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Inelastic scattering of fast electrons by crystals

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Generalized fundamental equations for electron diffraction in crystals, which include the effect of inelastic scattering described by a nonlocal interaction, are derived. An expression is obtained for the cross section for any specific type of inelastic scattering (e.g., inner-shell ionization, Rutherford backscattering). This result takes into account all other (background) inelastic scattering in the crystal leading to absorption from the dynamical Bragg-reflected beams (in practice mainly due to thermal diffuse scattering). There is a contribution to the cross section from all absorbed electrons, which form a diffuse background, as well as from the dynamical electrons. The approximations involved in assuming that the interactions leading to inelastic scattering can be described by a local potential are discussed, together with the corresponding expression for the cross section. It is demonstrated by means of an example for K-shell electron energy loss spectroscopy that nonlocal effects can be significant.

I. INTRODUCTION

The inelastic scattering of electrons in electron diffraction plays a vital role in many experimental procedures involving the scattering of electrons in a crystalline environment. Inelastic scattering not only leads to an energy loss for the electrons. They may be scattered through an angle large enough such that the electron is no longer part of the dynamical wave function describing the diffraction of the electrons. Electron microscopists say that such an inelastic scattering event has led to absorption from dynamical beams (which is not true absorption in the usual sense).[1] The main inelastic mechanisms we consider[1,2] are (i) single-electron excitations, (ii) collective atomic excitations [phonons, leading to thermal diffuse scattering (TDS)], and (iii) collective electronic excitations (plasmons). Plasmon excitations are not necessarily considered absorptive since the electrons are mostly scattered through small angles.[3]

In this work we are mainly concerned with the scattering of fast electrons in crystalline solids. For electrons in the energy range of several keV to MeV, exchange interactions can be ignored. The Coulombic crystal potential can be considered to be essentially local. The absorptive scattering is also very often represented in terms of a complex energy-dependent local potential.[1,4–6] However, it is often not appreciated that, unlike scattering from the crystal potential, inelastic scattering can have substantial nonlocal character.

In Sec. II we derive general dynamical scattering equations for electrons incident on a crystal of a given finite thickness which are a generalization of those given by Yoshioka[7] which in turn are a generalization of those derived by Bethe[8] in 1928. These fundamental scattering equations follow from a Schrödinger equation containing a nonlocal integral kernel that represents inelastic scattering (including virtual inelastic scattering). We show that, with appropriate assumptions and simplifications, our dynamical scattering equations become independent of thickness and reduce to those given by Yoshioka.

In Sec. III we derive a general form for the cross section for any particular type of inelastic scattering in a crystal from the nonlocal formulation obtained in Sec. II. This general cross section expression consists of two terms. One is due to inelastic scattering of the dynamical Bloch waves describing electron diffraction. The other is due to a diffuse background of electrons that have scattered out of the dynamical waves, in practice mainly as a consequence TDS.

In Sec. IV we show how local approximations may be used to represent nonlocal inelastic scattering, making clear the assumptions made. An expression for the cross section is then obtained in terms of a local inelastic potential which, if the local potential is represented by a δ function, reduces to the previous result of Cherns *et al.*[9]

In Sec. V we consider the effects of nonlocality in the cross section by comparing nonlocal and local cross sections for K-shell ionization in electron energy loss spectroscopy (EELS) for 120 keV electrons incident on Al.

II. FUNDAMENTAL SCATTERING EQUATIONS

A. Generalized fundamental scattering equations

As shown by Yoshioka,[7] the scattering of fast electrons incident on a crystal, taking into account absorption, can be described by an integro-differential equation of the form

$$\left[\nabla^2 + k_0^2 - \frac{2m}{\hbar^2}H'_{00}(\mathbf{r})\right]\psi_0(\mathbf{r}) - \frac{2m}{\hbar^2}\int A(\mathbf{r},\mathbf{r}')\psi_0(\mathbf{r}')d\mathbf{r}' = 0 , \qquad (2.1)$$

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where $\psi_0(\mathbf{r})$ describes elastic scattering of the fast electron. This result can be viewed as an equation for a one-electron state with damping due to the nonlocal kernel,[10] which is given by

$$A(\mathbf{r},\mathbf{r}') = -\frac{m}{2\pi\hbar^2}\sum_{m\neq 0} H'_{0m}(\mathbf{r})H'_{m0}(\mathbf{r}')\frac{\exp\left(ik_m|\mathbf{r}-\mathbf{r}'|\right)}{|\mathbf{r}-\mathbf{r}'|}\ , \tag{2.2}$$

where k_m is the magnitude of the wave vector of the scattered electron. In general the interaction matrix elements $H'_{mn}(\mathbf{r})$ are given by

$$H'_{mn}(\mathbf{r}) = \int a^*_m(\mathbf{r}_1,\ldots,\mathbf{r}_N)H'(\mathbf{r};\mathbf{r}_1,\ldots,\mathbf{r}_N)a_n(\mathbf{r}_1,\ldots,\mathbf{r}_N)d\mathbf{r}_1,\ldots,d\mathbf{r}_N\ , \tag{2.3}$$

where $H'(\mathbf{r};\mathbf{r}_1,\ldots,\mathbf{r}_N)$ describes the interaction of the incident electron (coordinate $\mathbf{r}$) with the crystal particles (coordinates $\mathbf{r}_j$) and $a_n(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ represents the nth stationary state of the crystal. The approximation has been made that only excitations from the ground state contribute significantly to the scattering,[11] i.e., $H'_{m0}(\mathbf{r}) >> H'_{mn}(\mathbf{r})$ $(n\neq 0)$. A treatment of inelastic scattering which does not neglect the terms $H'_{mn}(\mathbf{r})$ $(n\neq 0)$ is discussed in Ref. 10. More exact but more complicated forms for $A(\mathbf{r},\mathbf{r}')$ can be obtained.[10,12,13]

For fast electrons the interaction matrix element $H'_{00}(\mathbf{r})$ can be assumed to represent the local crystal potential due to elastic Coulomb scattering and exchange is ignored.[14,15] [At lower energies another nonlocal term representing exchange could be included in the Schrödinger equation or a local, approximately equivalent, contribution could be included in $H'_{00}(\mathbf{r})$.] Because of the periodicity of the crystal lattice, $H'_{00}(\mathbf{r}) = H'_{00}(\mathbf{r}+\mathbf{R}_\alpha)$ for any lattice vector $\mathbf{R}_\alpha$ and $H'_{00}(\mathbf{r})$ can be expanded in a Fourier series

$$H'_{00}(\mathbf{r}) = -\sum_{\mathbf{g}} V_{\mathbf{g}}\exp\left(i\mathbf{g}\cdot\mathbf{r}\right)\ , \tag{2.4}$$

where $V_{\mathbf{g}}$ are the Fourier coefficients and the $\mathbf{g}$'s are reciprocal lattice vectors. The minus sign has not been absorbed into the $V_{\mathbf{g}}$'s so that the usual definition of the Fourier coefficients used in electron diffraction is preserved.[1] The inelastic scattering of the fast electron is represented by the additional term containing the nonlocal kernel $A(\mathbf{r},\mathbf{r}')$. In general $A(\mathbf{r},\mathbf{r}')$ depends on the energy of the incident electron. It has the periodicity property

$$A(\mathbf{r},\mathbf{r}') \approx A(\mathbf{r}+\mathbf{R}_\alpha,\mathbf{r}'+\mathbf{R}_\alpha)\ , \tag{2.5}$$

for any lattice vector $\mathbf{R}_\alpha$. The approximate equality reflects the fact that in principle such a symmetry is only approximate. For example, after a core excitation the interaction between the core hole and the valence electrons destroys translational symmetry.[16] However, such contributions to $A(\mathbf{r},\mathbf{r}')$ are small so that equality in Eq. (2.5) is assumed from this point onwards, as done by others.[7,17] Because of the periodicity of $H'_{00}(\mathbf{r})$ and $A(\mathbf{r},\mathbf{r}')$, the general solution to Eq. (2.1) can be written as a sum of Bloch states $\phi^i(\mathbf{r})$, such that

$$\psi_0(\mathbf{r}) = \sum_i \alpha^i\sum_{\mathbf{g}} C^i_{\mathbf{g}}\exp\left[i(\mathbf{k}^i+\mathbf{g})\cdot\mathbf{r}\right] \equiv \sum_i \alpha^i\phi^i(\mathbf{r})\ . \tag{2.6}$$

α^i is the amplitude of the ith Bloch state $\phi^i(\mathbf{r})$. Each Bloch state is individually a solution to Eq. (2.1) and has an associated complex wave vector $\mathbf{k}^i$. The boundary conditions require that these Bloch wave vectors have the same tangential component along the crystal surface, and hence they can only differ by a component in the direction along the (inwardly directed) surface normal $\hat{\mathbf{n}}$. With these boundary conditions $\mathbf{k}^i = \mathbf{K}+\lambda^i\hat{\mathbf{n}}$, where $\mathbf{K}$ is the incident wave vector in the crystal corrected for refraction such that $K^2 = k_0^2 + 2mV_0/\hbar^2$. The complex quantities λ^i can be written as

$$\lambda^i = \gamma^i + i\eta^i\ , \tag{2.7}$$

where γ^i are the real parts (anpassung) and η^i are the absorption coefficients.

Using Eq. (2.4) and also substituting the Bloch state expansion of the wave function (2.6) into Eq. (2.1), premultiplying by $1/V\ \exp\left[-i(\mathbf{k}^{i*}+\mathbf{g})\cdot\mathbf{r}\right]$, and integrating over the crystal volume, we obtain

$$\begin{aligned}&\sum_{\mathbf{h}}[K^2-(\mathbf{k}^i+\mathbf{h})^2]C^i_{\mathbf{h}}\frac{1}{V}\int_V \exp\left[i(\mathbf{h}-\mathbf{g}+\mathbf{k}^i-\mathbf{k}^{i*})\cdot\mathbf{r}\right]d\mathbf{r}\\ &\quad+\frac{2m}{\hbar^2}\sum_{\mathbf{f}\neq 0}V_{\mathbf{f}}\sum_{\mathbf{h}}C^i_{\mathbf{h}}\frac{1}{V}\int_V \exp\left[i(\mathbf{f}+\mathbf{h}-\mathbf{g}+\mathbf{k}^i-\mathbf{k}^{i*})\cdot\mathbf{r}\right]d\mathbf{r}\\ &\quad-\frac{2m}{\hbar^2}\sum_{\mathbf{h}}C^i_{\mathbf{h}}\frac{1}{V}\int_V\int_V \exp\left[-i(\mathbf{k}^{i*}+\mathbf{g})\cdot\mathbf{r}\right]A(\mathbf{r},\mathbf{r}')\exp\left[i(\mathbf{k}^i+\mathbf{h})\cdot\mathbf{r}'\right]d\mathbf{r}d\mathbf{r}' = 0\ .\end{aligned} \tag{2.8}$$

We now make some assumptions about the scattering geometry. We assume that the real-space diffracting planes are perpendicular to the crystal surface. Therefore the reciprocal-space vectors **h** and **g** pertinent to the scattering lie in a plane parallel to the crystal surface (i.e., perpendicular to $\hat{\mathbf{n}}$). The plane defined by the **h** and **g** vectors is called the xy plane. The xy plane in turn defines the z direction, and in this case $\hat{\mathbf{n}}$ (and hence $\lambda^i\hat{\mathbf{n}}$) is along the z direction. If in addition we assume that the surface area A of the crystal is very large, the integrations over the crystal volume in Eq. (2.8) reduce to

$$\begin{aligned}\frac{1}{V}\int_V \exp[i(\mathbf{h}-\mathbf{g}+\mathbf{k}^i-\mathbf{k}^{i*})\cdot\mathbf{r}]d\mathbf{r} &= \frac{1}{A}\int_A \exp[i(\mathbf{h}-\mathbf{g})\cdot\mathbf{r}_{xy}]d\mathbf{r}_{xy}\frac{1}{t}\int_0^t \exp[i(\mathbf{k}^i-\mathbf{k}^{i*})\cdot\mathbf{z}]dz\\ &= \delta_{\mathbf{h},\mathbf{g}}L^{ii}(t)\ ,\end{aligned} \tag{2.9}$$

where t is the thickness of the crystal in the direction of the surface normal $\hat{\mathbf{n}}$. We assume that t is much smaller than the surface dimensions A of the crystal and we do not obtain a δ function in this direction. This is a crucial assumption, the importance of which has been previously emphasized.[18,19] Physically, the assumption of a δ function in the z direction would imply that the detector(s) in our scattering experiment is inside the crystal and that we could resolve the different λ^i's, which is not possible. The dimensionless quantity $L^{ii}(t)$ is given by

$$L^{ii}(t) = \frac{\exp[i(\lambda^i-\lambda^{i*})t]-1}{i(\lambda^i-\lambda^{i*})t} = \frac{1-\exp(-2\eta^i t)}{2\eta^i t}\ , \tag{2.10}$$

where we have used Eq. (2.7). The scattering equations (2.8) reduce, with the assumptions given below them, to

$$[K^2-(\mathbf{k}^i+\mathbf{g})^2]L^{ii}(t)C^i_{\mathbf{g}} + \frac{2m}{\hbar^2}\left[L^{ii}(t)\sum_{\mathbf{h}\neq\mathbf{g}}V_{\mathbf{g}-\mathbf{h}}C^i_{\mathbf{h}} + \sum_{\mathbf{h}}W^{ii}_{\mathbf{g},\mathbf{h}}C^i_{\mathbf{h}}\right] = 0\ , \tag{2.11}$$

where

$$W^{ii}_{\mathbf{g},\mathbf{h}} = -\frac{1}{V}\int_V\int_V \exp[-i(\mathbf{k}^{i*}+\mathbf{g})\cdot\mathbf{r}]A(\mathbf{r},\mathbf{r}')\exp[i(\mathbf{k}^i+\mathbf{h})\cdot\mathbf{r}']d\mathbf{r}d\mathbf{r}'\ . \tag{2.12}$$

This is the general form of the dynamical scattering equations allowing for inelastic scattering, for the case of a crystal of finite thickness t. These fundamental dynamical equations, which have to be solved in a self-consistent way, are a generalization of those given by Yoshioka[7] which in turn generalize those derived by Bethe.[8]

B. Reduction of scattering equations to those of Yoshioka

The reduction of our equations to those of Yoshioka is now discussed. Since $A(\mathbf{r},\mathbf{r}')$ given by Eq. (2.2) is not Hermitian, $W^{ii}_{\mathbf{g},\mathbf{h}}$ [Eq. (2.12)] is also not Hermitian. However, we may split $W^{ii}_{\mathbf{g},\mathbf{h}}$ into two parts which are individually Hermitian as follows: $W^{ii}_{\mathbf{g},\mathbf{h}} \equiv (W^{ii}_{\mathbf{g},\mathbf{h}})^{(r)} + i(W^{ii}_{\mathbf{g},\mathbf{h}})^{(i)}$, where

$$(W^{ii}_{\mathbf{g},\mathbf{h}})^{(r)} = -\frac{1}{2V}\int_V\int_V \exp[-i(\mathbf{k}^{i*}+\mathbf{g})\cdot\mathbf{r}][A(\mathbf{r},\mathbf{r}')+A^*(\mathbf{r}',\mathbf{r})]\exp[i(\mathbf{k}^i+\mathbf{h})\cdot\mathbf{r}']d\mathbf{r}d\mathbf{r}'\ , \tag{2.13}$$

$$(W^{ii}_{\mathbf{g},\mathbf{h}})^{(i)} = -\frac{1}{2iV}\int_V\int_V \exp[-i(\mathbf{k}^{i*}+\mathbf{g})\cdot\mathbf{r}][A(\mathbf{r},\mathbf{r}')-A^*(\mathbf{r}',\mathbf{r})]\exp[i(\mathbf{k}^i+\mathbf{h})\cdot\mathbf{r}']d\mathbf{r}d\mathbf{r}'\ . \tag{2.14}$$

We note that for a centrosymmetric crystal, $(W^{ii}_{\mathbf{g},\mathbf{h}})^{(r)}$ and $(W^{ii}_{\mathbf{g},\mathbf{h}})^{(i)}$ are both real quantities. The term $(W^{ii}_{\mathbf{g},\mathbf{h}})^{(i)}$ represents the actual inelastic scattering of the incident electron, while the term $(W^{ii}_{\mathbf{g},\mathbf{h}})^{(r)}$ represents the virtual inelastic scattering. We note that $|(W^{ii}_{\mathbf{g},\mathbf{h}})^{(r)}|$ is several orders of magnitude smaller than $|(W^{ii}_{\mathbf{g},\mathbf{h}})^{(i)}|$ at high incident energies[15,20] and so will be neglected for the remainder of this work. In turn $|(W^{ii}_{\mathbf{g},\mathbf{h}})^{(i)}|$ is usually an order of magnitude smaller than the magnitude of the elastic potential coefficients $|V_{\mathbf{g}}|$.[1,14]

With the assumptions about the scattering geometry discussed above, and bearing in mind that the thickness of the crystal is small compared to the surface dimensions, the $(W^{ii}_{\mathbf{g},\mathbf{h}})^{(i)}$ can be written in the form [cf. Appendix A and in particular Eq. (A26)]

$$(W^{ii}_{\mathbf{g},\mathbf{h}})^{(i)} = L^{ii}(t)X^{ii}_{\mathbf{g},\mathbf{h}}\ , \tag{2.15}$$

where

$$X^{ii}_{\mathbf{g},\mathbf{h}} = \frac{4\hbar^2}{ma_0^2}\frac{1}{V}\frac{1}{(1-a)}\sum_{m\neq 0}\int\frac{F^*_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}')}{|\mathbf{k}^i+\mathbf{g}-\mathbf{K}'|^2}\frac{F_{m0}(\mathbf{k}^i+\mathbf{h}-\mathbf{K}')}{|\mathbf{k}^i+\mathbf{h}-\mathbf{K}'|^2}\delta(K'^2-k_m^2)d\mathbf{K}'\ . \tag{2.16}$$

The Bohr radius $a_0 = (4\pi\hbar^2\epsilon_0)/(me^2)$, and a is the band dispersion factor of the initial state.[19] The quantity $\mathbf{q} = \mathbf{K} - \mathbf{K}'$ is the momentum transfer from the incident electron to the scattered electron. The transition matrix element $F_{m0}(\mathbf{k}^i + \mathbf{h} - \mathbf{K}')$ between the ground state $u_0(\mathbf{r})$ and excited state $u_m(\mathbf{r})$ of the crystal is given by

$$F_{m0}(\mathbf{k}^i + \mathbf{h} - \mathbf{K}') = \int_V u_m{}^*(\mathbf{r}) \exp\left[i(\mathbf{k}^i + \mathbf{h} - \mathbf{K}') \cdot \mathbf{r}\right] \times u_0(\mathbf{r}) d\mathbf{r} \,. \tag{2.17}$$

Using Eq. (2.15) the thickness-dependent factor in Eq. (2.11) cancels and the dynamical scattering equations reduce to

$$[K^2 - (\mathbf{k}^i + \mathbf{g})^2] C^i_{\mathbf{g}} + \frac{2m}{\hbar^2} \sum_{\mathbf{h} \neq \mathbf{g}} V_{\mathbf{g}-\mathbf{h}} C^i_{\mathbf{h}} + \frac{2m}{\hbar^2} \sum_{\mathbf{h}} X^{ii}_{\mathbf{g},\mathbf{h}} C^i_{\mathbf{h}} = 0 \,. \tag{2.18}$$

To a good approximation for fast electrons $|\mathbf{k}^i| \approx |\mathbf{K}|$. If in addition to this approximation we assume that the $\lambda^i \hat{\mathbf{n}}$ component of the wave vector $\mathbf{k}^i$ only has a small effect on the transition matrix elements of Eq. (2.17), then the λ^i dependence of $X^{ii}_{\mathbf{g},\mathbf{h}}$ becomes weak. Consistent with this assumption is that $L^{ii}(t) \approx 1$. Ignoring the i dependence we can write [from Eq. (2.15)] $X^{ii}_{\mathbf{g},\mathbf{h}} \rightarrow X_{\mathbf{g},\mathbf{h}} = (W_{\mathbf{g},\mathbf{h}})^{(i)}$, and Eq. (2.18) reduces to

$$[K^2 - (\mathbf{k}^i + \mathbf{g})^2] C^i_{\mathbf{g}} + \frac{2m}{\hbar^2} \sum_{\mathbf{h} \neq \mathbf{g}} V_{\mathbf{g}-\mathbf{h}} C^i_{\mathbf{h}} + \frac{2m}{\hbar^2} \sum_{\mathbf{h}} W_{\mathbf{g},\mathbf{h}} C^i_{\mathbf{h}} = 0 \,, \tag{2.19}$$

the form of the fundamental equations given by Yoshioka.[7]

III. CROSS SECTION FOR INELASTIC SCATTERING

A. Cross section for absorptive scattering

The cross section for absorptive scattering of a particular type, or "absorption" from the elastic scattered electron flux, is given by the number of electrons per unit volume multiplied by the probability that an inelastically scattered electron will cross the crystal surface, per incident flux per unit area, i.e.,

$$\sigma = \left[\rho \sum_{n \neq 0} \int_S \mathbf{j}_n(\mathbf{r}) \cdot d\mathbf{s}\right] \Big/ (\rho v) \,, \tag{3.1}$$

where ρ is the number of electrons per unit volume and $v = \hbar k_0/m$ is the incident electron velocity. Furthermore, $\mathbf{j}_n(\mathbf{r})$ is the electron probability current density vector corresponding to an event that leaves the crystal in the state n. In the usual way, $\mathbf{j}_n(\mathbf{r})$ can be defined as

$$\mathbf{j}_n(\mathbf{r}) = \frac{\hbar}{2im}[\psi^*_n(\mathbf{r}) \nabla \psi_n(\mathbf{r}) - \psi_n(\mathbf{r}) \nabla \psi^*_n(\mathbf{r})] \,. \tag{3.2}$$

The integral over the crystal surface S in Eq. (3.1) summed over all $n \neq 0$ is the probability that an inelastically scattered electron will exit the crystal surface. Because the total number of electrons is conserved, the *net* probability of any scattered electrons exiting the solid is of course zero. Therefore

$$\sum_{n \neq 0} \int_S \mathbf{j}_n(\mathbf{r}) \cdot d\mathbf{s} = -\int_S \mathbf{j}_0(\mathbf{r}) \cdot d\mathbf{s} \,. \tag{3.3}$$

The sum of the electron probability currents flowing out from the crystal by inelastic scattering must be equal to the *net* flux of electrons from the elastic scattered part $\psi_0(\mathbf{r})$ *into* (minus sign) the crystal. The electrons that contribute to the inelastic scattering are effectively absorbed in the crystal as far as the elastic scattering part $\psi_0(\mathbf{r})$ is concerned. We can therefore write the inelastic cross section in terms of the elastic electron probability current density vector as

$$\sigma = -\frac{1}{v} \int_S \mathbf{j}_0(\mathbf{r}) \cdot d\mathbf{s} \,. \tag{3.4}$$

Furthermore, it can be shown after some algebra[17] that

$$\int_S \mathbf{j}_0(\mathbf{r}) \cdot d\mathbf{s} = \frac{1}{i\hbar} \int_V \int_V \psi^*_0(\mathbf{r})[A(\mathbf{r},\mathbf{r}') - A^*(\mathbf{r}',\mathbf{r})] \times \psi_0(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \,. \tag{3.5}$$

Consequently the general expression for the cross section for inelastic scattering is given by

$$\sigma = -\frac{1}{i\hbar v} \int_V \int_V \psi^*_0(\mathbf{r})[A(\mathbf{r},\mathbf{r}') - A^*(\mathbf{r}',\mathbf{r})] \psi_0(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \,. \tag{3.6}$$

The quantity $-1/i\hbar[A(\mathbf{r},\mathbf{r}') - A^*(\mathbf{r}',\mathbf{r})]$ expresses the spatial distribution of the nonlocal "absorption power," with the amount of absorption depending on the values of $\psi_0(\mathbf{r})$ at the points $\mathbf{r}$ and $\mathbf{r}'$.[17]

B. Cross section due to dynamical electrons

The cross section for inelastic scattering of the dynamical fast electron Bloch states in the crystal can then be written using Eq. (2.6) in Eq. (3.6) as

$$\sigma_{\text{dyn}} = -NV_c \frac{m}{i\hbar^2 k_0} \sum_{i,j} \alpha^i \alpha^{j*} \sum_{\mathbf{g},\mathbf{h}} C^i_{\mathbf{g}} C^{j*}_{\mathbf{h}} \frac{1}{V} \int_V \int_V \exp\left[-i(\mathbf{k}^{j*} + \mathbf{h}) \cdot \mathbf{r}\right][A(\mathbf{r},\mathbf{r}') - A^*(\mathbf{r}',\mathbf{r})] \exp\left[i(\mathbf{k}^i + \mathbf{g}) \cdot \mathbf{r}'\right] d\mathbf{r} d\mathbf{r}' \,. \tag{3.7}$$

From Eq. (2.14) this becomes

$$\sigma_{\mathrm{dyn}} = NV_c \frac{2m}{\hbar^2 k_0} \sum_{i,j} \alpha^i \alpha^{j*} \sum_{\mathbf{g},\mathbf{h}} C^i_{\mathbf{g}} C^{j*}_{\mathbf{h}} (W^{ji}_{\mathbf{h},\mathbf{g}})^{(i)} \ , \qquad (3.8)$$

and we may rewrite this in turn as

$$\sigma_{\mathrm{dyn}} = \frac{2m}{\hbar^2 k_0} NV_c \sum_{i,j} B^{ij}(t) \sum_{\mathbf{g},\mathbf{h}} C^i_{\mathbf{g}} C^{j*}_{\mathbf{h}} X^{ji}_{\mathbf{h},\mathbf{g}} \ , \qquad (3.9)$$

where $X^{ji}_{\mathbf{h},\mathbf{g}}$ is given by Eq. (A27) and

$$B^{ij}(t) = \alpha^i \alpha^{j*} L^{ij}(t) \ , \qquad (3.10)$$

with $L^{ij}(t)$ as given by Eq. (A25). Letting

$$\frac{2m}{\hbar^2 k_0} X^{ji}_{\mathbf{h},\mathbf{g}} = \mu^{ji}_{\mathbf{h},\mathbf{g}} \ , \qquad (3.11)$$

we then have

$$\sigma_{\mathrm{dyn}} = NV_c \sum_{i,j} B^{ij}(t) \sum_{\mathbf{g},\mathbf{h}} C^i_{\mathbf{g}} C^{j*}_{\mathbf{h}} \mu^{ji}_{\mathbf{h},\mathbf{g}} \ . \qquad (3.12)$$

Assuming, as before, that the i and j dependences of the $X^{ji}_{\mathbf{h},\mathbf{g}}$ are weak, we can drop the i and j dependence in $\mu^{ji}_{\mathbf{h},\mathbf{g}}$ and write

$$\sigma_{\mathrm{dyn}} = NV_c \sum_{i,j} B^{ij}(t) \sum_{\mathbf{g},\mathbf{h}} C^i_{\mathbf{g}} C^{j*}_{\mathbf{h}} \mu_{\mathbf{h},\mathbf{g}} \ , \qquad (3.13)$$

which is similar to the result obtained using a different approach in Ref. 19. This result can also be obtained from the transition matrix element in Ref. 10 provided the approximation below Eq. (2.3) is made.

C. Cross section due to diffuse background

Electrons may be scattered in such a way that they are no longer described by a wave function of the form given by Eq. (2.6). This is often referred to as "anomalous absorption." Due to this absorption, represented by the absorption coefficients η^i implicit in Eq. (2.6), the dynamical Bloch waves decrease in intensity as they propagate further into the crystal. Ultimately, for sufficiently thick crystals, the cross section due to the electrons in the dynamical Bloch waves σ_{dyn} should approach zero. However, the decrease in dynamical Bloch wave intensity leads to a corresponding increase in intensity of a diffuse background of electrons which have been absorbed. These (in practice mostly TDS) electrons in the diffuse background contribute to further inelastic scattering, and must be included in the total cross section.

To obtain the cross section σ_{dif} for the electrons in the diffuse background we require the wave function for these electrons. After they have been absorbed, the electrons propagate through the crystal along directions different from their initial direction. It is unlikely that these electrons undergo strong Bragg reflection, and so they can be described by plane waves and form a diffuse background. We assume that the final states of the electrons in the diffuse background can be written

$$\psi_{\mathrm{dif}}(\mathbf{r}) = \sum_n \alpha^n(\hat{\mathbf{n}} \cdot \mathbf{r}) \exp(i\mathbf{k}^n \cdot \mathbf{r}) \ , \qquad (3.14)$$

where $\mathbf{k}^n$ are the (real) wave vectors of the electrons in the diffuse background. The sum could be replaced by an integral[21] but the above form is appropriate for our purposes. The amplitudes of these plane waves,

$$\alpha^n(\hat{\mathbf{n}} \cdot \mathbf{r}) = \alpha^n[1 - \exp(-\eta^n \hat{\mathbf{n}} \cdot \mathbf{r})] \ , \qquad (3.15)$$

are a function of distance normal to (or depth into) the crystal surface. The amplitudes of the diffusely scattered waves are zero at the entrance surface, $\alpha^n(0) = 0$, and all the electrons are in the dynamical beams. As the dynamical waves propagate through the crystal the amplitudes of the diffusely scattered waves increase until, for a sufficiently thick crystal, they saturate to α^n. Because the individual plane waves in the diffuse background act independently, the cross section for the diffuse electrons σ_{dif} is simply that obtained incoherently from the plane waves of wave vector $\mathbf{k}^n$ and amplitude, $\alpha^n(\hat{\mathbf{n}} \cdot \mathbf{r})$, i.e.,

$$\sigma_{\mathrm{dif}} = -\frac{1}{i\hbar v} \sum_n \int_V \int_V \alpha^{n*}(\hat{\mathbf{n}} \cdot \mathbf{r}) \exp(-i\mathbf{k}^n \cdot \mathbf{r})[A(\mathbf{r},\mathbf{r}') - A^*(\mathbf{r}',\mathbf{r})]\alpha^n(\hat{\mathbf{n}} \cdot \mathbf{r}') \exp(i\mathbf{k}^n \cdot \mathbf{r}') d\mathbf{r} d\mathbf{r}' \ . \qquad (3.16)$$

Inserting $\alpha^n(\hat{\mathbf{n}} \cdot \mathbf{r})$ into Eq. (3.16) we can separate this cross section into four terms and write

$$\sigma_{\mathrm{dif}} = NV_c \frac{2m}{\hbar^2 k_0} \sum_n |\alpha^n|^2 [(W^{nn}_{0,0})^{(i)} + (W^{\bar{n}\bar{n}}_{0,0})^{(i)} - (W^{\bar{n}n}_{0,0})^{(i)} - (W^{n\bar{n}}_{0,0})^{(i)}] \ , \qquad (3.17)$$

where

$$(W^{nn}_{0,0})^{(i)} = -\frac{1}{2iV} \int_V \int_V \exp(-i\mathbf{k}^n \cdot \mathbf{r})[A(\mathbf{r},\mathbf{r}') - A^*(\mathbf{r}',\mathbf{r})] \exp(i\mathbf{k}^n \cdot \mathbf{r}') d\mathbf{r} d\mathbf{r}' \ , \qquad (3.18)$$

$$(W^{\bar{n}\bar{n}}_{0,0})^{(i)} = -\frac{1}{2iV} \int_V \int_V \exp(-i\overline{\mathbf{k}}^{n*} \cdot \mathbf{r})[A(\mathbf{r},\mathbf{r}') - A^*(\mathbf{r}',\mathbf{r})] \exp(i\overline{\mathbf{k}}^{n} \cdot \mathbf{r}') d\mathbf{r} d\mathbf{r}' \ , \qquad (3.19)$$

$$(W^{\bar{n}n}_{0,0})^{(i)} = -\frac{1}{2iV} \int_V \int_V \exp(-i\overline{\mathbf{k}}^{n*} \cdot \mathbf{r})[A(\mathbf{r},\mathbf{r}') - A^*(\mathbf{r}',\mathbf{r})] \exp(i\mathbf{k}^{n} \cdot \mathbf{r}') d\mathbf{r} d\mathbf{r}' \ , \qquad (3.20)$$

and

$$(W_{0,0}^{n\bar{n}})^{(i)} = -\frac{1}{2iV}\int_V\int_V \exp(-i\mathbf{k}^n\cdot\mathbf{r})[A(\mathbf{r},\mathbf{r}') - A^*(\mathbf{r}',\mathbf{r})]\exp(i\overline{\mathbf{k}}^n\cdot\mathbf{r}')d\mathbf{r}d\mathbf{r}' , \tag{3.21}$$

with $\overline{\mathbf{k}}^n = \mathbf{k}^n + i\eta^n\hat{\mathbf{n}}$.

Now Eq. (A26) can be applied to each of Eqs. (3.18)–(3.21) and we can write

$$\sigma_{\text{dif}} = NV_c\sum_n |\alpha^n|^2[\mu_{0,0}^{nn} + L^{\bar{n}\bar{n}}(t)\mu_{0,0}^{\bar{n}\bar{n}} - L^{\bar{n}n}(t)(\mu_{0,0}^{n\bar{n}} + \mu_{0,0}^{\bar{n}n})] , \tag{3.22}$$

where

$$\mu_{0,0}^{nn} = \frac{2m}{\hbar^2 k_0}\frac{W_{0,0}^{nn}}{L^{nn}(t)} , \tag{3.23}$$

and similarly for the other $\mu_{0,0}$ terms. We have also made use of the properties [see Eq. (2.10)] $L^{nn}(t) = 1$ [as $L^{nn}(t)$ is constructed from a real wave vector] and $L^{\bar{n}n}(t) = L^{n\bar{n}}(t)$.

At high incident energies $|\mathbf{k}^i| \approx |\mathbf{K}|$ and $|\mathbf{k}^n| \approx |\mathbf{K}|$. The latter is true because TDS is the dominant contribution to absorption and, while TDS can be through large angles, it involves relatively little change in energy.[22,23] We can then drop the n and $\bar{n}$ dependence in the μ terms [but not in the $L(t)$ terms]. The cross section for the diffuse electrons can then be written as

$$\sigma_{\text{dif}} = NV_c\sum_n |\alpha^n|^2[1 + L^{\bar{n}\bar{n}}(t) - 2L^{\bar{n}n}(t)]\mu_{0,0} . \tag{3.24}$$

The diffuse electron plane wave amplitudes $\alpha^n(\hat{\mathbf{n}}\cdot\mathbf{r})$ and wave vectors $\mathbf{k}^n$ are not known directly. However, they can be related to the known scattered Bloch wave amplitudes. We know that an electron must be in one of the states of either the dynamical or the diffuse background wave function. From conservation of particles the total probability of finding an electron in any of these states must be equal to 1. We can write this as

$$1 = \frac{1}{V}\int_V \sum_n |\alpha^n(\hat{\mathbf{n}}\cdot\mathbf{r})\exp(i\mathbf{k}^n\cdot\mathbf{r})|^2 d\mathbf{r} + \frac{1}{V}\int_V \left|\sum_i \alpha^i \sum_{\mathbf{g}} C_{\mathbf{g}}^i \exp[i(\mathbf{k}^i + \mathbf{g})\cdot\mathbf{r}]\right|^2 d\mathbf{r} . \tag{3.25}$$

The integral involving the dynamical wave function becomes

$$\frac{1}{V}\int_V \left|\sum_i \alpha^i \sum_{\mathbf{g}} C_{\mathbf{g}}^i \exp[i(\mathbf{k}^i + \mathbf{g})\cdot\mathbf{r}]\right|^2 d\mathbf{r} = \sum_{i,j} B^{ij}(t)\sum_{\mathbf{g}} C_{\mathbf{g}}^i C_{\mathbf{g}}^{j*} . \tag{3.26}$$

The integral involving the diffuse background wave function can be written

$$\frac{1}{V}\int_V \sum_n |\alpha^n[1 - \exp(-\eta^n z)]\exp(i\mathbf{k}^n\cdot\mathbf{r})|^2 d\mathbf{r} = \sum_n |\alpha^n|^2[1 + L^{\bar{n}\bar{n}}(t) - 2L^{\bar{n}n}(t)] . \tag{3.27}$$

Conservation of particles [Eq. (3.25)] then entails that

$$\sum_n |\alpha^n|^2[1 + L^{\bar{n}\bar{n}}(t) - 2L^{\bar{n}n}(t)] = 1 - \sum_{i,j} B^{ij}(t)\sum_{\mathbf{g}} C_{\mathbf{g}}^i C_{\mathbf{g}}^{j*} , \tag{3.28}$$

so that Eq. (3.24) may be rewritten as

$$\sigma_{\text{dif}} = NV_c\left[1 - \sum_{i,j} B^{ij}(t)\sum_{\mathbf{g}} C_{\mathbf{g}}^i C_{\mathbf{g}}^{j*}\right]\mu_{0,0} . \tag{3.29}$$

D. Total cross section for inelastic scattering

The total cross section can be obtained from Eqs. (3.13) and (3.29) in terms of the known Bloch wave amplitudes and coefficients as

$$\begin{aligned} \sigma &= \sigma_{\text{dif}} + \sigma_{\text{dyn}} \\ &= NV_c\left\{\left[1 - \sum_{i,j} B^{ij}(t)\sum_{\mathbf{g}} C_{\mathbf{g}}^i C_{\mathbf{g}}^{j*}\right]\mu_{0,0} + \sum_{i,j} B^{ij}(t)\sum_{\mathbf{g},\mathbf{h}} C_{\mathbf{g}}^i C_{\mathbf{h}}^{j*}\mu_{\mathbf{h},\mathbf{g}}\right\} . \end{aligned} \tag{3.30}$$

While the $\mu_{\mathbf{h},\mathbf{g}}$ refer to the specific inelastic scattering under consideration, the scattering coefficients λ^i implicit in the $B^{ij}(t)$ and the Bloch state coefficients $C^i_{\mathbf{g}}$ come from solution of the total scattering equations. Hence in principle they include all absorptive scattering which is concurrently occurring. If there is no diffraction, then Eq. (3.30) reduces to the kinematic value

$$\sigma_{\mathrm{kin}} = NV_c\mu_{0,0}\ . \tag{3.31}$$

In the limit as $t \to \infty$ the $B^{ij}(t) \to 0$ and we also obtain the kinematic result given by Eq. (3.31).

IV. LOCAL APPROXIMATION

A. Approximately equivalent local potential

Nonlocal interactions are often approximated by local potentials[24] for ease of application or visualization. We now construct a local potential $V_L(\mathbf{r})$ approximately equivalent to the nonlocal inelastic scattering potential in Eq. (2.1), by which we mean that

$$V_L(\mathbf{r})\psi_0(\mathbf{r}) \approx \int A(\mathbf{r},\mathbf{r}')\psi_0(\mathbf{r}')d\mathbf{r}'\ . \tag{4.1}$$

When we solve the scattering equations with this local potential, we should then obtain coefficients $C^i_{\mathbf{g}}$ and wave vectors $\mathbf{k}^i$ that are similar to those obtained from the nonlocal scattering potential. We consider the nonlocal term as follows:

$$\int A(\mathbf{r},\mathbf{r}')\psi_0(\mathbf{r}')d\mathbf{r}' = \int A(\mathbf{r},\mathbf{r}+\mathbf{s})\psi_0(\mathbf{r}+\mathbf{s})d\mathbf{s}\ , \tag{4.2}$$

where we have let $\mathbf{r}' = \mathbf{r}+\mathbf{s}$. Let us approximate the right-hand side of Eq. (4.2) as follows:

$$\int A(\mathbf{r},\mathbf{r}+\mathbf{s})\psi_0(\mathbf{r}+\mathbf{s})d\mathbf{s} \approx \sum_\alpha A(\mathbf{r},\mathbf{r}+\mathbf{R}_\alpha) \times\psi_0(\mathbf{r}+\mathbf{R}_\alpha)V_c\ , \tag{4.3}$$

where $\mathbf{R}_\alpha$ are real-space lattice vectors and V_c is the unit cell volume. From Eq. (2.6) and as $\exp(i\mathbf{g}\cdot\mathbf{R}_\alpha) = 1$, it follows that

$$\begin{aligned}\psi_0(\mathbf{r}+\mathbf{R}_\alpha) &= \sum_i \alpha^i \sum_{\mathbf{g}} C^i_{\mathbf{g}} \exp[i(\mathbf{k}^i+\mathbf{g})\cdot(\mathbf{r}+\mathbf{R}_\alpha)] \\ &= \sum_i \alpha^i \exp(i\mathbf{k}^i\cdot\mathbf{R}_\alpha) \\ &\quad\times \sum_{\mathbf{g}} C^i_{\mathbf{g}} \exp[i(\mathbf{k}^i+\mathbf{g})\cdot\mathbf{r}]\ .\end{aligned} \tag{4.4}$$

Since $|\lambda^i\hat{\mathbf{n}}| \ll |\mathbf{K}|$, we make the assumption that

$$\exp(i\mathbf{k}^i\cdot\mathbf{R}_\alpha) \equiv \exp[i(\mathbf{K}+\lambda^i\hat{\mathbf{n}})\cdot\mathbf{R}_\alpha] \approx \exp(i\mathbf{K}\cdot\mathbf{R}_\alpha)\ . \tag{4.5}$$

Equation (4.4) then becomes [using Eq. (2.6)]

$$\psi_0(\mathbf{r}+\mathbf{R}_\alpha) = \exp(i\mathbf{K}\cdot\mathbf{R}_\alpha)\psi_0(\mathbf{r})\ . \tag{4.6}$$

The effect of $\exp(i\mathbf{K}\cdot\mathbf{R}_\alpha)$ is to translate the electron wave function by a reciprocal lattice vector $\mathbf{R}_\alpha$ (to a good approximation). Therefore Eq. (4.3) can be written as

$$\int A(\mathbf{r},\mathbf{r}+\mathbf{s})\psi_0(\mathbf{r}+\mathbf{s})d\mathbf{s} \approx \sum_\alpha A(\mathbf{r},\mathbf{r}+\mathbf{R}_\alpha)\exp(i\mathbf{K}\cdot\mathbf{R}_\alpha)\psi_0(\mathbf{r})V_c\ . \tag{4.7}$$

The inverse Fourier transform of Eq. (2.12) (ignoring the i dependence) is

$$A(\mathbf{r},\mathbf{r}') = -\frac{1}{V}\sum_{\mathbf{g},\mathbf{h}} W_{\mathbf{g},\mathbf{h}} \exp[i(\mathbf{K}+\mathbf{g})\cdot\mathbf{r}]\exp[-i(\mathbf{K}+\mathbf{h})\cdot\mathbf{r}']\ . \tag{4.8}$$

It follows that

$$A(\mathbf{r},\mathbf{r}+\mathbf{R}_\alpha) = -\frac{1}{V}\sum_{\mathbf{g},\mathbf{h}} W_{\mathbf{g},\mathbf{h}} \exp[i(\mathbf{g}-\mathbf{h})\cdot\mathbf{r}]\exp(-i\mathbf{K}\cdot\mathbf{R}_\alpha)\exp(-i\mathbf{h}\cdot\mathbf{R}_\alpha)\ . \tag{4.9}$$

Substituting Eq. (4.9) and Eq. (4.6) into Eq. (4.3) we obtain

$$\int A(\mathbf{r},\mathbf{r}+\mathbf{s})\psi_0(\mathbf{r}+\mathbf{s})d\mathbf{s} \approx -\sum_{\mathbf{g},\mathbf{h}} W_{\mathbf{g},\mathbf{h}} \exp[i(\mathbf{g}-\mathbf{h})\cdot\mathbf{r}]\psi_0(\mathbf{r})\ , \tag{4.10}$$

where we have used the relation $\sum_\alpha \exp(i\mathbf{h}\cdot\mathbf{R}_\alpha) = N$ and $NV_c = V$. We therefore obtain the approximate equivalent local potential [cf. Eq. (4.1)] as

$$V_L(\mathbf{r}) = -\sum_{\mathbf{g},\mathbf{h}} W_{\mathbf{g},\mathbf{h}} \exp[i(\mathbf{g}-\mathbf{h})\cdot\mathbf{r}]\ . \tag{4.11}$$

The $W_{\mathbf{g},\mathbf{h}}$ are clearly the Fourier coefficients of the equivalent local inelastic potential corresponding to the vectors $\mathbf{g}-\mathbf{h}$ [with sign convention as discussed for the Fourier coefficients of the elastic crystal potential after Eq. (2.4)].

As such, the $W_{\mathbf{g},\mathbf{h}}$ should depend only on the difference of the two vectors, $\mathbf{g}-\mathbf{h}$. Let us now make more explicit why this is indeed the case. If we assume at the outset that $A(\mathbf{r},\mathbf{r}')$ is local, i.e., given by $V_L(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$, then $W_{\mathbf{g},\mathbf{h}}$ (ignoring the i dependence) becomes

$$\begin{aligned}W_{\mathbf{g},\mathbf{h}} &= -\frac{1}{V}\int_V\int_V \exp\left[-i(\mathbf{K}+\mathbf{g})\cdot\mathbf{r}\right]V_L(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\exp\left[i(\mathbf{K}+\mathbf{h})\cdot\mathbf{r}'\right]d\mathbf{r}d\mathbf{r}' \\ &= -\frac{1}{V}\int_V \exp\left[-i(\mathbf{g}-\mathbf{h})\cdot\mathbf{r}\right]V_L(\mathbf{r})d\mathbf{r}\;. \end{aligned} \tag{4.12}$$

We see from inspection (i.e., by direct substitution) that $W_{\mathbf{g},\mathbf{h}} = W_{\mathbf{g}-\mathbf{h},\mathbf{0}}$, and so we can write Eq. (4.11) as

$$V_L(\mathbf{r}) = -\sum_{\mathbf{g},\mathbf{h}} W_{\mathbf{g}-\mathbf{h},\mathbf{0}}\exp\left[i(\mathbf{g}-\mathbf{h})\cdot\mathbf{r}\right]\;. \tag{4.13}$$

B. Cross section in the local approximation

In the local approximation we can rewrite the cross section expression [Eq. (3.30)] as

$$\sigma = NV_c\left\{\left[1-\sum_{i,j}B^{ij}(t)\sum_{\mathbf{g}}C^i_{\mathbf{g}}C^{j*}_{\mathbf{g}}\right]\mu^L_0 + \sum_{i,j}B^{ij}(t)\sum_{\mathbf{g},\mathbf{h}}C^i_{\mathbf{g}}C^{j*}_{\mathbf{h}}\mu^L_{\mathbf{h}-\mathbf{g}}\right\}\;. \tag{4.14}$$

The superscript L denotes "local," and $\mu^L_{\mathbf{h}-\mathbf{g}} \equiv \mu_{\mathbf{h}-\mathbf{g},\mathbf{0}}$. Equation (4.14) is the expression used in previous work[25] and in the case of a δ function interaction ($\mu^L_0 \approx \mu^L_{\mathbf{h}-\mathbf{g}}$ for all $\mathbf{h},\mathbf{g}$) reduces to the expression obtained by Cherns *et al.*[9] The work of Cherns *et al.* has been elaborated on by Taftø[26] and also Krishnan.[27] An expression similar to Eq. (4.14) has recently been used in Ref. 28.

The $\mu^L_{\mathbf{h}-\mathbf{g}}$ are related to the Fourier coefficients of the local potential by

$$\mu^L_{\mathbf{h}-\mathbf{g}} = \frac{2m}{\hbar^2 k_0}W_{\mathbf{h}-\mathbf{g},\mathbf{0}}\;. \tag{4.15}$$

We have discussed the local approximation for the coefficients $\mu^{ji}_{\mathbf{h},\mathbf{g}}$ for the inelastic scattering of interest (for example K-shell ionization). This inelastic scattering may also be absorptive (for the given example of K-shell ionization it is) and thus contributes to the absorption coefficients η^i and η^j implicit in the $B^{ij}(t)$. Other absorptive processes contributing to the absorption coefficients (TDS is the dominant contribution) may be treated as nonlocal interactions or also in a local approximation.

Equation (4.14) can be derived more directly by assuming a local potential at the outset but the approximations made in assuming a local potential are then not as apparent as they are here. The generalization of Eq. (4.14) to explicitly include diffraction of the scattered electron has been done in Ref. 29.

V. NONLOCALITY IN INNER-SHELL IONIZATION CROSS SECTIONS

Applications of Eq. (3.30) have very recently been made to energy-dispersive x-ray (EDX) analysis[30,31] and Rutherford backscattering,[32] where the correct form for the nonlocal cross section was conjectured from the corresponding local expression [Eq. (4.14)] used in previous work,[25,29] which in turn improved on earlier work only containing the dynamical term.[33–37] The rigorous proof given in this paper puts the nonlocal expression on a solid foundation and the example we will now discuss shows the importance of the more exact result.

We will now illustrate the theoretical results by an application of the formalism to EELS, in particular for K-shell ionization in aluminum. Our calculations are for 120 keV electrons incident on Al at room temperature and for the case of a $\{111\}$ systematic row. The scattering equations [Eq. (2.19)] were solved to obtain the Bloch state coefficients in a similar manner to that disscused in Ref. 31. The elastic potential was calculated in the standard way for high energy electrons, from the Doyle-Turner[38] x-ray scattering form factors for neutral atoms via the Mott formula. The TDS form factors were calculated in the Einstein model,[39] with the Debye-Waller parameter taken from Ref. 40. A collection aperture of 25 mrad has been assumed and the energy window is 200 eV above the ionization threshold. Some of our calculations can then be compared with the experimental results of Stobbs and Bourdillon.[41] They used a slightly off-center collection aperture with angular radius 25 mrad, allowing passage of zeroth- and first-order Bragg beams. In our calculations the detector is placed symetrically about the z axis and also includes these two beams and it is reasonable to compare the experimental results with our calculations. The appropriate form for the coefficients $\mu^{ji}_{\mathbf{h},\mathbf{g}}$ for K-shell ionization is derived in Appendix B. They have been evaluated using a hydrogenic model.[42]

First the cross section (per atom) has been calculated using Eq. (3.30) for a range of different incident beam directions and thicknesses. Fifteen beams [or Bloch state components in the summations in Eq. (3.30)] were required in the calculation to obtain fully converged results. The contribution from the dynamic term in Eq. (3.30) is shown in Fig. 1(a). Note the logarithmic scale for the thickness of the crystal. The incident beam orientation in the calculated cross section varies by up to approximately 60 mrad either side of the symmetrical position (indicated by 0). A value of unity indicates that (111) is in the exact Bragg orientation. Orientation dependence (as a function of crystal thickness) in the cross section is initially absent but then becomes increasingly important. As the thickness continues to increase the dynamical contribution to the cross section shows an overall decrease due to absorptive scattering (in this case assumed to be

TDS and K-shell ionization). The contribution to the cross section due to the diffuse background of electrons [Fig. 1(b)] increases with thickness, starting initially from zero. It starts to become important from about 100 Å and becomes the dominant contribution to the cross section for thick crystals. The total cross section, which is just the sum of the dynamical and diffuse components, is shown in Fig. 1(c). For very thin crystals the cross section has the kinematic value $\sigma_{\mathrm{kin}} = 3.15 \times 10^{-6}$ Å^2, and is orientation independent. For increasing thickness it shows strong orientation dependence before once again tending to the kinematic value for very large thicknesses.

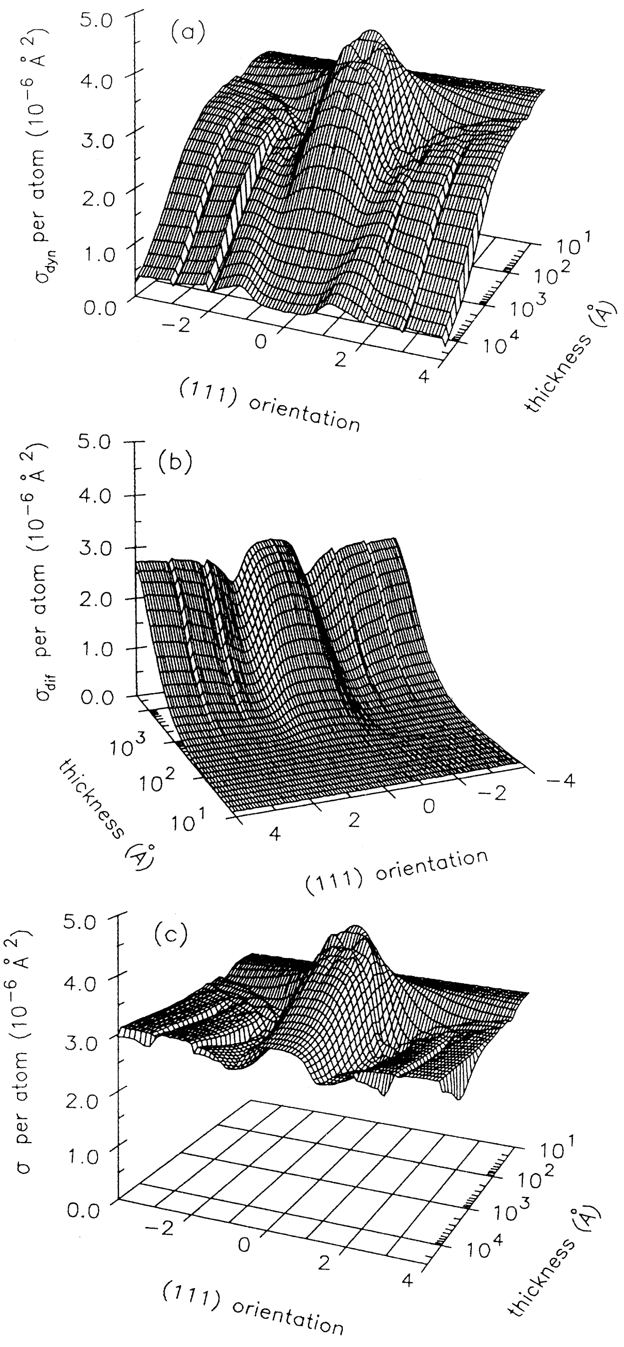

FIG. 1. (a) Dynamical part of the cross section per atom for K-shell EELS for 120 keV electrons at room temperature on Al and for a $\{111\}$ systematic row orientation. An orientation value of unity indicates that (111) is in the exact Bragg orientation. Crystal thickness increases towards the front of the plot. (b) Cross section for the diffuse background. Crystal thickness increases towards the back of the plot. (c) The total cross section per atom.

The calculations in Fig. 1 were made assuming the K-shell ionization interaction is nonlocal. In Fig. 2 we show the appropriate form factor $f_{\mathbf{h},\mathbf{g}}$ defined in Eq. (B9) used to calculate $\mu_{\mathbf{h},\mathbf{g}}$ for use in the cross section expression [Eq. (3.30)]. If we choose to treat the ionization interaction in the local approximation discussed above and calculate the cross sections via Eq. (4.14), then we are making the approximation $f_{\mathbf{h},\mathbf{g}} \approx f_{\mathbf{h}-\mathbf{g},\mathbf{0}}$. In Fig. 2 we compare the nonlocal form factor $f_{\mathbf{h},\mathbf{g}}$ [Fig. (2a)] to the corresponding value expected in the local approximation $f_{\mathbf{h}-\mathbf{g},\mathbf{0}}$ [Fig. (2b)]. The diagonal values $f_{\mathbf{g},\mathbf{g}}$ are clearly smaller than $f_{\mathbf{0},\mathbf{0}}$ for $\mathbf{g} \neq \mathbf{0}$, contrary to what is expected in the local approximation. However, the off diagonal terms ($f_{\mathbf{h},\mathbf{g}}$, $\mathbf{h} \neq \mathbf{g}$) are not very different from the local

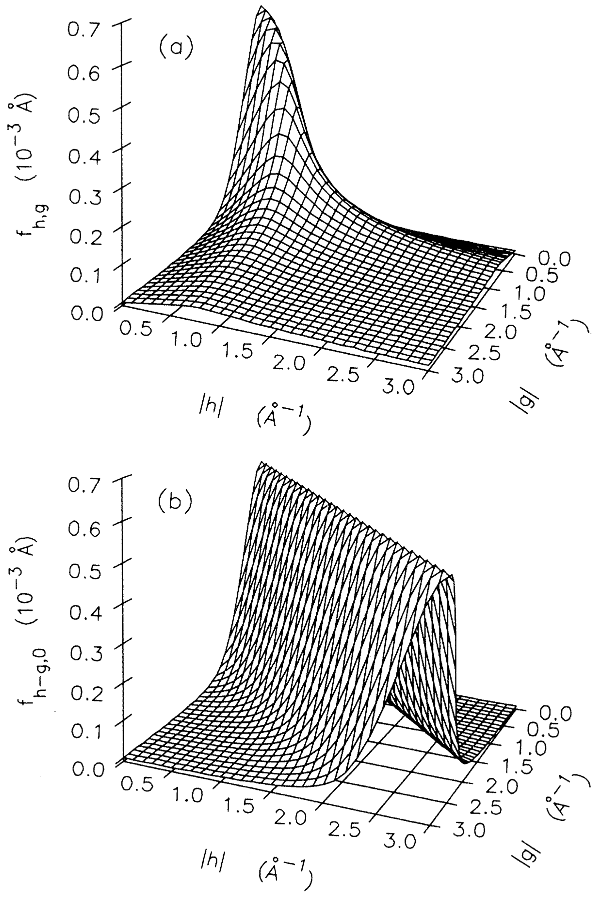

FIG. 2. (a) The atomic K-shell ionization form factor $f_{\mathbf{h},\mathbf{g}}$, for 120 keV electrons incident on Al. (b) The quantity $f_{\mathbf{h}-\mathbf{g},\mathbf{0}}$ used in the local approximation to the ionization form factor.

approximation $f_{\mathbf{h}-\mathbf{g},\mathbf{0}}$. We note that the diagonal terms $f_{\mathbf{g},\mathbf{g}}$ for $\mathbf{g} \neq \mathbf{0}$ only occur in the dynamical component of the cross section, and hence any manifestation of inaccuracy in the local approximation $f_{\mathbf{g},\mathbf{g}} \approx f_{\mathbf{0},\mathbf{0}}$ will only show itself in this term.

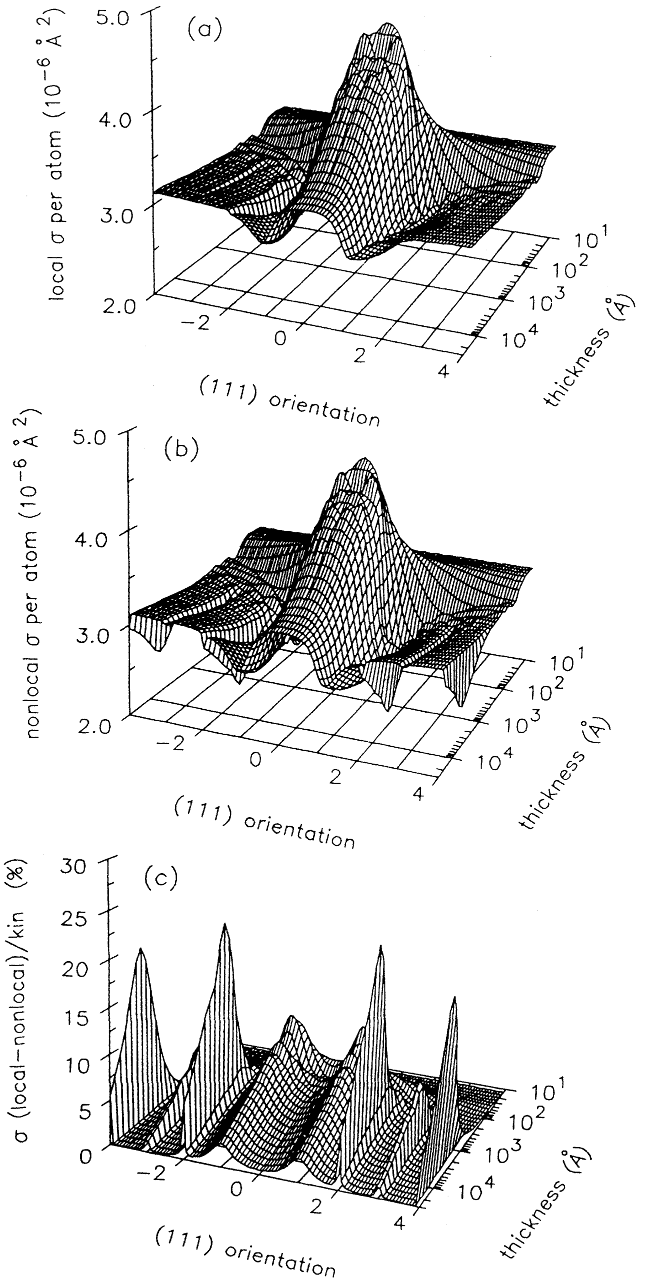

FIG. 3. (a) Total cross section per atom for K-shell EELS for 120 keV electrons on Al at room temperature and for a {111} systematic row orientation calculated in the local approximation. (b) Total cross section using the nonlocal formalism. (c) Difference between the local and nonlocal cases plotted as a percentage of the kinematic value.

The implications of the local approximation are shown in Fig. 3. The cross section in the local approximation is shown in Fig. 3(a) and can be compared with the full nonlocal result shown in Fig. 3(b). While overall the two cross sections are similar, there is more structure in the nonlocal case as successive Brillouin zone boundaries are crossed. The comparison is made more explicit in Fig. 3(c) where the difference between local and nonlocal cross sections is shown as a percentage of the kinematic value. This effectively scales the difference between the local and nonlocal cross sections to give some measure of how important the differences between the two cases are.

We note, referring to Fig. 1(c), that there is considerable variation in structure in the cross section between about 200 and 1000 Å. This is shown in more detail on a linear scale in Fig. 4(a). Experimental data taken by Stobbs and Bourdillon[41] for a sample of thickness approximately equal to one extinction distance ($\approx$ 600 Å) are compared in Fig. 4(b) with the cross section calcu-

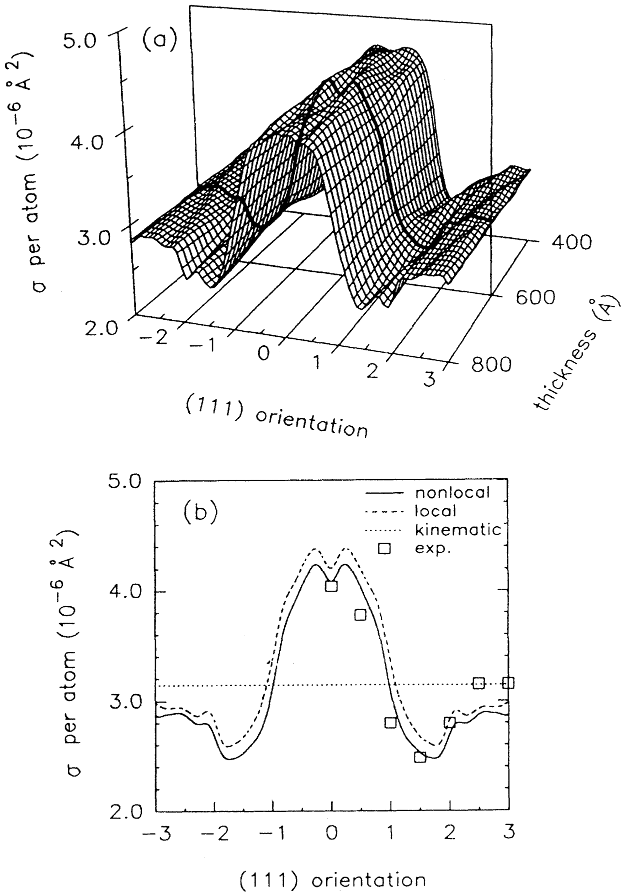

FIG. 4. (a) Total cross section per atom for K-shell EELS for 120 keV electrons on Al at room temperature and for a {111} systematic row orientation calculated using the nonlocal formalism. (b) Comparison of nonlocal and local results with experiment for a thickness of 600 Å. The kinematic result is also shown.

lated in both the local and nonlocal cases. The pertinent thickness slice for the nonlocal case is also indicated in Fig. 4(a). For this particular thickness, the local approximation to the cross section is significantly higher than the nonlocal result. It should be pointed out that an exact comparison with experiment is difficult. This is due to uncertanties in the exact crystal thickness and the often quite large experimental uncertanties. These in turn relate to difficulties in obtaining accurate systematic row conditions unaffected by nonsystematic reflections, etc.[30] However, the local calculation appears not to fit the experimental results as well as the nonlocal calculation does.

VI. CONCLUSIONS

We have extended the work of Yoshioka to obtain generalized dynamical scattering equations, for scattering of electrons from a crystal of finite thickness, where the inelastic scattering is assumed to be represented by a nonlocal interaction.

A rigorous derivation has been made of the cross section for any chosen specific type of inelastic scattering [e.g., inner-shell ionization, Rutherford backscattering,[32,43] dynamical TDS (Refs. 44–46)] which also takes into account absorption occurring concurrently in the crystal. The wide general applicability of this result is emphasized.

Furthermore, the assumptions made in representing the inelastic scattering under consideration by a local interaction have been made manifest here and we have shown by means of an example that significant "nonlocal effects" can be expected in certain situations.

ACKNOWLEDGMENT

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APPENDIX A: THE INELASTIC SCATTERING COEFFICIENTS

The main purpose of this appendix is a derivation of Eq. (2.15) and the associated Eq. (2.16). Making use of the standard Green's function identity

$$\frac{1}{4\pi}\frac{\exp(ik_n|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}=\lim_{\delta\to 0^+}\frac{1}{(2\pi)^3}\int\frac{\exp[i\mathbf{K}'\cdot(\mathbf{r}-\mathbf{r}')]}{K'^2-k_n^2-i\delta}d\mathbf{K}' , \tag{A1}$$

in the definition of $A(\mathbf{r},\mathbf{r}')$ in Eq. (2.2), we can write

$$\begin{aligned}A(\mathbf{r},\mathbf{r}')-A^*(\mathbf{r}',\mathbf{r})=&-\frac{2m}{\hbar^2}\sum_{m\neq 0}H'_{0m}(\mathbf{r})H'_{m0}(\mathbf{r}')\\&\times\left\{\lim_{\delta\to 0^+}\frac{1}{(2\pi)^3}\int\frac{\exp[i\mathbf{K}'\cdot(\mathbf{r}-\mathbf{r}')]}{K'^2-k_m^2-i\delta}d\mathbf{K}'-\lim_{\delta\to 0^+}\frac{1}{(2\pi)^3}\int\frac{\exp[i\mathbf{K}'\cdot(\mathbf{r}-\mathbf{r}')]}{K'^2-k_m^2+i\delta}d\mathbf{K}'\right\} .\end{aligned}\tag{A2}$$

Using the standard relation

$$\lim_{\delta\to 0^+}\frac{f(x)}{(x-b)+i\delta}=f(x)P\frac{1}{x-b}-i\pi f(x)\delta(x-b) \tag{A3}$$

and its complex conjugate, we can rewrite Eq. (A2) in the form

$$A(\mathbf{r},\mathbf{r}')-A^*(\mathbf{r}',\mathbf{r})=-\frac{2m}{\hbar^2}\sum_{m\neq 0}H'_{0m}(\mathbf{r})H'_{m0}(\mathbf{r}')\frac{i}{(2\pi)^2}\int\exp[i\mathbf{K}'\cdot(\mathbf{r}-\mathbf{r}')]\delta(K'^2-k_m^2)d\mathbf{K}' . \tag{A4}$$

Therefore the inelastic scattering coefficient $(W^{ji}_{\mathbf{h},\mathbf{g}})^{(i)}$ [cf. Eq. (2.14)] becomes

$$(W^{ji}_{\mathbf{h},\mathbf{g}})^{(i)}=\frac{m}{(2\pi)^2\hbar^2 V}\sum_{m\neq 0}\int E^*_{m0}(\mathbf{k}^j+\mathbf{h}-\mathbf{K}')E_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}')\delta(K'^2-k_m^2)d\mathbf{K}' , \tag{A5}$$

where

$$E_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}')=\int_V H'_{m0}(\mathbf{r})\exp[i(\mathbf{k}^i+\mathbf{g}-\mathbf{K}')\cdot\mathbf{r}]d\mathbf{r} . \tag{A6}$$

We will now examine the form of $E_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}')$ in more detail. In an independent electron description of the crystal (a good approximation for our purposes) we represent the many-electron wave function $a_m(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ of the crystal in terms of Bloch states $b_m(\mathbf{p},\mathbf{r}')$, where $\mathbf{p}$ is the wave vector for the Bloch electron in the crystal. Due to the periodicity of the Bloch states on the reciprocal lattice, $b_m(\mathbf{p}+\mathbf{g},\mathbf{r}') = b_m(\mathbf{p},\mathbf{r}')$ for any reciprocal lattice vector $\mathbf{g}$ and we can expand the crystal Bloch states in a Fourier series

$$b_n(\mathbf{p}_n,\mathbf{r}') = \frac{1}{\sqrt{N}}\sum_\alpha \exp\left(i\mathbf{p}_n\cdot\mathbf{R}_\alpha\right)u_n(\mathbf{r}'-\mathbf{R}_\alpha)\,, \qquad n=0,m\,, \tag{A7}$$

where N is the number of lattice sites and $\mathbf{R}_\alpha$ are the lattice vectors. We note that in the "tight-binding" approximation the Wannier functions $u_n(\mathbf{r}'-\mathbf{R}_\alpha)$ are simply the atomic wave functions.[47] For a transition in the crystal from the ground state with wave vector $\mathbf{p}_0$ to the state m with wave vector $\mathbf{p}_m$ and assuming that $H'(\mathbf{r};\mathbf{r}_1,\ldots,\mathbf{r}_N)\equiv H'(\mathbf{r}-\mathbf{r}')$, where

$$H'(\mathbf{r}-\mathbf{r}') = \frac{e^2}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|}\,, \tag{A8}$$

we can write the interaction matrix elements $H'_{m0}(\mathbf{r})$ [Eq. (2.3)] as

$$H'_{m0}(\mathbf{r}) = \frac{e^2}{4\pi\epsilon_0 N}\sum_\alpha \exp\left[i(\mathbf{p}_0-\mathbf{p}_m)\cdot\mathbf{R}_\alpha\right]\int_V u_m^*(\mathbf{r}'-\mathbf{R}_\alpha)\frac{1}{|\mathbf{r}-\mathbf{r}'|}u_0(\mathbf{r}'-\mathbf{R}_\alpha)d\mathbf{r}'\,. \tag{A9}$$

We have used the orthogonality property of the Wannier functions, $\int u_m^*(\mathbf{r}'-\mathbf{R}_\alpha)u_0(\mathbf{r}'-\mathbf{R}_\beta)d\mathbf{r}'=0$, unless $\alpha=\beta$. Inserting Eq. (A9) into $E_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}')$ [Eq. (A6)] we obtain, by integrating over $\mathbf{r}$,

$$\begin{aligned} E_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}') &= \frac{e^2}{4\pi\epsilon_0 N}\frac{4\pi}{|\mathbf{k}^i+\mathbf{g}-\mathbf{K}'|^2}\sum_\alpha \exp\left[i(\mathbf{p}_0-\mathbf{p}_m)\cdot\mathbf{R}_\alpha\right] \\ &\quad\times\int_V u_m^*(\mathbf{r}'-\mathbf{R}_\alpha)u_0(\mathbf{r}'-\mathbf{R}_\alpha)\exp\left[i(\mathbf{k}^i+\mathbf{g}-\mathbf{K}')\cdot\mathbf{r}'\right]d\mathbf{r}'\,. \end{aligned} \tag{A10}$$

Letting $\mathbf{r}'=\mathbf{R}_\alpha+(\mathbf{r}'-\mathbf{R}_\alpha)$, we can write Eq. (A10) as

$$E_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}') = \frac{e^2}{\epsilon_0 N}\frac{1}{|\mathbf{k}^i+\mathbf{g}-\mathbf{K}'|^2}\sum_\alpha \exp\left[i(\mathbf{p}_0-\mathbf{p}_m+\mathbf{k}^i+\mathbf{g}-\mathbf{K}')\cdot\mathbf{R}_\alpha\right]F_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}')\,, \tag{A11}$$

where

$$F_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}') = \int_V u_m^*(\mathbf{r}')\exp\left[i(\mathbf{k}^i+\mathbf{g}-\mathbf{K}')\cdot\mathbf{r}'\right]u_0(\mathbf{r}')d\mathbf{r}'\,. \tag{A12}$$

We now focus on the summation over the lattice sites α in Eq. (A11). Writing $\mathbf{p}_{0m}\equiv\mathbf{p}_0-\mathbf{p}_m$,

$$\begin{aligned} S &= \sum_\alpha \exp\left[i(\mathbf{p}_{0m}+\mathbf{k}^i+\mathbf{g}-\mathbf{K}')\cdot\mathbf{R}_\alpha\right] \\ &\approx \frac{1}{V_c}\int_V \exp\left[i(\mathbf{p}_0-\mathbf{K}_\mathbf{G}+\lambda^i\hat{\mathbf{n}})\cdot\mathbf{r}\right]d\mathbf{r}\,, \end{aligned} \tag{A13}$$

assuming the argument of the exponent in the summand varies slowly over the unit cell. We have used the fact that $\exp(i\mathbf{g}\cdot\mathbf{R}_\alpha)=1$, and $\mathbf{G}$ is a reciprocal lattice vector such that $\mathbf{K}_\mathbf{G}=(\mathbf{K}'-\mathbf{K}+\mathbf{p}_m)-\mathbf{G}$ is a vector in the first Brillouin zone. We now make the same assumptions about the scattering geometry that were made in Sec. II. We assume that all the reciprocal lattice vectors which contribute to diffraction lie in a plane (the xy plane), and that this plane is parallel to the crystal surface. The z direction is perpendicular to the xy plane, and hence along the crystal surface normal $\hat{\mathbf{n}}$. The crystal surface is assumed to be very large (of area A), but strictly finite and of much smaller dimension (thickness t) in the $\hat{\mathbf{n}}$ direction. We then obtain, as $\lambda^i\hat{\mathbf{n}}$ now only has a component along the z direction,

$$\begin{aligned} S &= \frac{1}{V_c}\int_A \exp\left[i(\mathbf{p}_0-\mathbf{K}_\mathbf{G})\cdot\mathbf{r}_{xy}\right]d\mathbf{r}_{xy}\int_0^t \exp\left[i(p_{0_z}-K_{G_z}+\lambda^i)z\right]dz \\ &= \frac{(2\pi)^2}{V_c}\delta(\mathbf{p}_0-\mathbf{K}_\mathbf{G})_{xy}\int_0^t \exp\left[i(p_{0_z}-K_{G_z}+\lambda^i)z\right]dz\,. \end{aligned} \tag{A14}$$

Inserting Eq. (A14) into Eq. (A11) we obtain

$$E_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}') = \frac{e^2}{\epsilon_0 N}\frac{(2\pi)^2}{V_c}\frac{1}{|\mathbf{k}^i+\mathbf{g}-\mathbf{K}'|^2}\delta(\mathbf{p}_0-\mathbf{K}_\mathbf{G})_{xy}F_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}')\int_0^t \exp\left[i(p_{0_z}-K_{G_z}+\lambda^i)z\right]dz\,. \tag{A15}$$

Now substituting Eq. (A15) for $E_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}')$ in Eq. (A5) but using Eq. (A11) for $E^*_{m0}(\mathbf{k}^j+\mathbf{h}-\mathbf{K}')$ we obtain

$$(W^{ji}_{\mathbf{h},\mathbf{g}})^{(i)} = \frac{m}{(2\pi)^2\hbar^2 V}\left(\frac{e^2}{\epsilon_0 N}\right)^2 \frac{(2\pi)^2}{V_c}\sum_{m\neq 0}\int \frac{F^*_{m0}(\mathbf{k}^j+\mathbf{h}-\mathbf{K}')}{|\mathbf{k}^j+\mathbf{h}-\mathbf{K}'|^2}\frac{F_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}')}{|\mathbf{k}^i+\mathbf{g}-\mathbf{K}'|^2}\delta(K'^2-k_m^2)d\mathbf{K}'$$

$$\times\delta(\mathbf{p}_0-\mathbf{K}_\mathbf{G})_{xy}\sum_\alpha \exp\left[-i(\mathbf{p}_0-\mathbf{K}_\mathbf{G}+\lambda^{j*}\hat{\mathbf{z}})\cdot\mathbf{R}_\alpha\right]\int_0^t \exp\left[i(p_{0_z}-K_{G_z}+\lambda^i)z\right]dz\ . \qquad \text{(A16)}$$

The ground state of the crystal is specified in this notation by the wave vector $\mathbf{p}_0$, which is of course just convenient notation for the multitude of allowed initial band states. Scattering from all these states is allowed, and so we must sum over all possible initial band wave vectors $\mathbf{p}_0$. In the limit of a large crystal, we replace this summation by an integral, i.e., $\sum_{\mathbf{p}_0}\rightarrow V/(2\pi)^3\int d\mathbf{p}_0$. Due to the surface δ function $\delta(\mathbf{p}_0-\mathbf{K}_\mathbf{G})_{xy}$, we are left with an integral over p_{0_z},

$$(W^{ji}_{\mathbf{h},\mathbf{g}})^{(i)} = \frac{m}{(2\pi)^2\hbar^2 V}\left(\frac{e^2}{\epsilon_0 N}\right)^2 \frac{(2\pi)^2}{V_c}\frac{N}{t}\frac{V}{(2\pi)^3}\sum_{m\neq 0}\int \frac{F^*_{m0}(\mathbf{k}^j+\mathbf{h}-\mathbf{K}')}{|\mathbf{k}^j+\mathbf{h}-\mathbf{K}'|^2}\frac{F_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}')}{|\mathbf{k}^i+\mathbf{g}-\mathbf{K}'|^2}\delta(K'^2-k_m^2)d\mathbf{K}'$$

$$\times\int_0^t\int_0^t \exp\left[i(\lambda^i z'-\lambda^{j*}z)\right]\left\{\int_{-\infty}^{\infty}\exp\left[i(p_{0_z}-K_{G_z})(z-z')\right]dp_{0_z}\right\}dz\,dz'\ . \qquad \text{(A17)}$$

In order to perform the integration over p_{0_z} we proceed as follows. From the definition of $\mathbf{K}_\mathbf{G}$ we may write

$$\frac{\partial K_{G_z}}{\partial p_{0_z}} = \frac{\partial p_{m_z}}{\partial p_{0_z}} \approx \frac{m}{\hbar^2 p_{m_z}}\frac{\partial\varepsilon_m}{\partial p_{0_z}}\ , \qquad \text{(A18)}$$

for nearly free dispersing final states of energy $\varepsilon_m \approx \hbar^2 {p_m}^2/2m$. From conservation of energy

$$E_0 - E_m = \varepsilon_m - \varepsilon_0\ , \qquad \text{(A19)}$$

it is clear that

$$\frac{\partial\varepsilon_m}{\partial p_{0_z}} = \frac{\partial\varepsilon_0}{\partial p_{0_z}}\ , \qquad \text{(A20)}$$

because the incident electron energy E_0 and scattered electron energy E_m are known and are not explicitly a function of p_{0_z}. Therefore from Eq. (A18)

$$\frac{\partial K_{G_z}}{\partial p_{0_z}} \approx \frac{m}{\hbar^2 p_{m_z}}\frac{\partial\varepsilon_0}{\partial p_{0_z}} \approx a\ , \qquad \text{(A21)}$$

where a is the dispersion factor of the initial band which we may take to be approximately constant. This approximation is valid only for linearly dispersing bands. We note that for "flat" bands (such as those pertaining to inner shell electrons) a=0. Integrating we then obtain

$$K_{G_z} \approx a p_{0_z} + c\ , \qquad \text{(A22)}$$

where c is a constant. Hence the integration over p_{0_z} can be approximated by

$$\int_{-\infty}^{\infty}\exp\left[i(p_{0_z}-K_{G_z})(z-z')\right]dp_{0_z} \approx \exp\left[-ic(z-z')\right]\frac{2\pi}{(1-a)}\delta(z-z')\ . \qquad \text{(A23)}$$

As pointed out by Young and Rez[18] the delta function $\delta(z-z')$ implies that crystal layers of different z contribute incoherently to the cross section.

Returning to Eq. (A17) and using Eq. (A23) we perform the integrations over z and z' as follows:

$$\begin{aligned}\frac{1}{t}\int_0^t\int_0^t &\exp\left[i(\lambda^i z'-\lambda^{j*}z)\right]\left\{\int_{-\infty}^{\infty}\exp\left[i(p_{0_z}-K_{G_z})(z-z')\right]dp_{0_z}\right\}dz\,dz' \\ &\approx \frac{2\pi}{(1-a)t}\int_0^t\int_0^t \exp\left[i(\lambda^i z'-\lambda^{j*}z)\right]\exp\left[ic(z-z')\right]\delta(z-z')dz\,dz' \\ &= \frac{2\pi}{(1-a)t}\int_0^t \exp\left[i(\lambda^i-\lambda^{j*})z\right]dz \\ &= \frac{2\pi}{(1-a)}L^{ij}(t)\ ,\end{aligned} \qquad \text{(A24)}$$

where $L^{ij}(t)$ is given by

$$L^{ij}(t)=\frac{\exp[i(\lambda^{i}-\lambda^{j*})t]-1}{i(\lambda^{i}-\lambda^{j*})t}\,. \tag{A25}$$

Substituting Eq. (A24) into Eq. (A17) and gathering the constants, we obtain our final expression as

$$(W^{ji}_{\mathbf{h},\mathbf{g}})^{(i)}=L^{ij}(t)X^{ji}_{\mathbf{h},\mathbf{g}}\,, \tag{A26}$$

where

$$X^{ji}_{\mathbf{h},\mathbf{g}}=\frac{4\hbar^2}{ma_0^2}\frac{1}{V}\frac{1}{(1-a)}\sum_{m\neq 0}\int\frac{F^{*}_{m0}(\mathbf{k}^j+\mathbf{h}-\mathbf{K}')}{|\mathbf{k}^j+\mathbf{h}-\mathbf{K}'|^2}\frac{F_{m0}(\mathbf{k}^i+\mathbf{g}-\mathbf{K}')}{|\mathbf{k}^i+\mathbf{g}-\mathbf{K}'|^2}\delta(K'^2-k_m^2)d\mathbf{K}'\,. \tag{A27}$$

APPENDIX B: THE INELASTIC SCATTERING COEFFICIENTS FOR INNER-SHELL IONIZATION

Here we derive the form of the $\mu^{ji}_{\mathbf{h},\mathbf{g}}$ for inner-shell ionization from a particular atom species (denoted by β) in the crystal lattice. The general form [cf. Eq. (2.16) and Eq. (3.11)] is

$$\mu^{ji}_{\mathbf{h},\mathbf{g}}=\frac{8}{k_0Va_0^2}\frac{1}{(1-a)}\sum_{m\neq 0}\int\frac{F^{*}_{m0}(\mathbf{Q}^j_{\mathbf{h}})}{|\mathbf{Q}^j_{\mathbf{h}}|^2}\frac{F_{m0}(\mathbf{Q}^i_{\mathbf{g}})}{|\mathbf{Q}^i_{\mathbf{g}}|^2}\times\delta(K'^2-k_m^2)d\mathbf{K}'\,, \tag{B1}$$

where $\mathbf{Q}^i_{\mathbf{g}}=\mathbf{k}^i+\mathbf{g}-\mathbf{K}'$. The "tight-binding" approximation describes the inner-shell electron states to a good approximation. We replace the Wannier functions $u_m(\mathbf{r})$ and $u_0(\mathbf{r})$ occurring in the transition matrix elements $F_{m0}(\mathbf{Q}^i_{\mathbf{g}})$ [cf. Eq. (A12)], by the sum of atomic wave functions $u^{\beta}_m(\mathbf{r})$ and $u^{\beta}_0(\mathbf{r})$ at each atomic site $\boldsymbol{\tau}_{\beta_n}$ (labeled by n) in the unit cell. We then obtain

$$F_{m0}(\mathbf{Q}^i_{\mathbf{g}})=\sum_n\exp(i\mathbf{g}\cdot\boldsymbol{\tau}_{\beta_n})F^{\beta}_{m0}(\mathbf{Q}^i_{\mathbf{g}})\,, \tag{B2}$$

where

$$F^{\beta}_{m0}(\mathbf{Q}^i_{\mathbf{g}})=\int_V u^{\beta}_m{}^{*}(\mathbf{r})\exp[i\mathbf{Q}^i_{\mathbf{g}}\cdot\mathbf{r}]u^{\beta}_0(\mathbf{r})d\mathbf{r}\,. \tag{B3}$$

For ionization we replace the summation over all discrete final states m of the crystal, by the equivalent integral over all the possible final continuum state wave vectors (denoted by $\boldsymbol{\kappa}$) of the ejected electron, $\sum_{m\neq 0}\rightarrow V/(2\pi)^3\int d\boldsymbol{\kappa}$. Furthermore, the discrete atomic transition matrix elements [Eq. (B3)] must be replaced by their equivalent continuum forms:

$$F^{\beta}(\mathbf{Q}^i_{\mathbf{g}},\boldsymbol{\kappa})=\int_V\sqrt{NV}b^{\beta*}(\boldsymbol{\kappa},\mathbf{r})\exp[i\mathbf{Q}^i_{\mathbf{g}}\cdot\mathbf{r}]u^{\beta}_0(\mathbf{r})d\mathbf{r}\,. \tag{B4}$$

The final state wave function $u^{\beta}_m(\mathbf{r})$ has been replaced by the *dimensionless* orthogonal plane wave continuum state $\sqrt{NV}b^{\beta}(\boldsymbol{\kappa},\mathbf{r})$. The continuum state is normalized to the crystal volume and hence $\sqrt{NV}b^{\beta}(\boldsymbol{\kappa},\mathbf{r})$ is dimensionless. We can then write

$$\sum_{m\neq 0}F^{\beta*}_{m0}(\mathbf{Q}^j_{\mathbf{h}})F^{\beta}_{m0}(\mathbf{Q}^i_{\mathbf{g}})=\frac{nN}{(2\pi)^3}\int F^{\beta*}(\mathbf{Q}^j_{\mathbf{h}},\boldsymbol{\kappa})\times F^{\beta}(\mathbf{Q}^i_{\mathbf{g}},\boldsymbol{\kappa})d\boldsymbol{\kappa}\,. \tag{B5}$$

An additional factor of n is included to take into account the number of electrons in a particular given shell in the atom, e.g., n=2 for the K shell. Before we proceed further we evaluate the $\mathbf{K}'$ integration in Eq. (B1), in terms of the scattered electron wave vector $\mathbf{k}_m$:

$$\begin{aligned}\int G(\mathbf{K}')\delta(K'^2-k_m^2)d\mathbf{K}'&=\int\int\frac{K'}{2}G(\mathbf{K}')\delta(K'^2-k_m^2)d\Omega_{K'}dK'^2\\&=\int\frac{k_m}{2}G(\mathbf{k}_m)d\Omega_{k_m}\\&=\int\frac{K'}{2}G(\mathbf{K}')d\Omega_{K'}\,,\end{aligned} \tag{B6}$$

where we have relabled the scattered electron wave vector as $\mathbf{K}'$ for convenience.

We may now evaluate the $\mu^{ji}_{\mathbf{h},\mathbf{g}}$ from Eq. (B1) by using Eq. (B6) and Eq. (B5), obtaining

$$\mu^{ji}_{\mathbf{h},\mathbf{g}}=\frac{4n}{(2\pi)^3k_0V_ca_0^2}\frac{1}{(1-a)}\mathcal{F}[\text{site}]\int K'\kappa^2\left[\int\left(\int\frac{F^{\beta*}(\mathbf{Q}^j_{\mathbf{h}},\boldsymbol{\kappa})F^{\beta}(\mathbf{Q}^i_{\mathbf{g}},\boldsymbol{\kappa})}{|\mathbf{Q}^j_{\mathbf{h}}|^2|\mathbf{Q}^i_{\mathbf{g}}|^2}d\Omega_{\kappa}\right)d\Omega_{K'}\right]d\kappa\,, \tag{B7}$$

where $d\boldsymbol{\kappa}=\kappa^2d\kappa d\Omega_{\kappa}$, and

$$\mathcal{F}[\text{site}]=\sum_n\exp[-M_{\beta}(\mathbf{g}-\mathbf{h})]\exp[i(\mathbf{g}-\mathbf{h})\cdot\boldsymbol{\tau}_{\beta_n}]\,. \tag{B8}$$

The Debye-Waller factor $M_\beta(\mathbf{g}-\mathbf{h})$ has been inserted in Eq. (B8) following Ref. 9, to take into account the delocalization of the ionization interaction at each atomic site, due to the thermal motion of the target atom.

In the high-incident-energy approximation $|\mathbf{Q}^i_\mathbf{g}| \approx |\mathbf{Q}_\mathbf{g}|$ and we can neglect the i and j dependences in Eq. (B7). Further setting $a = 0$ (a good approximation for tightly bound inner-shell states) gives the form of the $\mu_{\mathbf{h},\mathbf{g}}$'s for inner-shell ionization from the atoms of species β,

$$\begin{aligned}\mu_{\mathbf{h},\mathbf{g}} &= \frac{4n}{(2\pi)^3 k_0 V_c a_0^2}\mathcal{F}[\text{site}]\int K'\kappa^2\left[\int\left(\int\frac{F^{\beta *}(\mathbf{Q}_\mathbf{h},\kappa)F^{\beta}(\mathbf{Q}_\mathbf{g},\kappa)}{|\mathbf{Q}_\mathbf{h}|^2|\mathbf{Q}_\mathbf{g}|^2}d\Omega_\kappa\right)d\Omega_{K'}\right]d\kappa\\ &= \frac{1}{k_0 V_c}\mathcal{F}[\text{site}]f_{\mathbf{h},\mathbf{g}}\;,\end{aligned}\tag{B9}$$

where $f_{h,g}$ is the inner-shell ionization form factor.

The above expression for the inner-shell ionization coefficients integrates over all possible scattered electron orientations and all possible energy losses. This is appropriate for experimental situations such as EDX spectroscopy where the scattered electron is not detected. In many cases (such as for EELS) the scattered electron is detected within a well-defined aperture and energy loss window above the ionization threshold energy. The appropriate inelastic scattering coefficients are then obtained simply by constraining the integrations over $\Omega_{K'}$ and κ appropriately.[29]

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