Theory underpinning multislice simulations with plasmon energy losses

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Abstract

The theoretical conditions for small angle inelastic scattering where the incident electron can effectively be treated as a particle moving in a uniform potential is examined. The motivation for this work is the recent development of a multislice method that combines plasmon energy losses with elastic scattering using Monte Carlo methods. Since plasmon excitation is delocalised it was assumed that the Bloch wave nature of the incident electron in the crystal does not affect the scattering cross-section. It is shown here that for a delocalised excitation the mixed dynamic form factor term of the scattering cross-section is zero and the scattered intensities follow a Poisson distribution. These features are characteristic of particle-like scattering and validate the use of Monte Carlo methods to model plasmon losses in multislice simulations.

Keywords: plasmons, multislice, Monte Carlo methods, mixed dynamic form factor.

Quantitative electron microscopy requires accurate modelling of all interactions of the high energy electron beam with the solid. Frozen phonon multislice simulations include both elastic [1] and thermal diffuse scattering [2], and can be extended to include core ionisation losses as well [3-4]. Recently plasmon energy losses have also been combined with multislice simulations using Monte Carlo methods [5]. In Monte Carlo the high energy incident electron is assumed to be a particle moving in a uniform potential [6]. Strictly speaking incident electrons in a crystal are Bloch waves [7], but the effect this has on the scattering cross-section was overlooked, since plasmon excitations are delocalised [8-9]. The scattering angles for individual plasmon excitation events are then governed by a Lorentz cross-section derived for an incident electron plane wave [10]. Furthermore, the scattering path length is governed by Poisson statistics with a constant mean free path [5]. Computer generated random numbers are used to estimate the scattering depth and scattering angle from the Poisson distribution and Lorentz cross-section respectively. Many such plasmon ‘configurations’ can be generated, similar to modelling thermal diffuse scattering using frozen phonons. For a given plasmon configuration the transmission and propagator functions in the multislice simulation are updated to that of a tilted beam following plasmon excitation [5]. Averaging over many plasmon configurations then gives a statistically valid image or diffraction pattern. For example, it has been demonstrated that plasmon scattering reduces the Kikuchi band contrast in diffraction patterns as well as the atom column intensity in high angle annular dark field (HAADF) images [5].

In this letter quantum mechanics is used to rigorously demonstrate that inelastic scattering of a Bloch electron in a crystal is similar to a particle in a uniform potential provided the excitation is delocalised. Specifically it is shown that for a delocalised excitation the mixed dynamic form factor [11] is zero, due to the close relationship between the form factor and interaction potential in reciprocal space [4,12]. This means that apart from ‘preservation of elastic contrast’ [13-14] the periodic intensity oscillations in a Bloch electron are not important for inelastic scattering. This is in contrast to localised excitations such as core shell ionisation, where channeling of the incident beam is important [15]. Furthermore, it is shown that for a delocalised excitation the inelastic scattered intensities follow a Poisson distribution [16], which is also characteristic of particle-like scattering [6].

Following Yoshioka [17] the inelastic wavefunction ψ_m for the m^{th}-excited state (wavenumber k_m) is given by:

$$\left(\nabla^2 + 4\pi^2 k_m^2 + \frac{2me}{\hbar^2} V_{mm}(\mathbf{r})\right)\psi_m(\mathbf{r}) = -\frac{2me}{\hbar^2}\sum_{n\neq m} V_{mn}(\mathbf{r})\psi_n(\mathbf{r})$$

… (1)

$V_{mn}(\mathbf{r})$ is the potential for inelastic scattering from the n^{th} to m^{th} excited state with state '0' being the ground state. The other parameters are the electron charge (e) and mass (m), and Planck's reduced constant ($\hbar$).

Within the Born approximation only the elastic wave ψ_0 has appreciable intensity to scatter into the ψ_m inelastic channel. Furthermore, set $V_{mm}(\mathbf{r}) = 0$ in Equation (1); this means that elastic scattering of ψ_m in the crystal is suppressed. The resulting cross-section $d\sigma/d\Omega$ can therefore be directly compared to a particle in a uniform potential without the influence of channeling of the inelastic wave as it propagates through the crystal. Under these conditions the solution to Equation (1) is given by [17-18]:

$$\psi_m(\mathbf{r}) = \frac{me}{2\pi\hbar^2}\int \frac{\exp(2\pi i k_m|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} V_{m0}(\mathbf{r}')\psi_0(\mathbf{r}')d\mathbf{r}'$$

… (2)

In a crystal ψ_0 is a linear superposition of Bloch waves [7]:

$$\psi_0(\mathbf{r}) = \sum_{j,\mathbf{g}} \varepsilon^{(j)} C_{\mathbf{g}}^{(j)} \exp[2\pi i(\mathbf{k}_0 + \mathbf{g} + \boldsymbol{\gamma}^{(j)})\cdot\mathbf{r}]$$

… (3)

where for an incident wavevector $\mathbf{k}_0$ the j^{th}- Bloch wave has excitation $\varepsilon^{(j)}$, change in wavevector $\boldsymbol{\gamma}^{(j)}$ and expansion coefficient $C_{\mathbf{g}}^{(j)}$ for the $\mathbf{g}$ reciprocal vector. In principle $\varepsilon^{(j)}$ is a function of the depth z within the crystal due to inelastic scattering, but since the Born approximation is assumed this dependence is ignored. In the far field ψ_m has the form of a distorted spherical wave $f_m(\theta)[\exp(2\pi i k_m r)/r]$, where $f_m(\theta)$ is the inelastic scattering factor. Substituting Equation (3) in (2) and taking the asymptotic $r\rightarrow\infty$ value [18] gives:

$$f_m(\theta) = \frac{me}{2\pi\hbar^2}\sum_{j,\mathbf{g}} \varepsilon^{(j)} C_{\mathbf{g}}^{(j)} \int V_{m0}(\mathbf{r}')\exp\left[2\pi i(\mathbf{k}_0 - \mathbf{k}_m + \mathbf{g} + \boldsymbol{\gamma}^{(j)})\cdot\mathbf{r}'\right]d\mathbf{r}' \quad \ldots (4)$$

The integral is the Fourier transform of V_{m0}, i.e. $\tilde{V}_{m0}(\mathbf{q})$ where $\mathbf{q} = \mathbf{k}_m - \mathbf{k}_0 - \mathbf{g} - \boldsymbol{\gamma}^{(j)}$. For delocalised excitations $\tilde{V}_{m0}(\mathbf{q})$ is non-zero when $\mathbf{q} \approx \mathbf{0}$. Furthermore, $\mathbf{k}_m \approx \mathbf{k}_0$ for small angle scattering and small energy loss, such as plasmon excitations, so that $\mathbf{g} = \mathbf{0}$ (recall that $\boldsymbol{\gamma}^{(j)}$ is much smaller compared to $\mathbf{g}$, $\mathbf{k}_m$ or $\mathbf{k}_0$ [7]). Equation (4) therefore simplifies to:

$$f_m(\theta) \approx \frac{me}{2\pi\hbar^2}\left(\sum_j \varepsilon^{(j)} C_{\mathbf{0}}^{(j)}\right)\tilde{V}_{m0}(\mathbf{0}) = \frac{me}{2\pi\hbar^2}\phi_0(z=0)\tilde{V}_{m0}(\mathbf{0}) \quad \ldots (5)$$

where the substitution $\phi_0(z) = \Sigma\varepsilon^{(j)}C_{\mathbf{0}}^{(j)}\exp(2\pi i\gamma^{(j)}z)$ has been made [7], with ϕ_0 being the unscattered beam amplitude at depth z. The inelastic scattering cross-section $d\sigma$ over the solid angle $d\Omega$ is given by $(k_m/k_0)|f_m(\theta)|^2 d\Omega$ [18-19], so that from the normalisation condition $|\phi_0(z = 0)|^2 = 1$ and Equation (5) we obtain:

$$\frac{d\sigma}{d\Omega} = \frac{m^2e^2}{4\pi^2\hbar^4}\left(\frac{k_m}{k_0}\right)\left|\tilde{V}_{m0}(\mathbf{0})\right|^2 \quad \ldots (6)$$

Importantly Equation (6) does not contain a mixed dynamic form factor (i.e. terms of the form $\tilde{V}_{m0}(\mathbf{q}_1)\tilde{V}_{m0}^*(\mathbf{q}_2)$ where $\mathbf{q}_1 \neq \mathbf{q}_2$). The mixed dynamic form factor represents the interference contribution in inelastic scattering [11], an example being the interference of Bragg diffracted beams that gives rise to the periodic intensity oscillations of Bloch electrons. Equation (6) indicates that channeling of the incident electrons does not affect the inelastic scattering cross-section when the excitation is delocalised.

Next consider the inelastic scattered intensities. Expressing ψ_0 and ψ_m as $\Phi_0(\mathbf{r})\exp(2\pi i\mathbf{k}_0\cdot\mathbf{r})$ and $\Phi_m(\mathbf{r})\exp(2\pi i\mathbf{k}_m\cdot\mathbf{r})$ respectively and substituting in Equation (1) we obtain the inelastic amplitude Φ_m generated within an infinitesimal slice of thickness Δz at depth z as [3-4]:

$$\frac{d\Phi_m(\mathbf{R},z)}{dz} = i\sigma_m V_{m0}(\mathbf{R},z)\exp[-2\pi i(k_m - k_0)\mathrm{z}]\Phi_0(\mathbf{R},z)$$

… (7a)

$$\Phi_m(\mathbf{R},z) = i\sigma_m V_{m0}^{p}(\mathbf{R})\Phi_0(\mathbf{R},z)$$

… (7b)

$$V_{m0}^{p}(\mathbf{R}) = \int_{z-\frac{\Delta z}{2}}^{z+\frac{\Delta z}{2}} V_{m0}(\mathbf{R},z)\exp[-2\pi i(k_m - k_0)z]\,dz$$

… (7c)

here σ_m is the inelastic interaction constant ($me/2\pi\hbar^2 k_m$) and $\mathbf{R}$ is the position vector in the xy-plane. In deriving Equation (7a) it is assumed that the Born approximation is valid (i.e. only ψ_0 is included in the right hand side of Equation 1), backscattering is neglected (i.e. $\partial^2\Phi_m/\partial z^2$ is zero) and $\mathbf{k}_0$, $\mathbf{k}_m$ are parallel to the z-axis (i.e. small angle scattering at normal beam incidence). Equation (7b) is the integral of (7a) assuming $\Phi_0(\mathbf{R},z)$ does not vary significantly in ‘z’ within the slice. For a delocalised excitation $V_{m0}(\mathbf{R},z)$ and $V_{m0}^{p}(\mathbf{R})$ are slowly varying and can therefore effectively be treated as constants denoted by V and V^p respectively. Assuming small energy loss (i.e. $k_m \approx k_0$) the rate of generation of inelastic intensity, dI_m^{gen}/dz, is given by:

$$\frac{dI_m^{\mathrm{gen}}}{dz} = \int \frac{d(\Phi_m\Phi_m^*)}{dz}d\mathbf{R} = 2\mathrm{Re}\left(\int \Phi_m\frac{d\Phi_m^*}{dz}d\mathbf{R}\right) = \frac{1}{\lambda}I_0(z)$$

…. (8)

where $\lambda = [2\sigma_m^2\mathrm{Re}(V^*\cdot V^p)]^{-1}$ and ‘Re’ denotes the real part of a complex number. Equation (8) can be generalised to multiple plasmon scattering, i.e.:

$$\frac{dI_{m,n}^{\text{gen}}}{dz} = \frac{1}{\lambda} I_{m,n-1}(z)$$

… (9)

where $I_{m,n}$ denotes n^{th}-order multiple scattering. The derivation is similar to Equation (8) and assumes that $\psi_{m,n}$ is primarily generated by inelastic scattering of $\psi_{m,n\text{-}1}$, analogous to the Born approximation used for single inelastic scattering. As an example the double plasmon scattered intensity is due to inelastic scattering of single plasmon loss electrons. Double plasmon excitation of elastic electrons or energy gain of triple plasmon loss electrons are considered to be unlikely events. Furthermore, it has been shown previously that plasmon excitation does not perturb the crystal potential significantly [5], so that the inelastic potential terms V_{mn} for multiple scattering are similar to single scattering, and consequently 'λ' in Equation (9) is unchanged from Equation (8).

The intensity $I_{m,n}(z)$ at depth z is given by:

$$\frac{dI_{m,n}}{dz} = \frac{dI_{m,n}^{\text{gen}}}{dz} - \frac{dI_{m,n+1}^{\text{gen}}}{dz} = \frac{1}{\lambda}\left[I_{m,n-1}(z) - I_{m,n}(z)\right]$$

… (10)

The $-dI_{m,n+1}^{\text{gen}}/dz$ term represents the rate of intensity loss due to inelastic scattering of $I_{m,n}$ to $I_{m,n+1}$. By inspection it is clear that $I_{m,n}$ has a Poisson distribution, i.e. $I_{m,n}(z) = [(z/\lambda)^n\exp(-z/\lambda)]/n!$. A characteristic feature of Poisson statistics is that individual events are independent of one another and have the same average rate [16]. This is also the expected behaviour for the scattering path length of a particle [6], with the average 'rate' here being the mean free path λ. Since $\lambda = [2\sigma_m^2\text{Re}(V^{*}\cdot V^{p})]^{-1}$ it would appear that the mean free path is a function of the slice thickness Δz through the V^p term (Equation 7c), although in reality λ is a constant. In fact the smallest slice thickness that preserves the properties of the inelastic scattering event should be used to calculate λ. For core losses Δz is roughly the size of the ionised atom. The bulk plasmon energy depends on the electron density [20] and consequently Δz for plasmon losses should be of the order of the unit cell dimension.

In summary it is shown that both the scattering path length and cross-section for Bloch electrons are particle-like when the excitation is delocalised. This justifies the use of Monte Carlo methods to model plasmon energy losses in multislice simulations.

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