec{k})$ consists of a nonscattering term and a term with at least one single-scattering process. The sum of these two terms corresponds to including all different scattering paths and is equal to

$$\begin{aligned}
&\eta^{\alpha_1}+\sum_{\substack{q=0 \\ \alpha\neq\alpha_1}}^{\infty}\left(1+\sum_{\substack{i,j=0 \\ j\neq\alpha}}^{\infty}T^{ij}G^{jq}\right)\tau^\alpha G^{\alpha\alpha_1}\eta^{\alpha_1} \\
&= \left(1+\sum_{\substack{i,j=0 \\ j\neq\alpha_1}}^{\infty}T^{ij}G^{jq}\right)\eta^{\alpha_1}.
\end{aligned}$$

Then

$$\begin{aligned}
B(\vec{k}) &= Y(\vec{k})\sum_{\alpha\in\mathcal{K}\mathcal{C}}\left(1+\sum_{\substack{i,j=0 \\ j\neq\alpha}}^{\infty}T^{ij}G^{jq}\right) \\
&\quad \times [\eta^\alpha+(1-X^\alpha)^{-1}(\lambda^\alpha+t^\alpha G^{\alpha\alpha}\eta^\alpha)]. \tag{56}
\end{aligned}$$

Equation (56) can be further simplified by noting that

$$\lambda^\alpha+t^\alpha G^{\alpha\alpha}\eta^\alpha = \sum_{\beta(\alpha)} e^{-i\vec{k}\cdot\vec{R}_\beta} m^\beta + t^\alpha G^{\alpha\alpha} \sum_{\beta(\alpha)} e^{-i\vec{k}\cdot\vec{R}_\beta} S^\beta. \tag{57}$$

From Eqs. (30) and (31), we see that

$$m_L^\beta = F_L^\beta - S_L^\beta,$$

where

$$\begin{aligned}
F_L^\beta &= D \int_{\beta^+} d^3r_\beta e^{i\delta_i^\beta} R_i^f(r_\beta) \\
&\quad \times Y_L^*(\vec{r}_\beta)\vec{A}\cdot\vec{\nabla}V(r_\beta)f_\beta(\vec{r}_\beta). \tag{58}
\end{aligned}$$

Thus we obtain

$$\eta^a + (1 - X^a)^{-1}(\lambda^a + t^a G^a \eta^a) = \sum_{\beta(a)} e^{-i\vec{k} \cdot \vec{R}_\beta} [S^\beta + (1 - X^a)^{-1} [F^\beta - (1 - t^a G^a) S^\beta]]. \quad (59)$$

Using Eq. (49), we have

$$\begin{aligned} \eta^a + (1 - X^a)^{-1}(\lambda^a + t^a G^a \eta^a) &= \sum_{\beta(a)} e^{-i\vec{k} \cdot \vec{R}_\beta} [S^\beta + (1 - X^a)^{-1} F^\beta - (1 - X^a)^{-1} (1 - X^a) S^\beta] \\ &= (1 - X^a)^{-1} \sum_{\beta(a)} e^{-i\vec{k} \cdot \vec{R}_\beta} F^\beta. \end{aligned} \quad (60)$$

Putting Eqs. (60) and (56) into Eq. (55), we obtain

$$\psi(\vec{R}) = -\left(\frac{2m}{\hbar^2}\right) \left(\frac{1}{2\pi^2}\right) \int d^3k \frac{e^{i\vec{k} \cdot \vec{R}}}{k_0^2 - k^2} Y(\vec{k}) \sum_{a \in KC} \left(1 + \sum_{\substack{i, j=0 \\ j \neq a}}^{\infty} T^{ij} G^{ja}\right) (1 - X^a)^{-1} \Gamma^a, \quad (61)$$

where

$$\Gamma^a = \sum_{\beta(a)} e^{-i\vec{k} \cdot \vec{R}_\beta} F^\beta, \quad (62)$$

and F^β is defined in Eq. (58). Equation (61) is reduced to the core-state photoemission formulation if the cluster consists of one atom at the origin.

VII. EVALUATING FINAL-STATE SCATTERING IN K -SPACE REPRESENTATION

The expression given in Eq. (61) may be used to evaluate the photoemission amplitude. However, evaluating the final-state scattering can be a lengthy computational operation. From lessons learned in dynamical LEED calculations, in the presence of inelastic damping, it is much faster to evaluate final-state scatterings using perturbation schemes. We shall now transform Eq. (61) into K -space representation.

The interlayer structural propagator G^{ij} ($i \neq j$) expressed in K -space representation is²⁶

$$\begin{aligned} G_{LL}^{ij}(\vec{k}) &= \gamma_0 e^{-i\vec{k} \cdot (\vec{d}_i - \vec{d}_j)} \sum_{\vec{g}} \frac{e^{i\vec{k}^{\pm}(\vec{g}) \cdot (\vec{d}_i - \vec{d}_j)}}{k_1^{\pm}(\vec{g})} \\ &\quad \times Y_L^*(\vec{k}^{\pm}(\vec{g})) Y_L(\vec{k}^{\pm}(\vec{g})), \end{aligned} \quad (63)$$

where the (+) sign is for layer i above and (-) sign for layer i below layer j . Also, $\gamma_0 = -(8\pi^2 i/A)(2m/\hbar^2)$, A is the area of the unit cell and

$$\vec{k}^{\pm}(\vec{g}) = [\vec{k}_{\parallel} + \vec{g}; \pm(k_0^2 - (\vec{k}_{\parallel} + \vec{g})^2)^{1/2}]. \quad (64)$$

In Eq. (63), \vec{g} is a two-dimensional reciprocal lattice of a layer and the coordinate system is chosen such that $\vec{k}^+(\vec{g})$ propagates outward and $\vec{k}^-(\vec{g})$ propagates into the crystal. The vector \vec{d}_{\perp} is from the origin at the surface into the crystal to the origin of a given layer i . The positive \vec{d}_{\perp} direction is pointed away from the solid.

If the photoemission detector is placed at direction given by

$$\vec{k}_f = (\vec{k}_{\parallel}^f; +\vec{k}_{\perp}^f) \quad (65)$$

from the origin, then through scattering from the crystal lattice, only electrons with momenta \vec{k} given by

$$\vec{k}_{\parallel} = \vec{k}_{\parallel}^f + \vec{g} \quad (66)$$

have a chance to be collected. Using the relation

$$\delta_{\vec{k}_{\parallel}, \vec{k}_{\parallel}^f + \vec{g}} = \frac{(2\pi)^2}{NA} (\delta_{\vec{k}_{\parallel} - \vec{k}_{\parallel}^f - \vec{g}}), \quad (67)$$

where N is the number of atoms in a layer, the integral in Eq. (61) becomes

$$[\psi(\vec{R})]_{\vec{k}_{\parallel}^f, \vec{g}} = -\left(\frac{2m}{\hbar^2}\right) \frac{2}{NA} \int_{-\infty}^{\infty} dk_{\perp}^f(\vec{g}) \frac{e^{i\vec{k}^+(\vec{g}) \cdot \vec{R}}}{k_0^2 - k^2(\vec{g})} Y(\vec{k}(\vec{g})) \sum_{a \in KC} \left(1 + \sum_{\substack{i, j=0 \\ j \neq a}}^{\infty} T^{ij} G^{ja}\right) (1 - X^a)^{-1} \Gamma^a. \quad (68)$$

This integral is done in Appendix E, Ref. 26, and

$$[\psi(\vec{R})]_{\vec{k}_{\parallel}^f, \vec{g}} = \left(\frac{2m}{\hbar^2}\right) \frac{2\pi i}{NA} \left[\frac{Y(\vec{k}^+(\vec{g}))}{k_1^+(\vec{g})} \sum_{a \in KC} \left(1 + \sum_{\substack{i, j=0 \\ j \neq a}}^{\infty} T^{ij} G^{ja}\right) (1 - X^a)^{-1} \Gamma^a \right] e^{i\vec{k}^+(\vec{g}) \cdot \vec{R}} \quad (69)$$

$$= C(\vec{k}^+(\vec{g})) e^{i\vec{k}^+(\vec{g}) \cdot \vec{R}}. \quad (70)$$

The factor $e^{i\vec{k}^*(\vec{g})\cdot\vec{R}}$ represents a set of outgoing plane waves towards the detector at directions $\vec{k}_n^* + \vec{g}$. Thus the coefficients $C(\vec{k}^*(\vec{g}))$ are the photoemission amplitudes in these directions. Evaluating the coefficients in Eq. (69) results in the photoemission amplitudes of a set of directions, related by \vec{g} , including for $\vec{g}=0$ the \vec{k}_f direction.

Using the K -space representation of G^{ij} in Eq. (63), and defining layer scattering matrices for the q th layer as²⁶

$$M_{\epsilon_1\epsilon_2}^{q\pm\pm} = \gamma_0 \sum_{LL'} \frac{Y_L(\vec{k}^*(\vec{g}_1)) \tau_{LL'}^q(k_0) Y_{L'}^*(\vec{k}^*(\vec{g}_2))}{k_L(\vec{g}_1)}, \quad (71)$$

we can write multiple scatterings in Eq. (69) as a series of matrix products such as

$$[P^+ M^{++} P^+ (1 + M^{++}) P^+]_{\epsilon_1\epsilon_2}. \quad (72)$$

In Eq. (72), the P^\pm are diagonal matrices corresponding to outward (+) and inward (-) propagations defined by

$$P_{\epsilon_1\epsilon_2}^\pm = e^{i\vec{k}^*(\vec{g}_1)\cdot\vec{a}} \delta_{\epsilon_1\epsilon_2}. \quad (73)$$

In Eq. (73), $\vec{a} = \vec{d}_{i+1} - \vec{d}_i$ is an interlayer spacing and P^\pm , of course, depends on the layer index i . Note that $\vec{a} = (\vec{a}_\parallel, -\vec{a}_\perp)$ and $\vec{k}^-(\vec{g}) = (\vec{k}_\parallel^* + \vec{g}; -k_\perp(\vec{g}))$ points into the crystal.

We now define the photoexcited source from layer q as

$$Q^q(\vec{k}^*(\vec{g})) = \alpha_0 \sum_{LL'} \frac{Y_L(\vec{k}^*(\vec{g}))}{k_L^+(\vec{g})} (1 - X^q)_{LL'}^{-1} \bar{\Gamma}_{L'}^q(\vec{g}), \quad (74)$$

$$\int d^3 r_\beta g(\vec{r}_\beta) \vec{\nabla} V(\vec{r}) = \lim_{\epsilon \rightarrow 0^+} \left(\int_0^{b_\beta - \epsilon} d^3 r_\beta g(\vec{r}_\beta) \vec{\nabla} V^\epsilon(\vec{r}_\beta) \right) + \int_{b_\beta - \epsilon}^{b_\beta + \epsilon} d^3 r_\beta g(\vec{r}_\beta) \vec{\nabla} V^\epsilon(\vec{r}_\beta) + \int_{b_\beta + \epsilon}^\infty d^3 r_\beta g(\vec{r}_\beta) \vec{\nabla} V^\epsilon(\vec{r}_\beta), \quad (77)$$

where we have replaced $V(\vec{r})$ by the smooth potential $V^\epsilon (V^\epsilon - V \text{ as } \epsilon \rightarrow 0)$. The first term is just the integral inside β and the last term is equal to zero because $\vec{\nabla} V = 0$ in that region. The radial

$$\int_{b_\beta^+} d^3 r_\beta g(\vec{r}_\beta) \vec{\nabla} V(\vec{r}) = \int_0^{b_\beta} d^3 r_\beta g(r_\beta) \vec{\nabla} V(r_\beta) + \int g(b_\beta) [V_{\text{II}} - V(b_\beta)] d\Omega_\beta. \quad (78)$$

where $\alpha_0 = (2m/\hbar^2)(2\pi i/NA)$ and

$$\bar{\Gamma}_{L'}^q(\vec{g}) = \sum_{\beta(q)} e^{-i\vec{k}^*(\vec{g})\cdot(\vec{R}_\beta - \vec{R}_q^0)} F_{L'}^\beta, \quad (75)$$

where \vec{R}_q^0 is an origin in the q th layer. It could be one of the $\beta(q)$ atoms. The quantity $Q^q(\vec{k}^*(\vec{g}))$ represents electron amplitudes excited from the q th layer in directions outwards (+ sign) and inwards (- sign). Subsequent scattering are done by matrices $M_{\epsilon_1\epsilon_2}^{q\pm\pm}$ at layer q and propagations by $P_{\epsilon_1\epsilon_2}^\pm$ in between layers. Summing the layer scatterings to convergence can then be done by perturbation methods, such as RFS or layer doubling.²⁷

VIII. EVALUATION OF F^β

From Eqs. (58) and (23), we have

$$F_L^\beta = D \int_{\rho^+} d^3 r_\beta e^{i\delta_i^\beta} R_i^f(r_\beta) Y_L^*(\vec{r}_\beta) \vec{A} \cdot \vec{\nabla} V(r_\beta) \times \sum_{L_i} C_{L_i}^\beta \bar{R}_{i_i}^\beta(r_\beta) \bar{Y}_{L_i}(\vec{r}_\beta), \quad (76)$$

where

$$D = -(-i)^l (-i\hbar) \left(\frac{e}{mc} \right) \frac{1}{\epsilon_f - \epsilon_i}.$$

First we note that because of the muffin-tin-type potential, there is a discontinuity of V across the sphere surface. Thus, in the evaluation of F_L^β , the integral should be written as

integral of the second term can be shown, by the mean theorem, to be $g(b_\beta)[V_{\text{II}} - V(b_\beta)]$, where V_{II} is the constant potential in the intersphere region. Thus, we have

Secondly, we note that although the vector potential \vec{A} is spatially dependent, i.e., $\vec{A}(\vec{r}) = \vec{A}_0 e^{-i\vec{q}\cdot\vec{r}}$, for ultraviolet light frequencies, $|\vec{k}_f| \gg |\vec{q}|$ and \vec{A} may be taken as constant inside the cluster. Then Eq. (76) becomes

$$F_L^\beta = D \sum_{L_i} C_{L_i}^\beta e^{i\delta_{L_i}^\beta} \vec{L}_i \cdot \int_{B^+} d^3r_\beta R_{L_i}^\beta(r_\beta) Y_{L_i}^*(\vec{r}_\beta) \vec{\nabla} V(r_\beta) \vec{R}_{L_i}^\beta(r_\beta) \vec{Y}_{L_i}(\vec{r}_\beta). \quad (79)$$

We note that

$$\vec{\nabla} V(r_\beta) = \left(\frac{4\pi}{3}\right)^{1/2} \frac{dV(r_\beta)}{dr_\beta} \sum_{p=-1}^1 (-1)^p \hat{e}_p \vec{Y}_{1p}(\vec{r}_\beta), \quad (80)$$

where $\hat{e}_1 = \hat{x}$, $\hat{e}_{-1} = \hat{y}$ and $\hat{e}_0 = \hat{z}$. Then we have

$$F_L^\beta = D \sum_{L_i} C_{L_i}^\beta e^{i\delta_{L_i}^\beta} \left(\frac{4\pi}{3}\right)^{1/2} \sum_{p=-1}^1 (-1)^p A_{\vec{L}_i}(L; 1, p; L_i) \int_{B^+} dr_\beta r_\beta^2 R_{L_i}^\beta(r_\beta) \frac{dV(r_\beta)}{dr_\beta} \vec{R}_{L_i}^\beta(r_\beta) \quad (81)$$

where

$$\vec{I}(L_1, L_2, L_3) = \int d\Omega_\beta Y_{L_1}^*(\vec{r}_\beta) \vec{Y}_{L_2}(\vec{r}_\beta) \vec{Y}_{L_3}(\vec{r}_\beta), \quad (82)$$

and

$$A_1 = A_x, \quad A_{-1} = A_y, \quad A_0 = A_z. \quad (83)$$

IX. REFLECTION AND REFRACTION OF A AT THE INTERFACE

If the incident photon makes angles (θ, ϕ) with the surface coordinate system (θ measured from the surface normal), then we define p (parallel) and s (perpendicular) polarization components of the vector potential by

$$A_x(p) = A \sin\theta; \quad A_x(s) = 0; \quad (84)$$

$$A_x(p) = -A \cos\theta \cos\phi; \quad A_x(s) = -A' \sin\phi; \quad (85)$$

$$A_y(p) = -A \cos\theta \sin\phi; \quad A_y(s) = A' \cos\phi. \quad (86)$$

At the interface of two mediums, the photon field above (incident plus reflected \vec{A}) and below (refracted \vec{A}) are different. For the photon field above the boundary,

$$A_x^T(p) = (1 + \beta_2) A_x(p); \quad A_x^T(s) = 0; \quad (87)$$

$$A_x^T(p) = (1 - \beta_2) A_x(p); \quad A_x^T(s) = (1 + \beta_1) A_x(s); \quad (88)$$

$$A_y^T(p) = (1 - \beta_2) A_y(p); \quad A_y^T(s) = (1 + \beta_1) A_y(s); \quad (89)$$

where

$$\beta_1 = \frac{\cos\theta - (n^2 - \sin^2\theta)^{1/2}}{\cos\theta + (n^2 - \sin^2\theta)^{1/2}}, \quad (90)$$

$$\beta_2 = \frac{n^2 \cos\theta - (n^2 - \sin^2\theta)^{1/2}}{n^2 \cos\theta + (n^2 - \sin^2\theta)^{1/2}}, \quad (91)$$

and $n = (\epsilon_2/\epsilon_1)^{1/2}$ is the ratio of dielectric constants

of the two mediums. Note that β_1, β_2, n are complex and the positive roots are taken in Eqs. (90) and (91). The light travels from material with ϵ_1 into ϵ_2 . The photon field below the interface, i.e., the reflected wave can be written as

$$A_x^R(p) = \alpha_2 \cos\theta A_x(p); \quad A_x^R(s) = 0; \quad (92)$$

$$A_x^R(p) = \alpha_2 (n^2 - \sin^2\theta)^{1/2} A_x(p); \quad A_x^R(s) = \alpha_1 A_x(s); \quad (93)$$

$$A_y^R(p) = \alpha_2 (n^2 - \sin^2\theta)^{1/2} A_y(p); \quad A_y^R(s) = \alpha_1 A_y(s). \quad (94)$$

Here again, α_1 and α_2 are complex and defined as

$$\alpha_1 = \frac{2 \cos\theta}{\cos\theta + (n^2 - \sin^2\theta)^{1/2}}, \quad (95)$$

$$\alpha_2 = \frac{2}{n^2 \cos\theta + (n^2 - \sin^2\theta)^{1/2}}. \quad (96)$$

In Eq. (83), the proper components of the \vec{A} vector given in Eqs. (87)–(89) and (92)–(94) are to be substituted.

Finally, the energy and momentum factor to be multiplied to the coefficient $|C(\vec{k}^*(\vec{g}))|^2$ given in Eq. (70) to obtain the measured photoemission intensity per incident photon is

$$I \propto |\vec{k}_f^{\text{out}}| (k_{1f}^{\text{out}})^2 \frac{1}{\omega_{\text{ph}}} |C(\vec{k}^*(\vec{g}))|^2 \quad (97)$$

where \vec{k}_f^{out} is the outside electron momentum and ω_{ph} is the photon frequency.

X. RESULTS OF c(2X2) O AND S ON Ni(001) OVERLAYER SYSTEMS

Photoemission intensity spectra using Eq. (97) are calculated from the adsorbate induced p levels

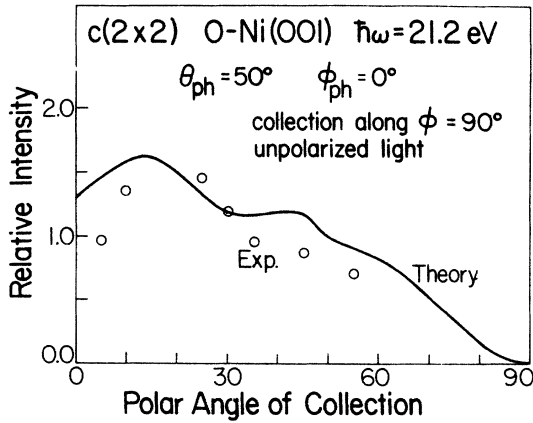


FIG. 1. Polar emission plots for $c(2 \times 2)$ O-Ni(001). Solid line: theory; circles: experiment.

of $c(2 \times 2)$ O and S overlayer systems on Ni(001). The initial states are obtained from cluster wave functions of one adsorbate (S or O) and five nickel atoms. The adsorbate sits at a four-fold site at vertical spacing 0.9 Å for O and 1.3 Å for S.²⁸ The nickel atoms are arranged with four atoms in one plane forming a square and the fifth atom occupies the four-fold location in the layer below. Bulk bond distances are used between the nickel atoms. Dynamical inputs used in LEED calculations are employed here for the final-state electron scattering process, i.e., inner potential $V_0 = 11.2$ eV and inelastic damping $V_i = 2.5$ eV. Below the vacuum-solid interface, the refracted vector potential \vec{A}^R given in Eqs. (92)–(94) are used. The optical constants ϵ_1, ϵ_2 are taken for nickel from Ref. 29.

In Fig. 1, we show the calculated polar emission plot for $c(2 \times 2)$ O-Ni(001) at $\theta_{ph} = 50^\circ$, $\hbar\omega = 21.2$ eV, using unpolarized light. The calculated results are compared with the data of Weeks and Plummer.³ The convention used to describe the azimuthal direction of the photon incident plane is shown in Fig. 2.

The dependences of polar emission profiles on photon incident azimuthal directions are shown in

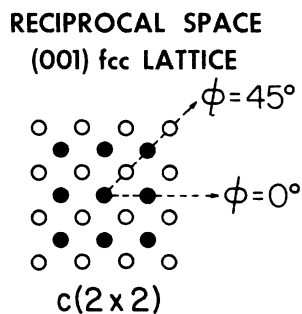


FIG. 2. Convention used to describe the azimuthal direction of the photon incident plane.

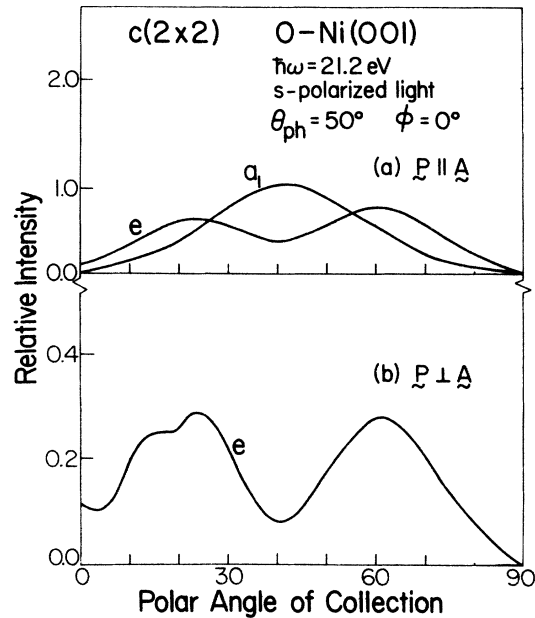


FIG. 3. Polar emission plots for $c(2 \times 2)$ O-Ni(001) using s -polarized light. Photon incident along $\phi = 0^\circ$. (a) Emission parallel to the incident plane; (b) emission perpendicular to the incident plane.

Figs. 3 and 4 for $c(2 \times 2)$ O-Ni(001) and in Fig. 5 for $c(2 \times 2)$ S-Ni(001). For the O-Ni(001) system, s -polarized light is used with the \vec{A} vector along the $\phi = 0^\circ$ and $\phi = 45^\circ$ directions, respectively. For

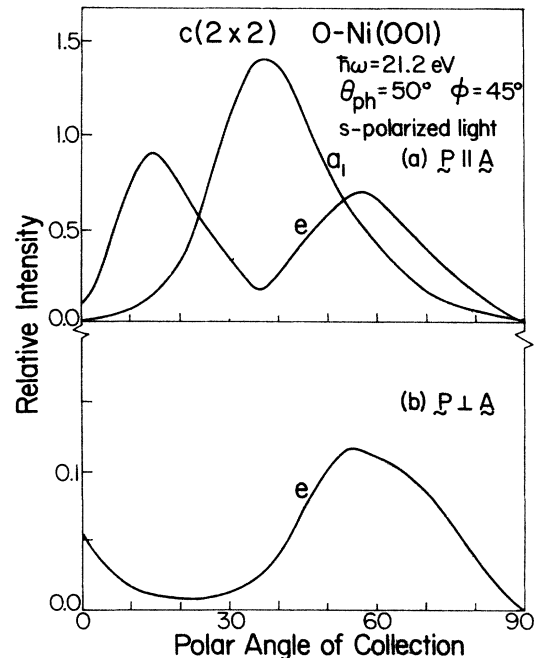


FIG. 4. Polar emission plots for $c(2 \times 2)$ O-Ni(001) using s -polarized light. Photon incident along $\phi = 45^\circ$. (a) Emission parallel to the incident plane; (b) emission perpendicular to the incident plane.

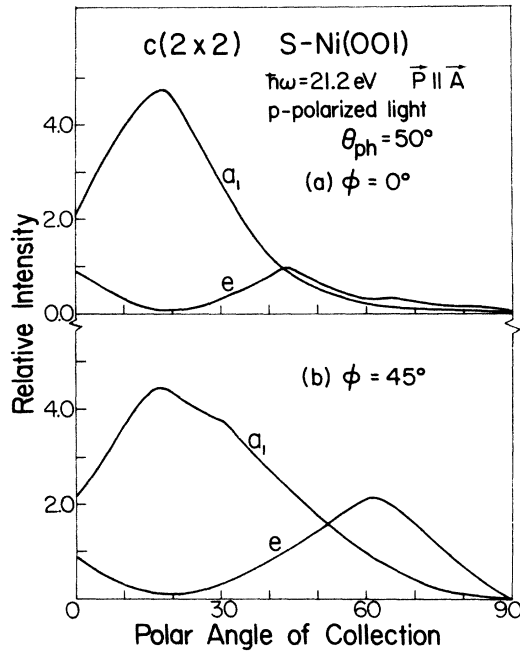


FIG. 5. Polar emission plots for $c(2 \times 2)$ S-Ni(001) using p -polarized light. Emission parallel to the incident plane. (a) Photon incident along $\phi = 0^\circ$; (b) photon incident along $\phi = 45^\circ$.

the S-Ni(001) system, p -polarized light is used. In the case of O-Ni(001), we note that for the \vec{A} vector along $\phi = 45^\circ$, the emissions along the plane parallel to \vec{A} ($\vec{P} \parallel \vec{A}$) and the emissions along the plane perpendicular to \vec{A} ($\vec{P} \perp \vec{A}$) separate complete-

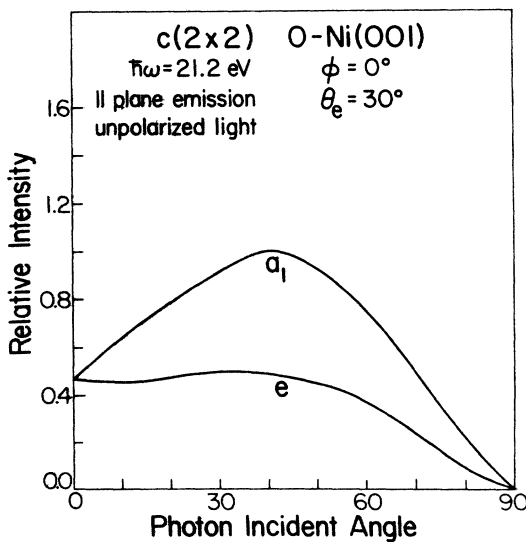


FIG. 6. Variation of electron emission as a function of photon incident angle for $c(2 \times 2)$ O-Ni(001). Emission parallel to the plane of incidence. Photon incident along $\phi = 0^\circ$.

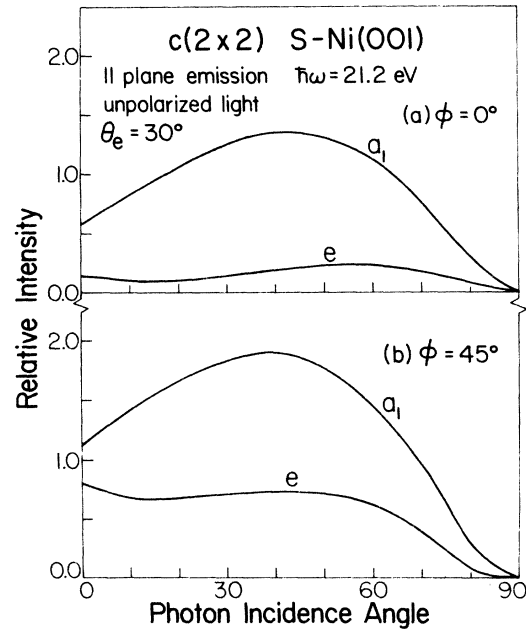


FIG. 7. Variation of electron emission as a function of photon incident angle for $c(2 \times 2)$ S-Ni(001). Emission parallel to the plane of incidence. (a) Photon incident along $\phi = 0^\circ$; (b) photon incident along $\phi = 45^\circ$.

ly contributions from a_1 and e states for θ_{emission} between 30° and 45° . This is a good example when surface states having different symmetries are separated by measuring along different polarization directions.

The variations of electron emission as a function of photon incident angle are shown in Figs. 6 and 7 for $c(2 \times 2)$ O-Ni(001) and $c(2 \times 2)$ S-Ni(001), respectively. We use unpolarized light $\hbar\omega = 21.2$ eV for both systems. For O-Ni system, the plane of incidence is along $\phi = 0^\circ$, while for the S-Ni system, results of both $\phi = 0^\circ$ and $\phi = 45^\circ$ are shown. In Fig. 6, we note that for the O-Ni system, both a_1 and e states have substantial contributions. In contrast, we note in Fig. 7(a) that for the S-Ni system, the a_1 state dominates the electron emission at most angles. This is interesting because in the calculations, both O and S are put at four-fold registry sites. Thus, the different emission behaviors cannot be explained by arguing that O and S sit at different "types" of sites. We trace the differences in the emission partly to different amounts of wave function overlaps the O and S p levels have with the nickel atoms. We also suspect that this behavior is photon energy dependent.

ACKNOWLEDGMENT

This work supported in part by NSF DMR 73-02614.

APPENDIX A: EQUIVALENCE OF THE \vec{V} AND $\vec{\nabla}V$ FORM
FOR THE INTERACTION HAMILTONIAN

In Eq. (1) we have

$$\psi(\vec{R}) = \int d^3r G(\vec{R} - \vec{r}) \left(-\frac{e}{mc} \right) \vec{A} \cdot \vec{P} \psi_i(\vec{r}),$$

where ψ_i and G satisfy

$$H|\psi_i\rangle = \epsilon_i |\psi_i\rangle,$$

$$H(\vec{r})G(\vec{R} - \vec{r}) = \epsilon_f G(\vec{R} - \vec{r}) - \delta(\vec{R} - \vec{r}),$$

with H as the unperturbed Hamiltonian for the entire system

$$H = -(\hbar^2/2m)\nabla^2 + V(\vec{r}).$$

Then we have

$$\begin{aligned} & \int d^3r G(\vec{R} - \vec{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right) \vec{\nabla} \psi_i(\vec{r}) \\ &= \int d^3r \epsilon_f G(\vec{R} - \vec{r}) \vec{\nabla} \psi_i(\vec{r}) - \int d^3r \delta(\vec{R} - \vec{r}) \vec{\nabla} \psi_i(\vec{r}) \\ &= \epsilon_f \int d^3r G(\vec{R} - \vec{r}) \vec{\nabla} \psi_i(\vec{r}) - [\vec{\nabla} \psi_i(r)]_{\vec{r}=\vec{R}}. \end{aligned} \quad (\text{A1})$$

The second term vanishes because $\psi_i(\vec{r})$ is supposed to be a localized state inside the cluster and \vec{R} is the observation point far away from the sample. Thus,

$$\begin{aligned} \int d^3r G(\vec{R} - \vec{r}) \vec{\nabla}(\epsilon_i \psi_i(\vec{r})) &= \int d^3r G(\vec{R} - \vec{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \vec{\nabla} \psi_i(\vec{r}) + \int d^3r G(\vec{R} - \vec{r}) [\vec{\nabla} V(\vec{r})] \psi_i(\vec{r}) \\ &= \epsilon_f \int d^3r G(\vec{R} - \vec{r}) \vec{\nabla} \psi_i(\vec{r}) + \int d^3r G(\vec{R} - \vec{r}) [\vec{\nabla} V(\vec{r})] \psi_i(\vec{r}), \end{aligned}$$

where the first term is obtained from Eq. (A1). Therefore,

$$\begin{aligned} & \int d^3r G(\vec{R} - \vec{r}) \vec{\nabla} \psi_i(\vec{r}) \\ &= -\frac{1}{\epsilon_f - \epsilon_i} \int d^3r G(\vec{R} - \vec{r}) [\nabla V(\vec{r})] \psi_i(\vec{r}) \end{aligned}$$

and

$$\begin{aligned} \psi(\vec{R}) &= \int d^3r G(\vec{R} - \vec{r}) \left(-\frac{e}{mc} \right) \vec{A} \cdot \vec{P} \psi_i(\vec{r}) \\ &= \int d^3r G(\vec{R} - \vec{r}) \left(-i\hbar \frac{e}{mc} \frac{1}{\epsilon_f - \epsilon_i} \right) \vec{A} \cdot \vec{\nabla} V(\vec{r}) \psi_i(\vec{r}). \end{aligned}$$

Hence, the $\vec{\nabla}$ form of the interaction Hamiltonian is equivalent to $\vec{\nabla}V$ form as in Eqs. (13) and (15).

APPENDIX B: SEPARATION OF THE FINAL STATE

Let us consider the single-scattering term $G_0 t_\alpha G_0 |\phi\rangle$ in Eq. (10)

$$\begin{aligned} G_0 t_\alpha G_0 |\phi\rangle &= \int d^3r_1 d^3r_2 d^3r G_0(\vec{R} - \vec{r}_1) \\ &\quad \times t_\alpha(\vec{r}_1 - \vec{R}_\alpha, \vec{r}_2 - \vec{R}_\alpha) G(\vec{r}_2 - \vec{r}) \phi(\vec{r}). \end{aligned} \quad (\text{B1})$$

$$\begin{aligned} G_0 t_\alpha G_0 |\phi\rangle &= -ik_0 \left(\frac{2m}{\hbar^2} \right) \sum_L h_L^{(\alpha)}(k_0 | \vec{R} - \vec{R}_\alpha |) Y_L(\vec{R} - \vec{R}_\alpha) \\ &\quad \times \int d^3\rho \left(\int \rho_1^2 d\rho_1 \rho_2^2 d\rho_2 j_L(k_0 \rho_1) t_L^{(\alpha)}(\rho_1 \rho_2) G_L(\rho_2 \rho) \right) Y_L^*(\vec{\rho}) \phi(\vec{\rho} + \vec{R}_\alpha). \end{aligned}$$

Let

$$\vec{\rho}_1 = \vec{r}_1 - \vec{R}_\alpha, \quad \vec{\rho}_2 = \vec{r}_2 - \vec{R}_\alpha, \quad \vec{\rho} = \vec{r} - \vec{R}_\alpha,$$

and

$$t_\alpha(\vec{\rho}_1, \vec{\rho}_2) = \sum_{L_1} t_{L_1}^{(\alpha)}(\rho_1 \rho_2) Y_{L_1}(\vec{\rho}_1) Y_{L_1}^*(\vec{\rho}_2), \quad (\text{B2})$$

$$G_0(\vec{\rho}_2 - \vec{\rho}) = \sum_{L_2} G_{L_2}(\rho_2 \rho) Y_{L_2}(\vec{\rho}_2) Y_{L_2}^*(\vec{\rho}). \quad (\text{B3})$$

Also,

$$\begin{aligned} G_0(\vec{R} - \vec{r}_1) &= -ik_0 \left(\frac{2m}{\hbar^2} \right) \sum_L h_L^{(\alpha)}(k_0 | \vec{R} - \vec{R}_\alpha |) \\ &\quad \times Y_L(\vec{R} - \vec{R}_\alpha) \\ &\quad \times j_L(k_0 \rho_1) Y_L^*(\vec{\rho}_1), \end{aligned} \quad (\text{B4})$$

where the last equality holds only when $|\vec{R} - \vec{R}_\alpha| > \rho_1$. Indeed, this condition is satisfied since the integration in Eq. (B1) is only over the α th sphere because of the finite range of the potential due to the α th sphere. Substituting Eqs. (B2), (B3), and (B4) into Eq. (B1) and using the orthonormality of the spherical harmonics, we have

For a spherical potential $V(r_\alpha)$, the quantity inside the bracket is just $e^{i\delta_\alpha} R_i^\alpha(r_\alpha) - j_i(k_0 r_\alpha)$, where $R_i^\alpha(r_\alpha)$ is the normalized radial part of the solution to Schrödinger's equation inside sphere α . Putting $\vec{\rho} = \vec{r} - \vec{R}_\alpha$, we have

$$G_0 t_\alpha G_0 |\phi\rangle = ik_0 \left(\frac{2m}{\hbar^2} \right) \sum_L (-i)^{-l} h_l^{(1)}(k_0 |\vec{R} - \vec{R}_\alpha|) \times Y_L(\vec{R} - \vec{R}_\alpha) M_L^\alpha,$$

where M_L^α is as defined in Eq. (17).

Just as in the case of core level photoemission, the multiple-scattering term is

$$G_0 T'_\alpha G_0 t_\alpha G_0 |\phi\rangle = ik_0 \left(\frac{2m}{\hbar^2} \right) \sum_{LL'} (-i)^{-l} h_l^{(1)}(k_0 |\vec{R} - \vec{R}_\alpha|) Y_{L'}(\vec{R} - \vec{R}_\alpha) \left(\sum_{i,j=0}^{\infty} T^{ij} G^{jq(\alpha)} \right) \sum_{L''} M_{L''}^\alpha,$$

with T^{ij} , G^{jq} as the multilayer T matrix and structure constants defined as follows

$$T^{ij} = \tau^i \delta_{ij} + \tau^i \sum_{q \neq i} G^{iq} T^{qj},$$

$$\tau^i = (1 - t^i G^{ii})^{-1} t^i,$$

$$G_{LL}^{ii} = -4\pi i \left(\frac{2m}{\hbar^2} \right) k_0 \sum_{L_1} \sum_{\vec{P} \neq 0} i^{l_1} a(LL'L_1) h_{l_1}^{(1)}(k_0 |\vec{P}|) Y_{L_1}(\vec{P}) e^{-i\vec{k}_0 \cdot \vec{P}},$$

$$G_{LL}^{ij} = -4\pi i \left(\frac{2m}{\hbar^2} \right) k_0 \sum_{L_1} \sum_{\vec{P} \neq 0} i^{l_1} a(LL'L_1) h_{l_1}^{(1)}(k_0 |\vec{P} + \vec{d}_i - \vec{d}_j|) Y_{L_1}(\vec{P} + \vec{d}_i - \vec{d}_j) e^{-i\vec{k}_0 \cdot (\vec{P} + \vec{d}_i - \vec{d}_j)} \quad (i \neq j),$$

$$a(LL'L_1) = \int d\Omega Y_{L'}^*(\vec{r}) Y_{L'}(\vec{r}) Y_{L_1}(\vec{r}),$$

and \vec{d}_i, \vec{d}_j are the vectors from the reference origin to the i th and j th layer. (d_i^z is negative into the crystal.)

By summing over all the contributions from different spheres α , we obtain the expression for $\psi(\vec{R})$ as in Eq. (16).

APPENDIX C: EXPANSION THEOREM FOR

$$[e^{i\delta_\alpha} R_i^\alpha(r_\alpha) - j_i(k_0 r_\alpha)] Y_{L'}^*(\vec{r}_\alpha)$$

When \vec{r}_α lies outside of sphere α and is inside sphere β , we have

$$\begin{aligned} [e^{i\delta_\alpha} R_i^\alpha(r_\alpha) - j_i(k_0 r_\alpha)] Y_{L'}^*(\vec{r}_\alpha) &= ie^{i\delta_\alpha} \sin \delta_\alpha h_l^{(1)}(k_0 r_\alpha) Y_{L'}^*(\vec{r}_\alpha) \\ &= ie^{i\delta_\alpha} \sin \delta_\alpha 4\pi \sum_{L''} i^{l''} a(LL_1 L'') h_{l''}^{(1)}(k_0 R_{\alpha\beta}) Y_{L''}(\vec{R}_{\alpha\beta}) j_{l''}(k_0 r_\beta) Y_{L_1}^*(\vec{r}_\beta), \end{aligned}$$

which follows by expanding $h_l^{(1)}(k_0 r_\alpha) Y_{L'}^*(\vec{r}_\alpha)$ about \vec{R}_β . Noting that

$$t_i^\alpha(k_0) = -\frac{\hbar^2}{2m} \frac{1}{k_0} e^{i\delta_\alpha} \sin \delta_\alpha$$

and

$$\begin{aligned} G_{LL_1}^{\alpha\beta}(k_0) &= -4\pi i \left(\frac{2m}{\hbar^2} \right) k_0 \sum_{L''} i^{l''} a(LL_1 L'') h_{l''}^{(1)} \\ &\quad \times (k_0 R_{\alpha\beta}) Y_{L''}(\vec{R}_{\alpha\beta}), \end{aligned}$$

we have

$$\begin{aligned} [e^{i\delta_\alpha} R_i^\alpha(r_\alpha) - j_i(k_0 r_\alpha)] Y_{L'}^*(\vec{r}_\alpha) \\ = t_i^\alpha \sum_{L_1} G_{LL_1}^{\alpha\beta} j_{l_1}(k_0 r_\beta) Y_{L_1}^*(\vec{r}_\beta). \end{aligned}$$

Also, note that $G_{LL_1}^{ij}$, $G_{LL_1}^{ii}$, and $G_{LL_1}^{\alpha\beta}$ are related by

$$\begin{aligned} G_{LL_1}^{ii}(\vec{k}) &= \sum_{\substack{\alpha(i) \\ \alpha \neq \beta}} e^{-i\vec{k} \cdot \vec{R}_{\alpha\beta}} G_{LL_1}^{\alpha(i)\beta(i)}(\vec{k}), \\ G_{LL_1}^{ij}(\vec{k}) &= \sum_{\alpha(i)} e^{-i\vec{k} \cdot \vec{R}_{\alpha\beta}} G_{LL_1}^{\alpha(i)\beta(j)}(\vec{k}), \end{aligned}$$

where the index $\alpha(i)$ represents the α th atom in the i th layer, and $\beta(j)$ is an arbitrary atom in layer j .

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