Online Supplementary Materials for

Scanning Confocal Electron Energy Loss Microscopy using Valence-Loss Signals

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Derivation of the SCEELM formulation

Using the paraxial approximation the incident wave function formed by the pre-specimen lens is

$$\psi(r - r_p, z) = \exp(-i2\pi K_0 z) \int A(\boldsymbol{k}, \Delta f = z - \Delta f_0) \exp\left(-\boldsymbol{i2\pi k}(\boldsymbol{r} - r_p)\right) d^2\boldsymbol{k} \quad (1)$$

Here r is the coordinate with an origin that coincides with the location of the atom. r_p is the scanned position of the probe and Δf is the defocus of the beam.

Then the incident electron scatters with an electron of a target atom. Here we treat the scattering according to the Born approximation which calculates the scattering amplitude according to Fermi's golden rule (Batson, 1993) and assumes the scattered electrons do not have an angular dependent phase shift, i.e.

$$s(\boldsymbol{k}, \boldsymbol{k}') = < \boldsymbol{k}', f|V|i, \boldsymbol{k} >$$

The atom coordinate (r') and the incident electron coordinate (r) shares the same origin.

$$|i > = \phi_0(R')$$
$$< f| = \phi_n^*(R')$$
$$|k > = \exp(-i2\pi K_0 z)\exp(-i2\pi \boldsymbol{k}(r - r_p))$$
$$< k'| = \exp(i2\pi K_n z)\exp(i2\pi \boldsymbol{k}' r)$$
$$V = \frac{1}{|R - R'|}$$

Where $\boldsymbol{R} = (\boldsymbol{r}, z)$ is the coordinate of the incident electron and $\boldsymbol{R}' = (\boldsymbol{r}', z)$ is the coordinate of the core electron. $\boldsymbol{k}$ and $\boldsymbol{k}'$ are the transverse wave vectors before and after scattering.

The scattered wave function is

$$\psi'(\boldsymbol{R}'') = \exp(-i2\pi K_n \boldsymbol{z}'') \int A(\boldsymbol{k}, \Delta f) s(\boldsymbol{k}, \boldsymbol{k}') \exp(-i2\pi \boldsymbol{k}'\boldsymbol{r}'') d\boldsymbol{k}\, d\boldsymbol{k}'$$

$$= \exp(-i2\pi K_n z'') \iint A(\boldsymbol{k}, \Delta f)\exp(i2\pi K_n z)\exp(i2\pi \boldsymbol{k}'\boldsymbol{r})\phi_n^*(\boldsymbol{R}') \frac{1}{|\boldsymbol{R} - \boldsymbol{R}'|} \times$$
$$\phi_0(\boldsymbol{R}')\exp(-i2\pi K_0 z)\exp(-i2\pi \boldsymbol{k}(\boldsymbol{r} - \boldsymbol{r}_p))d\boldsymbol{R}'\exp(-i2\pi \boldsymbol{k}'\boldsymbol{r}'')d\boldsymbol{k}d\boldsymbol{k}'$$

$$= \exp(-i2\pi K_n z'') \int \exp(-i2\pi q_z z)\, \phi_n^*(\boldsymbol{R}') \frac{1}{|\boldsymbol{R} - \boldsymbol{R}'|} \phi_0(\boldsymbol{R}') d\boldsymbol{R}'$$
$$x \int A(\boldsymbol{k}, \Delta f) \exp(i2\pi \boldsymbol{k}'\boldsymbol{r}) \exp\left(-i2\pi \boldsymbol{k}(\boldsymbol{r} - \boldsymbol{r}_p)\right) \exp(-i2\pi \boldsymbol{k}'\boldsymbol{r}'')\, d\boldsymbol{k}d\boldsymbol{k}'$$

Where $\boldsymbol{R}'' = (\boldsymbol{r}'', z)$ and $q_z = K_0 - K_n$. Here K_n is the wave vector after the energy loss.

Then the wave function is imaged through the post-specimen lens. The image is also shifted back to the origin. Therefore a phase factor of $\exp\left(-i2\pi \boldsymbol{k}'\boldsymbol{r_p}\right)$ needs to be applied.

$$I\left(r'' - r_p\right) =$$
$$= \left| \begin{matrix} \exp(-i2\pi K_n z'') \int \exp(-i2\pi q_z z)\, \phi_n^*(\boldsymbol{R}') \frac{1}{|\boldsymbol{R} - \boldsymbol{R}'|} \phi_0(\boldsymbol{R}') d\boldsymbol{R}' \\ \times \int A(\boldsymbol{k}, \Delta f) \exp(i2\pi \boldsymbol{k}' r) \exp\left(-i2\pi \boldsymbol{k}(\boldsymbol{r} - \boldsymbol{r}_p)\right) \exp(-i2\pi \boldsymbol{k}'\boldsymbol{r}'')\, A'(\boldsymbol{k}', -\Delta f) \exp\left(-i2\pi \boldsymbol{k}'\boldsymbol{r_p}\right) d\boldsymbol{k}d\boldsymbol{k}' \end{matrix} \right|^2$$

Then we apply the rejection pinhole. Here we use a vanishingly small pinhole, i.e. only intensity from $r'' = 0$ is used.

$$I(r_p, \Delta f_0) =$$
$$= \left| \iint \exp(-i2\pi q_z z)\, \phi_n^*(R') \frac{1}{|R - R'|} \phi_0(R') dR' \int A(\boldsymbol{k}, \Delta f)\, A'(\boldsymbol{k}', -\Delta f) \exp\big(i2\pi \boldsymbol{k}'(r - r_p)\big) \exp\left(-i2\pi \boldsymbol{k}(r - r_p)\right) d\boldsymbol{k} d\boldsymbol{k}' \right|^2$$

$$= \left| \begin{array}{c} \int A'(\boldsymbol{k}', -\Delta f) \exp\left(i2\pi \boldsymbol{k}'(r - r_p)\right) d\boldsymbol{k}' \times \\ \int \exp(-i2\pi q_z z)\, \phi_n^*(R') \frac{1}{|R - R'|} \phi_0(R') dR' \times \\ \int A(\boldsymbol{k}, \Delta f) \exp\left(-i2\pi \boldsymbol{k}(r - r_p)\right) d\boldsymbol{k} \end{array} \right|^2$$

According to our definition in Eqn. (1),

$\psi_0 = \int A(\boldsymbol{k}, \Delta f) \exp\left(-i2\pi \boldsymbol{k}(r - r_p)\right) d\boldsymbol{k}$ is the slow-varying part of the 3-D wave function of the incident beam formed by the pre-specimen lens, and $\varphi^* = \int A'(\boldsymbol{k}', -\Delta f) \exp\left(i2\pi \boldsymbol{k}'(r - r_p)\right) d\boldsymbol{k}'$ is the complex conjugate of the 3-D wave function of the post-specimen lens. We denote $V_{0n} = \int \exp(-i2\pi q_z z)\, \phi_n^*(R') \frac{1}{|R - R'|} \phi_0(R') dR'$. Therefore, the simplified form of SCEELM imaging of a single atom of transition $0 \rightarrow n$ is:

$$I(\boldsymbol{r}_p, \Delta f_0) = \left| \iiint \varphi^*(\boldsymbol{r} - \boldsymbol{r}_p, z) V_{0n}(\boldsymbol{r}, z) \psi_0(\boldsymbol{r} - \boldsymbol{r}_p, z) d^2\boldsymbol{r}' dz' \right|^2 \qquad (2)$$

Equation (2) is the 3-D formulation of the SCEELM imaging model; however, to date in all spatial-resolved inelastic scattering calculations and most elastic scattering calculations, the projection approximation is used, i.e. the scattering is sudden. This approximation is justified when the Ewald sphere of the incident electron is relatively flat and q_z is relatively small within the collection range. Here we applied this approximation to Eqn. (2) and applied a change of variable, we arrive at the first Eqn. in the main text:

$$I(\boldsymbol{r}_p, \Delta f_0) = \left| \iint \varphi^*(\boldsymbol{r}, -\Delta f_0) V_{n0}(\boldsymbol{r} + \boldsymbol{r}_p) \psi_0(\boldsymbol{r}, \Delta f_0) d^2\boldsymbol{r} \right|^2$$

And the projected transition potential $V_{n0}(\mathbf{r} + \mathbf{r}_p)$ is

$$\mathrm{V_{n0}}(\mathbf{r}) = \int \int \phi_\mathrm{n}^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_0(\mathbf{r}') \mathrm{d}^3\mathbf{r}' \; \mathrm{e}^{-\mathrm{i}2\pi \mathrm{q_z z}} \, \mathrm{dz}$$

References

BATSON, P.E. (1993). Symmetry-selected electron-energy-loss scattering in diamond. *Physical Review Letters* **70**, 1822-1825.