The spatial resolution of core-loss imaging in the STEM

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Abstract. We have investigated the resolution of scanning transmission electron microscope images for single, isolated atoms. The images are simulated from first principles using a nonlocal model for electron core-loss spectroscopy. We have examined the role of the width of the probe in determining the localisation of the images.

1. Introduction
Atomic resolution microscopy has found use in the nanotechnology and bioengineering fields for such purposes as investigating the properties of materials containing dopants or the characterisation of biological samples. The scanning transmission electron microscope (STEM) is able to provide images at atomic resolution, the more so if fitted with a field emission gun and a spherical aberration corrector. As the advent of aberration correctors allows for the formation of an aberration balanced probe, it is now possible to increase the probe forming aperture size, which results in a smaller, finer probe. Small probe sizes have led to the successful detection of single atoms on the surface [1] and recently the spectroscopic identification of a single atom within the bulk [2]. This latter result was achieved with the use of electron energy loss spectroscopy (EELS). This technique detects electrons which have undergone an energy loss associated with a particular inelastic scattering event and have been scattered through an angular range determined by the detector geometry. It provides a means of identification, as an atomic ‘signature’ may be measured by setting an energy window about the threshold energy of an ionisation event. One possible application of combining EELS with STEM is column-by-column spectroscopy. Thus, the spatial resolution of core-loss EELS becomes an important issue.

Images formed using annular dark field (ADF) detectors are highly localised at the atomic locations. In addition, the ADF interaction is readily described using a local potential whose width may be used as a measure of the localisation of the interaction. The EELS interaction is however, most accurately described by an effective nonlocal potential [3] and treating this nonlocality correctly can be essential when calculating STEM images based on core-loss spectroscopy [4]. For zone-axis illumination, the effective nonlocal potential is a four dimensional function and so cannot be used to provide a simple measure of the interaction localisation. The peak widths of the STEM EELS image will be used instead as an unambiguous measure of the resolution obtainable for various combinations of probe sizes and interaction delocalisation.
Previous work has suggested either definite localisation [5] or considerable delocalisation [6] of STEM EELS images. The results of Ref. [5] are calculated using a local formalism and contain an error in the formulation of the mixed dynamic form factors (MDFFs) which results in a local potential that is significantly too narrow. The results presented here are in reasonable agreement with those presented in Ref. [6].

We have investigated the spatial resolution for EELS imaging in the STEM by ignoring sample-dependent effects such as multiple scattering and channelling of the probe. To provide an optimal measure of the STEM image width, we have considered an isolated atom without the additional smearing of thermal motion. Even by ignoring these effects we would still expect to obtain a reasonable estimate of the delocalisation of the EELS image of a particular element, regardless of its local environment. The width of the probe achievable in current machines is the primary limitation on the width of single atom EELS features.

2. Theoretical Background
In the multislice formulation, an incoherent STEM image for an isolated atom formed by inelastic scattering may be calculated via [7],

$$\sigma(R) = \frac{1}{2\pi k V_c V_A} \left[ \sum_{g,h} \Psi^*(K, R, h, z) \Psi(K, R, g, z) f_{h,g} \right] \Delta z.$$  

(1)

The term $\Psi(K, R, g, z)$ is the Fourier transform of the wave function, where $K$ (magnitude $K$) is the wave vector of the incident electron corrected for refraction. In the case of imaging a single atom, $K \approx k$; the incident wave vector of magnitude $k$ is not significantly refracted by one atom. The probe position is denoted by $R$ and $z$ denotes the distance in the direction of propagation. The momentum space vectors $g$ and $h$ are those related to the supercell. Here, $V_c$ is the volume of the fundamental unit cell and $V$ the volume of the supercell of area $A$.

The atomic scattering factors for inner-shell ionisation are given by the terms $f_{h,g}$. Details of their calculation is described in [8]. It is important to note that here the scattering factors are calculated using realistic atomic wave functions and calculations are not limited to K-shell ionisation. Relativistic corrections have been made to Hartree-Fock wave functions and continuum states are described by Hartree-Slater wave functions.

A unit cell of dimensions 10 Å by 10 Å was constructed with the single atom placed at the origin. This unit cell was tiled in the direction perpendicular to propagation to produce an 8 x 8 supercell which was distributed over 512 x 512 pixels. The calculation was performed using a single slice of thickness $\Delta z = 2$ Å.

3. STEM EELS Imaging of Single Atoms
Simulated STEM images were made for single, isolated atoms using an incident probe energy of 300 keV, assuming an aberration free probe. The EELS detector has a collection semi-angle $\beta = 20$ mrad and an energy window of $\Delta E = 40$ eV above the threshold energy for ionisation. The full width at half maximum (FWHM) of the STEM images was used to quantify the resolution obtainable with the simulated probe.

Shown in Figure 1 is the variation of the FWHM of the STEM EELS images as a function of atomic number $Z$ for K-shell ionisation with probe forming aperture sizes of $\alpha = 10$ mrad (filled circles) and $\alpha = 20$ mrad (filled triangles). The results are plotted for atomic numbers ranging from $Z = 6$ (carbon) to $Z = 20$ (calcium). Obvious for both aperture sizes shown is the reduction of the FWHM as a function of $Z$, due to the tighter binding of the K-shell electrons in heavier atoms. There is also a significant reduction in the FWHM of the STEM images formed using the 20 mrad probe.
Figure 1. FWHM as a function of atomic number for STEM images resulting from K-shell ionisation. Results are shown for probe forming aperture sizes of $\alpha = 10$ mrad and $\alpha = 20$ mrad for scattering into an EELS detector with collection semi-angle $\beta = 20$ mrad and energy window of $\Delta E = 40$ eV.

Figure 2. STEM images based on the K-shell ionisation of carbon showing the appearance of a ‘volcano’ for the largest condenser aperture with an EELS detector semi-angle of 20 mrad.

For large probe forming aperture sizes and small detector collection semi-angles, the inelastic STEM images exhibit additional structure. As $\alpha$ increases, the probe size in real space becomes smaller. For a probe tightly focused on an atomic site, electrons tend to be scattered through large angles, which may be outside the range of the detector and so they are not detected. This leads to a diminished EELS signal at the atomic site and the appearance of volcano-like structures in the images. Such structures had previously been calculated by Kohl and Rose [6]. The development of these structures as a function of $\alpha$ is shown in Figure 2. The STEM image is sharply peaked for $\alpha = 15$ mrad but as the aperture is increased to 20 mrad, the top of the image flattens out which leads to a small increase in the FWHM. By increasing the aperture size further to $\alpha = 30$ mrad, a well defined ‘volcano’ appears in the image and the FWHM is reduced.

Not only is the FWHM of the STEM EELS images dependent upon probe size but it is also dependent upon the size of the EELS detector. Plotted in Figure 3 is the variation of the FWHM as a function of both the probe forming aperture and EELS detector semi-angle for images based on K-shell ionisation of carbon. There are two interesting points to note. Indicated on the plot is a thick black line marking a diagonal ridge. This ridge represents the point at which volcano-like structures appear in the STEM image. These types of images occur on the large $\alpha$ side of the ridge. By increasing the detector size $\beta$, electrons scattered through larger angles are detected and as a result the FWHM is reduced as the interaction is more ‘localised’. This is clearly seen for small values of $\alpha$ but distorted somewhat by the ridge. The second point to note is that for $\alpha = 40$ mrad, where all images have a volcano-like appearance, the FWHM increases slightly with increasing collection angle. The calculations show that especially for weakly bound orbitals, small collection angles actually enhance the ‘nonlocal nature’ of the interaction [9].
4. Conclusion
The ‘delocalisation’ of STEM EELS images is a crucial issue for the ultimate spatial resolution of core-loss spectroscopy in the electron microscope. Images for single atoms were simulated from first principles using a nonlocal model for electron core-loss spectroscopy. We have elucidated the role of the probe width relative to the underlying ionisation interaction and examined the dependence of the resolution on the EELS detector size. The results indicate that, with future advances in electron microscopy, column-by-column spectroscopy of crystal samples using core-loss spectroscopy will be a feasible procedure.

Acknowledgments
The authors acknowledge fruitful discussions with Scott Findlay. M P Oxley and L J Allen acknowledge support by the Australian Research Council. S J Pennycook acknowledges support by the Laboratory Directed Research and Development Program of ORNL, managed by UT-Battelle, LLC, for the US Department of Energy under Contract no. DE-A C05-00OR22725.

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Figure 3. Variation of FWHM of STEM images with probe forming aperture and EELS detector semi-angle for the K-shell ionisation of carbon.