J. Mustre de Leon, J.J. Rehr, C.R. Natoli, C.S. Fadley, J. Osterwalder

SPHERICAL-WAVE CORRECTIONS IN PHOTOELECTRON DIFFRACTION

.

Spherical-wave corrections in photoelectron diffraction

J. Mustre de Leon and J. J. Rehr

Department of Physics (FM-15), University of Washington, Seattle, Washington 98195

C. R. Natoli

Laboratori Nazionali di Frascati dell'Istituto Nazionale di Fisica Nucleare, Cassella Postale 13, I-00044 Frascati (Roma), Italy

C. S. Fadley and J. Osterwalder

Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822

(Received 11 April 1988; revised manuscript received 28 June 1988)

We present a formulation of photoelectron diffraction which generalizes that based on the plane-wave approximation. Explicit expressions for K- and L-shell photoemission are given. Single-scattering terms are treated exactly in terms of effective distance-dependent scattering amplitudes $f^{(i)}(\theta,R)$. Spherical-wave corrections in the theory can be approximated with use of asymptotic expansions for the one-particle propagators. This spherical-wave approximation (SWA) explains observed corrections to the plane-wave approximation and is found to be in good agreement with the full, single-scattering, spherical-wave treatment. The relation between photoelectron diffraction and x-ray-absorption fine structure (XAFS) is discussed with use of a generalized optical theorem.

I. INTRODUCTION

In photoelectron diffraction (PD), the variation of the differential photoemission cross section with either energy or direction can be used to investigate the local environment of a particular atom.[1] The energy-dependent form is often termed angle-resolved photoemission extended fine structure (ARPEFS), and it bears a close relationship to x-ray-absorption fine structure (XAFS). In the plane-wave approximation to PD,[2] the differential photoemission cross section $d\sigma/d\Omega$ for emission from a core orbital ψ_c into a direction $\hat{k}$ is proportional to $|\langle \psi_k|\hat{\epsilon}\cdot r|\psi_c\rangle|^2$; in the presence of a scatterer at a distance R from the absorbing atom this is readily evaluated and for a K-shell core state gives

$$\frac{d\sigma}{d\Omega} \propto \left| \hat{\epsilon}\cdot\hat{k} + \frac{e^{ikR(1-\cos\theta)}}{R}\hat{\epsilon}\cdot\hat{R}f(\theta) \right.$$

$$\left. + \frac{e^{i2kR}}{R^2}\hat{\epsilon}\cdot\hat{R}f(\pi)f_c(\pi-\theta) \right|^2 . \tag{1}$$

where $f(\theta)$ and $f_c(\theta)$ are the plane-wave scattering amplitudes of the scatterer and absorbing atom, respectively. Here, we include second-order scattering events that are necessary to ensure conservation of flux, although these are often omitted in analysis of PD data.[1] However, the plane-wave approximation is found to be inadequate even at moderately high energies (100–200 eV), and it is thus necessary to take into account the spherical-wave nature of the photoelectron final state.[3,4] This spherical-wave generalization is carried out in detail here. In contrast to the treatment of Barton and Shirley,[3] who consider the photoelectron wave function to be simply an outgoing spherical wave of a given angular momentum, our formalism is based on an exact, time-reversed scattering

state for the photoelectron.[5] Thus our treatment explicitly takes into account possible interference between different angular momentum channels which will be important in PD from any non-s subshell, while that of Ref. 3 does not consider this complication. Consequently, our treatment allows us to determine the PD for a core state of arbitrary angular momentum as well as the partial differential cross section $d\sigma/d\Omega$. When $d\sigma/d\Omega$ is integrated over all possible directions one must obtain the total absorption and consequently the correct XAFS formula. We show that this reduction is the result of a generalized optical theorem for spherical waves.

In Sec. II we evaluate the differential cross section for a single scatterer and discuss its plane-wave limit. Section III contains explicit spherical-wave corrections to the plane-wave approximation for K- and $L_{2,3}$-shell absorption. The spherical-wave corrections can be approximated accurately by asymptotic expansions for the single-particle propagator, the "spherical-wave approximation" of Ref. 4. We show that the basic structure of Eq. (1) is preserved provided one generalizes the plane-wave scattering amplitude $f(\theta)$ to a linear combination of effective scattering amplitudes, $f^{(i)}(\theta,R)$, which depend on the distance between absorbing atom and scatterer. In this section, we also discuss other aspects of photoelectron diffraction theory, e.g., the inclusion of lattice vibrations, inelastic losses, and the presence of a surface. In Sec. IV we show numerical comparisons between PD calculated with the plane-wave scattering amplitude $f(\theta)$ and with the spherical-wave theory. Finally, in Sec. V, we show how solid-angle integration of the differential photoemission cross section leads to the correct XAFS formula.

II. PHOTOEMISSION CROSS SECTION IN THE PLANE-WAVE LIMIT

The photoelectron final state in the photoabsorption process can be viewed as a time-reversed scattering state.[5]

For an isolated atom, this state $|\psi_\mathbf{k}^0\rangle$ consists of *incoming spherical waves* centered at the origin $\langle \mathbf{r}|L^-,0\rangle = i^l h_l^-(kr)Y_L(\hat{\mathbf{r}})$, and an *outgoing plane wave* $\langle \mathbf{r}|\mathbf{k}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}$ in the observation direction $\hat{\mathbf{k}}$,

$$|\psi_\mathbf{k}^0\rangle = (1 + G^- t_c^\dagger)|\mathbf{k}\rangle = |\mathbf{k}\rangle + 4\pi \sum_L Y_L^*(\hat{\mathbf{k}})t_l^{c*}|L^-,0\rangle,$$

$$(2)$$

where t^c denotes the dimensionless central-atom t matrix, G^- is the incoming free-particle propagator [i.e., $G^- = (k^2/2 - H_0 - i0^+)^{-1}$], Y_L denotes a spherical harmonic of angular momentum L ($\equiv \{l,m\}$), and h_l^- is a spherical Bessel function. Throughout this paper we use atomic units, $e = \hbar = m_e = 1$. The photoelectron state in the presence of a scatterer at site $\mathbf{R}$ is given, to linear order in $t_\mathbf{R}$, by

$$|\psi_\mathbf{k}\rangle = (1 + G_c^- t_\mathbf{R}^\dagger)|\psi_\mathbf{k}^0\rangle,$$

$$(3)$$

where $t_\mathbf{R}$ is the t matrix of the scatterer at $\mathbf{R}$ with components $t_l = e^{i\delta_l}\sin\delta_l$ (site index suppressed) and G_c^- is the exact incoming propagator in the presence of the absorbing atom, (i.e., $G_c = G + Gt_cG$).

Now consider the dipole matrix element between a core state $|\psi_c\rangle$ and the final photoelectron state $|\psi_\mathbf{k}\rangle$, i.e., the fully relaxed final state which is calculated in the presence of the core hole,

$$M_{c\mathbf{k}} = \langle\psi_c|\hat{\mathbf{\varepsilon}}\cdot\mathbf{r}|\psi_\mathbf{k}\rangle = \langle\psi_c|\hat{\mathbf{\varepsilon}}\cdot\mathbf{r}(1 + G_c^- t_\mathbf{R}^\dagger)|\psi_\mathbf{k}^0\rangle.$$

$$(4)$$

Throughout this paper we shall use the phase convention $\psi_L(\mathbf{r}) = \langle\mathbf{r}|\psi_L\rangle = i^l R_l(kr)Y_L(\hat{\mathbf{r}})$ to denote eigenstates of the Hamiltonian with angular momentum L, where the radial wave function $R_l(kr)$ is regular at the origin and normalized by the condition $R_l(kR_{MT}) = j_l(kR_{MT})\cos\delta_l^c - n_l(kR_{MT})\sin\delta_l^c$, where R_{MT} denotes the muffin-tin radius. This condition and continuity of R_l' at R_{MT} defines the phase shifts δ_l. The outgoing part $|\psi_L^+\rangle$ is denoted by the same formula with R_l replaced by R_l^+, where $R_l^+(kR_{MT}) = e^{i\delta_l^c}h_l^+(kR_{MT})$. Similarly, free particle states of angular momentum L centered at $\mathbf{r} = \mathbf{R}$ are denoted by $|L,\mathbf{R}\rangle$, where $\langle\mathbf{r}|L,\mathbf{R}\rangle = i^l j_l(k|\mathbf{r}-\mathbf{R}|)Y_L(\Omega_\mathbf{R})$, and the outgoing part $|L^+,\mathbf{R}\rangle$ is given by the same formula with j_l replaced by h_l^+. Now using the decomposition of the propagator, $G_c = \sum_L |\psi_L^+\rangle\langle\psi_L| = (G_c^-)^\dagger$, in Eq. (4) we obtain

$$M_{c\mathbf{k}}^* = \langle\psi_\mathbf{k}^0|\hat{\mathbf{\varepsilon}}\cdot\mathbf{r}|\psi_c\rangle + \sum_L \langle\psi_\mathbf{k}^0|t_\mathbf{R}|\psi_L^+\rangle\langle\psi_L|\hat{\mathbf{\varepsilon}}\cdot\mathbf{r}|\psi_c\rangle.$$

$$(5)$$

Using the alternative representation $|\psi_\mathbf{k}^0\rangle = 4\pi\sum_L Y_L^*(\hat{\mathbf{k}}) \times e^{-i\delta_l^c}|\psi_L\rangle$ to evaluate the first term in Eq. (5) and Eq. (2) to evaluate the second, one obtains

$$M_{c\mathbf{k}}^* = \sum_{L_f} \left[4\pi Y_{L_f}(\hat{\mathbf{k}}) + \sum_L \langle\mathbf{k}|t_\mathbf{R}|L,\mathbf{R}\rangle G_{L,L_f}(\mathbf{R}) \right.$$

$$\left. + 4\pi \sum_{L,L'} Y_{L'}(\hat{\mathbf{k}})t_{l'}^c\langle L'^-,0|t_\mathbf{R}|L,\mathbf{R}\rangle G_{L,L_f}(\mathbf{R}) \right]$$

$$\times \langle\psi_{L_f}|\hat{\mathbf{\varepsilon}}\cdot\mathbf{r}|\psi_c\rangle e^{i\delta_{l_f}^c},$$

$$(6)$$

where we have used $\langle\mathbf{r}|\psi_L^+\rangle = e^{i\delta_l^c}\langle\mathbf{r}|L^+,0\rangle$, for $\mathbf{r}$ outside the muffin tin radius of the central atom, and the identity $\langle L,\mathbf{R}|L'^+,\mathbf{R}'\rangle \equiv G_{L,L'}(\mathbf{R}-\mathbf{R}')$. Here $G_{LL'}(\mathbf{R}-\mathbf{R}') = \langle L,\mathbf{R}|G|L',\mathbf{R}'\rangle$ denotes the outgoing free-particle propagator in an angular momentum representation. The sum over L_f goes over all final states allowed by the dipole selection rules, e.g., p states for K-shell core states. Expanding the plane-wave state $|\mathbf{k}\rangle$ in terms of states $|L,\mathbf{R}\rangle$ centered at the scatterer, we then get

$$M_{c\mathbf{k}}^* = \sum_{L_f} \left[Y_{L_f}(\hat{\mathbf{k}}) + e^{-i\mathbf{k}\cdot\mathbf{R}}\sum_L Y_L(\hat{\mathbf{k}})t_l G_{L,L_f}(\mathbf{R}) \right.$$

$$\left. + \sum_{L',L} Y_{L'}(\hat{\mathbf{k}})t_{l'}^c G_{L',L}(-\mathbf{R})t_l G_{L,L_f}(\mathbf{R}) \right]$$

$$\times m_{L_f c}^* e^{i\delta_{l_f}^c},$$

$$(7)$$

with $m_{Lc}^* = 4\pi\langle\psi_L|\hat{\mathbf{\varepsilon}}\cdot\mathbf{r}|\psi_c\rangle$. The terms in large parentheses in this sum are interpreted as the direct, single-scattering, and double-scattering terms, respectively. With the approximation of linearity in $t_\mathbf{R}$ in Eq. (3), we ignore repeated scatterings by the atom at $\mathbf{R}$, i.e., triple-scattering and higher-order terms.

In the plane-wave limit $G_{L,L'}(\mathbf{R}) = 4\pi(e^{ikR}/kR) \times Y_L^*(\hat{\mathbf{R}})Y_{L'}(\hat{\mathbf{R}})$. Substituting this in Eq. (7) leads for the case of K-shell absorption to the plane-wave result of Eq. (1), which was previously derived by Lee.[2]

III. SPHERICAL-WAVE CORRECTIONS IN PHOTOEMISSION

To recast Eq. (7) in a form similar to Eq. (1), we take as a starting point the exact z-axis expansion for the propagator of Rehr *et al.*[4]

$$G_{L',L}(\mathbf{R}) = \sum_\mu G_{L',L}^{(\mu)}(\mathbf{R})$$

$$= 4\pi\frac{e^{ikR}}{kR} Y_{l'0}^*(\hat{\mathbf{z}})Y_{l0}(\hat{\mathbf{z}})\sum_\mu D_{L'L}^{(\mu)}g_{l'}^{(|\mu|)}(kR),$$

$$(8)$$

where $g_{ll'}^{(\mu)}$ are dimensionless, z-axis propagators defined in Ref. 4 and the quantity $D_{L'L}^{(\mu)} = D_{\mu m'}^{l'*}(0,\theta_R,\pi-\phi_R) \times D_{\mu m}^l(0,\theta_R,\pi-\phi_R)$, where $D_{\mu m}^l$ are the rotation matrices corresponding to a rotation that takes the vector $\mathbf{R} = (R,\theta_R,\phi_R)$ into the z axis[6] and μ runs over the values $-l_m$ to l_m, where $l_m = \min[l,l']$. Below we shall consider explicitly the cases of K- and $L_{2,3}$-shell photoemission and choose the z axis along the polarization direction $\hat{\mathbf{\varepsilon}}$. For K-shell emission we calculate the single-scattering term of Eq. (7) using Eq. (8). The dominant contribution [$\mu = 0$ in Eq. (8)] is

$$\sum_L Y_L(\hat{\mathbf{k}})t_l G_{L,10}^{(0)}(\mathbf{R}) = \frac{e^{ikR}}{kR} Y_{10}(\hat{\mathbf{R}})$$

$$\times \sum_l (2l+1)t_l P_l(\hat{\mathbf{k}}\cdot\hat{\mathbf{R}})g_{1l}^{(0)}(kR),$$

$$(9)$$

and similarly, the $\mu=\pm1$ corrections, which are smaller than the $\mu=0$ term by a factor $O(1/kR)$, are

$$\sum_L Y_L(\hat{\mathbf{k}})t_l G_{L,10}^{(\pm1)}(\mathbf{R})=\frac{e^{ikR}}{kR}\sum_L t_l Y_L(\hat{\mathbf{k}})D_{\pm1m}^{*l}Y_{l0}^*(\hat{\mathbf{z}})$$

$$\times D_{\pm10}^l Y_{10}(\hat{\mathbf{z}})g_{1l}^{(1)}(kR) .$$

(10)

Summing both contributions and substituting explicit expressions for the spherical harmonics and rotation matrices,[6] the differential photoemission cross section, correct to linear order in f, can be expressed as

$$\frac{d\sigma}{d\Omega}\propto\left|\hat{\boldsymbol{\epsilon}}\cdot\hat{\mathbf{k}}+\frac{e^{ikR(1-\cos\theta)}}{R}[\hat{\boldsymbol{\epsilon}}\cdot\hat{\mathbf{R}}f^{(0)}(\theta,R)\right.$$

$$\left.+\sin\theta_R\cos\phi\, f^{(1)}(\theta,R)]\right|^2 ,$$

(11)

where

$$f^{(0)}(\theta,R)=(1/k)\sum_l(2l+1)t_l P_l(\cos\theta)g_{1l}^{(0)}(kR) ,$$ (12a)

$$f^{(1)}(\theta,R)=(1/k)\sum_l(2l+1)t_l P_l^1(\cos\theta)$$

$$\times\sqrt{2/l(l+1)}g_{1l}^{(1)}(kR) .$$

(12b)

Here $P_l^m(x)$ is the associated Legendre polynomial of order l and degree m, θ is the scattering angle, and ϕ is the dihedral angle between $\hat{\mathbf{k}}$ and $\hat{\boldsymbol{\epsilon}}$ through $\hat{\mathbf{R}}$.[3] In terms of the spherical correction factors $c_l(x)$ to the plane-wave limit of the spherical Hankel functions $h_l^+(x)=i^l(e^{ix}/x)c_l(x)$, we have[4]

$$g_{1l}^{(0)}(kR)=[(l+1)c_{l+1}(kR)+lc_{l-1}(kR)]/(2l+1)$$ (13a)

$$g_{1l}^{(1)}(kR)=i\sqrt{l(l+1)/2}c_l(kR)/kR .$$ (13b)

Because of the factor $1/kR$ in (13b) the term proportional to $f^{(1)}$ in Eq. (11) is generally much smaller than the term proportional to $f^{(0)}$, except near the nodes of the latter or for polarization perpendicular to $\hat{\mathbf{R}}$. The factor $g_{1l}^{(0)}$ in $f^{(0)}$ corrects the plane-wave result for the variation of the radial part of the photoelectron wave function due to the centrifugal barrier in the scattering region (i.e., the muffin-tin sphere centered at the scattering atom).[4] Consequently, this term has the same polarization dependence as the plane-wave result. The term proportional to $g_{1l}^{(1)}$ in $f^{(1)}$ corrects the plane-wave result for the variation of the angular part of the photoelectron wave function in the scattering region,[3] and is smaller by a factor of order $1/kR$.

We define χ to be the normalized, oscillatory part of the PD differential cross section, i.e., $\chi=[d\sigma/d\Omega-(d\sigma/d\Omega)_0]/(d\sigma/d\Omega)_0$, where $(d\sigma/d\Omega)_0$ is the atomic photoemission differential cross section. From Eq. (11), keeping only terms linear in f, we obtain the single-scattering K-shell PD formula

$$\chi=2\,\mathrm{Re}\left[\frac{e^{ikR(1-\cos\theta)}}{R}\left[\frac{\hat{\boldsymbol{\epsilon}}\cdot\hat{\mathbf{R}}f^{(0)}(\theta,R)+\sin\theta_R\cos\phi\, f^{(1)}(\theta,R)}{\hat{\boldsymbol{\epsilon}}\cdot\hat{\mathbf{k}}}\right]\right] .$$

(14)

This expression can be shown to be equivalent to the exact single-scattering expression derived by Barton and Shirley,[3] who assumed the photoelectron wave function to be simply an outgoing spherical wave of a given angular momentum. However, for general shell photoemission that assumption does not take into account interference between different angular momentum channels, e.g., that between s and d channels in $L_{2,3}$-shell photoemission. The point is that the final state $|\psi^0\rangle$ is a linear combination of s and d states of well-defined relative phases.

A similar expression can be worked out for PD from the $L_{2,3}$ shell. For this case one must average over initial states of fixed total angular momentum, i.e., $j=\frac{3}{2}$ for L_3-shell photoemission or $j=\frac{1}{2}$ for L_2-shell photoemission. It is easy to show that the average over initial m_j states is equivalent to an average over initial p states. In this case we get for the single-scattering $L_{2,3}$-shell PD modulation,

$$\chi=2\,\mathrm{Re}\left[\frac{e^{ikR(1-\cos\theta)}}{R}\right.$$

$$\left.\times\left[\frac{Af_s+A_0f_d^{(0)}+A_1f_d^{(1)}+A_2f_d^{(2)}}{B}\right]\right] .$$

(15)

Formulas for the A's, f's, and B are given in Appendix A. Equations (14) and (15) give exact single-scattering contributions to χ.

As an additional, though not essential approximation, one can replace the coefficients c_l by the spherical-wave approximation of Ref. 4, i.e., by the asymptotic expansion

$$c_l\approx\left[1+\frac{l(l+1)}{2(kR)^2}\right]^{1/2}e^{il(l+1)/2kR} .$$ (16)

This high-energy approximation remains valid to within several eV of threshold and hence is highly accurate for most photoemission experiments.[4] In the plane-wave limit $kR\to\infty$; in this limit, $c_l(kR)\to1$, and $f^{(1)}(\theta,R)$, $f_d^{(1)}(\theta,R)$, and $f_d^{(2)}(\theta,R)$ vanish, while $f^{(0)}(\theta,R)$, $f_s(\theta,R)$, and $f_d^{(0)}(\theta,R)$ reduce to the plane-wave scattering amplitude $f(\theta)$.

To estimate the double-scattering term we make the additional approximation of a separable Green's function,[4] a form which can be shown to be equivalent to the point-scattering approximation of Lee and Pendry,[7] i.e.,

$$G_{L,L'}(\mathbf{R})\approx4\pi\frac{e^{ikR}}{kR}Y_L^*(\hat{\mathbf{R}})Y_{L'}(\hat{\mathbf{R}})c_l(kR)c_{l'}(kR) .$$ (17)

This leads to a double-scattering contribution of the form

$$\sum_{L',L} Y_{L'}(\hat{\mathbf{k}})t_{l'}^c G_{L',L}(-\mathbf{R})t_l G_{L,10}(\mathbf{R})$$

$$= Y_{10}(\hat{\mathbf{R}})\frac{e^{i2kR}}{R^2}f_s^c(\pi-\theta)\bar{f}(\pi) , \qquad (18)$$

$$f_s^c(\theta,R)=(1/k)\sum_l(2l+1)t_l^c P_l(\cos\theta)c_l(kR) , \qquad (18a)$$

$$\bar{f}(\theta,R)=(1/k)\sum_l(2l+1)t_l P_l(\cos\theta)c_l^2(kR)c_1(kR) , \qquad (18b)$$

where f_s^c denotes and s-wave effective scattering amplitude for the central atom and $\bar{f}$ that for the scattering atom. Hence we obtain

$$\frac{d\sigma}{d\Omega} \propto \left| \hat{\mathbf{e}}\cdot\hat{\mathbf{k}} + \frac{e^{ikR(1-\cos\theta)}}{R}[\hat{\mathbf{e}}\cdot\hat{\mathbf{R}}f^{(0)}(\theta,R)+\sin\theta_R\cos\phi f^{(1)}(\theta,R)] + \frac{e^{i2kR}}{R^2}\hat{\mathbf{e}}\cdot\hat{\mathbf{R}}f_s^c(\pi-\theta,R)\bar{f}(\pi,R) \right|^2 , \qquad (19)$$

which reduces to Eq. (1) in the plane-wave limit.

The theory outlined above does not take into account, for example, lattice vibrations or disorder, inelastic scattering of the photoelectron, intrinsic many-electron effects, or the presence of a surface, although such effects have been considered in previous discussions of PD theory.[1,3] For the more accurate model we are using, lattice vibrations can be taken into account by considering a thermal average of Eq. (14) [or Eq. (15) for $L_{2,3}$-shell absorption]. If one ignores the variation of coefficients c_l with fluctuations in R, one must compute the thermal average of the term $e^{ikR(1-\cos\theta)}$. In the harmonic approximation for the interaction potential between atoms we obtain[1,3]

$$\langle e^{ikR(1-\cos\theta)} \rangle = e^{ik\bar{R}(1-\cos\theta)}e^{-q^2\sigma_R^2(\hat{\mathbf{q}})/2} , \qquad (20)$$

where $\bar{R}$ is the mean distance between the absorbing atom and the scatterer, $\mathbf{q}=\mathbf{k}-k\hat{\mathbf{R}}$, and $\sigma_R^2(\hat{\mathbf{q}}) = \langle[\hat{\mathbf{q}}\cdot(\mathbf{u}_R-\mathbf{u}_0)]^2\rangle$, is the correlated mean-square displacement, with $\mathbf{u}_0$ and $\mathbf{u}_R$ being the local displacement vectors from equilibrium. Unlike the case of XAFS Debye-Waller factors[8] the relative mean-square displacement is projected along the momentum-transfer direction $\hat{\mathbf{q}}$ and not the bond direction $\hat{\mathbf{R}}$.[1,3] The contribution from the spherical-wave corrections is, however, not necessarily negligible. Taking account of the factor c_l, using Eq. (16), and assuming the harmonic approximation we obtain

$$\langle e^{ikR(1-\cos\theta)}c_l(kR) \rangle \cong e^{ik\bar{R}(1-\cos\theta)}c_l(k\bar{R})e^{-q_l^2\sigma_R^2(\hat{\mathbf{q}}_l)/2} , \qquad (21)$$

where $\mathbf{q}_l=\mathbf{k}-\hat{\mathbf{R}}[k-l(l+1)/2k\bar{R}^2]$, and $\sigma_R^2(\hat{\mathbf{q}}_l) = \langle[\hat{\mathbf{q}}_l\cdot(\mathbf{u}_R-\mathbf{u}_0)]^2\rangle$. Furthermore, we can make the approximation

$$e^{-q_l^2\sigma_R^2(\hat{\mathbf{q}}_l)/2} \cong e^{-q^2\sigma_R^2(\hat{\mathbf{q}})/2}e^{+(1-\cos\theta)[l(l+1)/\bar{R}^2]\sigma_R^2(\hat{\mathbf{q}})/2} . \qquad (22)$$

The correction term in Eq. (22) is thus l dependent and is not negligible for $l \sim l_{max}$, where $l_{max} \sim kR_{MT}$ is the maximum value of l for which scattering is appreciable. The correction is opposite in sign and smaller in magnitude than the exponent of the Debye-Waller factor in Eq. (20) by a factor $(lR_{MT}/l_{max}\bar{R})^2$.

Inelastic scattering of the photoelectron can be taken

into account crudely by the introduction of an *ad hoc* mean free path (i.e., $kR \to kR + iR/\lambda$).[1,3,9] An alternative and more satisfactory approach, we feel, would be to construct a complex-valued scattering potential and hence complex phase shifts $\delta_l \to \delta_l + i\beta_l$ that explicitly take into account inelastic processes, as is conventionally done in EXAFS calculations.[10,11]

Unlike XAFS, in photoelectron diffraction the photoelectron can be detected within a narrow energy range.[1(b),3] It is therefore argued that only the primary channel contributes to the differential cross section, which is reduced from the single-particle value by the square of the overlap integral $\langle \Phi_0|\Phi_0' \rangle$ between passive electrons.[12] However, this overlap factor is not important for PD, since it cancels in the normalized definition of χ. Note too that the use of a correct core-hole potential is not relevant for K-shell PD, since the central-atom phase shift cancels out, but it may be important for $L_{2,3}$-shell PD.

The effect of a surface is normally approximated by considering the refraction suffered by the photoelectron by a planar barrier of constant height V_0.[1,8] However, as discussed by Barton et al.,[3] one expects this potential to depend on the photoelectron energy, and, moreover, the case of a nonplanar geometry will not be correctly described by this approximation. Alternatively, one might incorporate non-muffin-tin corrections arising from a more accurate treatment of the potential in the surface region.

IV. NUMERICAL RESULTS

Comparisons with experiment using the results in Sec. III for K-shell and L_3-shell PD have been presented separately.[13,14] Here we only show comparisons between the single-scattering exact spherical-wave result [Eq. (14)] and its asymptotic form obtained using Eq. (16) in Eqs. (13), to illustrate the accuracy of this approximation. In Figs. 1 and 2 we present a comparison between the exact spherical-wave result, and expressions for χ based on the plane-wave scattering amplitude $f(\theta)$, on the asymptotic form of $f^{(0)}(\theta,R)$ above, and on the most accurate asymptotic form of $[f^{(0)}(\theta,R)+\sin\theta\cos\phi'f^{(1)}(\theta,R)]$. We have used phase shifts derived from a muffin-tin potential for Ni, with the nearest-neighbor distance at
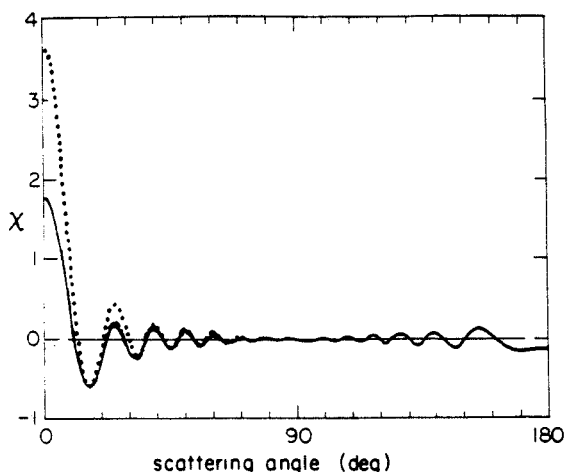
FIG. 1. PD χ from model calculations of photoemission from a Ni K shell as a function of the scattering angle for a single Ni scatterer at a distance $R = 2.492$ Å from the emitter. Polarization is parallel to the emission direction ($\theta_k = 0°$) and $E = 950$ eV: exact spherical wave [Eq. (14)] (solid line), ($f^{(0)} + \tan\theta \cos\phi' f^{(1)}$) approximated using Eq. (16) (dashed line), $f^{(0)}$ approximated using Eq. (16) (long dash) and plane wave (dotted line). Note that solid and dashed curves are indistinguishable.

$R = 2.49$ Å. When we use Eq. (14), omitting the correction term proportional to $f^{(1)}$ we find good agreement with the exact treatment even at 100 eV, the lowest energy studied. The term proportional to $f^{(1)}$ vanishes at small angles but can be important when the energy is low, at observation angles away from the forward and backward directions (see Fig. 2). The double-scattering term
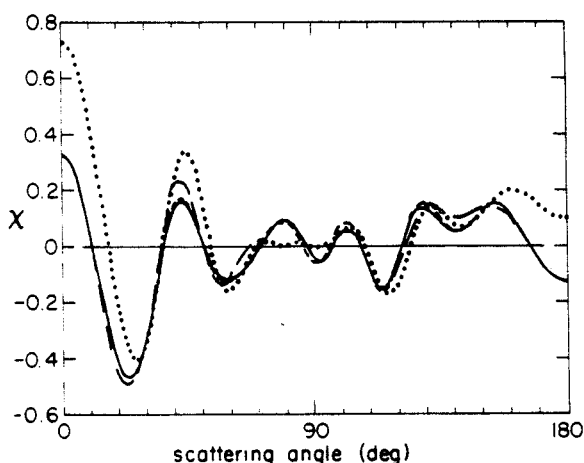

FIG. 2. PD χ from model calculations of photoemission from a Ni K shell as a function of the scattering angle for a single Ni scatterer at a distance $R = 2.492$ Å from the emitter. Polarization is parallel to the emission direction ($\theta_k = 0°$) and $E = 100$ eV: exact spherical wave [Eq. (14)] (solid line), ($f^{(0)} + \tan\theta \cos\phi' f^{(1)}$) approximated using Eq. (16) (dashed line), $f^{(0)}$ approximated using Eq. (16) (long dash) and plane wave (dotted line). Note that in the forward and backward directions the solid and dashed curves are indistinguishable.

is important in geometries in which the photoelectron is backscattered ($\hat{k} = -\hat{R}$), in which case shadowing by the absorbing atom occurs. In this case one should use Eq. (19) instead of Eq. (11). Also, this contribution must be retained in order to recover the XAFS result, as shown in Sec. V.

V. GENERALIZED OPTICAL THEOREM AND XAFS

It is of interest to see how the XAFS formula is recovered when $d\sigma/d\Omega$ is integrated over all angles. The previous reduction based on the plane-wave approximation and the optical theorem[2] must be modified when spherical-wave corrections are taken into account. Here it is convenient to use an alternative, angular momentum representation of the photoelectron final state in the presence of an absorbing atom at the origin [cf. Eq. (2)], i.e.,

$$|\psi_k^0\rangle = 4\pi \sum_L Y_L^*(\hat{k}) e^{-i\delta_l^c} |\psi_L\rangle .$$ (23)

By Eq. (4) the dipole matrix element is given by

$$M_{ck}^* = \sum_{L_f} m_{cLf} \left[Y_{L_f}(\hat{k}) e^{i\delta_l^c} \right.$$

$$\left. + \sum_L e^{i\delta_l^c} Y_L(\hat{k}) \langle \psi_L | t_R | \psi_{L_f}^+ \rangle \right] .$$ (24)

For K-shell absorption the total photoabsorption cross-section $\sigma \propto \int d\hat{k} |M_{ck}|^2$ is thus

$$\sigma = \sigma_0 (1 + 2 \text{Re} \langle \psi_{10} | t_R | \psi_{10}^+ \rangle + \langle \psi_{10}^+ | t_R^\dagger t_R | \psi_{10}^+ \rangle) ,$$ (25)

where σ_0 is the atomic photoabsorption cross section. With $|\psi_{10}\rangle = (|\psi_{10}^+\rangle - |\psi_{10}^-\rangle)/2i$, and introducing a complete set of angular momentum eigenstates $|L, R\rangle$, we find

$$\sigma = \sigma_0 \left[1 + \text{Im} \sum_L \langle \psi_{10}^- | L, R \rangle t_l \langle L, R | \psi_{10}^+ \rangle \right.$$

$$\left. - \text{Im} \sum_L t_l |\langle L, R | \psi_{10}^+ \rangle|^2 + \sum_L |t_l|^2 |\langle L, R | \psi_{10}^+ \rangle|^2 \right] .$$

(26)

Since $t_l = e^{i\delta_l} \sin\delta_l$, $\text{Im} t_l = |t_l|^2$, and, hence, the last two terms cancel identically. In the plane-wave limit $\langle L, R | \psi_{10}^+ \rangle = [Y_{10}(\hat{R}) e^{i\delta_l^c}] Y_L^*(\hat{k}) e^{ikR}/kR$, and this cancellation is just a statement of the optical theorem[2] $\int d\Omega |f(\theta)|^2 = \text{Im} f(0)/4\pi k$. In the present case this cancellation occurs l by l, though there does not appear to be a simple relation between the total scattered intensity in Eq. (12) and $f^{(0)}(0,R)$ (the term proportional to $f^{(1)}$ vanishes in the forward direction). Writing $\sigma = \sigma_0(1 + \tilde{\chi})$ (Where $\tilde{\chi}$ refers to the XAFS χ rather than the PD χ) and using the identify $\langle r | \psi_{10}^+ \rangle = e^{i\delta_l^c} \langle r | 10^+, 0 \rangle$, valid outside the central-atom muffin-tin radius, we obtain

$$\tilde{\chi} = \text{Im} e^{i2\delta_l^c} \sum_L G_{10,L}(R) t_l G_{L,10}(-R) .$$ (27)

Finally, with the expansion for the propagator given in Eq. (9) we obtain the K-shell polarized XAFS formula

$$\chi = -\text{Im}\frac{e^{i(2kR+2\delta_1^c)}}{kR^2}[(\hat{\epsilon}\cdot\hat{R})^2\bar{f}^{(0)}(\pi,R)$$

$$+\sin^2\theta_R\bar{f}^{(1)}(\pi,R)] ,\qquad (28)$$

with $\bar{f}^{(m)}(\pi,R)=(1/k)\sum_l(2l+1)(-1)^lt_l[g_{1l}^{(m)}(kR)]^2$.

Although the form is slightly different, Eq. (28) is equivalent to that obtained by Barton and Shirley.[3] After averaging Eq. (28) over all angles $\hat{\epsilon}$, one obtains the exact result for K-shell absorption in polycrystalline materials.[4] This result implies that to get the correct XAFS expression it suffices to use the outgoing part of the wave function [i.e., $|\psi_L^+\rangle$ instead of $|\psi_L\rangle$ in Eq. (23)]. However, to determine the total absorption, the atomic dipole matrix element m_{cL} must be calculated with the correct atomic wave function $|\psi_L\rangle$, which is regular at the origin, and not just $|\psi_L^+\rangle$. The above reduction was carried out for the case of a single scatterer at R, and only including single scatterings at site R. In Appendix B we show the generalization of this cancellation theorem when multiple scattering to all orders is considered.

ACKNOWLEDGMENTS

APPENDIX A

In this Appendix we give explicit formulas for the coefficients for $L_{2,3}$-shell photoelectron diffraction, Eq. (15), obtained following the same steps leading to Eq. (14) for K-shell absorption. We assume equal occupation of the core levels $l=1$, $m=0,\pm1$. The effective scattering amplitudes are

$$f_s=\sum_l t_l(2l+1)c_lP_l(\cos\theta) ,\qquad (A1)$$

$$f_d^{(0)}=\tfrac{1}{2}\sum_l t_l\left[\frac{(l+2)(l+1)}{2l+3}c_{l+2}+\frac{2l(l+1)(2l+1)}{3(2l+3)(2l-1)}c_l\right.$$

$$\left.+\frac{l(l-1)}{2l-1}c_{l-2}\right]P_l(\cos\theta) ,\qquad (A2)$$

$$f_d^{(1)}=\sum_l t_l\left[\frac{l+2}{2l+3}c_{l+2}-\frac{2l+1}{(2l+3)(2l-1)}c_l\right.$$

$$\left.-\frac{(l-1)}{2l-1}c_{l-2}\right]P_l^1(\cos\theta) ,\qquad (A3)$$

$$f_d^{(2)}=\tfrac{1}{2}\sum_l t_l\left[\frac{c_{l+2}}{2l+3}-\frac{2(2l+1)}{(2l+3)(2l-1)}c_l\right.$$

$$\left.+\frac{c_{l-2}}{2l-1}\right]P_l^2(\cos\theta) .\qquad (A4)$$

The terms f_s and $f_d^{(0)}$ correct the plane-wave result for the variation of the radial part of the photoelectron wave function in the scattering region. Consequently, the con-

tribution $A_0f_d^{(0)}+Af_s$ has the same angular polarization dependence as the plane-wave result. The contribution $A_1f_d^{(1)}+A_2f_d^{(2)}$ corrects the plane-wave result for the angular variation of the photoelectron wave function in the scattering region. In the plane-wave limit, f_s and $f_d^{(0)}$ reduce to the plane-wave scattering amplitude f while $f_d^{(1)}$ and $f_d^{(2)}$ vanish, as can be checked by substituting $c_l=1$ in Eqs. (A1)–(A4).

The coefficients in Eq. (15), which depend only on scattering angles and atomic quantities but not on the absorbing-atom–scatterer distance, are given by

$$A=-C\frac{m_0}{2m_2}e^{i(\delta_0-\delta_2)} ,\qquad (A5)$$

$$A_0=CP_2(\cos\theta_R)+\tfrac{1}{4}P_2^1(\cos\theta_k)P_2^1(\cos\theta_R)\cos\phi' ,\qquad (A6)$$

$$A_1=CP_2^1(\cos\theta_R)\cos\phi$$

$$-\tfrac{1}{4}P_2^1(\cos\theta_k)[\cos(2\theta_R)\cos\phi'\cos\phi$$

$$+\cos\theta_R\sin\phi'\sin\phi] ,\qquad (A7)$$

$$A_2=C\frac{P_2^2(\cos\theta_R)\cos(2\phi)}{4}$$

$$+\frac{P_2^1(\cos\theta_k)}{4}[P_2^1(\cos\theta_R)\cos(2\phi)\cos\phi'$$

$$-3\sin\theta_R\sin(2\phi)\sin\phi'] ,\qquad (A8)$$

$$B=|C|^2+\tfrac{1}{4}[P_2^1(\cos\theta_k)]^2 ,\qquad (A9)$$

$$C=P_2(\cos\theta_k)-\frac{m_0}{2m_2}e^{-i(\delta_0-\delta_2)}\qquad (A10)$$

Here $B=(d\sigma/d\Omega)_0$ is the atomic partial differential photoemission cross section, $m_l=i^{1-l_c}\int_0^\infty dr\, r^3R_l(kr)$ $\times R_c(r)$ is the radial part of the atomic dipole matrix element and δ_0 and δ_2 are the corresponding s- and d-atomic phase shifts. The angle ϕ is the dihedral angle between $\hat{R}$ and $\hat{k}$ through $\hat{\epsilon}$ and $\phi'=\phi_R-\phi_k$. The term C arises from the contribution of the $(l,m)=(2,0)$ and $(0,0)$ channels, present in the emission from the $(1,0)$ core level, and shows explicitly the interference between the s and d channels. The term proportional to $P_2^1(\cos\theta_k)$ represents emission from the $(1,\pm1)$ core levels. Note that this term does not exhibit interference with the s-channel contribution since it originates from a different core state. The ratio m_0/m_2 is typically $-\tfrac{1}{5}$ and relatively energy independent,[15] thus terms that are quadratic in this ratio can be neglected. Specifically, in the case of Ni $2p$ absorption $m_0/m_2=-0.222$ at an energy of 1000 eV.[16]

APPENDIX B

In this section we demonstrate the equivalence of the Green's-function approach[17] and the wave-function approach to the calculation of the total photoemission cross section in the multiple-scattering theory. This is the generalization of the cancellation theorem of Sec. V, carried to all orders in the multiple-scattering expansion.

Defining the full scattering state $\psi^+(r)$ as

$$|\psi^+\rangle = |\mathbf{k}\rangle - i \sum_{j,L} h_L^+ B_L^j , \tag{B1}$$

the multiple-scattering equations in T-matrix normalization for a cluster of scatterers is

$$(\cot\delta_l^i - i)B_L^i + \sum_{j,L'}(1-\delta_{ij})G_{LL'}^{ij} \cdot B_{L'}^j = -J_{LL''}^{i0} . \tag{B2}$$

The structure factors $G_{LL'}^{ij}$ are the free propagators in the partial-wave representation,

$$G_{LL'}(\mathbf{R}_{ij}) \equiv G_{LL'}^{ij} = 4\pi \sum_{L''} C_{LL''}^{L'} h_{L''}^+(\mathbf{R}_{ij}) = N_{LL'}^{ij} - iJ_{LL'}^{ij} , \tag{B3}$$

where $h_L^+(\mathbf{R}_{ij}) = i^l h_l^+(kR_{ij})Y_L(\hat{\mathbf{R}}_{ij}) \equiv j_L - in_L$. The quantities $J_{LL'}$ and $N_{LL'}$ are defined similarly by replacing h_L^+ in (B3) with j_L or n_L, respectively. Inside the muffin-tin spheres Ω, the wave function is taken to be

$$\psi(\mathbf{r}_j) = \sum_L C_L^j R_L^j , \tag{B4}$$

where $R_L^j = i^l R_l^j(r_j)Y_L(\hat{\mathbf{r}}_j)$, is the solution of the Schrödinger equation in cell Ω_j, which is regular at the origin, and $\mathbf{r}_j = \mathbf{r} - \mathbf{R}_j$. Imposing continuity conditions of the wave function and its derivative at the sphere boundary, as given in Eqs. (B1) and (B4), one generates the set of Eqs. (B2) together with the relations

$$B_L^j = k\rho_j^2 W[j_l, R_l]_{\rho_j} C_L^j \tag{B5}$$

by extensive use of the expansion theorem for Hankel functions. Notice that for each exciting partial wave L'' there is a set of solutions of Eq. (B2) for the coefficients B_L^j, and in turn for C_L^j in Eq. (B5), so that they can be labeled accordingly as $B_L^j(L'')$ and $C_L^j(L'')$. The total photoabsorption cross section from a deep core level localized at site 0 is given by

$$\sigma(E) = \sum_{L''} |\langle \psi_{L''}^- |\hat{\varepsilon}\cdot\mathbf{r}|\psi_c\rangle|^2 , \tag{B6}$$

where $\psi_{L''}^-$ is a time-reversed scattering state given an incoming spherical wave of angular momentum L''. Since spin is neglected, $\psi_{L''}^- = (\psi_{L''}^+)^*$. At site 0

$$\psi_{L''}^-(\mathbf{r}_0) = \sum_L C_L^0(L'')R_L^0 \tag{B7}$$

and using Eq. (B5), we have

$$\langle \psi_L^- |\hat{\varepsilon}\cdot\mathbf{r}|\psi_{\text{in}}\rangle = \sum_L (k\rho_0^2)^{-1}(W[j_l, R_l])_{\rho_0}^{-1}$$

$$\times B_L^0 \langle R_L^0 Y_L|\hat{\varepsilon}\cdot\mathbf{r}|\psi_{\text{in}}\rangle , \tag{B8}$$

where the sum over L runs over final states L_f. Noting that $\bar{R}_l^0 \equiv (k\rho_0^2)^{-1}(W[j_l, R_l])_{\rho_0}^{-1}R_l^0$ is the solution of the Schrödinger equation inside the sphere that matches smoothly to $j_l\cos\delta_l - n_l\sin\delta_l$ at the sphere boundary,

$$\cot\delta_l = W[n_l, R_l^0]/W[j_l, R_l^0] . \tag{B9}$$

Hence we can write

$$\sigma(E) = \sum_{L,L',L''} \langle \psi_L|\hat{\varepsilon}\cdot\mathbf{r}|\psi_c\rangle B_L^0(L'')$$

$$\times B_{L'}^{*0}(L'')\langle \psi_{L'}|\hat{\varepsilon}\cdot\mathbf{r}|\psi_c\rangle^* , \tag{B10}$$

where $\langle \mathbf{r}|\psi_L\rangle = i^l \bar{R}_l^0(r_0)Y_L(\hat{\mathbf{r}}_0)$ and L and L' run over final states L_f.

As stated in the beginning our aim is to show that this expression is equivalent to the result using the Green's-function approach.[17] To this purpose we write Eq. (B2) as

$$(M - i\Delta)\mathbf{B}(L'') = -\mathbf{J}(L'') , \tag{B11}$$

where $M_{LL'}^{ij} = \cot\delta_l^i \delta_{ij}\delta_{LL'} + (1-\delta_{ij})N_{LL'}^{ij}$, and $\Delta_{LL'}^{ij} = J_{LL'}^{ij}$ are Hermitian matrices and $\mathbf{B}(L'') = B_L^i(L'')$, $\mathbf{J}(L'') = J_{LL''}^{i0}$. Hence

$$B_L^i(L'') = \sum_{j,L'} [(M - i\Delta)^{-1}]_{LL'}^{ij} J_{L'L''}^{j0} . \tag{B12}$$

Since $J_{LL'}^{ij} = \sum_{L''} J_{LL''}^{i0} J_{L''L'}^{0j}$, we obtain

$$\sum_{L''} B_L^{i*}(L'')B_{L'}^j(L'') = \frac{1}{2i}[(M - i\Delta)^{-1} - (M + i\Delta)^{-1}]_{LL'}^{ij} . \tag{B13}$$

To obtain this result we used $[(M - i\Delta)^{-1}]^\dagger = (M + i\Delta)^{-1}$. Equation (B13) is a generalization of the optical theorem. Substitution in Eq. (B10) gives the total photoabsorption cross section

$$\sigma(E) = \sum_L \sum_{L'} m_{cL}(\hat{\varepsilon}) \frac{1}{2i}[(M - i\Delta)^{-1} - (M + i\Delta)^{-1}]_{LL'}^{ij}$$

$$\times m_{cL'}^*(\hat{\varepsilon}) , \tag{B14}$$

where $m_{cL}(\hat{\varepsilon}) = \langle \psi_L|\hat{\varepsilon}\cdot\mathbf{r}|\psi_c\rangle$. Now noting that $M - i\Delta = (T^{-1})_L^i \delta_{ij}\delta_{LL'} + (1-\delta_{ij})H_{LL'}^{ij}$, where $(T^{-1})_L^i = e^{-i\delta_l^i}/(\sin\delta_l^i)$, we have

$$\sigma(E) = \sum_{L_f} m_{cL_f}(\hat{\varepsilon}) \frac{1}{2i}\text{Im}[(I + TH)^{-1}T]_{L_fL_f}^{00} m_{cL_f}^*(\hat{\varepsilon}) , \tag{B15}$$

which is the result derived using the Green's-function formalism by Durham et al.[17]

---

[1]See (a) reviews by C. S. Fadley, in Progress in Surface Science, edited by S. Davison (Pergamon, New York, 1984), Vol. 16; Phys. Scr. T17, 39 (1987); (b) discussion of the theory of ARPEFS in M. Sagurton, E. L. Bullock, and C. S. Fadley, Surf. Sci. 182, 287 (1987).

[2]P. A. Lee, Phys. Rev. B 13, 5261 (1976).

[3]J. J. Barton and D. A. Shirley, Phys. Rev. B 32, 1892 (1985); Phys. Rev. A 32, 1019 (1985); J. J. Barton, S. W. Robey, and D. A. Shirley, Phys. Rev. B 34, 778 (1986); J. J. Barton, Ph.D. thesis, University of California, Berkeley, 1985.

[4]J. J. Rehr, R. C. Albers, C. R. Natoli, and E. A. Stern, Phys. Rev. B 34, 4350 (1986); J. J. Rehr and R. C. Albers (unpub-

lished).

[5]G. Breit and H. Bethe, Phys. Rev. 93, 888 (1954).

[6]A. Messiah, *Quantum Mechanics* (Wiley, New York, 1963), Vol. 2, p. 1068.

[7]P. A. Lee and J. B. Pendry, Phys. Rev. B 11, 2795 (1975).

[8]E. Sevillano, H. Meuth, and J. J. Rehr, Phys. Rev. B 20, 4908 (1979).

[9]P. J. Orders and C. S. Fadley, Phys. Rev. B 27, 781 (1983); E. L. Bullock, C. S. Fadley, and P. J. Orders, 28, 4867 (1983).

[10]P. A. Lee and G. Beni, Phys. Rev. B 15, 2862 (1977).

[11]D. Lu, J. Mustre de Leon, and J. J. Rehr, Physica B (to be published).

[12]J. J. Rehr, E. A. Stern, R. L. Martin, and E. R. Davidson, Phys. Rev. B 17, 560 (1978).

[13]M. Sagurton, E. Bullock, R. Saiki, A. Kaduwela, C. R. Brundle, C. S. Fadley, and J. J. Rehr, Phys. Rev. B 33, 2207 (1986).

[14]J. Osterwalder, E. A. Stewart, D. Cyr, C. S. Fadley, J. Mustre de Leon, and J. J. Rehr, Phys. Rev. B 35, 9859 (1987); and unpublished.

[15]P. A. Lee, P. H. Citrin, and B. M. Kincaid, Rev. Mod. Phys. 53, 769 (1980).

[16]S. Goldberg, C. S. Fadley, and S. Kono, J. Electron Spectrosc. Relat. Phenom. 21, 285 (1980).

[17]P. J. Durham, J. B. Pendry, and C. H. Hodges, Comput. Phys. Commun. 25, 193 (1982).