Scattering delocalization and radiation damage in STEM-EELS

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Abstract

We discuss the delocalization of the inelastic scattering of 60 – 300 keV electrons in a thin specimen, for energy losses below 50 eV where the delocalization length exceeds atomic dimensions. Analytical expressions are derived for the point spread function (PSF) that describes the radial distribution this scattering, based on its angular distribution and a dielectric representation of energy loss. We also compute a PSF for energy deposition and show how the dispersive properties of delocalization allow a reduction in the radiolysis damage created by a small-diameter probe. Based on these ideas, we propose a “leapfrog” scanning procedure to minimize the damage when recording energy-selected images of a beam-sensitive specimen.

Keywords: TEM, STEM, EELS, inelastic scattering, delocalization, radiation damage

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1. Introduction

The purpose of this paper is to develop analytical formulas, based on wave optics and dielectric theory, to describe the spatial extent of inelastic scattering and the resulting energy deposition that leads to radiolysis damage in a beam-sensitive TEM specimen. Measurements show that the delocalization distance is a few nm for valence-electron scattering, and tens of nm for vibrational-mode losses, implying that the EELS signal is generated mainly outside the electron probe, for the very small probes used for high-resolution STEM. Although scattering delocalization is generally a disadvantage, since it limits the spatial resolution of energy-loss spectroscopy and energy-filtered imaging, it can be exploited in particular circumstances to minimize radiation damage, as already demonstrated for aloof-beam spectroscopy of vibrational energy losses [1 – 3].

The aloof mode (electron probe beyond the edge of the specimen) is useful for spectroscopy but it examines limited regions of the specimen (adjacent to the edge) and is largely incapable of measuring the spatial distribution of the energy-loss signal. Therefore we will explore the situation for transmission-mode measurements and propose a STEM procedure that should allow mapping of the signal with less radiation damage. The delocalization formulas will also be applied to previous EELS measurement on polymers, to provide an explanation for the apparent reduction in radiation sensitivity with decreasing probe diameter.
2. Delocalization of inelastic scattering

TEM images and diffraction patterns arise from the *elastic* scattering of primary electrons by the electrostatic field of atomic nuclei. In a neutral atom, this field terminates on the surrounding atomic electrons and the scattering is localized to subatomic dimensions, allowing atomic-resolution images. The signal used in electron energy-loss spectroscopy (EELS) arises from the *inelastic* scattering by atomic electrons, which can be excited by a primary electron passing some distance away. This electron-electron scattering is therefore delocalized over a region of size $L(E)$, the delocalization length, whose value depends on the energy loss $E$ involved in the scattering.

For valence-electron scattering ($1 \text{ eV} < E < 50 \text{ eV}$), $L(E)$ can be shown to be a few nm by recording the inelastic signal as a STEM probe is scanned across the edge of a specimen [4 – 8] or a sharp internal boundary [9]. Similar measurements for vibrational losses (0.1 – 0.5 eV) give values of several tens of nm [1]. The general situation is illustrated in Fig. 1, which includes $L(E)$ values estimated from various kinds of TEM measurements (filled data points). The data is scattered (due to experimental error and the different methods, geometry and definitions used) but demonstrates how the delocalization distance is inversely related to energy loss.

![Fig. 1. Delocalization length $L(E)$, adjusted to an incident energy of $E_0 = 100 \text{ keV}$, based on measurements [1 – 13] and calculations [24 – 30]. The dashed line represents Eq. (2) and the dotted red line is based on Eq. (4).](image_url)
For core-electron excitation giving rise to an ionization edge at some hundreds of eV, \( L(E) \) is of subatomic dimensions but is important for the interpretation of channeling measurements on crystalline specimens [14–20]. Here delocalization effects have been calculated using Bloch-wave or multislice methods [21–30] and are complicated by the influence of elastic scattering, which occurs on a length scale similar to that of the core-loss scattering.

The lines on Fig.1 are based on relatively simple considerations. For example, we can use the Heisenberg uncertainty principle \( \Delta p_x \Delta x \approx h \) to estimate a delocalization distance \( \Delta x \), taking the momentum uncertainty as \( \Delta p_x = \pm (h/\lambda)\theta_{50} \) where \( h \) is Planck’s constant, \( \lambda \) is the primary-electron wavelength and \( \theta_{50} \) is the angular width containing 50% of the scattering. Assuming an inverse correlation between impact parameter and scattering angle, the length containing half of the inelastic scattering is:

\[
\Delta x \approx h/(2\Delta p_x) = 0.5 (\lambda/\theta_{50})
\]  

Except for Cerenkov and surface-mode losses, inelastic scattering is dominated by a dipole component that has a Lorentzian angular distribution with half-width \( \theta_E = E/2E_0 \) and a cutoff around an angle \( \theta_c \), giving \( \theta_{50} = (\theta_E \theta_c)^{1/2} \). A Bethe-ridge cutoff at \( \theta_c = (2\theta_E)^{1/2} \) leads to:

\[
\Delta x = 0.5\lambda/(\theta_E \theta_c)^{1/2} \approx (0.42)\lambda/(\theta_E)^{3/4} \approx (0.71)\lambda(E_0/E)^{3/4}
\]  

as given by the dashed line in Fig.1. In this figure, the black dash-dot curve represents Eq.(2) combined (by quadrature addition) with the diffraction limit imposed by a 10mrad spectrometer-collection aperture. The effect of the aperture is important only for large energy losses; for \( E < 50 \) eV, \( \theta_E < 1 \) mrad and almost all the inelastic signal passes through the aperture.

Invoking Fourier optics, we can compare the inelastic scattering of electrons with the diffraction of light of wavelength \( \lambda \) from a circular aperture of radius \( a \). Observed on a distant screen, the first minimum in the Airy-function intensity corresponds to a deflection angle of \( \theta_1 = 0.61\lambda/a \), which forms the basis of the Rayleigh criterion for resolution: \( \Delta x = 0.61\lambda/\theta_1 \). However, the angular range containing half of the photons is \( \theta_{50} = 0.263(\lambda/a) \) and the diameter (within the aperture) from which these photons emerge is \( d_{50} = (2a)/2^{1/2} \), giving a value:

\[
d_{50} = (0.263)(2^{1/2})(\lambda/\theta_{50}) \approx 0.37 (\lambda/\theta_{50})
\]  

that is slightly smaller than Eq.(1).

Using \( \Delta p_x \Delta x \approx h \) and similar arguments, Pennycook [17] obtained an expression for the root-mean-square (RMS) impact parameter \( b_{\text{RMS}} \) (weighted over the Lorentzian angular distribution) that can also be interpreted as a delocalization length:
\[
\text{b}_{\text{RMS}} \approx \left( \frac{\hbar}{2\pi} \right) (v/E) \left( \log_\text{\text{e}} \left( \frac{2}{\theta E} \right) \right) = \left( \frac{\hbar}{2\pi} \right) (v/E) \left( \log_\text{\text{e}} \left( \frac{4E_0}{E} \right) \right)
\] (4)

Equation (4) predicts an energy-loss dependence close to \( E^{-1} \) rather than \( E^{-3/4} \) but provides an equally good fit to experimental data, as shown in Fig. 1.

These various approximations indicate that the delocalization of inelastic scattering is highly dispersive, with an inverse dependence on the energy loss. It is this property that allows a reduction in radiation damage if the analytical signal corresponds to a low value of \( E \).

### 3. Point spread function for inelastic scattering.

The success of Eq.(3) in predicting delocalization suggests using the methods of Fourier optics to relate the spatial distribution of the scattering (which we will call its point-spread function, PSF) to its angular distribution, which is easily recorded as an intensity variation at a distant plane (Fraunhofer diffraction pattern). In light optics, the PSF is related to the Fourier transform of the angular distribution of scattered intensity or scattered amplitude, depending on the lateral coherence length of the illumination [31]. For the elastic scattering of electrons, this coherence length exceeds atomic dimensions and the object-plane potential is related to the scattered amplitude [32,33]. Extending this idea to the inelastic scattering of electrons suggests:

\[
\text{PSF}(r) \propto [\text{FT}(dI/d\Omega)^{1/2}]^2
\] (5)

where \( r \) is an object-plane radial coordinate and \( \text{FT} \) represents a two-dimensional Fourier transform. Under most conditions, the angular distribution of inelastic intensity is close to a Lorentzian function: \( (dI/d\Omega) \propto (\theta^2 + \theta E^2)^{-1} \), with an amplitude \( (\theta^2 + \theta E^2)^{-1/2} \) whose Fourier transform has a simple analytical form [34], giving:

\[
\text{PSF}(r) \propto [\text{FT}(\theta^2 + \theta E^2)^{-1/2}]^2 = (k_0 r)^{-2} \exp(-2\theta_E k_0 r)
\] (6)

where \( k_0 = 2\pi/\lambda \) is the incident-electron wavenumber, making the product \( k_0 r \) dimensionless. The exponential behaviour at large \( r \) is consistent with aloof-EELS measurements of Muller and Silcox [7]. The \( 1/r^2 \) dependence at small \( r \) agrees with calculations of inner-shell excitation by Ritchie [22] and Wentzel-potential estimates of Rose [21], summing over all energy loss.

Introducing a gradual cutoff of the Lorentzian angular distribution around some large angle \( (\theta_c) \) makes Eq.(6) more realistic by removing the singularity at \( r = 0 \), and can be simulated by replacing the \( 1/r^2 \) dependence in Eq.(6) by a Lorentzian function, giving:

\[
\text{PSF}(r) \propto (r^2 + r_c^2)^{-1} \exp(-2\theta_E k_0 r)
\] (7)

Figure 2 shows that Eq.(7) matches quite well with the PSF calculated using Eq.(5).
Fig. 2. Point-spread function for inelastic scattering with (a) \( E = 0.45 \) eV and \( E_0 = 60 \) keV, (b) \( E = 6 \) eV and \( E_0 = 200 \) keV. The blue curves were calculated using Eq.(5), assuming \( dI/d\Omega \propto (\theta^2 + \theta_E^2) \), with gradual (Lorentzian) cutoff around \( \theta_c = (2\theta_E)^{1/2} \). Red curves are calculated from Eq.(7) with \( r_c = (2k_0\theta_c)^{-1} \). The green dashed lines depict \( 1/r^2 \) behavior. Vertical lines show the values of \( b_{\text{min}} \) and \( b_{\text{max}} \).

4. Properties of the inelastic PSF

The inelastic point spread function can be written more precisely in terms of the probability \( (d^2P/dEdV) \) that a primary electron interacts with a volume \( dV \) of specimen, located at a radial distance \( r \) from the path of the primary electron and resulting in an energy loss between \( E \) and \( E + dE \). Following Eq.(7), we write:

\[
d^2P/dEdV = C(r^2 + b_{\text{min}}^2)^{-1} \exp(-2r/b_{\text{max}})
\]  

(8)

where \( C \) is an \( E \)-dependent coefficient (to be determined) and

\[
b_{\text{max}} \approx 1/(k_0\theta_E) = 1/[(2\pi mv/h)(\hbar \omega/2\pi)/(mv^2)] = v/\omega
\]  

(9)

as in Eq. (7). The length \( b_{\text{max}} \) is known as the Bohr adiabatic limit because at larger distances \( (r >> b_{\text{max}}) \) the electrostatic field of the primary electron changes slowly enough to allow atomic electrons to respond adiabatically, without making a transition to a higher energy state. In fact, the inelastic interaction starts to fall off exponentially at \( r = b_{\text{max}}/2 \), as indicated by Eq. (8). This behavior is sometimes referred to as dynamical screening [7] and is directly related to the characteristic angle of the inelastic scattering: \( \theta_c = E/(mv^2) \), as seen from Eq.(9).

The length \( b_{\text{min}} \) arises because the angular distribution of dipole-mode scattering remains Lorentzian only up to some angle \( \theta_c \) such that:

\[
b_{\text{min}} = 1/(2k_0\theta_c) = (b_{\text{max}}/2)(\theta_E/\theta_c)
\]  

(10)
In the case of plasmon excitation, $\theta_c$ is the angle at which momentum conservation allows the transfer of energy to single-electron transitions at the Fermi energy, leading to heavy plasmon damping. In the case of single-electron excitation, $\theta_c \approx (E/E_0)^{1/2} = (2\theta E)^{1/2}$ is the Bethe-ridge angle at which momentum conservation permits energy transfer to a free electron, rather than inducing dipole transitions. In the case of vibrational-EELS peaks (in the range 0.1 eV to 0.5 eV), $\theta_c$ may be the angle at which dipole transitions give way to impact scattering. Because its value is currently unknown, we will use a Bethe-ridge cutoff since it gives approximate agreement with measured delocalization lengths, represented by the square data points on the left in Fig. 1.

As seen in Fig. 3, the ratio $b_{\text{max}}/b_{\text{min}}$ is typically in the range 10 – 50 for inner-shell excitations (core losses), of the order of 100 for plasmon and valence-electron excitation and as high as 500 for vibrational losses [3]. So for low energy losses, the inelastic PSF is close to a $1/r^2$ power law over much of its range, with (typically) less than 10% of the intensity lying below $r = b_{\text{min}}$ and less than 5% above $r = b_{\text{max}}/2$. Therefore the probability that inelastic scattering occurs inside a radius $r$ is roughly

$$\left(\frac{dP}{dE}\right)_< r = \int (C/r^2) \, dV = C \log_e (r/b_{\text{min}})$$

(11)

and the probability that it lies outside this radius $r$ is approximately

$$\left(\frac{dP}{dE}\right)_> r = \int (C/r^2) \, dV = C \log_e (b_{\text{max}}/2r)$$

(12)

where we have integrated Eq. (8), taking $dV = (2\pi rt) dt$ with $t$ representing specimen thickness. Equating these two integrals provides an estimate for the median radius $r_{50}$, containing 50% of the inelastic scattering with energy loss $E$:

$$r_{50} = (b_{\text{min}} b_{\text{max}}/2)^{1/2}$$

(13)

For valence or core-electron excitation, where $\theta_c \approx (E/E_0)^{1/2} = (2\theta E)^{1/2}$, the diameter containing half the scattering is therefore:

$$d_{50} = 2r_{50} = 2k_0^{-1} (4\theta E \theta_c)^{-1/2} = 0.16\lambda/(\theta E \theta_c)^{1/2}$$

(14)

This result is similar in form to Eq.(3) but about a factor of 2 smaller, suggesting that Eq.(5) may underestimate the spatial extent of delocalization. However, we will continue with the coherent approximation for now and return to the question of accuracy later.
Values of $b_{\text{min}}$, $b_{\text{max}}$ and $r_{50}$ calculated from Eqs. (9) – (13) as a function of energy loss $E$, for $E_0 = 60$ keV and 200 keV. An angular cutoff at $\theta_c = (E/E_0)^{1/2}$ is assumed, giving $b_{\text{min}} \propto E^{-1/2}$, $b_{\text{max}} \propto 1/E$ and $r_{50}$ proportional to $E^{-3/4}$ but nearly independent of $E_0$.

Integrating Eq. (8) from $r = b_{\text{min}}$ to $r = b_{\text{max}}/2$ equivalent to replacing the exponential attenuation with a sharp cutoff at $b_{\text{max}}/2$, gives:

$$dP/dE = C \int (r^2 + b_{\text{min}}^2)^{-1} (2\pi r) \, dr = (\pi Ct) \int (r^2 + b_{\text{min}}^2)^{-1} \, d(r^2 + b_{\text{min}}^2)$$

$$= (\pi Ct) \log_e[(b_{\text{max}}^2/4 + b_{\text{min}}^2)/b_{\text{min}}^2] = (\pi Ct) \log_e[1 + \theta_c^2/\theta_E^2]$$

(15)

where $t$ is specimen thickness and Eq.(10) has been used for $b_{\text{max}}/b_{\text{min}}$. Equation (4) is of identical form to the result obtained from the dielectric theory of energy loss:

$$dP/dE = t(\pi a_0 m_0 v^2)^{-1} \text{Im}[-1/\varepsilon(E)] \log_e[1 + \theta_c^2/\theta_E^2]$$

(16)

where $a_0 = 52.9$ pm is the Bohr radius, $m_0$ is the electron rest mass and $v$ is the speed of the primary electrons [35]. Im[-1/$\varepsilon(E)$] is the so-called energy-loss function, which can be calculated if the permittivity $\varepsilon$ of the specimen is known at a photon frequency $E/h$, but which becomes a constant factor if we want to describe the spatial dependence of $dP/dE$ at a fixed value of energy loss.

Equation (15) was derived by integration over real space, whereas Eq. (16) comes from integration of reciprocal space. Equating these two expressions gives the coefficient used in Eq. (8) as $C = (\pi^2 a_0 m_0 v^2)^{-1} \text{Im}[-1/\varepsilon(E)]$, allowing the inelastic PSF to be written as:

$$d^2P/dEdV = (\pi^2 a_0 m_0 v^2)^{-1} \text{Im}[-1/\varepsilon(E)] \, (r^2 + b_{\text{min}}^2)^{-1} \exp(-2r/b_{\text{max}})$$

(17)
5. Electron beam of arbitrary radius

In the case of a broad incident beam, each primary electron has its own PSF that governs the spatial extent of energy loss. In the center of the beam these functions overlap to create a uniform rate of scattering and energy deposition. At the edge of the beam, the PSF tails extend into the surrounding material, to an extent that depends on the energy loss $E$. The fraction of scattering outside the incident probe will be largest in the case of a small-diameter probe and a low value of $E$.

We will assume that the spatial distribution of inelastic scattering is a two-dimensional convolution of the inelastic PSF with the current-density profile of the beam. For convenience, we take the latter to be a rectangular (top-hat) function.

The geometry involved in the convolution is shown in Fig. 4. The incident beam (electron probe) has a radius $R$ and is centered on the origin of the coordinate system. We first calculate the intensity $I_P$ of inelastic scattering at a point $P$ outside the probe, allowing for electrons incident at all points within the area $A$ of the probe. This can be done by summing over the incident intensity within arcs $AC$ (of radius $\rho$ and thickness $d\rho$), using the fact that point $A$ lies the intersection of circles of radius $\rho$ and $R$ and therefore has coordinates: $x_A = (R^2 + r^2 - \rho^2)/(2r)$ and $y_A = (R^2 - x_A)^{1/2}$. From geometry of the triangle $ABP$, $\sin(\phi) = (y_A/\rho)$ and the length of arc $AC$ is $S = 2\phi$. The number of incident electrons per second contained within the arc-shaped region is $J_\rho S(d\rho)$, where $J_\rho = I_\rho/(\pi R^2)$ for a beam current $I_\rho$ electrons/sec and a uniform current density $J_\rho$ electrons/m$^2$/s. The number of electrons/m$^2$/s inelastically scattered at point $P$ is therefore:

$$I_P(r) = J_\rho \int \left( \frac{d^2 P}{dEdV} \right) dA = J_\rho \int S \left( \frac{d^2 P}{dEdV} \right) d\rho$$

(18)

where the limits of integration are from $\rho = r - R$ to $\rho = r + R$. The total signal (electrons/s) from inelastic scattering outside the probe is given by a second integration:

$$I_{\text{sig}}(R) = \int I_P(r) \ (2\pi r) d\rho = \int I(P) \ (2\pi r^2) \ d[\log_e(r)]$$

(19)

where the integration is from $r = R$ to $r > R + b_{\text{max}}$. The use of a logarithmic grid to evaluate Eq.(25) helps to maintain accuracy (with reasonable computing time) for a large range of signal radius $r$. 
Using Eq. (19), the fraction of the inelastic signal that lies outside the probe can be calculated, and is shown in Fig. 5. For 60keV electrons, this fraction remains appreciable (> 10%) for probe radii up to about 17 nm \((E = 6 \text{ eV})\) or 150 nm \((E = 0.45 \text{ eV})\). If Eq.(8) is accurate for small \(r\), about 84% of the 0.45eV scattering and 57% of the 6eV scattering lies outside a 60keV probe of radius 1 nm \((\text{diameter} = 2 \text{ nm})\). Figure 5 also demonstrates how the delocalization depends strongly on the energy loss \(E\) but only weakly on the incident energy \(E_0\) [35].

![Diagram of electron probe and geometry](Diagram.png)

**Fig. 4.** Incident electron probe (solid circle, radius \(R\)) and geometry needed to calculate the inelastic intensity at point \(P\), a distance \(r\) from the center of the probe.

**Fig. 5.** Fraction of the inelastic scattering occurring outside an electron probe of radius \(R\). Upper red curve: \(E = 0.45 \text{ eV}, E_0 = 60 \text{ keV}\); middle black curve: \(E = 6 \text{ eV}, E_0 = 200 \text{ keV}\); lower blue curve: \(E = 6 \text{ eV}, E_0 = 60 \text{ keV}\).
Our preceding equations have assumed a parallel incident beam, whereas in reality the very small probes involved in STEM have an appreciable convergence semi-angle $\alpha$. From the point of view of the spatial distribution of scattering, the main effect of this convergence is probably an increase in beam diameter, by an amount $\alpha t$ at the top and bottom surfaces if the probe is focused at the midplane of a specimen of thickness $t$, giving an increase $\alpha t/2$ if averaged over the thickness of the film. For small probes this effect could be significant and might incorporated approximately by adding $\alpha t/2$ to the value of $R$ used in Eq.(18) and Eq.(19).

For an incident beam of large radius, the rate of inelastic scattering will be a uniform in the center but will decrease towards the edge and beyond it. For $R >> L(E)$, the edge approximates to a straight edge and the geometry simplifies to that shown in Fig. 6. The intensity beyond the edge of the beam is still given by integration over arcs AC whose length is $S = (2\varphi r)$, with $\varphi = \frac{\varphi}{r}$. The inelastic intensity (electrons/m$^2$/s) at a distance $b$ outside the edge is:

$$I(b) = J_e t \int \left( \frac{d^2 P}{dE dV} \right) (2\varphi r) \, dr$$

(20)

where $J_e$ is the current density (electrons/m$^2$/s) within the probe and the integration limits are from $r = b$ up to some large value ($> b_{max}$). Within the illuminated area, the intensity at a distance $b$ inside the edge is just $I(-b) = I(0) - I(b)$. In other words, the intensity profile is symmetric, as shown by the data points in Fig. 7.

Fig. 6. Geometry for calculating the inelastic intensity at point P, a distance $b$ outside the edge ABC of an electron beam of large radius. The contributions of arcs of specimen AC (radius $r$, thickness $dr$) are summed over $r$ to give the total EELS signal at point P.
Fig. 7. Inelastic intensity near the edge of an electron beam of large radius and uniform intensity. Blue data points correspond to \( E = 6 \) eV, red data points to \( E = 0.2 \) eV. The calculations assume an incident energy of \( E_0 = 100 \) keV.

It is tempting to apply Eq.(17) to the case of a small-diameter aloof beam at point P, a distance \( b \) from the edge AC of the specimen, integrating from \( r = b \) to some large value in order to calculate the energy-loss signal \( S(b) \) as a function of the impact parameter \( b \). This would allow comparison with measurements of \( S(b) \) for vibrational EELS [1] and valence–electron excitation [7,8]. But the electric field of an aloof electron does not have the radial symmetry of the PSF, which may make such a comparison inaccurate. In any event, the form of \( S(b) \) appears to be well matched [1] by the formula:

\[
S(b) \propto (m_0v^2)^{-1} K_0(4\pi bE/\gamma v h) = (m_0v^2)^{-1} K_0(2\theta_E k_0 b)
\]

(21)
derived from the dielectric response to an electron travelling parallel to a planar surface [36–38].

6. Point spread function for energy deposition.

Radiation damage to a beam-sensitive TEM specimen arises predominantly from inelastic scattering, through the process referred to as radiolysis [33,39,40]. This same process is responsible for the damage caused by x-rays, and in both cases the amount of damage is believed to be proportional to the energy deposited per unit volume of specimen. Almost all inelastic events contribute to this energy deposition, but in proportion to the energy loss suffered in each event, so the energy \( H \) deposited per unit volume \( V \) by a single primary electron is:

\[
dH/dV = \int E \left( \frac{d^2P}{dEdV} \right) dE
\]

(22)
where $P$ represents the probability of an energy loss $E$ per primary electron, as in Eq.(8), and the integral is from some threshold energy loss ($E_{\text{min}} \sim 5$ eV) to a large value, which can be taken as 100 eV [3]. In the case of a STEM probe, both $P$ and $H$ are functions of the distance $r$, measured from the center of the probe.

In Eq.(22), $dH/dV$ has units of eV/m$^3$ but multiplying by $e = 1.6 \times 10^{-19}$ converts $dH/dV$ into J/ m$^3$. Dividing by the specimen density $\rho$ (in kg/m$^3$) then gives the local radiation dose $g(r)$ per primary electron, expressed in Gray:

$$g(r) = e(dH/dV)/\rho$$  \hspace{1cm} (23)

To relate $g(r)$ to the case of a parallel electron beam whose diameter is small compared to the delocalization length, we can multiply $g(r)$ by the number of primary electrons to get the radiation dose $G(r)$ at a distance $r$ from the beam:

$$G(r) = e(dH/dV)\rho^{-1} \left( I_b/e \right) T = (dH/dV)\rho^{-1} I_b T$$  \hspace{1cm} (24)

where $I_b$ is the primary-beam current in Amp, $(I_b/e)$ is the current in electrons/sec, and $T$ is the irradiation time in sec.

With $(d^2P/dEdV)$ given by Eq.(17), both $dH/dV$ and the dose $G(r)$ will decrease with increasing radius $r$ from the beam. But because delocalization is dispersive, high-$E$ scattering causes energy deposition mainly at small $r$ and low-$E$ scattering mainly at larger distances from the probe. Even so, the local extent of radiolysis should depend only on the total energy deposition per kg, as described by Eq.(27), Eq.(25) and Eq.(17). Radiation damage starts close to the beam and gradually spreads outwards.

To calculate $G(r)$ we need to sum over a range of energy loss, using Eq. (22) and Eq.(17), which requires a knowledge of the energy-loss function $\text{Im}[-1/\varepsilon(E)]$. The latter can be obtained from the energy-loss spectrum $S(E)$ of the specimen, measured with a broad electron beam and a collection aperture of semiangle $\beta$, based on the standard dielectric theory [35]:

$$S(E) = I_b \cdot t \left( \alpha a_0 m_0 v^2 \right)^{-1} \text{Im}[-1/\varepsilon(E)] \log_e(1 + \beta^2 / \theta \varepsilon^2)$$  \hspace{1cm} (25)

where (as elsewhere in this analysis) we assume that the specimen thickness $t$ is small enough to make plural inelastic scattering unimportant.

Alternatively, the energy-loss function can be simulated by using the Drude model for valence-electron excitation, giving:

$$\text{Im}[-1/\varepsilon(E)] = \left[ E(\Delta E_p)E_p^2 \right] / \left[ (E^2 - E_p^2)^2 + (E\Delta E_p)^2 \right]$$  \hspace{1cm} (26)

where $E_p$ and $\Delta E_p$ are the energy and width of the valence-loss peak [35]. By using Eq. (26), we neglect the energy deposition arising from inner-shell excitation, which is less important in light-element solids.
Taking $E_p = 25$ eV and $\Delta E_p = 25$ eV gives an energy-loss function (see Fig. 8) that is typical of an organic compound and this function was used in the present calculations. The mean energy loss is 26 eV, defined by:

$$E_{av} = \frac{\int E \text{Im}[\frac{-1}{\epsilon(E)}] \, dE}{\int \text{Im}[\frac{-1}{\epsilon(E)}] \, dE}$$  \hspace{1cm} (27)$$

K-shell excitation increases $E_{av}$ to typically 35 – 40 eV in an organic compound, but inner-shell energy deposition occurs very close to the electron probe and in practice be indistinguishable from energy deposition within the probe. More generally, $E_{av} \approx 7Z$ and becomes large in materials of high atomic number $Z$, due to inner-shell contributions [35]. However, most of these materials are less radiation-sensitive.

Fig. 8. Red dots: energy-loss function $\text{Im}[\frac{-1}{\epsilon(E)}]$ for a typical organic specimen (calculated using a Drude model), which represents the variation of scattering probability with energy loss. The corresponding inelastic mean free path is $\lambda_i = 170$ nm at $E_0 = 200$ keV. Blue crosses show the product $(E/E_{av}) \text{Im}[\frac{-1}{\epsilon(E)}]$, where $E_{av} = 26$ eV, which represents the corresponding energy deposition, assuming a thin specimen (single-scattering approximation).
Fig. 9. Fraction of energy deposited outside an electron beam of diameter $d$, calculated on the basis of Eqs. (17) and (19), assuming a uniform current density within the beam and the energy-loss function shown in Fig. 10.

Calculated using Eqs. (17), (22) and (26), Fig. 9 shows the fraction of energy deposited (within an organic specimen) outside an electron beam of a given diameter. This fraction increases slightly with primary-beam energy because of the increasing delocalization length.

If the energy deposition occurs within a beam-sensitive specimen, radiolysis causes a characteristic signal (e.g. diffracted intensity or an energy-loss peak) to diminish with increasing radiation dose $G$, usually in an exponential manner. We therefore assume that the radial distribution of the EELS signal (energy loss $E$) is modified according to:

$$\text{PSF}(r,E,T) = \text{PSF}(r,E,0) \exp[-G(r)/G_c]$$

(28)

where $G(r)$ is the radiation dose at a distance $r$ from the probe, after an exposure time $T$; $G_c$ is a characteristic (or critical) dose, measured using a broad electron beam, which is an inverse measure of the radiation sensitivity of the specimen. In Eq. (31) we assume that radiation damage does not significantly change the inelastic scattering properties the specimen.

Electron microscopists commonly measure radiation dose as an electron fluence: the product of beam-current density and exposure time: $D = JT$, where $D$ is in $C/m^2$. The corresponding dose in Gray:

$$G = (D/\rho)(dE/dz) = (D/\rho)(E_{av}/\lambda_i)$$

(29)
where $\frac{dE}{dz}$ is the linear energy transfer (LET) or stopping power, which can be calculated by dividing the mean energy loss $E_{av}$ per inelastic collision (in eV) by the mean distance $\lambda_i$ between collisions.

Expressed in Gray, the characteristic dose $G_c$ varies greatly between different materials but is independent of electron energy $E_0$. Because $\lambda_i$ increases with increasing $E_0$, the corresponding characteristic fluence $D_c$ depends on both the material and the electron energy. Typical values for a beam-sensitive polymer are $G_c = 25$ MGy and $E_{av} = 35$ eV, giving $\frac{dE}{dz} = 2.5 \times 10^8$ eV/m and $D_c = 100$ C/m$^2$ at $E_0 = 100$ kV.

Figure 10 shows the effect of radiolysis due to a small-diameter (sub-nm) beam of electrons traveling through an organic specimen, calculated using Eq. (28) and based on Eqs. (17) and (26). Blue curves represent the radial dependence of energy deposition, which is more localized than either the 6eV or 0.45eV signals since the average energy loss exceeds 25 eV. Green curves are based on Eq. (17) and demonstrate the increased delocalization at lower energy loss, as in Fig.1 and Fig. 2. The red curves show how radiolysis reduces the energy-loss signal generated close to the centre of the electron probe, the signal from larger distances being hardly affected. This behavior is particularly evident for vibrational-mode losses ($E < 0.5$ eV, Fig. 10a), where the delocalization distance $L(E)$ is tens of nm.

Fig. 10. Dark blue curves: PSF for energy deposition, calculated using Eq. (27) for a beam-sensitive specimen having the energy-loss function shown in Fig. 4. For comparison, light blue curves show the PSF for $E = 40$ eV, the mean energy loss for a typical organic compound. Green curves are the PSF from Eq.(17), for an energy-loss signal at (a) 0.45 eV and (b) 6eV, assuming no damage. Red curves are based on Eq. (22) and Eq. (28), and show the spatial distribution of the EELS signal after substantial damage has occurred around the electron probe.
7. Optimization of the signal/damage ratio

The dispersive property of delocalization can be exploited to reduce the effect of radiolysis on an energy-loss signal. This possibility has been discussed for the aloof-beam case [41,42], particularly for damage created by inner-shell excitations. Reduced damage was subsequently demonstrated for aloof-beam EELS using a vibrational-mode signal [2], where calculations suggest that that the signal/damage ratio may increase by a factor of $10^5$ as the impact parameter $b$ (distance of the beam from the specimen edge) is increased from 10 nm to 60 nm [3]. The penalty associated with increasing $b$ is a loss of spatial resolution, since the specimen area contributing to the energy-loss signal is of the order of $(2.5)b^2$ [3].

A tradeoff between damage and resolution is familiar in electron microscopy: for a broad beam (diameter $d$) of electrons traveling through a specimen, the radiation dose is proportional to $1/d^2$, for a given beam current and recording time. Therefore a six-fold increase in diameter should improve the signal/damage ratio by a factor of 36 in transmission mode. The much larger improvement in aloof mode arises because the total energy deposition is much less; the energy that would be deposited in the specimen within a few nm of the electron probe is no longer deposited if the electrons are traveling in a vacuum. However, a measurable signal can only be detected if the delocalization length exceeds a few nm, meaning valence-electron excitations below about 10 eV or vibrational-mode peaks.

The aloof mode is attractive for spectroscopy of beam-sensitive specimens but it lacks the ability to map the two-dimensional distribution of the signal. Transmission-mode STEM measurements can perform such mapping but only if radiation damage does not destroy the signal, a major limitation if the specimen is beam-sensitive.

The usual way of creating a STEM image is to scan a small probe (diameter $d$) in the form of a digital raster with a jump distance $s$ (pixel spacing) approximately equal to $d$. The case of $s > d$ represents undersampling and is usually avoided because the irradiated area is then only a fraction of the scanned area, suggesting increased radiation damage. For lower-magnification images, sub-pixel scanning is sometimes used to address this problem and reduce the damage. While this strategy may be advantageous for core-loss images or x-ray elemental maps, low-loss images represent a different situation, because of the greater delocalization of the signal. Undersampling can then be favorable because the regions between the directly-irradiated areas can contribute to the energy-loss signal, while suffering relatively little damage.

Figure 11a illustrates the principle involved [43]. It shows a quickly-scanned HAADF STEM image of a calcium hydroxide specimen, recorded using the Nion HERMES STEM at Arizona State University. This instrument incorporates a high-resolution monochromator and energy-loss spectrometer, giving an energy resolution ($< 15$ meV at $E_0 = 60$ keV) sufficient to detect vibrational-mode energy-loss peaks that are characteristic of hydrogen or specific chemical bonds [1]. The region within the
green square was previously scanned using a coarse digital raster ($s = 10$ nm, $d = 1$ nm) and with a probe current high enough to cause substantial radiation damage, visible as dark spots that indicate reduced specimen thickness (mass loss). During this scanning, however, the presence of hydrogen could be continuously detected from its 0.45 eV vibrational peak, whose inelastic scattering is delocalized over at least 30 nm.

![Image](image_url)

(a) Finely-scanned HAADF image showing the effect of using a coarse digital raster ($s = 10$ nm, $d = 1$ nm) on a specimen of Ca(OH)$_2$. Dark spots show locations where the electron beam caused mass loss due to radiation damage, while the hydrogen vibEELS signal remained largely unaltered after three complete scans. (b) Fraction of the inelastic scattering contained within a given diameter surrounding a sub-nm probe, calculated from Eq.(17) for several values of energy loss and incident energy.

Subsequent “leapfrog” scanning of guanine [44] showed a similar array of dark spots (indicating substantial damage within the 1nm probe) but little observable decrease in the H-bond (0.3 – 0.4eV) signal if the step size was increased from $s = 10$ nm to $s = 30$ nm. However, increasing $s$ reduces the spatial resolution of the image and to demonstrate that leapfrog scanning is beneficial, it is necessary to show that the technique provides a larger signal for the same spatial resolution.

This possibility is illustrated in Fig. 12a, which shows the H-bond signal (integrated over a diameter $s$) as a function of irradiation time. For a regular scan ($d = s$) the energy-loss signal falls exponentially with increasing radiation dose, whereas with a leapfrog scan ($d << s$) it falls rapidly at first (as each beam location becomes heavily damaged) but then much more slowly, allowing signal to be
collected (via scattering delocalization) from largely undamaged material between each beam position. The spatial resolution of the inelastic image should be approximately $s$ for both types of scan, so leapfrog scanning (using a vibrational-EELS signal) could be beneficial for mapping the presence of hydrogen or a particular chemical bond in a beam-sensitive specimen, at a resolution of around 30 nm.

The situation for a 6 eV signal (e.g. $\pi^*$ peak, characteristic of double bonds) is illustrated in Fig. 12b. In this case, the leapfrog signal becomes higher only after the material has been substantially damaged. Leapfrog scanning might also be useful for imaging changes in the energy gap of a semiconductor or insulator (or bandgap states) where the characteristic signal corresponds to an energy loss of a few eV or less.

![Energy-loss signal as a function of time](image)

**Fig. 12.** Energy-loss signal as a function of time (relative units) for a regular scan ($d = s$, blue curves) and leapfrog scan ($d << s$, red curves). Solid lines are for $s = 30 \text{ nm}$, dashed lines are for $s = 10 \text{ nm}$. The incident energy is (a) 60 keV and (b) 300 keV.
Unlike the case of aloof-mode spectroscopy, the leapfrog technique does not reduce the total energy deposited in the specimen, but its highly non-uniform distribution can lead to a reduction in the overall damage. To outperform a regular \((s \approx d)\) scan, however, it appears necessary to damage a substantial fraction of the specimen, judged by the location of the crossovers in Fig. 12.

8. Damage measurements on polymers

The energy-loss spectra of organic materials contain a broad peak centered around 20 – 25 eV (as in Fig. 8) that is usually interpreted as a highly-damped plasmon resonance of the valence electrons. However, compounds with double bonds also exhibit a smaller peak at 6 – 7 eV, attributed to \(\pi-\pi^*\) interband transitions. The presence of this peak provides evidence of \(\pi\)-bonding and its fading during electron irradiation indicates bond scission due to radiolysis. Among many radiation-damage investigations of polymers are studies [45 – 47] in which the intensity \(I_n\) of the \(\pi^*\) peak was monitored as a function of irradiation time, for a fixed beam current \(I_b\) but using different values of the electron-beam diameter \(d\). Plotting \(\log(I_n)\) against irradiation time yielded a characteristic time \(T_c\) (for double-bond scission) that decreased as \(d\) was reduced (as expected when the current density or dose rate is increased) but remained nearly constant for \(d < 100\) nm. If the characteristic dose (fluence) is calculated as \(D_c = (\pi/4)(I_b/d^2) T_c\), the constancy of \(T_c\) implies that \(D_c\) increased proportional \(1/d^2\), by a factor as large as \(10^6\) at \(d = 0.3\) nm [47]. Further experiments, in which \(I_b\) was varied at constant \(d\), showed that this unexpected behavior was not a dose-rate effect \((D_c\) dependent on \(J\)) but was directly related to beam diameter.

However, this apparent reduction in radiation sensitivity (for small probes) assumes that all of the energy deposition occurs within the incident beam, ignoring the delocalization of inelastic scattering. As already illustrated in Fig. 12b, the initial damage within a small probe is very rapid, so what was measured (over a period of a few seconds) likely corresponded to the slow decay of the 6eV signal from regions outside the probe.

Figure 13 shows the result of PSF calculations designed to model the experiments on polystyrene [47], where the beam current was adjusted to give a 2.5-fold decay in the \(\pi^*\) intensity (over 5 seconds) for \(d = 300\) nm, represented by the black circular data points. The case of a very small (0.3nm) probe is represented by the red-square data points, the first of which would be unobservable because it corresponds to zero dose (undamaged specimen). Subsequent red data points show a slope very similar to that for \(d = 300\) nm, leading to a measured time constant \(T_c\) independent of beam diameter, as observed experimentally.
Figure 13. Time dependence of the 6eV $\pi^*$ energy-loss peak recorded from polystyrene, for 300keV incident electrons and beam diameters of 300 nm and 0.3 nm. The calculations take account of damage and signal generated outside the probe (due to the delocalization of inelastic scattering) but not damage arising from secondary electrons.

The fact that $T_e$ remained constant for beam diameters as large as 100 nm is at first surprising. The diameter $2b_{\text{max}}$ within which the 6eV signal is generated is about 64 nm at $E_0 = 300$ keV and would be larger if Eq. (5) underestimates the delocalization. In fact, a large part (e.g. 80%) of the radiolysis of organic materials is known to arise from secondary-electron production [48]. A simplified analysis [49] of fast-secondary ($E > 50$eV) transport suggests a mean range of the order of 10 nm, consistent with Monte Carlo calculations [46] and PMMA lithography [50].

Secondary electron production undoubtedly causes damage outside a small probe but not up to a radius of 50 nm as the experiments suggest. Therefore the major factor underlying these remarkable experimental results is likely to be the delocalization of inelastic scattering.

9. Discussion.

We have confined our attention to energy losses due to valence-electron or phonon excitation, where the delocalization distance is much larger than atomic dimensions and is determined by $b_{\text{max}}$ and the $1/r^2$ dependence of the point spread function. These properties derive from the kinematics of electron interaction rather than internal dynamics of an atom, as expressed in terms of the generalized oscillator strength for example [51]. Such dynamical effects will influence the PSF for $r < b_{\text{min}}$ but this contribution to the inelastic signal is small for low values of energy loss.
The situation is different for inner-shell energy losses, where the region $0 < r < b_{\text{min}}$ represents a larger part of the PSF and greatly affects the probability of core-electron excitation. Here the delocalization lengths of the inelastic and elastic scattering are comparable to each other, leading to a coupling that complicates the interpretation of atomic-resolution inelastic images recorded from crystalline specimens. Such complications are unlikely to be important for the low energy losses considered here.

Vibrational (phonon) energy losses have been measured for many years using medium-energy electrons reflected from the surfaces of crystalline specimens [52]. The EELS signal is found to contain two components: a dipole mode concentrated around Bragg-reflected beams, and an “impact” component that can be measured between the Bragg beams [53,54]. The latter has a broad angular distribution, indicating a high degree of localization around atomic cores. In fact, calculations of the transmission-mode phonon signal have predicted atomic resolution [55-58] and recent STEM measurements have confirmed that a resolution better than 2 nm is possible [59]. These measurements were made in a dark-field mode on a crystalline BN specimen, with the incident beam tilted so that the central and diffracted beams were excluded by the (small) spectrometer entrance aperture, giving a high-resolution signal about 1% of the bright-field phonon signal. Under such conditions, the equations derived above will not apply, since we have assumed bright-field spectroscopy where the dipole component dominates the vibrational-mode signal.

The theory presented here is based on Eq.(5), which assumes a coherent summation of amplitudes, ignoring any change of phase as a function of angle. This assumption may be justified for excitations to a bound state [12] but is questionable in the case of excitation to a continuum, which involves an extra degree of internal freedom related to the direction of the escaping secondary electron [23]. Based on a comparison of Eq.(14) with Eq. (3) or Eq.(2), it seems quite likely that the coherent approximation underestimates the delocalization of inelastic scattering.

If we take an opposite extreme and assume a completely incoherent summation of intensities, Eq.(5) is replaced by:

$$\text{PSF}(r) \propto \text{FT}(dI/d\Omega)$$

(30)

With no cutoff to the Lorentzian angular distribution, the analytical solution is [34]:

$$\text{PSF}(r) \propto \text{FT}[(\theta^2 + \theta_E^2)^{-\frac{1}{2}}] = K_0(\theta_E k_0 r)$$

(31)

where $K_0$ is the same Bessel function as used in Eq.(23) but without a factor of 2 within the argument. As seen in Fig. 14, Eq. (34) predicts much more extensive delocalization than Eq.(17); the diameter $d_{50}$ (containing 50% of the scattered electrons) is around 1000 nm for $E = 0.2$ eV, decreasing to 10 nm at $E = 25$ eV, values an order of magnitude larger than the trend shown in Fig. 1. Numerical evaluation
of Eq.(30) with a Bethe-ridge angular cutoff leads to the same conclusion: that incoherent addition considerably overestimates the degree of delocalization.

Fig. 14. Fraction of inelastic intensity within a radius \( r \), calculated using Eq. (31) (green curve, incoherent approximation) and Eq. (17) (blue curve, coherent approximation), for \( E = 6 \) eV and \( E_0 = 60 \) keV.

An attractive feature of the coherent approximation is that it predicts an exponential falloff of intensity at around \( b_{\text{max}}/2 \), as verified experimentally [7]. In contrast, Eq.(31) leads to an \( r \)-integrated intensity that does not saturate until about \( 6b_{\text{max}} \) implying very broad delocalization.

There appears to be a direct correlation between inelastic delocalization and the lateral coherence length \( L_c(E) \) involved in inelastic scattering. Kimoto and Matsui [60] measured \( L_c(E) \) from the focus dependence of lattice-fringe contrast and found values similar to those given by Eq.(2), for \( E \) between 10 eV and 400 eV. Holographic measurements are also possible [61]. Schattschneider and Werner [62] have argued that inelastic scattering by plasmon excitation is highly coherent and that inelastic scattering in general has a large coherent component.

Certainly there is a need for experimental data to verify or refine the simple theory presented here. \textit{Ab-initio} calculations of delocalization for valence-electron and vibrational losses, perhaps based on the approach of Ritchie and Howie (22), would also be valuable. Especially if it can be cast in analytical form, the resulting PSF could be used in place of Eq. (17) and used to predict the properties discussed here.
Our equations have assumed single inelastic scattering in the specimen, which becomes a poor approximation when the specimen thickness approaches or exceeds the mean from path $\lambda_i$ for the inelastic process being detected. The value of $\lambda_i$ is of the order of 100 nm for valence-electron (plasmon) scattering but many micrometers for dipole-mode vibrational (optical-phonon) scattering. Plural scattering leads to a broadening of the measured angular distribution of inelastic scattering [35] but does not obviously change the delocalization.

We have also ignored the simultaneous presence of elastic scattering in the specimen, whose extent is described (inversely) by an elastic mean free path $\lambda_e$ in the case of a non-crystalline material. Low-loss spectra are typically recorded using a spectrometer entrance aperture subtending a collection semiangle $\beta$ that is large enough to include a major part of the inelastic scattering but small enough to exclude most of the elastic scattering, which has a much larger angular width. For electrons transmitted through a specimen of thickness $t$, the fraction that escape elastic scattering is $\exp(-t/\lambda_e)$ and the energy-loss signal is reduced (at the aperture) by this factor. For a thin specimen with roughly uniform composition and thickness, the elastic scattering should not significantly affect the delocalization properties of the inelastic scattering.

In a thicker specimen, plural elastic scattering can lead to “beam spreading” or “beam broadening” that degrades the spatial resolution of analysis and for which formulas are available [35]. Since this effect is not correlated with the inelastic scattering, it could be combined in quadrature with the delocalization length.

In calculating the PSF for energy deposition, we ignored the contribution from inner-shell excitation, which increases the average energy loss and would make the PSF narrower, perhaps comparable to the light-blue curve in Fig. 10. The calculated advantage of leapfrog scanning would then increase. Inner-shell contributions would become important for higher specimens of medium or high atomic number.

10. Conclusions

We have discussed the delocalization of inelastic scattering in terms of a point spread function (PSF), assuming it to be a Lorentzian function with an exponential cutoff around the Bohr adiabatic limit. This particular form leads to delocalization distances of a few nm for valence-electron losses in the range 5 – 30 eV and several tens of nm for vibrational-mode losses between 0.1 and 0.5 eV. Knowing the PSF, the fraction of inelastic scattering occurring outside an electron probe of a given diameter can be predicted.

By summing over energy losses between 5 eV and 100 eV, we calculated the radial distribution of energy deposition created by a sub-nm STEM probe in an organic specimen. This distribution can be interpreted as a PSF for radiolysis damage and its width is less than that of the PSF for inelastic scattering, for energy
losses below 10 eV. Consequently, an energy loss signal can be recorded from regions outside the probe that damage relatively slowly, resulting in an increase in signal/damage ratio. This possibility should allow a coarse digital raster to be used to map hydrogen or specific chemical bonds in a beam-sensitive specimen, with less damage than would occur with regular STEM scanning.

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References


[38] F.J. Garcia de Abajo, Rev. Mod. Phys. 82 (2010) 209.


[54] R. F. Willis, in Vibrational Spectroscopy of Adsorbates, Ed.: R.F. Willis (Springer Verlag, 1980), Ch. 1 and Ch.4


