ATOMIC RESOLUTION IMAGING IN TWO AND THREE DIMENSIONS

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Submitted in total fulfilment of the requirements of the degree of Doctor of Philosophy

School of Physics
The University of Melbourne
Australia
January 2010
Abstract

This thesis explores theoretical aspects of scanning transmission electron microscopy (STEM) and the comparison of simulation with experiment.

The long standing contrast mismatch problem between theory and experiment in conventional high resolution transmission electron microscopy (HRTEM) is examined using the principle of reciprocity and bright field scanning transmission electron microscopy (BFSTEM). It is found that quantitative agreement between theoretical and experimental images is possible provided that theory suitably accounts for the spatial incoherence of the source, and that experimental images are placed on an absolute scale with respect to the incident beam current. Agreement between theory and experimental image contrast is found to be independent of specimen thickness and probe defocus.

Core-loss electron energy-loss spectroscopy (EELS) is a powerful experimental tool with the potential to provide atomic-resolution information about the electronic structure at defects and interfaces in materials and nanostructures. Interpretation, however, is nonintuitive due to the nonlocal ionization potential. Novel improvements in microscope design and operating environment have enabled two dimensional chemical maps. This has permitted a more thorough theoretical analysis. This thesis compares experimental STEM EELS images of LaMnO$_3$, BiSrMnO$_3$ and Si samples to the relevant theoretical simulations. Image features which at first appear counter intuitive are discussed and explained with the accompanying theoretical simulations. It is demonstrated, using a sample of SrTiO$_3$, that more direct interpretation of atomic resolution chemical maps is possible when using energy dispersive x-ray spectroscopy (EDS) in STEM.

This thesis considers extending chemical mapping in STEM EELS to three dimensions using depth sectioning. It explores, theoretically, the feasibility to depth section zone-axis aligned crystals that contain embedded impurities. In STEM
EELS this is found to be possible for point defects but not for larger extended objects such as nanoparticles.

The theory describing the mechanism by which contrast is obtained in elastic scanning confocal electron microscopy (SCEM) is developed. It is shown that there is no first order phase contrast in SCEM and thus low image contrast. Finally, energy filtered scanning transmission electron microscopy (EFSCM) is developed theoretically. The fundamental equation describing image formation is derived and an efficient computation method is developed to allow the rapid calculation of EFSCM images.
Declaration

This is to certify that:

1. The thesis comprises only my original work towards the PhD except where indicated in the Preface.

2. Due acknowledgement has been made in the text to all other material used.

3. The thesis is less than 100,000 words in length, exclusive of tables, bibliographies and appendices.

Adrian John D’Alfonso
Preface

The work in this thesis is the result of many fruitful collaborations. The nature of the collaboration and the portions of the work which the author claims as original are listed below.

**Chapter 1** This chapter introduces the field of electron microscopy. It puts the work in a historical perspective as well as discussing current attempts to progress the field. This chapter provides a brief outline of the thesis and what topics have been investigated.

**Chapter 2** This chapter presents a brief review of the background theory developed by many scientists over the past 50 years. The analysis of multislice slicing schemes is the authors own work and all theoretical simulations are the authors own.

**Chapter 3** This chapter addresses questions concerning the validity of current models of elastic and thermal scattering within the context of electron microscopy. The experimental work was performed by J.M. LeBeau from the University of California Santa Barbara with all theoretical simulations performed by the author.

**Chapter 4** This chapter introduces imaging based on core-loss spectroscopy in scanning transmission electron microscopy. Calculations are the authors own unless otherwise stated.

**Chapter 5** This chapter contains a experimental work that was performed at Oak Ridge National Laboratory as part of a collaboration. Theoretical simulations were performed by the author.
Chapter 6 This chapter contains a large amount of experimental work from various collaborations and is based on the work of several papers. Experimental work was performed at the SuperSTEM laboratory in Daresbury and at FEI corporation. All theoretical simulations were once again performed by the author.

Chapter 7 This chapter is all the candidates original work unless otherwise stated.

Chapter 8 This chapter contains theoretical work that was a result of a collaboration between Oxford University and the theoretical condensed matter physics group at the University of Melbourne. All simulations are the authors own work.

Chapter 9 This chapter contains theoretical work that was a result of a collaboration between Oxford University and the TCMP group. All simulations are the authors own work.
Acknowledgements

The work in this thesis was only possible because of the rich and generous contributions of many people. I thank my supervisor Les Allen for his guiding influence, patience and help throughout my candidature. Thank-you for indulging my idiosyncrasies and allowing me to explore ideas.

Special thanks go out to Scott Findlay for his help and willingness to respond to my never ending questions. Your technical advice regarding computing and the physical principles was invaluable. Lastly, thank-you for your friendship and being sympathetic to a doctoral student struggling to find his feet.

Thank-you to Mark Oxley for your early guidance and discussions. Thanks are also extended to the people I met during my visit to Oak Ridge National Laboratory: Steve Pennycook, Maria Varela and Klaus van Benthem for your hospitality. Also, thank-you to Pete Nellist and Gavin Behan for their hospitality during my visit to Oxford University.

Special thanks to Elaine Miles for your support, understanding and guidance along this journey. Your irrepressible good spirit and encouragement were an essential contribution to this thesis. Thank-you to Chris Witte and to Andrew Martin my fellow PhD students, for our discussions, coffees and lunches where we debated all manner of topics. Thank-you for your help, friendship and support.

I am grateful to Les Allen, Scott Findlay, Chris Witte and Elaine Miles for proof reading my thesis and offering valuable suggestions.

To my parents Agostino and Silvana D’Alfonso I extend my deepest thanks and gratitude. Your support and patience over the past 28 years is appreciated more than words can express. Finally, thank-you to my older brother Justin D’Alfonso for being an exceptional role model.
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List of acronyms

- BFSTEM – bright field scanning transmission electron microscopy
- CSOM – confocal scanning optical microscopy
- CTF – contrast transfer function
- EDS – energy dispersive x-ray spectroscopy
- EELS – electron energy-loss spectroscopy
- EFSCN – energy filtered scanning confocal electron microscopy
- FWHM – full width at half maximum
- HAADF – high angle annular dark field
- HRTEM – high resolution transmission electron microscopy
- MDFF – mixed dynamical form factor
- MTF – modulation transfer function
- OTF – optical transfer function
- PCA – principal component analysis
- PSF – point spread function
- STEM – scanning transmission electron microscopy
- SCEM – scanning confocal electron microscopy
- ZLP – zero loss peak
List of publications

  Depth sectioning in scanning transmission electron microscopy based on core-loss spectroscopy.

  Interpreting atomic resolution spectroscopic images.

  Two-dimensional mapping of chemical information at atomic resolution.

  Volcano structure in atomic resolution core-loss images.

  Depth sectioning using electron energy loss spectroscopy.
LIST OF PUBLICATIONS

  Three-dimensional imaging using aberration-corrected scanning transmission and confocal electron microscopy.

  Theoretical interpretation of electron energy loss spectroscopic images.


  Three dimensional imaging in double aberration-corrected scanning confocal electron microscopy. Part II: Inelastic scattering.

  Contrast reversal in atomic-resolution chemical mapping.

  Quantitative comparisons of contrast in experimental and simulated bright-field scanning transmission electron microscopy images.

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CHAPTER 1

Introduction

1.1 Motivation and overview

In his famous talk, Plenty of Room at the Bottom (1959) [1], Richard P. Feynman said

“It would be very easy to make an analysis of any complicated chemical structure; all one would have to do would be to look at it and see where the atoms are. The only trouble is that the electron microscope is one hundred times too poor... I put this out as a challenge: Is there no way to make the electron microscope more powerful?”

This sentiment has been echoed by materials scientists many times in the intervening years. It has been the desire to map locally, in real space, the atomic distribution of a material that has been the driving force behind the development of the electron microscope. The continued development of electron microscopy has led to atomic resolution images, initially of a single atom [2] and more recently to sub-Ångström two-dimensional crystal maps [3, 4]. Because of its singular strength in sub-nanometer-scale imaging, electron scattering has historically played the leading role in the characterization of defects – structural and chemical inhomogeneities – that control many of the functional properties of materials. High-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) are two of the most powerful techniques capable of investigating these defects. Whilst the physical processes driving the image formation in both
techniques are the same, the imaging process is fundamentally different. HRTEM uses plane wave illumination of the sample by high energy electrons whereas STEM uses a finely focused convergent probe. The two modes have their own complementary strengths and weaknesses. In HRTEM an image of the transmitted electrons is formed with the insertion of a post-specimen objective lens, Fig. 1.1(a). The subsequent measurement can be made in either the back focal or the image plane (Fig. 1.1(a) shows the image plane measurement) with an energy filter to discriminate between electrons that have undergone different energy losses. Typically HR-TEM is performed in bright field mode where images are taken that are designed to be comprised mostly of coherent elastically scattered electrons. As atoms are weak phase objects, information regarding the specimen’s structure is contained in the phase of the transmitted electron wave function. The point resolution in HRTEM is limited by the aberrations of the objective lens, which until recently were too great to directly achieve sub-Ångström resolution imaging. Circumvention of these limitations traditionally relied upon the exit-plane wave function reconstruction [5–8]. The practical implementation of HRTEM aberration correctors [9–11] finally allowed direct imaging at sub-Ångström resolution and is, perhaps, the single most important technological advance since the electron microscope’s initial creation.

STEM approaches imaging from a different direction: the convergent probe illuminates a single point of the sample and the transmitted electrons are then collected in the diffraction plane (or the back focal plane of some post-specimen lens). Depicted in Fig 1.1(b) is a schematic of STEM showing the resultant convergent beam electron diffraction (CBED) pattern. By raster scanning the probe across a sample it is possible to build up a series of electron scattering experiments. The annular detector in Fig. 1.1(b) collects those electrons scattered to high angles, the on axis electron energy loss spectrometer allows the construction of spatially resolved energy-loss maps and the energy dispersive x-ray spectrometer records the spatially resolved x-ray emission spectrum. This geometry allows the simultaneous recording of structural, compositional and bonding information.

A third novel approach was first proposed by Frigo et al. [12]. It is the logical combination of HRTEM and STEM, and is shown in Fig 1.1(c) and is called scanning confocal electron microscopy. In SCEM there are both pre- and post-specimen lenses. A convergent probe is incident onto the sample and raster scanned in a similar fashion to STEM. However, unlike STEM, the transmitted electrons are then
1.2. QUANTITATIVE ELECTRON MICROSCOPY

imaged as they typically would be in HRTEM. Focussing the both the pre- and post-
specimen lenses to the same plane within the specimen (the confocal condition) and
recording specific changes in the image plane (i.e. with a pinhole detector) as a
function of probe position, including focal plane, allows this alternative form of
imaging. While HRTEM uses plane wave illumination conditions and the illumina-
tion for STEM and SCEM consists of a finely focused probe, interpretation of
images in all three techniques relies heavily on image simulations [13, 14].

Image simulation involves the theoretical modelling of the interaction of a beam
of electrons with a specimen. As such, it is a challenging and complex many body
quantum mechanical problem. Since the first application of the Schrödinger equa-
tion by Bethe [15], many people have worked to produce a sufficiently accurate
theory that qualitatively reproduces the features present in electron scattering ex-
periments. The theme of this thesis is the simulation and quantification of electron
microscopy images with an eye toward three-dimensional characterisation on the
atomic scale. It traverses all three modes of imaging discussed. Firstly it aims
towards quantification of HRTEM images using STEM and the principle of reciprocity [16], secondly it investigates energy loss mapping in STEM in one, two and
three dimensions, and finally it presents a theory for calculating SCEM images.

1.2 Quantitative electron microscopy

In spite of the advances in the theories describing the fast-electron sample inter-
action, experiment and theoretical models in high-resolution electron microscopy
images do not agree quantitatively: there is a large contrast mismatch which has
become known as the Stobbs factor [17] and is typically in the range between two
and five. A large body of literature has addressed the origin of the Stobbs factor
with numerous experimental and theoretical approaches [14, 17–21]. The Stobbs
factor persists even when all electrons that have undergone inelastic scattering with
energy losses of greater than \(\sim 1\) eV are excluded from the image using an energy
filter [14, 22]. Electrons which have been involved in phonon excitation, also known
as thermal diffuse scattering (TDS), have energy losses on the order of meV and are
not excluded by the energy filter. Consequently, there has been speculation that
the inadequate modeling of TDS might be the cause of the Stobbs factor [23, 24].
Figure 1.1: A schematic of the three microscope geometries considered in this thesis. (a) conventional HRTEM with plane wave incidence, (b) STEM showing a HAADF detector which integrates the diffraction pattern over some annular detector, the smaller on axis EELS detector (and accompanying energy loss spectrum) and the energy dispersive x-ray spectroscopy detector, and (c) SCEM with the pre- and post-specimen lenses with the pinhole detector located at some point in the image plane producing the raster image underneath. In (b) and (c) the image is recorded serially as a function of probe position whereas the HRTEM image is recorded in parallel.
1.3 CHEMICAL MAPPING

This is supported by results reported in off-axis electron holography, a technique in which an almost perfectly energy filtered image can be obtained [25], where a reduced contrast mismatch is observed [26]. Other inelastic scattering mechanisms, such as plasmon scattering, have also been suggested to play a role [27]. Opposing this view is that rather than an inadequate description of inelastic scattering the origin of the Stobbs factor lies in an inadequate description of the imaging process [28, 29]. Quantitative agreement in STEM high-angle annular dark field (HAADF) imaging [30–32], which critically relies on inelastic scattering and particularly TDS to form an image, further supports the notion that the Stobbs factor is a consequence of the HRTEM imaging procedure. Until resolved, the Stobbs factor raises questions as to whether the current understanding of image formation is adequate.

1.3 Chemical mapping

Even though the HRTEM Stobbs factor problem has persisted for over a decade the success of qualitatively matching the image features between simulation and experiment has been remarkable. Nevertheless, alternate STEM methods have been developed for structure determination. One popular technique has been STEM HAADF which, due to its incoherent nature [33], provides structural images which are relatively insensitive to focusing errors and provides visual identification of compositional changes (as the contrast scales approximately with atomic number as $Z^{1.7}$ [34]). The STEM HAADF image usually permits direct visual identification and its utility for structure determination has been recognised for many years with numerous examples present in the literature (see for example Refs. [35–38]). Compositional analysis based only on STEM HAADF, whilst possible due to the $Z^{1.7}$ contrast scaling, remains a dubious prospect for crystals containing atoms of a similar atomic number or light atoms surrounded by heavy neighbours. Imaging based on electron energy-loss spectroscopy (EELS) has dominated recent scientific attention as it allows unambiguous atomic species identification. It involves recording energy-loss spectra along a contiguous sequence of points [39–41]. The correlation of structure, composition and physical properties using STEM has predominantly been achieved by using the HAADF image as a probe position reference to record energy-loss spectra at select, structurally significant points [42, 43].
CHAPTER 1. INTRODUCTION

The spectra contain information about the unoccupied density of states above the Fermi energy and, in the case of core-loss ionization, can be integrated up over some energy window to construct a compositional map [44, 45]. The theoretical development of STEM EELS has progressed from single atom images [46] to dynamical simulations [47–49], and finally dynamical simulations incorporating the effect of the ionized atom’s local environment [50]. From an experimental perspective, the implementation of stable microscope environments [51, 52] coupled with STEM aberration correctors [53–55] finally allowed results of sufficient quality to test these theories and their non-intuitive predictions [56, 57]. This has culminated with the production of atomic resolution two-dimensional chemical maps based on EELS [51, 52, 58–60] and emboldened materials scientists, both theoreticians and experimentalists, to aspire to full three-dimensional reconstructions.

1.4 Three-dimensional imaging and depth sectioning

Images produced by transmission electron microscopy are by definition a projection of the object’s three-dimensional structure onto a two-dimensional plane. Electron tomography [61–64] and optical depth sectioning in STEM [65–67] are two techniques (among many such as atom probe tomography, x-ray tomography, confocal scanning optical microscopy (CSOM), etc.) which attempt to recover the three-dimensional structure from a collection of two-dimensional projection images\(^1\). For high-resolution (\(\sim 1 \text{ nm}\)) three-dimensional tomographic imaging using electron microscopy, images are recorded as a function of tilt angle about some tilt axis. Typically the images are then back-projected to form a three-dimensional reconstruction [63].

In general, the resolution of a reconstructed tomogram is governed by the number of images in the tilt series, their lateral resolution and the tilt range over which the series is recorded. In addition to these conditions the image formation process must also satisfy the projection requirement. The projection requirement simply states that the recorded signal be a monotonic function of some physical property [68]. In STEM HAADF imaging of thin specimens this is most likely to be sa-

\(^1\)We remind the reader that any form of three dimensional structure reconstruction using a series of two-dimensional images is tomography. Somewhat arbitrarily, we distinguish between the conventional tilt series tomography and the through focal series imaging.
tisfied as the contrast loosely scales with both the atomic number and the number of atoms. The development of STEM aberration-correcting electron optics resulted in sub-Ångström probes. Smaller probe size increases the transverse resolution of STEM while simultaneously reducing the depth of focus. Having a reduced depth of focus may jeopardise the projection requirement, and this coupled to limits on tilt angle imposed by sample holders, may hamper further development of electron tomography.

The reduction in the STEM depth of focus should improve matters somewhat for optical depth sectioning. Atomic resolution STEM imaging offers the tantalising possibility to depth section samples and so to extract three-dimensional atomic locations [65–67]. Depth sectioning (or optical slicing) involves recording a series of images as a function of defocus which are then used to reconstruct a three-dimensional model of the specimen. Just as tomography suffers from the missing wedge in Fourier space, due to the tilt limitations, STEM suffers from a similar elongation problem for extended objects and will most likely be limited to depth sectioning for point defects rather than nanoparticles [67, 69, 70]. Using the electron microscopy analogue of CSOM, SCEM attempts to remove the elongation problem. This technique is in formative stages, having successfully performed imaging at sub-micron resolution [12]. More recently the confocal alignment of pre- and post-specimen optics in a double aberration corrected microscope was successfully demonstrated [71].

1.5 Outline of thesis

As stated previously, the topic of this thesis is the simulation of electron microscopy images within the context of the ultimate goal of three-dimensional characterisation at the atomic scale. The thesis is structured such that the theoretical framework is developed as required. In chapter 2 a general overview of the theory of electron scattering with a phenomenological absorptive potential is derived. As the theory is drawn from several sources, notation and conventions are established. Two methods for solving the paraxial Schrödinger equation are given that are relevant for STEM imaging. Chapter 2 also introduces an alternative model for thermal scattering, the frozen phonon model, and evaluates the accuracy of the practical implementation
thereof within the frame work of the multislice algorithm [72]. Traditionally, in the multislice algorithm when applied to electron scattering, the atomic potential is projected into a single slice, or, for the sake of convergence, it is divided into a series of equally weighted slices. We explore the importance of calculating the full three-dimensional atomic potential in the context of single atoms, crystals and finally in full frozen phonon calculations.

The tools developed and discussed in chapter 2 are essential for the subsequent work presented in this thesis and are implemented and tested quantitatively in chapter 3. The quantitative agreement between the absorptive and frozen phonon model is compared to experimental results and shows agreement to within the experimental error. This work was performed in collaboration with colleagues at the University of California, Santa Barbara. This is explored using bright field STEM (BFSTEM) which, via reciprocity and under certain conditions, is equivalent to HRTEM and seeks to address the Stobbs factor problem. This quantitative agreement is the first significant outcome of the thesis. Chapters 4 through 6 turn attention towards EELS imaging, specifically core-loss EELS. Chapter 4 introduces the real space transition potential approach as well as the reciprocal space mixed dynamical form factor (MDFF) method. The imaging at a distance result of Oxley et al. [56] demonstrated the importance of detailed theoretical simulations in STEM EELS. Chapter 4 uses the real space transition potential approach to reveal many details not explicitly evident in the MDFF method. We revisit this result, in the single channelling approximation, revealing the exact mechanisms behind this seemingly anomalous result. The insight into the imaging procedure gained from making this exploration helps interpretation of experimental results presented in chapters 5 and 6.

In chapter 5, through collaboration with Oak Ridge National Laboratory, we explore experimental line scans of a sample of LaMnO₃. The appearance in the experimental results of the characteristic volcano structure, a long predicted [46, 73] consequence of the complicated nature of the ionization potential, is discussed and explained. The importance of the higher order multipole atomic transitions is discussed and is proven to be relevant to modern STEM instruments.

Chapter 6 presents the results of fruitful collaborations with the SuperSTEM laboratory and FEI. Two-dimensional chemical maps of Bi₀.₅Sr₀.₅MnO₃, Si and SrTiO₃ are discussed and presented. Their comparison, analysis and agreement with theory constitute another significant result of this thesis. EELS mapping in
two dimensions, as demonstrated in this chapter, allows for more convincing comparisons with simulations based on image features than is possible for the line scans in chapter 5. The energy dependence of the transition potential is demonstrated to lead to contrast reversals for EELS images taken at different regions of the energy loss spectrum from a crystal. The contrast reversals, and counter intuitive chemical maps obtained from EELS measurements, are shown to be avoided using energy dispersive x-ray spectroscopy.

Chapters 7 through 9 further extend chemical mapping, theoretically, to three dimensions. The possibility of depth sectioning to obtain three-dimensional information with atomic resolution laterally and nanometer resolution in depth is starting to be explored experimentally in STEM HAADF imaging [65–67]. Chapter 7 considers the depth sectioning scheme in the context of STEM EELS and explores the role of elastic channelling, detector and aperture collection angles, as well as the issue of precision versus resolution.

The last two substantive chapters present the theoretical description of SCEM, both elastic and inelastic, developed through a collaboration with Oxford University. This constitutes another significant and substantial result of this thesis. We develop the fundamental equations describing image formation in SCEM in both elastic and inelastic (energy filtered) contexts. A scheme is proposed that allows rapid calculation in the multislice framework. Simulations explore prospects for three-dimensional atomic resolution SCEM for, firstly, isolated impurities, and, secondly, clusters of impurities.

Chapter 10 concludes the thesis discussing and summarising the key results contained in this thesis.
CHAPTER 2

Background theory

This chapter presents the basic theoretical framework from which the major results of this thesis derive. It begins with a brief sketch of the Yoshioka equations and obtains the paraxial Schrödinger equation with a local projected absorptive potential. The latter part of the chapter introduces the two most common computational approaches, Bloch wave and multislice, used to solve these equations. It describes two methods to include absorption due to thermal scattering and discusses some subtle points necessary for accurate calculations. As our first interest is in calculating the elastic wave function with the view to understanding the Stobbs factor, we defer introducing the expression for calculating inelastic cross sections until chapter 4.

2.1 The Yoshioka equations

We begin our investigation by considering a fast electron incident onto the surface of a specimen of condensed matter with the system wave function $\Psi(r, \tau)$ which describes the particles comprising the specimen at positions $\tau = \{r_1, \ldots, r_N\}$ and the incident fast electron at position $r$. It is assumed that the wave function can be expanded into the form

$$\Psi(r, \tau) = \sum_n \psi_n(r) a_n(\tau),$$

(2.1)
a product of the fast electron wave function $\psi_n(r)$ and the crystal wave function $a_n(\tau)$ in the $n^{th}$ stationary state, such that $a_n$ satisfies

$$H_c(\tau)a_n(\tau) = \epsilon_n a_n(\tau),$$

(2.2)

where the crystal Hamiltonian is $H_c$ and the energy of the state is $\epsilon_n$. The series of coupled non-relativistic Schrödinger equations describing the fast electron is then [74–76]

$$\left[\nabla^2 + 4\pi^2 k_n^2 - \frac{2m}{\hbar^2}H_{nm}(r)\right] \psi_n(r) = \frac{2m}{\hbar^2} \sum_{m \neq n} H_{nm}(r) \psi_m(r),$$

(2.3)

where the magnitude of the incident electron wave vector after scattering is $k_n$ and defines $\lambda_n = 1/k_n$ the electron wavelength. The energy associated with the scattered electron of mass $m$ (relativistically corrected) is

$$E_n = E - \epsilon_n \equiv \frac{2\pi^2 \hbar^2}{m} k_n^2.$$  

(2.4)

The quantity $H_{nm}$ is the transition matrix element defined by the relation

$$H_{nm}(r) = \int a_n^*(\tau) H'_{int}(r; \tau) a_m(\tau) d\tau,$$

(2.5)

describing the transition of the crystal from state $m$ to $n$. The interaction Hamiltonian between the fast electron and the crystal is $H_{int}(r; \tau)$ and we identify that the matrix element associated with elastic scattering of elastic ($n = 0$) and inelastic ($n \neq 0$) waves is $H_{0m}$. When $n = 0$ Eq. 2.3 becomes

$$\left[\nabla^2 + 4\pi^2 k_0^2 - \frac{2m}{\hbar^2} H_{00}(r)\right] \psi_0(r) = \frac{2m}{\hbar^2} \sum_{m \neq 0} H_{0m}(r) \psi_m(r).$$

(2.6)

Identifying the initial state $m = 0$ as the ground state and assuming that excitations from the ground state are the dominant source of inelastic waves ($H_{n0}(r) \gg H_{nm}(r)$) [77] Eq. 2.3 reduces to

$$\left[\nabla^2 + 4\pi^2 k_n^2\right] \psi_n(r) = \frac{2m}{\hbar^2} H_{n0}(r) \psi_0(r),$$

(2.7)
and describes the generation of inelastic waves (note $H_{nm} = H_{mn}^*$). For a particular excited state $n$ the solution of Eq. 2.6 can be written using the standard form

$$
\psi_n(r) = -\frac{m}{2\pi \hbar^2} \int \frac{e^{2\pi i k_n |r-r'|}}{|r-r'|} H_{n0}(r') \psi_0(r') dr'.
$$

(2.8)

(In Sec. 2.3.5 it will be shown how to account for multiply inelastically scattered electrons which excite multiple crystal phonons at the expense of an increased computational burden.) Substituting Eq. 2.8 into Eq. 2.6 allows the reduction of the uncountably infinite coupled channels equation into a single integro-differential equation

$$
\left[ \nabla^2 + 4\pi^2 k_0^2 - \frac{2m}{\hbar^2} H_{00}(r) \right] \psi_0(r) - \frac{2m}{\hbar^2} \int A(r, r') \psi_0(r') dr' = 0,
$$

(2.9)

with a nonlocal potential $A(r, r')$ defined by

$$
A(r, r') = -\frac{m}{2\pi \hbar} \sum_{m \neq 0} H_{0m}(r) H_{m0}(r') e^{2\pi i k_m |r-r'|} |r-r'|.
$$

(2.10)

The interpretation of Eq. 2.9 is that the evolution of the elastic wave, $\psi_0$, is modified by the presence of the inelastic source term which is a complex nonlocal potential. The nonlocal nature of the potential is a consequence of the way we solve the complicated many-body problem even though physically the interaction between the fast electron and the sample is the local Coulomb potential.

While the nonlocal potential is non-Hermitian, it is possible to break up the nonlocal potential into the linear combination of two Hermitian operators yielding a real component responsible for virtual inelastic scattering and an imaginary component that describes real inelastic scattering [78]:

$$
A(r, r') = \frac{1}{2} \left[ A(r, r') + A^*(r, r') \right] + \frac{1}{2i} \left\{ i \left[ A(r, r') + A^*(r, r') \right] \right\}.
$$

(2.11)

The distinction between the two is that virtual inelastic scattering effectively modifies the elastic potential whereas the imaginary component acts as either a source or sink of probability, essentially an absorptive potential. The virtual term is known to
be small and is neglected \[79\] so that

\[A(r, r') \approx -\frac{i}{2} \{i [A(r, r') + A^*(r, r')] \} \equiv -\frac{i}{2} W(r, r').\] (2.12)

Thus Eq. 2.9 becomes

\[
\left[ \nabla^2 + 4\pi^2 k_n^2 - \frac{2m}{\hbar^2} H_{00}'(r) \right] \psi_0(r) - \frac{im}{\hbar^2} \int W(r, r') \psi_0(r') dr' = 0. \] (2.13)

Using Eq. 2.10 and a standard identity it can be shown that \( W(r, r') \) is \[80\]

\[W(r, r') = \frac{2\pi m}{\hbar^2} \sum_{n \neq 0} H_{0n}(r) H_{n0}(r') k_n \int e^{2\pi i K' \cdot (r-r')} d\Omega_{K'} dK'. \] (2.14)

### 2.2 A local absorptive potential

We recap what has been developed thus far. Beginning with the non-relativistic Schrödinger equation we have collapsed the full many bodied problem into one integro-differential equation, Eq. 2.13, which describes the effect of all the inelastic channels on the evolution of the elastic channel. This effect is contained in the nonlocal absorptive potential in Eq. 2.14 that accounts for inelastic processes such as the excitation of a crystal phonon, inner-shell ionization, plasmon excitation and Bremsstrahlung radiation. For an electron microscope with an accelerating voltage of the order of hundreds of kV it is known that the dominant inelastic process which modifies elastic contrast is phonon excitation \[81–83\].

In Eq. 2.6 the tacit assumption was made that waves can only scatter inelastically once, multiple inelastic scattering has been ignored, any inelastic scattering to any angle acts as a probability sink on the elastic wave. For high energy electrons where \( k_n \) is considered large and using the flat Ewald sphere approximation, integrating over all possible scattering kinematics reduces Eq. 2.14 to \[80\]

\[W(r_\perp, r'_\perp) = \frac{2\pi m}{\hbar^2 k_n \Delta z} \sum_{n \neq 0} H_{0n}(r_\perp) H_{n0}(r'_\perp) \delta(r_\perp - r'_\perp) \equiv 2V'(r_\perp) \delta(r_\perp - r'_\perp),\] (2.15)

where we have performed a projection over thickness \( \Delta z \) and the variable \( r_\perp \) refers
to a vector that is in the plane perpendicular to the direction of propagation of the incident electron. If we assume that the incident wave is not greatly deviated from the $z$-axis, the incident wave function can be written as a modulated plane wave

$$\psi_0(r) \equiv \psi_0(r_\perp, z) = e^{2\pi i K z} \phi_0(r_\perp, z),$$  \hspace{1cm} (2.16)

where the refraction corrected wave vector is

$$K^2 = k_0^2 + \frac{m}{2\pi^2 \hbar^2} \bar{V}_0$$ \hspace{1cm} (2.17)

and using the definition for the mean inner potential as

$$V_0 = -\frac{1}{V} \int_V H_{00}(r) dr,$$ \hspace{1cm} (2.18)

for a crystal volume $V$. The variation of the potential about its mean is then

$$V(r) \equiv -H_{00}(r) - V_0.$$ \hspace{1cm} (2.19)

Using Eqs. 2.15, 2.16 and 2.18 in Eq. 2.13 after applying the paraxial approximation [84], where we discard the second derivative in $z$ and neglect back scattering, we obtain the paraxial Schrödinger equation with a projected absorptive potential,

$$4\pi i K \frac{\partial \phi_0(r_\perp, z)}{\partial z} + \nabla_\perp^2 \phi_0(r_\perp, z) + \frac{2m}{\hbar^2} V(r_\perp) \phi_0(r_\perp, z) + \frac{2mi}{\hbar^2} V'(r_\perp) \phi_0(r_\perp, z) = 0.$$ \hspace{1cm} (2.20)

It is understood that $\nabla_\perp$ refers to the gradient operator of the two-dimensional spatial variable $r_\perp$ which is parallel to the entrance surface of the specimen.

### 2.3 Solution of the paraxial Schrödinger equation

The solution for the fast electron wave function $\psi_0$ in Eq. 2.20 can be calculated using many methods (see for example Sec 4.4 in Ref. [85]). The work presented in the subsequent chapters of this thesis uses the Bloch wave [15] and the multislice [86] methods. Both of these methods with their respective approximations give almost identical numerical wave functions. Thus questions regarding which is preferred should be made on a pragmatic basis. The Bloch wave method exploits
the periodic nature of crystalline specimens much more readily than the multislice method can and in this situation can be significantly more efficient for calculations. Conversely, as the multislice method makes no direct assumptions regarding the sample periodicity it can also be more efficient for calculations simulating electron scattering from non-periodic objects.

2.3.1 The focused electron probe

We begin with a description of the electron probe in scanning transmission electron microscopy (STEM). The STEM probe is a focused collapsing spherical wave containing coherent distortions. The probe can be modelled in momentum space as,

\[ T(q) = A(q)e^{-i\frac{2\pi}{q} \chi(q)}, \quad (2.21) \]

a product of the aperture pupil function \( A(q) \) whose radius limits the range of transverse momentum components contained within the probe and the phase transfer function \( \chi(q) \) which describes the aberrations of the lens. It has been known for some time that all rotationally symmetric lenses contain spherical aberrations \[ 87 \] and much work has been devoted to both lens design in minimising these aberrations \[ 88 \] and more recently in their correction \[ 9, 10, 55, 89 \]. The most general form of the aberration function \( \chi(R, q, \lambda) \rightarrow \chi(r, \alpha, q, \theta, \lambda) \) is \[ 55, 90 \] \[ \chi(r, \alpha, q, \theta, \lambda) = \sum c_{m+1}^{m,va} \cos(v\alpha)r^m(\lambda q)^{m+1} \cos(n\theta), \quad (2.22) \]

where \( r \) and \( \alpha \) are polar spatial co-ordinates defined in the sample plane and \( q \) is the magnitude of the reciprocal space vector \( q \) and \( \theta \) the beam angle indicated as shown in Fig. 2.1. In the work that follows we consider the simplified case of rotationally invariant aberrations such that the labels \( a \) and \( b \) and associated quantities disappear. Furthermore the position dependent scanning aberrations are also neglected. With these assumptions we define the aberration function to be

\[ \chi(q, \lambda) = \frac{1}{2} \Delta f(\lambda q)^2 + \frac{1}{3} C_s(\lambda q)^4 + \frac{1}{6} C_5(\lambda q)^6. \quad (2.23) \]

\[ ^1 \text{There are two mutually orthogonal contributions for non axially symmetric aberrations which are denoted with the sub/super-scripts } a \text{ and } b. \text{ In Eq. } 2.22 \text{ replacing the label } a \text{ with } b \text{ requires a change of } \cos \text{ to } \sin. \]
Figure 2.1: Schematic diagram of the electron probe defined with the optic axis located in the lower left corner. The probe position $\mathbf{R}$, is defined as $\mathbf{R} = (r, \cos(\alpha))$.

The coefficients $\Delta f$, $C_s$ and $C_5$ correspond to defocus, 3rd and 5th order spherical aberrations respectively and are denoted in Eq. 2.22 with the coefficients $C_{1,0}$, $C_{3,0}$ and $C_{5,0}$. The real space STEM probe is then modelled using Eq. 2.21 as

$$T(r_\perp, \mathbf{R}) = \sum_q T(q)e^{-2\pi i q \mathbf{R}}e^{2\pi i q r_\perp}. \quad (2.24)$$

The position of the probe is accounted for with the inclusion of a phase term involving $\mathbf{R}$ using the Fourier shift theorem.

### 2.3.2 Bloch wave

Beginning with the paraxial wave equation in Eq. 2.20 and absorbing constants into the potential terms we have

$$4\pi i K \frac{\partial \phi_0(r)}{\partial z} + \nabla_\perp^2 \phi_0(r) + 4\pi^2 [U(r_\perp) + iU'(r_\perp)] \phi_0(r) = 0, \quad (2.25)$$

where

$$U(r_\perp) = \frac{m}{2\pi^2 \hbar^2} V(r_\perp) \quad \text{and} \quad U'(r_\perp) = \frac{m}{2\pi^2 \hbar^2} V'(r_\perp). \quad (2.26)$$
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For a crystalline specimen satisfying the condition

$$U(r_{\perp}) + iU(r_{\perp}) = U(r_{\perp} + \mathbf{\Upsilon}) + iU(r_{\perp} + \mathbf{\Upsilon}), \quad (2.27)$$

where $\mathbf{\Upsilon}$ is any lattice translation vector, the potential can be expanded in a Fourier series

$$U(r_{\perp}) + iU'(r_{\perp}) = \sum_{g \neq 0} U_g e^{2\pi i g \cdot r_{\perp}} + i \sum_{g} U'_g e^{2\pi i g \cdot r_{\perp}}. \quad (2.28)$$

We can exploit the crystal periodicity by using Bloch’s theorem [91]. Expressing the total fast electron wave function as a sum of Bloch states with excitation amplitude $a_i$,

$$\phi_0(r_{\perp}, z) = \sum_i a_i e^{2\pi i \lambda^i z} \sum_g C^i_g e^{2\pi i (K^i + g) \cdot r_{\perp}}, \quad (2.29)$$

where $g$ is a reciprocal lattice vector, the eigenvalue of each Bloch state is $\lambda^i = \gamma^i + i\eta^i$ with $\gamma^i$ the anpassung and $\eta^i$ the absorption coefficients. The associated wave vector of each Bloch state is $K^i$ and the $C^i_g$ is the $g^{th}$ order coefficient of the $i^{th}$ Bloch state. Using these constraints the Schrödinger equation can be cast into the eigenvalue problem [92–95]

$$\mathcal{A} \mathcal{C} = \mathcal{C} \left[2K\lambda^i\right]_{D}, \quad (2.30)$$

where the structure matrix $\mathcal{A}$ is constructed from the Fourier coefficients $W_g = U_g + iU'_g$ of the potential and is defined as

$$\mathcal{A} = \begin{pmatrix}
\vdots & -(k_{\perp}^2 + h^2 + iU_0') & W_{h-g} & W_h & W_{h+g} & W_{2h} & \vdots \\
\vdots & W_{g-h} & -(k_{\perp} + g)^2 + iU_0' & W_g & W_{2g} & W_{g+h} & \vdots \\
\vdots & W_{-h} & W_{-g} & -(k_{\perp} + h)^2 + iU_0' & W_{-g+h} & \vdots \\
\vdots & W_{-g-h} & W_{-2g} & W_{-g} & -(k_{\perp} + g)^2 + iU_0' & \vdots \\
\vdots & W_{-2h} & W_{-h-g} & W_{-h} & W_{-h+g} & -(k_{\perp} + h)^2 + iU_0' & \vdots \\
\end{pmatrix}. \quad (2.31)$$

The ordering of the columns and rows in $\mathcal{A}$ is arbitrary and can be chosen to display particular symmetries pertaining to the structure. We use the convention of Allen et al. [94, 95]. The $\mathcal{C}$ matrix contains the eigenvectors of $\mathcal{A}$ and the matrix $[2K\lambda^i]_{D}$, which is diagonal as denoted by the subscript $D$, contains the complex eigenvalues $\lambda^i$. Using continuity of the wave function at the entrance surface the excitation
amplitudes are found to be \( a_i = [C^{-1}]_i \) (the \( i^{th} \) element in the central column of \( C^{-1} \)) [85]. Thus by solving the eigenvalue equation the amplitude of the elastic beam composing the electron wave function at depth \( t \) can be obtained from Eq. 2.29. Therefore

\[
v_g(t) = \sum_i a_i C_i^e e^{2\pi i \lambda t}.
\]  

(2.32)

The matrix equation relating the vector representation of the entrance and exit surface wave functions, represented as \( u \) and \( v \) respectively, is then

\[
v = Su.
\]  

(2.33)

The \( S \)-matrix acts as an operator on the incident wave function and propagates it through the crystal and has the form

\[
S = e^{intA/K} = C\left[e^{2\pi i \lambda t}\right] D C^{-1}.
\]  

(2.34)

**Block diagonalisation**

Up to this point the form of the incident wave function is quite general. For plane wave incidence and for the exact zone axis orientation we have the incident beam composing the wave function defined as \( u = \delta_{g,0} \). The Laue condition requires that the scattered electron wave vector (for elastic scattering) must differ by a physical reciprocal lattice vector \( G \). Thus we restrict the set of \( g \) vectors used in constructing the \( S \) matrix to the physical reciprocal lattice vectors. This ensures that all the off diagonal elements in the \( A \) matrix are non-zero as the vector difference \( g - h \) is always a physical reciprocal lattice vector. STEM is slightly different in that the incident wave function is now a coherent superposition of plane waves. At high resolution the incident wave function is described using a nearly continuous set of reciprocal vectors \( g \). Taking the nearly continuous set of vectors \( q_l \) that lie in the first Brillouin zone allows the unique construction of any reciprocal space vector, \( g \), via the relation \( g = G + q_l \). Invoking the Laue condition requiring that any single momentum component comprising the STEM wave function can only scatter to reciprocal vectors which differ by a physical reciprocal lattice vector \( G \) means the \( A \)-matrix in Eq. 2.31 will only contain non-zero entries \( W_{g-h} \) when the continuous
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set of vectors differ by a physical $\mathbf{G}$:

$$W_{\mathbf{g} - \mathbf{h}} = W_{\mathbf{G} - \mathbf{H}} \delta_{l,m},$$

(2.35)

where $q_l$ and $q_m$ are elements of the set $q$. The Laue condition implies that for a STEM wave function incident onto a periodic specimen the $A$-matrix can be reordered in block diagonal form [97, 98], with each block having the same $q_l$ such that for STEM Eq. 2.30 is now

$$2K \begin{pmatrix} [A(q_1)] & [0] & \ldots & [0] \\ [0] & [A(q_2)] & \ldots & [0] \\ \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \ldots & [A(q_m)] \end{pmatrix} \begin{pmatrix} [C(q_1)] & [0] & \ldots & [0] \\ [0] & [C(q_2)] & \ldots & [0] \\ \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \ldots & [C(q_m)] \end{pmatrix} = \begin{pmatrix} [\lambda(q_1)] & [0] & \ldots & [0] \\ [0] & [\lambda(q_2)] & \ldots & [0] \\ \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \ldots & [\lambda(q_m)] \end{pmatrix}.$$ 

(2.36)

Thus it follows from Eq. 2.34 that the STEM $S$-matrix is also block diagonal. The exponentiation of a matrix can be achieved in many ways (for 19 dubious methods see Ref. [99]). As the Bloch wave method explicitly diagonalises the $A$ matrix to determine the Bloch states, one way of calculating the $S$ matrix amounts to the diagonalisation of the $l \times m$, sub-matrices contained in the $A$ matrix.

**Boundary conditions and excitation amplitudes**

The equivalence of global and phase-linked plane wave boundary conditions has been discussed extensively in Refs. [80, 100, 101]. Thus by using continuity of the wave function at the entrance surface it is expected that the excitation amplitudes in Eq. 2.29 will now depend on the phase distortion and position $R$ of the focused probe. Using Eq. 2.29 in conjunction with Eq. 2.24 the excitation amplitudes at the
entrance surface are given by the overlap integral,

\[ a_i(R) = \int \phi_i^*(r_\perp, z = 0) T(r_\perp, R) dr_\perp, \quad (2.37) \]

such that the position dependent excitation amplitude is [97, 102],

\[ a_i(R) = \sum_g [C^{-1}]_g^i \sum_q T(q) e^{-2\pi iqR} \int e^{2\pi i(q-g) \cdot r_\perp} dr_\perp. \quad (2.38) \]

Evaluating the integral in Eq. 2.38 and summing over all \( q \) reduces the excitation amplitude expression to

\[ a_i(R) = \sum_g [C^{-1}]_g^i T(g) e^{-2\pi igR}. \quad (2.39) \]

**Summary**

Using Eq. 2.39 in Eq. 2.32 allows dynamical calculation of the elastic STEM wave function at the exit surface of the specimen. The attenuation of the elastic wave function due to thermal scattering is accounted for via the complex potential in Eq. 2.20. Using the Bloch wave method allows the rapid calculation of the elastic wave function at the exit surface of a periodic specimen.

**2.3.3 Multislice**

An alternative approach to solving Eq. 2.25 can be elucidated using the physical optics approach of Cowley and Moodie [86]. In this method a three dimensional potential field is approximated by a series of closely spaced two dimensional potential distributions. Recasting the paraxial Schrödinger equation in Eq. 2.25 into the operator equation,

\[ \frac{d\phi_0(r_\perp, z)}{dz} = Q \phi_0(r_\perp, z), \quad (2.40) \]

the solution is

\[ \phi(z) = e^{Qz} \phi_0(r_\perp, 0). \quad (2.41) \]
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The operator $e^{Qz} = e^{(A + B)z}$, where $A = \frac{i}{4\pi K} \nabla_\perp^2$ and $B = \frac{i}{K} \tilde{U}(r_\perp)$, can be written as

$$e^{Qz} = e^{\frac{i}{4\pi} \nabla_\perp^2 z} e^{\frac{i}{K} \tilde{U}(r_\perp) z} + \frac{1}{2} \left[ \frac{i\pi}{K} \tilde{U}(r_\perp), \frac{i}{4\pi K} \nabla_\perp^2 \right] z^2 + O(z^3), \quad (2.42)$$

where $\tilde{U}(r_\perp) = U(r_\perp) + iU'(r_\perp)$. Henceforth it is assumed that for sufficiently small values of $z$ the error introduced from the commutation of the operators $A$ and $B$ is negligible. A subtle point not made explicit is that the projection distance of the potential $\tilde{U}(r_\perp)$ is the same as the propagation distance $z$, the consequences if this is not the case is discussed in the following section. Thus if the wave function is known at the depth $z$ then the wave function at the depth $z + \Delta z$ can be found using Eq. 2.42 to 1st order in $\Delta z$. Substituting it into Eq. 2.41 we obtain

$$\phi(r_\perp, z + \Delta z) = e^{\frac{i}{4\pi} \nabla_\perp^2 \Delta z} e^{\frac{i}{K} \tilde{U}(r_\perp) \Delta z} \phi(r_\perp, z). \quad (2.43)$$

Setting $\rho(r_\perp) = e^{\frac{i}{K} \tilde{U}(r_\perp) \Delta z}$ in the definition $\zeta(r_\perp, z) = \rho(r_\perp) \phi(r_\perp, z)$, and using a standard property of exponentials allows the wave function at depth $z + \Delta z$ to be written as

$$\phi(r_\perp, z + \Delta z) = \sum_n \frac{1}{n!} \left( \frac{i \nabla_\perp^2 \Delta z}{4\pi K} \right)^n \zeta(r_\perp, z)$$

$$= \sum_n \frac{1}{n!} \left( \frac{i \Delta z}{4\pi K} \right)^n (\nabla_\perp^2)^n \zeta(r_\perp, z). \quad (2.44)$$

Realising that the function $\zeta(r_\perp)$ can be written in terms of the inverse Fourier transform of the function $Z(q_\perp)$,

$$\zeta(r_\perp) = \int Z(q_\perp) e^{2\pi i q_\perp \cdot r_\perp} dq_\perp, \quad (2.45)$$

the action of the Laplacian operator on the wave function can be described using the operation,

$$(\nabla_\perp^2)^n \zeta(r_\perp) = (-1)^n \int (2\pi q_\perp)^2^n Z(q_\perp) e^{2\pi i q_\perp \cdot r_\perp} dq_\perp. \quad (2.46)$$
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Using the standard definitions

\[ Z(q_{\perp}) = \mathcal{F}\{\zeta(r_{\perp})\} \]

\[ \mathcal{F}^{-1}\left\{ (2\pi q_{\perp})^{2n} \right\} = \int (2\pi q_{\perp})^{2n} e^{2\pi i q_{\perp} \cdot r_{\perp}} \, dq_{\perp}, \]  

(2.47)

in Eq. 2.46 we find

\[ (\nabla_{\perp}^2)^n f(r_{\perp}) = \mathcal{F}^{-1}\left[ (2\pi q_{\perp})^{2n} \mathcal{F}\{\zeta(r_{\perp})\} \right] (-1)^n. \] 

(2.48)

Using Eq. 2.48 in 2.44 the wave function at a depth \( z + \Delta z \) can be written as

\[ \phi(r_{\perp}, z + \Delta z) = \sum_n \frac{1}{n!} \left( \frac{i \Delta z}{4\pi K} \right)^n \mathcal{F}^{-1}\left[ (2\pi q_{\perp})^{2n} \mathcal{F}\left\{ e^{i\bar{U}(r_{\perp}) \Delta z} \phi(r_{\perp}, z) \right\} \right] (-1)^n. \] 

(2.49)

Simplifying Eq. 2.49 reveals the multislice equations

\[ \phi(r_{\perp}, z + \Delta z) = \mathcal{F}^{-1}\left[ e^{-\frac{i \Delta z q_{\perp}^2}{K}} \mathcal{F}\left\{ e^{i\bar{U}(r_{\perp}) \Delta z} \phi(r_{\perp}, z) \right\} \right]. \] 

(2.50)

Or more succinctly, using the convolution theorem,

\[ \phi(r_{\perp}, z + \Delta z) = \xi(r_{\perp}) * \zeta(r, z), \] 

(2.51)

where \( \xi(r_{\perp}) \) is the inverse Fourier transform of the first exponential which is the free space propagator in the paraxial approximation,

\[ \Xi(q_{\perp}, \Delta z) = e^{-\frac{i \Delta z q_{\perp}^2}{K}}. \] 

(2.52)

Thus using the multislice equation we can operationally solve for the elastic wave function in the crystal as a function of depth. It is tempting when using the multislice equations to attempt to visualise the probe propagating in time from the entrance surface to exit surface. Note however that we are in a time independent picture. The wave function at a particular depth in the crystal is solved only by knowing the effect of the potential acting on the wave function in prior slices nearer to the entrance surface.
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2.3.4 Laue zones and the multislice slicing problem

The Bloch wave and multislice methods solve the paraxial Schrödinger equation with a local absorptive potential Eq. 2.20. Intuitively we justify this by considering that electrons that have been scattered inelastically are now incoherent with those that have scattered elastically. For coherent imaging techniques this allows us to consider the inelastically scattered electrons as being removed from the elastic scattering channel. By including a probability sink for the elastically scattered electron flux we neglect where the inelastically scattered electrons are scattered to and thus their contribution to the final image. It is argued that the improvement in the accuracy of the elastic wave function obtained by removing these electrons is greater than their contribution to the detected signal. Here we consider the accuracy of computing the elastic wave function in the context of the multislice equations.

In the multislice approach, the projected potential in Eq. 2.20 is replaced with a series of scattering planes onto which the average potential in the slice between \( z \) and \( z + \Delta z \) is projected. Free space propagation occurs between these planes. In the limit that \( \Delta z \to 0 \) and \( n \to \infty \) such that \( n\Delta z = Z \), where \( Z \) is the length of the specimen, the theory is exact. It effectively calculates the elastic wave function for a continuous cylinder of potential along the length of the specimen. By necessity, numerical calculations do not allow arbitrarily small propagation distances. This is observed with the error terms in Eq. 2.42.

In a zero order Laue zone calculation the natural \( z \) direction repeat of the crystal is used for the projection and propagation distance. The conventional multislice calculation may have intolerable errors present as this \( \Delta z \) may be large enough to cause the error terms in Eq. 2.42 to become appreciable. One approach to reduce this error is to further subslice the scattering potential such that the \( \Delta z \) now consists of \( N \Delta z/N \) steps.

Denoting the projected potential for the natural unit cell repeat distance, \( c \), as \( U(\mathbf{r}_\perp) \) the phase grating function for the full projected potential is

\[
\rho(\mathbf{r}_\perp, c) = e^{i \frac{K}{c} U(\mathbf{r}_\perp)}.
\] (2.53)

Dividing the multislice steps such that we now have \( N \) steps per repeat distance
plexical Schrödinger equation
implies
\[ \rho \left( r_\perp, \frac{c}{N} \right) = e^{i\frac{\pi}{N}U(r_\perp)} \frac{1}{N}. \]  
(2.54)

We have applied the average projected potential over \( N \) slices. The propagation function, using Eq. 2.52, is now
\[ \Xi \left( q_\perp, \frac{c}{N} \right) = e^{-\frac{i\pi q_\perp^2}{N}}, \]  
(2.55)

so that the conventional multislice expression, after a single slice for an incident probe wave function \( P(R, r_\perp) \), is
\[ \phi_1(r_\perp) = \xi \left( r_\perp, \frac{c}{N} \right) \ast \left[ P(R, r_\perp) \rho \left( r_\perp, \frac{c}{N} \right) \right]. \]  
(2.56)

For analytical analysis we make the following reasonable assumptions. Firstly we assume that the single scattering approximation holds for each multiplication of the phase grating,
\[ \rho(r_\perp, c/N) \approx 1 + i\frac{\pi}{K}U(r_\perp) \frac{c}{N}. \]

Secondly the probe is assumed to be sufficiently broad relative to the potential so that \( P(R, r_\perp)U(r_\perp) \approx P(R, 0)U(r_\perp) \) and finally, that the probe evolves sufficiently slowly so that \( \xi(r_\perp, c/N) \ast P(R, r_\perp) \approx P(R, r_\perp) \). Using these assumptions we find that Eq. 2.56 reduces to
\[ \phi_1(r_\perp) = P(R, r_\perp) + i\frac{\pi}{K} \frac{c}{N}U(r_\perp) \ast \xi \left( r_\perp, \frac{c}{N} \right). \]  
(2.57)

To obtain the wave function at the \( N^{th} \) slice we iterate \( N \) times. Discarding all nonlinear terms and concatenating the propagators together we obtain
\[ \phi_{N}(r_\perp) = P(R, r_\perp) + i\frac{\pi}{K} \frac{c}{N}U(r_\perp) \ast \left[ \sum_{n=1}^{N} \xi \left( r_\perp, \frac{nc}{N} \right) \right], \]  
(2.58)

which can be written in reciprocal space using Eq. 2.55 as
\[ \Psi_{N}(q_\perp) = \bar{P}(R, q_\perp) + i\frac{\pi}{K} \frac{c}{N} \bar{U}(q_\perp) \sum_{n=1}^{N} e^{-i\pi q_\perp^2 \frac{nc}{N}}. \]  
(2.59)

Equation 2.59 with its many assumptions reveals interesting behavior associated
with the multislice equations. For small scattering angles, the term in the sum in Eq. 2.59 is approximately unity. This reduces the above expression to the single scattering approximation applied to the whole unit cell in a single step ($N = 1$). At larger scattering angles, the terms in the summation begin to oscillate rapidly, reducing the quantity of scattering to high angles compared to that which would be produced by the application of a single phase grating and propagation across the unit cell. The effect of the attenuation of the high angle scattering can be seen in Fig. 2.2. Figure 2.2 shows the scattering from a single O atom placed in free space for a scattering potential subsliced (a) 1, (b) 2, (c) 4 and (d) 8 times per 4 Å repeat distance. Inelastic scattering as well as methods to include the thermal motion of the atom have not been included in Fig 2.2 and it has been plotted as a function of the fraction of the incident beam current scattered to a specific angle. Figure 2.2 shows explicitly the damping of the elastic scattering out to high angles as a consequence of subslicing the scattering potential. As the number of subsliced potential increases the oscillation term in Eq. 2.59 increases in frequency and the attenuation gets more severe.

Initially, it may seem that in certain circumstances it is impossible to simultaneously keep $\Delta z$ sufficiently small such that the error term in Eq. 2.42 is negligible without subslicing the scattering potential. However, Goodman and Moodie [103] demonstrated that the slice thickness need not necessarily correspond to atomic spacings or repeat distances. Furthermore, by using different potentials for the different atomic planes comprising the crystal allows for the inclusion of higher order Laue zone (HOLZ) effects [104]. This may however permit the appearance of false HOLZ lines if the slice thickness does not match the natural repeat distance of the specimen. Kilaas et al. [105] suggested that the optimum way to avoid false HOLZ lines was to calculate the full three-dimensional atomic potential and perform the projection integral for $U(r)$ over the suitably small multislice thickness $\Delta z$. This approach would ensure that the correct scattering potential in the region $z$ to $z + \Delta z$ is applied over a single phase grate. Simultaneously ensuring that no false HOLZ lines are present and that the calculated scattering out to high angles is correct, unlike Fig. 2.3. The results of one such calculation are shown in Fig. 2.3 where the unit cell is now divided into distinct potential slices with the correct projection replacing the previously used average over the unit cell. In Fig. 2.3 the three-dimensional potential was calculated with 128 sampling points over the 4 Å repeat distance $c$. 

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Figure 2.2: Scattering distribution from a single O atom’s projected potential subsliced (a) 1, (b) 2, (c) 4 and (d) 8 times per 4 Å repeat distance. The aberration free 100 keV STEM probe forming aperture semi-angle was 25 mrad. Calculations were performed on a 2048 × 2048 pixel grid for a 30 Å × 30 Å supercell.
The projection was then performed by summing the pixels in the region of each subdivision. Figure 2.3(a) shows that the full three-dimensional calculation with 16 distinct potentials returns similar results as the single projection result (1 distinct potential). The percentage difference between the three-dimensional and single projection is shown in Fig. 2.3(b). The difference begins to significantly diverge at the highest angles although, appreciating the logarithmic scale in Fig. 2.3(a), the numerical effect is small. The effect on high resolution transmission electron microscopy (HRTEM) calculations of the three dimensional potential is anticipated to be small, as the contribution to the image from electrons that have been scattered to high angles is negligible as the effective aperture, either real or virtual, as defined by partial coherence and the associated envelope functions removes these electrons from the image forming process. This is similar to the way that upper layer Laue zones are excluded from images, albeit through different mechanisms.
2.3. SOLUTION OF THE PARAXIAL SCHRÖDINGER EQUATION

2.3.5 Thermal scattering

As was stated in Sec. 2.2, the dominant form of inelastic scattering that modifies the elastic intensity is phonon scattering which is typically out to high angles and is commonly termed thermal diffuse scattering (TDS). Many methods to incorporate TDS in electron scattering calculations have been proposed [47, 106–111]. In this section we introduce the Fourier coefficients of the imaginary absorptive potential as well as discussing the frozen phonon algorithm. In light of the preceding section we shall discuss and explore practical computation using the frozen phonon algorithm in the multislice algorithm.

The absorptive coefficients

The Fourier coefficients of the absorptive potential using an Einstein model are [47, 81, 93, 112]

\[
\mu_{h,g} = \frac{\hbar}{4\pi^2 V_c} \sum_\alpha e^{2\pi i (g-h) \cdot \tau_\alpha} \int f_\alpha(q + g) f_\alpha^*(q + h) \times \left[ e^{-M_\alpha(g-h)} - e^{-M_\alpha(q+g) - M_\alpha(q+h)} \right] d\Omega.
\]  

(2.60)

For a local absorptive potential like that in Eq. 2.20 the Fourier coefficients become

\[
\mu_{h,0} = \frac{1}{4\pi^2 V_c} \sum_\alpha e^{-2\pi i h \cdot \tau_\alpha} \int f_\alpha(q) f_\alpha^*(q + h) [e^{-M_\alpha(h)} - e^{-M_\alpha(q) - M_\alpha(q+h)}] d\Omega.
\]  

(2.61)

In Eqs. 2.60 and 2.61 the term \(M_\alpha\) denotes the Debye-Waller factor and is \(M_\alpha(q) = 2\pi^2 \langle u^2 \rangle q^2\), where \(\langle u^2 \rangle\) is the projected mean square thermal displacement, for the atom type \(\alpha\) at position \(\tau_\alpha\) in a unit cell of volume \(V_c\). To calculate the total absorption due to phonon scattering the integration in Eqs. 2.60 and 2.61 is taken over the full solid angle. Restricting the range of integration in Eq. 2.61 to some high angle annular dark field (HAADF) collection angle, and monitoring the proportion of the incident beam which is lost in a calculation as a function of probe position allows the calculation of a STEM HAADF image [113].

For the theory shown thus far, where the potential has an imaginary component to account for anomalous absorption due to thermal scattering, the elastic potential accounts for the initial thermal state of the crystal atoms by including a Debye-
Waller factor in the elastic potential at the scattering site. This smears the elastic potential and limits elastic scattering out to high angles. Thus the high angle damping shown in Eq. 2.59 and Fig. 2.2 (b)-(d) is unable to manifest itself. (We remind the reader that the results in Figs. 2.2 and 2.3 were obtained without thermal motion of the target atom, and thus no Debye-Waller factor. The improvement in the accuracy of the elastic wave function attained by subdividing the unit cell (and thus minimising the multislice error term in Eq. 2.42) is greater than the error introduced by subslicing, for the calculation of scattering cross sections which critically rely upon accurate elastic wave functions this is an important detail.

The frozen phonon algorithm

An alternative and particularly successful method to incorporate phonon scattering in a quantitative manner is known as the frozen phonon method [72, 106, 114]. This model does not make a distinction between orthodox elastic and inelastic phonon scattering and treats both processes concurrently. The frozen phonon method performs a Monte Carlo integration over the elastically scattered electron wave functions produced by different atom configurations. The crystal potential is not smeared by a Debye-Waller factor as it is argued that modelling the finite temperature of the crystal accurately models elastic scattering which importantly, as there is no distinction between inelastic phonon and elastic scattering, effectively includes inelastic phonon scattering to all orders.

In the frozen phonon method the elastic (including phonon scattered) electron intensity in reciprocal space, \(I(q)\), is [106]

\[
I(q) = \int P_e(q|D) P_a(D) dD, 
\]

(2.62)

where \(D\) is the instantaneous displacement of the atoms in the specimen, \(P_a(D)\) is the probability of a particular configuration and \(P_e(q|D)\) is the probability of finding the incident electron at point \(q\) in the diffraction pattern for a given configuration \(D\). As the interaction time (classically or quantum mechanically) is much smaller than the vibration period of the lattice sites the scattering potential at the lattice sites is static and each experiment (i.e. elastic electron wave) is uncorrelated with respect to the last. The integral in Eq. 2.62 is performed using Monte Carlo
2.3. SOLUTION OF THE PARAXIAL SCHRÖDINGER EQUATION

methods and the atom position is the vector sum of $3N$ normal modes of vibration which can be evaluated using varying models of phonon dynamics \[115\].

As in the previous section we shall use the Einstein model where the probability distribution of the simple harmonic oscillator displacement associated with each atom is, as a function of temperature $T$ \[106\],

$$P_1(D, T) = \left[\frac{\omega m}{\pi \hbar} \tanh\left(\frac{\hbar \omega}{2k_B T}\right)\right]^{1/2} e^{-\left(\frac{\omega m}{\pi \hbar}\right) D^2 \tanh\left(\frac{\hbar \omega}{2k_B T}\right)}$$  \(2.63\)

or

$$P_1(D, T) = \left(\frac{\nu}{\pi}\right)^{1/2} e^{-\nu D^2}$$  \(2.64\)

with

$$\nu = \left(\frac{\omega m}{\pi \hbar}\right) \tanh\left(\frac{\hbar \omega}{2k_B T}\right),$$  \(2.65\)

where the mean square atomic displacement, which can be measured experimentally, is the standard deviation of the probability Gaussian $P_1$, the frequency of oscillation of each atom of mass $m$ is $\omega$ and $k_B$ is Boltzmann’s constant. Recently Muller et al. \[115\] implemented correlated phonon modes, demonstrating their importance in explaining fine details in CBED patterns. However, for STEM imaging where regions of the diffraction pattern are integrated over, these fine details are of little quantitative importance.

As the frozen phonon algorithm is most typically solved using multislice techniques the absence of a Debye-Waller factor significantly enhances the algorithms sensitivity to subslicing, especially for STEM HAADF calculations which critically rely on accurate high angle scattering. The effect of full three-dimensional frozen phonon calculations, in the Einstein model, is somewhat less clear. When we consider Fig. 2.3, it is anticipated that the quantitative effect of implementing fully three-dimensional frozen phonon calculations in STEM will be small.

The effect of including a three-dimensional atomic potential for a crystalline sample thicker than a single unit cell is shown in Fig. 2.4. The calculation includes thermal vibrations for a toy sample consisting of simple cubic Pb. The sample was 500 Å thick with each unit cell having the dimensions $4 \times 4 \times 4$ Å. It was chosen so that the multislice error from propagating through such a large repeat distance would have a sufficient number of slices to be observable. Conversely, the fully three-dimensional calculation had a propagation distance of only 0.125 Å.
with the correct scattering potential calculated for each subslice. The differences in the azimuthally averaged CBED patterns (Fig. 2.4(a)) only become pronounced, once again, at larger scattering angles, far beyond the inner angle typically seen in HAADF detectors. Looking at the percentage difference in Fig. 2.4 we see that at lower angles the difference is small and is most likely a consequence of the multislice commutation error ($O(z)$ in Eq. 2.42). It should be appreciated that the computation time for the three-dimensional calculation was at least an order of magnitude greater than the conventional projection of the full atomic potential into a single plane calculation. The differences between the methods, whilst not zero, are still small and one must be pragmatic when deciding between computational and accuracy considerations.

2.4 Discussion and conclusions

Beginning from the non-relativistic Schrödinger equation we have have derived, using the Yoshioka equations, a way to calculate the elastically scattered probe wave function which includes the effect of the inelastic channels on the elastic channel. Making suitable approximations we obtained the paraxial Schrödinger equation with an imaginary absorptive potential which can be solved using two different methods: Bloch wave and multislice. The infinite expansion of the wave function using Bloch waves is in practice limited to some finite number of beams $N$. For simple periodic structures with plane wave illumination the number of beams required for accurate simulations is small. Using a focused coherent probe for illumination introduces an aperiodicity which necessitates the use of supercells and thus increases the number of beams required. As the calculation of eigenvectors and values scales as $N^3$ this increases computation time significantly. Using block diagonalisation reduces the problem to solving the $l \times m$ plane wave $N$-beam problem. The aperiodicity of the crystal caused by the displaced atoms in the frozen phonon method prevents block diagonalisation, and this coupled to the increased amount of high angle scattering which increases the number of beams required for a calculation prevents Bloch wave from implementing the frozen phonon algorithm efficiently.

Using the convolution theorem allows the rapid numerical solution of the multislice equations using fast Fourier transforms (FFTs). Furthermore, the parallel
Figure 2.4: (a) The scattering distribution for a toy sample consisting of simple cubic Pb for the full three-dimensional atomic scattering potential projected over 1 (dashed line) and 32 (solid line) distinct regions per 4 Å repeat distance. (b) The percentage difference between the two methods. The CBED pattern for (c) 1 projected potential across the unit cell and (d) 32 distinct potentials across the unit cell (displayed on a log scale). The aberration free 100 keV STEM probe forming aperture semi-angle was 25 mrad. Calculations were performed on a $2048 \times 2048 \times 128$ pixel grid for a $30.0 \text{ Å} \times 30.0 \text{ Å} \times 4.0 \text{ Å}$ supercell. The crystal is 500 Å thick.
nature of the FFT algorithm lends itself naturally to a parallel implementation. This favourable scaling with the number of beams provides an efficient framework to implement the frozen phonon algorithm. This chapter discussed and highlighted some of the subtleties in performing an accurate multislice calculation. The projection of the potential and its subsequent subslicing. For numerical multislice calculations was found to have an appreciable effect on the amount of high angle scattering. As the multislice method can incorporate the absorptive and frozen phonon methods to include thermal scattering equally well the significance of this result depends critically on the method chosen. The quantitative effect of subslicing is small when the elastic potential is smeared by a Debye-Waller factor and an imaginary absorptive potential is used. When the frozen phonon model is used, which depends critically on accurately calculating the amount of high angle scattering, the slicing scheme was found to have some effect which would manifest itself in STEM HAADF simulations. Finally, the difference between projecting the full atomic potential into a single plane or calculating the full three-dimensional potential in the frozen phonon model was found to be small.
Quantitative match between theory and experiment in transmission electron microscopy

Image simulation techniques based on the tools in chapter 2 have been remarkably successful in reproducing qualitative electron microscopy image features [116–118]. However, it has long been recognised that the ability to perform quantitative transmission electron microscopy would allow determination of chemical composition, structure and stoichiometry. High resolution transmission electron microscopy (HRTEM) images have always been plagued by a large discrepancy between theory and experiment, which has become known as the Stobbs factor [17]. The Stobbs factor problem being the two to five times discrepancy in contrast predicted by theory and that measured in experimental images. The Stobbs factor persists even for the latest generation of aberration corrected instruments [119, 120]. Because interpretation of HRTEM critically relies on image simulations [13], confidence in the information that is extracted from HRTEM remains questionable as long as theory and experiment are not reconciled. Equally important, the inability to quantitatively describe the experiment raises doubts about the validity of current high-energy electron scattering theories that have been used to interpret electron microscopy images for many decades. In particular, it has been widely speculated that the contrast mismatch in HRTEM is due to an inadequate description of the interaction of fast electrons with the specimen [14, 20, 27].
This chapter presents a significant result of this thesis, quantitative agreement between experiment and theory in electron microscopy images based on elastic scattering without iterative fitting parameters. The ability to place electron microscopy images on an absolute scale has facilitated direct comparisons between theory and experiment in scanning transmission electron microscopy (STEM) high angle annular dark field (HAADF) [30, 32, 121, 122]. We use the combination of quantitative STEM, reciprocity and bright field imaging to address the Stobbs factor problem present in HRTEM. We apply the tools and insights developed in the previous chapter to ensure the accuracy of calculated images. The experimental results in this chapter were obtained through a collaboration with The University of California Santa Barbara and were taken by J.M. LeBeau and S. Stemmer.

3.1 Scanning transmission electron microscopy and its relationship to high resolution transmission electron microscopy via reciprocity

A complementary atomic resolution technique to the plane wave illumination conditions used in HRTEM is bright field scanning transmission electron microscopy (BFSTEM). The quantitative agreement between theory and experimental STEM HAADF images was recently demonstrated [30, 32]. The contrast in a STEM HAADF image is mainly formed from electrons scattered to high angles by TDS [123]. These results, for a range of atomic numbers and specimen thicknesses, strongly support the validity of current models of TDS. The results also suggest an approach for elucidating the cause of the Stobbs factor problem in HRTEM. The following section discusses reciprocity and its theoretical foundation. We then proceed to apply reciprocity in STEM to refine the HRTEM Stobbs factor problem.

3.1.1 Reciprocity, a formal proof

We begin with a statement of the reciprocity theorem, referring to Fig. 3.1:

The amplitude at B of a wave originating from a source A, and scattered by P, is equal to the scattered amplitude at A due to the same source placed at B,
3.1. SCANNING TRANSMISSION ELECTRON MICROSCOPY AND ITS RELATIONSHIP TO HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY VIA RECIPROCITY

![Diagram of HRTEM and STEM](image)

**Figure 3.1:** Reciprocity in the transmission electron microscope. On the left is HRTEM with a plane wave originating at point $A$, on the right is STEM with a convergent beam. The primes on the labels arbitrarily distinguish between HRTEM and STEM.

and was elucidated in these terms by Pogany and Turner [124]. This was quickly followed by Cowley [16] who explained the apparent similarity between STEM and HRTEM diffraction experiments using the reciprocity theorem.

The Bloch wave formalism described in chapter 2 using global boundary conditions for the incident wave function lends itself naturally to illustrate the reciprocity relationship between HRTEM and BFSTEM. This was developed in Findlay *et al.* [97] and is included here for completeness. We begin by considering STEM. Using Eq. 2.21 the incident STEM probe wave function in reciprocal space, at probe position $\mathbf{R}$, is

$$\Psi(\mathbf{q}) = T(\mathbf{q}) e^{-2\pi i \mathbf{q} \cdot \mathbf{R}}. \quad (3.1)$$

The action of transmission through the specimen of thickness $t$ can be achieved using the $S$ matrix (Eq. 2.34), where neglecting absorption means $C^{-1} = C^*$ and

$$S_{g,h} \equiv \sum_i C_{g}^{i} e^{2\pi i \lambda_{l}^{i} t} C_{h}^{i*}. \quad (3.2)$$
So the electron wave function at the exit surface is

$$\Psi_{A'}(p) = \sum_q S_{p,q} T(q) e^{2\pi i q \cdot R} \quad (3.3)$$

The axial bright field detector incoherently sums each diffracted beam intensity:

$$I(R) = \sum_p |\Psi(p)|^2. \quad (3.4)$$

For the special case of a point detector located at $p = 0$ (i.e. totally coherent), the bright field STEM amplitude is

$$A_{STEM}(R) = \Psi(0) = \sum_H \left[ \sum_i C_i^g e^{2\pi i \lambda_i t} C_{0 h}^i \right] T(H) e^{2\pi i H \cdot R}. \quad (3.5)$$

The change of summation variable from $p$ to $H$ is deliberate as, due to the Laue condition, only those momentum components contained in the probe that differ by a physical reciprocal lattice vector can scatter into the bright field detector located at $p = 0$.

Retaining the orientation depicted in Fig. 3.1 for HRTEM, propagation occurs in the negative $z$ direction. This backward propagation can be achieved by acting on the wave function with the inverse operation to forward propagation i.e. $S^{-1}$. Neglecting absorption implies that $S^{-1} \equiv S^\dagger$ as the $S$ matrix is unitary. The adjoint matrix is

$$S_{g,h}^\dagger = \sum_i C_{g}^{i} e^{-2\pi i \lambda_i t} C_{h}^{i*}. \quad (3.6)$$

For a perfectly coherent HRTEM experiment the entrance surface wave function is $\Psi(p) = \delta_{p,0}$. The exit surface wave function is then

$$\Psi_B(H) = \sum_i C_{H}^{i} e^{-2\pi i \lambda_i t} C_{0}^{i*}. \quad (3.7)$$

The real space exit surface wave function at the image plane is

$$A_{HRTEM}(R) = \sum_H \left[ \sum_i C_{H}^{i} e^{-2\pi i \lambda_i t} C_{0}^{i*} \right] T^*(H) e^{2\pi i H \cdot R}. \quad (3.8)$$
the variable $R$ now represents a two-dimensional real space position vector in the plane of the image. Equations 3.5 and 3.8 are simply the complex conjugates of each other. The quantity conjugate by reciprocity to the finite collection aperture size used in the STEM mode is an incoherent angular spread in the incident beam in HRTEM. Introducing spatial incoherence in the HRTEM experiment amounts to the incoherent sum over the incident wave functions. The quantity conjugate to the incoherent angular spread in the incident beam in HRTEM is by reciprocity the finite collection aperture size used STEM. Whilst the preceding derivation demonstrated the intimate relationship between HRTEM and STEM it is only strictly true for elastic scattering into a small collection angle; it has been shown to be an excellent approximation for thermal scattering as well as higher energy losses [124, 125] into point detectors.

### 3.1.2 Partial coherence

The STEM diffraction pattern (also known as the Ronchigram) can be written as a function of probe position as

$$|\Psi_A'(p, R)|^2 = \sum_{g, g'} S_{p, g} \Psi(g) S_{p, g'}^* \Psi^*(g') e^{-2\pi i (g - g') \cdot R}.$$  \hspace{1cm} (3.9)

We denote the combined effect of a finite illumination source size coupled with microscope and sample instabilities as the effective spatial incoherence [72, 126]. The effect of spatial incoherence is to effectively have a spread of point sources located perpendicular to the optical axis. The total intensity in the diffraction plane is thus a weighted integral over the source distribution, which amounts to small displacements about the probe position $R$, such that the Ronchigram is

$$|\Psi_A'(p, R)|^2 = \int \sum_{g, g'} S_{p, g} \Psi(g) S_{p, g'}^* \Psi^*(g') e^{-2\pi i (g - g') \cdot R} S(R) dR$$ \hspace{1cm} (3.10)

$$= \sum_{g, g'} S_{p, g} \Psi(g) S_{p, g'}^* \Psi^*(g') S(g - g').$$

Alternatively we can view this as amounting to a shift of the incident wave function. Since STEM images are constructed from a series of diffraction pattern measurements, this shift in the wave function has, by necessity, already been calculated
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Figure 3.2: Model structure of a SrTiO$_3$ unit cell in (a) a three dimensional perspective and (b) oriented along the [001] zone axis. The Sr atoms are coloured green, the Ti atoms are orange and the O atoms are red.

for the surrounding image pixels. The effect of spatial incoherence in STEM is a convolution with the function $s(R)$ that describes the effective source size, or more precisely, the distribution of point emitters perpendicular to the optical axis [30, 32, 58, 127].

Via reciprocity the finite source size in STEM is equivalent to the finite detector pixel size in the image plane of HRTEM [128]. Historically HRTEM experiments used photographic plates as the recording medium, which has subsequently been replaced with charge coupled devices (CCDs). The modulation transfer function (MTF), which describes the spatial-frequency impulse response of the recording CCD, defines an effective minimum pixel size and is the conjugate HRTEM quantity to the finite source size in STEM.

3.2 Quantitative bright field scanning transmission electron microscopy

In this section we directly compare experimental BFSTEM images of single crystal SrTiO$_3$ measured on an absolute scale to image simulations. A SrTiO$_3$ single crystal was thinned to electron transparency by wedge-polishing and Ar-ion milling for observation along the [100] zone axis. A model of this structure is shown in Fig. 3.2. A field emission electron microscope (FEI Titan 80-300) with a super-twin lens ($C_s = 1.2$ mm) operated at 300 kV was used for BFSTEM imaging. The probe
convergence semi-angle was 9.4 mrad. STEM HAADF images were acquired with a detector inner angle of 65 mrad. BFSTEM images were acquired with a 2.8 mrad collection aperture semi-angle (the HRTEM objective aperture) inserted directly below the sample. Though the aperture size used here is larger than typical HRTEM convergence angles, the transition to a smaller aperture is a well-defined limit [13] and our choice of aperture size therefore does not affect any conclusions regarding the scattering physics. The sample thickness was determined using position averaged convergent beam electron diffraction patterns [32]. BFSTEM simulations were performed using the multislice algorithm that takes into account inelastic thermal scattering using an absorptive potential based on the Einstein model as discussed previously. The calculations used a supercell of $13 \times 13$ unit cells ($50 \text{ Å} \times 50 \text{ Å}$), on a mesh of $1024 \times 1024$ pixels. Experimental BFSTEM images of a SrTiO$_3$ single crystal are shown in the left columns of Fig. 3.3 for a range of thickness and defocus values. The corresponding theoretical simulations are shown in the right hand columns. Contrast reversals and changes in the image pattern occur as a function of defocus and thickness, as is typical for HRTEM images [13]. The labels on each image state its measured/calculated contrast value, defined as the standard deviation of the image intensities about the mean image intensity. In the limit of a two pixel image this reduces to the standard Michelson contrast definition $\frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}}$.

The absorptive calculations give purely elastic images similar to those expected if a perfect energy filter was inserted post specimen. To quantitatively estimate the effect of the inelastically scattered electrons at the exit surface (i.e. those electrons that have excited a crystal phonon), frozen phonon calculations were carried out at strategic points in the parameter space, properly accounting for multiple phonon scattering. Frozen phonon calculations were were done on a finer mesh of $2048 \times 2048$ pixels to make sure that the sharp atomic potentials that occur in that model were adequately sampled. The average of the difference in contrast predicted by the two models was 0.1%, which is significantly less than the experimental error. Figure 3.3 shows that accounting for the finite source (c.f. Sec. 3.1.2 size with the convolution of a Gaussian with a full-width at half-maximum (FWHM) of 1.1 Å gives near perfect agreement of simulations with the experiments across the entire range of thickness and defocus values.

The bottom row in Fig. 3.3 shows HAADF images and comparisons with frozen phonon simulations that have been convolved with a Gaussian accounting for
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Figure 3.3: Experimental BFSTEM images (left panel in each column) compared to multislice absorptive model calculations (right panel in each column). The upper labels in each image show their contrast values. The lower (black background) labels state the defocus, with underfocus being negative. Note that all images are on an absolute intensity scale relative to the incident probe and reported as a fractional intensity. All simulations have been convolved with a Gaussian of 1.1 Å FWHM to account for the effects of a finite source size.
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Figure 3.4: Contrast in BFSTEM images as a function of defocus for region of the sample with thicknesses of approximately 140 Å (experiment) and 140 and 150 Å (simulations). As a visual aid, error bars of ±10% are shown for the experiments. The grey shaded region indicates a range of contrast values that lies between those calculated for the 140 Å and 150 Å thick samples.

Spatial incoherence. The HAADF images were recorded at the same locations as the BFSTEM images. The Gaussian (and associated half-width) which was used to account for spatial incoherence in the BFSTEM simulations has also yielded perfect agreement between simulation and experiment in HAADF imaging. Thus, a FWHM of 1.1 Å provides a realistic approximation for the spatial incoherence in STEM with this instrument (and is similar to others, see for example [31]), and is independent of the image formation and scattering processes, i.e. incoherent HAADF imaging and coherent BFSTEM. The average mismatch factor in contrast between experimental and simulated BFSTEM images was found to be 1.15.

This small residual mismatch is within the experimental uncertainty caused by the noise of the detector, residual astigmatism, drift and, most importantly, the thickness determination (±10 Å). This can be seen more clearly from Fig. 3.4, which, using one thickness dataset as an example, compares the experimental contrast with simulations with a thickness difference of 10 Å over a wide defocus range. The significant differences in contrast for the two thicknesses in Fig. 3.4 highlights the importance of accurate, independent thickness measurements. As the convolution operation conserves intensity, if the total absorption predicted is correct, the mean experimental and simulated image intensities should agree. A plot of the mean
Figure 3.5: Mean fractional intensities of each image as a function of thickness for the BFSTEM experiment.

image intensities for experimental and simulated experiments are shown in Fig. 3.5 and 3.6 exhibit excellent agreement.

3.3 Discussion and conclusions

Using the principle of reciprocity to obtain in STEM an image equivalent to an HR-TEM image provides a new insight into the Stobbs factor problem. The agreement demonstrated between theory and experiment is within the experimental accuracy, and is in sharp contrast to the mismatch of around two to three that has been reported in HRTEM experiments [14, 17, 18, 20]. The agreement is independent of probe defocus and specimen thickness. We considered two different models to account for inelastic thermal scattering that returned almost identical quantitative results. The conclusion is that inelastic scattering, which by reciprocity is present in these images as much as it would be in HRTEM, is not the origin of the contrast mismatch observed in the HRTEM literature for similar specimen thicknesses. The serial nature of the image recording process in STEM coupled to the excellent agreement between theory and experiment seems to suggest that the cause of the contrast mismatch may lie instead in the imaging/detector system used in HRTEM. As was noted previously, through reciprocity, the effective source size in BFSTEM is equivalent to the effective pixel size in HRTEM which is determined by the CCD MTF.
These results add to the evidence that the magnitude of the MTF has been underestimated in prior HRTEM experiments [28]. The MTF is more complex to measure and account for in HRTEM than the simple Gaussian convolution function that accounts for the effective source size in STEM. In the interim, STEM can provide quantitative imaging in both coherent and incoherent imaging modes.
CHAPTER 4

Imaging based on core-loss spectroscopy: theory

The traditional method for atomic-resolution analysis in scanning transmission electron microscopy (STEM) is high angle annular dark field (HAADF). It involves collecting electrons which have been scattered through large angles, usually by interaction with a phonon, and thus resembles in its dependence on atomic number the Rutherford scattering formula [72, 109]. For compositional analysis electron energy-loss spectroscopy (EELS) provides more scope for accurate chemical identification and the exploration of local bonding and other electronic properties [129, 130]. Correlating structural and chemical properties using high-resolution STEM is often carried out by using a HAADF image as a structural reference while recording energy-loss spectra at structurally significantly points [42, 43].

Implementing this is complicated by suggestions that high-resolution STEM images, both HAADF and EELS images, do not always admit direct, visual interpretation. There are three inter-related reasons for this: (i) the elastic scattering or dynamical spreading of the electron probe; (ii) the electron “absorption” (due to phonon excitation); and (iii) the delocalised and partially coherent nature of some inelastic scattering processes, which can lead to a non-intuitive connection between the probe density in the sample and the magnitude of the recorded signal. These complications demand that detailed theoretical simulations accompany experimental results. This chapter presents two methods for calculating electron microscopy images based on core-loss EELS. The theoretical tools developed and reviewed in
CHAPTER 4. IMAGING BASED ON CORE-LOSS SPECTROSCOPY: THEORY

this chapter will be integral to the remaining chapters in this thesis. The first presented is arguably more intuitive and direct to interpret. It is based on the work of Coene and Van Dyck [131] which was first applied to core-loss spectroscopy by Dwyer [48], and shall be referred to as the real space transition potential approach. It is most easily implemented using the multislice algorithm and, when implemented in the STEM framework, can just as easily accommodate aperiodic structures as it can periodic.

The second is that used by Allen and co-workers [43, 45, 56, 80, 100, 102, 132, 133], a reciprocal space method referred to as the mixed dynamical form factor method (MDFF). The MDFF method, when implemented in a Bloch wave calculation scheme, can rapidly calculate core-loss images for a range of thickness and probe parameters for periodic specimens. The MDFF method can also be implemented in a multislice scheme to calculate core-loss images for aperiodic specimens relatively more efficiently than the real space transition potential method. Whilst the final cross section expression for both approaches is equivalent, each method has its own strengths and weaknesses. In this chapter the real space transition potential approach is applied to the imaging at a distance result of Oxley et al. [56] as it gives further insight into the result not immediately clear from simulations using the MDFF approach. The relative merits of each approach is also discussed.

4.1 A real space transition potential approach

We start by considering a fast electron incident onto the surface of a crystal. The evolution of the electron wave function inside the crystal volume can be described using the coupled channels formulation in chapter 2. Restating Eq. 2.6 we have

\[ \nabla^2 \psi_n(r) + 4\pi^2 k_n^2 \psi_n(r) - \frac{2m}{\hbar^2} H_{nn}(r) \psi_n(r) = \sum_{m \neq n} \frac{2m}{\hbar^2} H_{nm}(r) \psi_m(r). \]  (4.1)

These equations can be evaluated in real space using a multislice formulation as described by Coene and Van Dyck [131]. Starting with the ansatz

\[ \psi_n(r) = \phi_n(r)e^{2\pi iknz}, \]  (4.2)
4.1. A REAL SPACE TRANSITION POTENTIAL APPROACH

using the standard paraxial approximation and assuming that the incident electron can only scatter inelastically from the ground state \((n = 0)\) gives the governing equation

\[
\frac{\partial}{\partial z} \phi_n(r) = D_n \phi_n(r) - \Lambda_n \frac{2m}{\hbar^2} H_{n0}(r) \phi_0(r) e^{2\pi i(k_0-k_n)z},
\]

where \(\Lambda_n = i/4\pi k_n\). The dynamical operator for elastic scattering of the inelastically scattered electron is

\[
D_n = \Lambda_n \left( \nabla^2 - \frac{2m}{\hbar^2} H_{nn} \right).
\]

Following Ref. [131] the multislice solution for inelastic scattering given by Eq. 4.3 is

\[
\phi_n(r_\perp, z + \Delta z) = e^{D_n \Delta z} \phi_n(r_\perp, z) - \frac{2m\Lambda_n}{\hbar^2} \int_z^{z+\Delta z} e^{D_n(z+\Delta z-z')} H_{n0}(r_\perp, z') \times \phi_0(r_\perp, z') e^{2\pi i(k_0-k_n)z'} dz'.
\]

The first term on the right hand side represents elastic scattering of the inelastic wave over the slice \(\Delta z\) in the region from \(z\) to \(z + \Delta z\) and the second term takes into account inelastic scattering in the slice. Considering the inner-shell ionization of a single atom lying between \(z\) and \(z + \Delta z\), assuming that inelastic scattering only occurs in this region and that \(e^{D_n(z+\Delta z-z')}\) is approximately unity, Eq. 4.5 reduces to

\[
\phi_n(r_\perp, z + \Delta z) \approx -\frac{2m\Lambda_n}{\hbar^2} \phi_0(r_\perp, z) \int_z^{z+\Delta z} e^{2\pi i(k_0-k_n)z'} H_{n0}(r_\perp, z') dz'.
\]

Calculation of the inelastic wave function can thus proceed provided that we can calculate the projected transition matrix element \(H_{n0}(r_\perp)\).

4.1.1 Inelastic transition potential

The projected transition matrices we shall consider are those pertaining to inner-shell ionization. However, these matrices do not need be restricted to just ionization and can be calculated for any inelastic process (phonon scattering being one such
example [21, 132]). Consider a single isolated atom which undergoes core electron excitation from some initial state \( u_0(\mathbf{r}) \) to a final continuum state \( u_n(\mathbf{r}) \) due to the passage of a fast electron. The core electron excitation proceeds via the Coulomb interaction so that the transition potential or matrix element \( H_{n0} \) is

\[
H_{n0}(\mathbf{r}) = \frac{e^2}{4\pi\varepsilon_0} \int u_n^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} u_0(\mathbf{r}') d\mathbf{r}',
\]

where \( e \) is the electron charge and \( \varepsilon_0 \) is the permittivity of free space. In the central potential model the initial and final state wave functions are:

\[
\begin{align*}
  u_0(\mathbf{r}) &= \frac{\tilde{u}_{n,l}(r)}{r} Y_{l,m}(\hat{r}) \\
  u_n(\mathbf{r}) &= \frac{\tilde{u}_{\epsilon,l'}(r)}{r} Y_{l',m'}(\hat{r}).
\end{align*}
\]

The radial wave function \( \tilde{u}_{n,l}(r) \) is for the atomic orbital specified by the quantum numbers \( n \) and \( l \). The functions \( Y_{l,m} \) are spherical harmonics with unit vector arguments (denoted by the hat). The continuum radial wave function is \( \tilde{u}_{\epsilon,l'} \) for an ejected electron of energy \( \epsilon \). We subsequently calculate the initial bound and final continuum state radial wave functions using a relativistically corrected Hartree-Fock and Hartree-Fock-Slater central potential respectively. This use of different potentials yields radial wave functions that are not strictly orthogonal, resulting in an extra monopole contribution which, in this thesis, is subtracted from the transition potential [134]. The projection of the transition potentials onto the plane is performed according to Eq. 4.6 using

\[
H_{n0}(\mathbf{r}_\perp) = \int H_{n0}(\mathbf{r}_\perp, z) e^{-2\pi i (k_n - k_0) z} dz = \int H_{n0}(\mathbf{q}_\perp, q_z = k_n - k_0) e^{2\pi i \mathbf{q}_\perp \cdot \mathbf{r}_\perp} d\mathbf{q}_\perp,
\]

where the second line follows from a generalized form of the Fourier projection theorem, and anticipates that evaluation is easier in reciprocal space:

\[
H_{n0}(\mathbf{q}) = \frac{e^2}{4\pi^2\varepsilon_0} \int \frac{u_n^*(\mathbf{r}') e^{-2\pi i \mathbf{q} \cdot \mathbf{r}'}}{\mathbf{q}_\perp^2 + q_z^2} u_0(\mathbf{r}') d\mathbf{r}'.
\]
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The numerator (the transition matrix element) in Eq. 4.10 can be evaluated using a standard exponential expansion [135]

\[ e^{-2\pi i \mathbf{q} \cdot \mathbf{r}} = 4\pi \sum_{\lambda=0}^{\infty} \sum_{m_\lambda=-\lambda}^{\lambda} i^\lambda j_\lambda(2\pi qr) Y_{\lambda,m_\lambda}^*(\mathbf{q}) Y_{\lambda,m_\lambda}(\mathbf{r}). \]  

(4.11)

with \( j_\lambda(2\pi qr) \) being a Bessel function of order \( \lambda \). Using the wave functions in Eq. 4.8 and noting that \( dr = r^2 dr d\mathbf{r} \) we have,

\[ F_{n0}(\mathbf{q}) = \int u_n^*(\mathbf{r}') e^{-2\pi i \mathbf{q} \cdot \mathbf{r}'} u_0(\mathbf{r}') d\mathbf{r}' \]

\[ = 4\pi \sum_{\lambda=0}^{\infty} \sum_{m_\lambda=-\lambda}^{\lambda} (-i)^\lambda Y_{\lambda,m_\lambda}(\mathbf{q}) \int_0^\infty \tilde{u}_{nl}(r) j_\lambda(2\pi qr) \tilde{u}_{e,l'}(r) dr \]

\[ \times \int Y_{l,m_l}(\mathbf{r}) Y_{\lambda,m_\lambda}^*(\mathbf{r}) Y_{l',m'_l}(\mathbf{r}) d\mathbf{r}. \]  

(4.12)

The integration over the unit vector \( \mathbf{r} \) can be evaluated using

\[ Y_{l',m'_l}(\mathbf{r}) = (-1)^{m'_l} Y_{l',-m'_l}(\mathbf{r}) \] and the relationship [136],

\[ \int Y_{l,m_l}(\mathbf{r}) Y_{\lambda,-m_\lambda}(\mathbf{r}) Y_{l',-m'_l}(\mathbf{r}) d\mathbf{r} = \]

\[ \sqrt{(2l+1)(2\lambda+1)(2l'+1)} \frac{4\pi}{\lambda} \left( \begin{array}{ccc} l' & \lambda & l \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} -m'_l & -m_\lambda & m_l \end{array} \right). \]  

(4.13)

Using Eq. 4.10 with Eq. 4.12 and Eq. 4.13 the projected transition potentials are

\[ H_{n,0}(\mathbf{r}_\perp) = \frac{e^2}{4\pi^2 \epsilon_0} 4\pi \sum_{\lambda=0}^{\infty} \sum_{m_\lambda=-\lambda}^{\lambda} (-i)^\lambda (-1)^{m_\lambda} (-1)^{m'_l} \]

\[ \times \sqrt{(2l+1)(2\lambda+1)(2l'+1)} \frac{4\pi}{\lambda} \left( \begin{array}{ccc} l' & \lambda & l \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} -m'_l & -m_\lambda & m_l \end{array} \right) \]

\[ \times \left[ \int \frac{Y_{\lambda,m_\lambda}(\mathbf{q}) G_{nl,el'}(q) \mathbf{q}_{\perp}}{q_{\perp}^2 + q_z} e^{2\pi i q_z \cdot \mathbf{r}_\perp} d\mathbf{q}_{\perp} \right]. \]  

(4.14)
Figure 4.1: Transition potentials for an isolated Al atom ionising a K-shell electron (initial state \( l = 0, m = 0 \)) to final state (a) \( l = 1, m = 0 \) and (b) \( l = 1, m = 1 \) 1 eV above ionization threshold. An incident electron energy of 200 keV is assumed. In (a) the transition potential is purely imaginary. In (b) the transition potential is complex and the plot shows the real component only (the imaginary component is the same size and shape but rotated by 90 degrees).

The bracketed array is the Wigner 3\( j \) symbol and the overlap integral, \( G_{nl,\ell'}(q) \), is defined as

\[
G_{nl,\ell'}(q) \equiv \int_0^\infty \tilde{u}_{nl}(r) j_\lambda(2\pi qr) \tilde{u}_{\ell'}(r) dr.
\] (4.15)

Two atomic transition matrix elements for different final states, calculated using Eq. 4.14, are shown in Fig. 4.1 for an isolated aluminum atom.

4.1.2 Spectroscopic imaging: a single channelling approximation

For a crystal of thickness \( t \) and an ionization event occurring in the slice \( z \) to \( z + \Delta z \) we use Eq. 4.6 to generate the inelastic wave function, which may then be propagated the remaining distance to the exit surface and its contribution to the energy-spectroscopic diffraction pattern determined. Imaging based on core-loss spectroscopy in STEM integrates this inelastic wave over some angular range. In the so-called single channelling approximation, in which further elastic scattering after the inelastic transition is neglected, the image as a function of probe position
4.1. A REAL SPACE TRANSITION POTENTIAL APPROACH

is,

$$I(R) = \int_{\text{detector}} \left[ \sum_n \frac{k_n}{k_0} |\Phi_n(q_\perp, R)|^2 \right] dq_\perp,$$  \hspace{1cm} (4.16)

where the inelastic wave generated at a depth $z$ is propagated in free space to the detector plane

$$\Phi_n(q_\perp, R, z) = -\frac{2m\Lambda_n}{\hbar^2} \int H_{n0}(r_\perp) \phi_0(r_\perp, R, z) e^{-2\pi i q_\perp \cdot r_\perp} dr.$$  \hspace{1cm} (4.17)

The factor $k_n/k_0$, which is less than unity, in Eq. 4.16 accounts for the reduction in the current as a consequence of the inelastic scattering event. Inserting Eq. 4.17 into 4.16 and expanding the modulus squared term we have

$$I(R) = \int_0^t \int \int \phi_0^*(r_\perp, R, z) \left[ \sum_{n \neq 0} \frac{k_n}{k_0 \Delta z} \Lambda_n^2 H_{n0}^*(r_\perp) H_{n0}(r_\perp') \right] e^{2\pi i q_\perp \cdot (r_\perp - r_\perp')} dq_\perp \phi_0(r_\perp', R, z) dr_\perp dr_\perp' dz,$$  \hspace{1cm} (4.18)

where the sum over slices has been turned into an integral over $z$ by including a factor $1/\Delta z$. This can be written as

$$I(R) \equiv \frac{2\pi}{hv} \int_0^t \int \int \phi_0^*(r_\perp, R, z) W(r_\perp, r_\perp') \phi_0(r_\perp, R, z) dr_\perp dr_\perp' dz,$$  \hspace{1cm} (4.19)

where

$$W(r_\perp, r_\perp') = \frac{2\pi m}{\hbar^2 \Delta z} \sum_{n \neq 0} \frac{1}{k_n} H_{n0}^*(r_\perp) H_{n0}(r_\perp') \int_{\text{detector}} e^{2\pi i q_\perp \cdot (r_\perp - r_\perp')} dq_\perp,$$  \hspace{1cm} (4.20)

and $v = \hbar k_0/m$, which is the same nonlocal potential as in Eq. 2.14, albeit projected. Later in this chapter we introduce a reciprocal space version of Eq. 4.19.

The single channelling approximation, whilst not accounting for the elastic scattering of the inelastically scattered electron inside the specimen, is usually taken to give a reasonable representation of the total signal obtained when integrating over a suitably large collection angle. Comparisons between full double channeling calculations (where subsequent elastic scattering of the inelastically scattered electron is explicitly taken into account) and the single channelling approximation showed...
that the orientation dependence of the aluminum $K$-shell EELS signal in systematic row conditions sufficed to reproduce experimental results using 120 keV plane wave illumination, provided that the detector semi-angle was around 20 mrad or larger [133]. In STEM the imaging process explicitly integrates over a collection angle, with current generation detectors having collection angles approaching 60 mrad [59, 60], elastic scattering changes the intensity distribution on such a small scale compared to the detector dimensions that the error introduced into the calculation by using the single channelling approximation is negligible [137]. In chapter 9, where the explicit form of the wave function is imaged onto some image plane, the fine details introduced by elastic scattering may not be neglected [138, 139]. It is in chapter 9 that we shall introduce a double channelling form of Eq. 4.19 relevant to energy filtered scanning confocal electron microscopy.

**Silicon carbide and imaging at a distance**

Dynamical elastic scattering and the form of the transition potentials clearly complicate the image formation process. A classic example of this is the simulation presented by Oxley *et al.* [56] for the $C K$-shell STEM EELS image in SiC showing significant, separate peaks on both the Si and C columns, with those on the Si column being larger. The structure of SiC when viewed along the [011] zone axis is shown in Fig. 4.2, with the distinct dumb-bell structure being obvious. While the parameters were carefully selected to illustrate a point and may not strictly allow the single channelling approximation, the result constitutes an image which if obtained experimentally could lead to erroneous conclusions about the specimen structure. The regime in which the most anomalous results arise can, at least in the next generation of microscopes, be avoided through judicious choice of experimental parameters [80, 140], but the highly nonintuitive result and its physical explanation is still important to our understanding of the inelastic scattering and imaging process.

The simulations of Oxley *et al.* [56] were based on the cross section expression in Eq. 4.19 but were solved using the Bloch wave method. Here we re-examine the result in Ref. [56] to explore and understand some subtleties in the interpretation of spectroscopic images.

Figure 4.3 shows $C K$-shell STEM EELS line scans in a 100 Å thick SiC sample
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Figure 4.2: Model structure of a SiC unit cell in (a) a three dimensional perspective and (b) oriented along the [011] zone axis. The Si atoms are coloured brown whereas the C atoms are coloured grey.

orientated along the [011] zone axis, using a 200 keV, aberration free probe with a 50 mrad semi-angle probe-forming lens, for both a 10 mrad detector semi-angle and a 50 detector mrad semi-angle and is essentially the same shape as the test case of Oxley et al. [56]. Since the approach based on summing inelastic waves as embodied in Eq. 4.17 does not lend itself to integration over an energy window, a fixed energy loss of 10 eV above the threshold was chosen, making the units here slightly different to those in Ref. [56]. The units in Fig. 4.3 should really be “fractional intensity per eV”, though alternately one could assume a 1 eV energy window. The 10 mrad detector results show peaks on both Si and C columns, with the larger peak on the Si. The 50 mrad detector results shows just a single peak on the C column, but a large background across the whole line scan. There are two aspects to an analysis of the scattering process based on Eq. 4.18. The first aspect is to identify all the contributing atoms and then to take into account all the significant transition potentials ($H_{n0}$) for each atom. The shape and position of these potentials relative to the elastic wave function determines how electrons in inelastic final states contribute to the imaging. The second aspect is the proportion of electrons in each inelastic state $\phi_n$ which contribute to the detected intensity. This is given by the fraction of the reciprocal space electron density of $\phi_n$ which lies within the region corresponding to the detector acceptance angle.

To investigate the first aspect, Fig. 4.4 shows profiles through a few select transition potentials, specifically those with final states characterized by angular momen-
CHAPTER 4. IMAGING BASED ON CORE-LOSS SPECTROSCOPY: THEORY

Figure 4.3: Carbon K-shell STEM EELS line scans in a 100 Å thick SiC sample orientated along the [011] zone axis, using a 200 keV, aberration free probe with a 50 mrad semi-angle probe-forming lens. Results for both 10 mrad and 50 mrad detector semi-angles are shown with separate axes, left and right respectively.

Figure 4.4: Carbon K-shell transition potential and probe intensity profiles. The transition potential to (0, 0) is purely real. That to (1, 0) is purely imaginary. In both cases only the modulus is plotted. The transition to (1, 1) is complex. Only the real part is plotted, its antisymmetric character hinting at the vortical phase ramp present in the full 2D transition potential.
tum quantum numbers \((l', m') = (0, 0), (1, 0)\) and \((1, 1)\). The transition to \((1, 0)\) is by far the widest of the three, but its maximum value is smaller than that of the other two potentials. The transition to final state \((0, 0)\) is seen to be highly peaked on the origin, while that to \((1, 1)\) peaks off-column. Fig. 4.4 also shows the probe intensity for the parameters given before, which is seen to have considerable overlap with the transition potential for the \((0, 0)\) final state. Assuming a C atom at the origin, the dashed vertical line shows the distance at which, in SiC, the nearest neighbour Si column would sit. If the probe were at this position, the relative size of the potentials is such that there would be a larger electron density in the inelastic channel for transition to the \((1, 1)\) state than there would to the \((1, 0)\) state. The probe does not, of course, retain the form it has on the surface as it propagates through the crystal. Rather than considering the detailed evolution of the wave function relative to the spatial distribution of these transition potentials, we can instead plot the contribution from each depth for transitions to a specific final state. Such plots are shown in Fig. 4.5. Assuming a 10 mrad detector collection semi-angle, Fig. 4.5(a) shows the total contribution per slice from all final states, while Figs. 4.5(b), (c) and (d) show the contribution from transitions to final states \((0, 0), (1, 0)\) and \((1, 1)\) respectively. (Note that the plot for transition to \((1, -1)\) is identical to that for \((1, 1)\).) The considerable spatial overlap between the probe intensity and the transition potential to final state \((0, 0)\) is evident in the large peak at small depths in Fig. 4.5(b), but this rapidly disappears beyond 20 Å as the probe diffuses through the specimen (bear in mind the large probe-forming semi-angle). For small depths, the contribution from transitions to \((1, 1)\) peaks to either side of the column position, the reason for which will readily be appreciated from the form of the transition potential in Fig. 4.4.

For larger depths, transitions to states \((1, 0)\) and \((1, 1)\) both give fairly consistent contributions when the probe is positioned on the C column but also when it is positioned on the Si column. Indeed for transitions to the \((1, 1)\) state, the contribution for the probe positioned on the Si column is notably larger than that for the probe on the C column. This leads to the dominance of the signal from the probe on the Si column (see Fig. 4.5(a), which, remember, integrates to give the 10 mrad detector plot in Fig. 4.3).

Figures 4.5(e)-(h) show equivalent plots assuming a 50 mrad detector collection semi-angle. Except in so much as the contribution is large for the first few slices and decreases rapidly the further into the crystal the probe is located, a simple conse-
Figure 4.5: Carbon K-shell signal per depth for transitions to: (a) all final states, (b) (0, 0), (c) (1, 0) and (d) (1, 1) for a 10 mrad detector collection semi-angle; and (e) all final states, (f) (0, 0), (g) (1, 0) and (h) (1, 1) for a 50 mrad detector collection semi-angle. Real space wave function intensity for the probe on the Si column at depths of (i) 0 Å, (j) 30 Å, (k) 61 Å and (l) 98 Å. Diffraction pattern intensity for: (m) (0, 0), (n) (1, 0) and (o) (1, 1) at 0 Å, (p) (1, 1) at 61 Å, all for the probe on Si; and (q) (0, 0), (r) (1, 0) and (s) (1, 1) at 0 Å, (t) (1, 1) at 61 Å, all for the probe on C. The 10 mrad and 50 mrad detector sizes relative to the reciprocal space intensity distributions are shown by the dashed circles in (t).
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quence of probe spreading, these figures are very different to those for the 10 mrad
detector. In particular, nothing distinguishes the case of the probe on the Si co-

column to most other probe positions, and the background signal is higher and more
consistent for all probe positions. It must be remembered that all that has changed
is the detector size. Neither the elastic wave function nor the transition potentials in
Eq. 4.17 have altered, and therefore neither have any of the inelastic wave functions
\( \phi_n \). All that distinguishes the form of Figs. 4.5(a)-(d) from that of Figs. 4.5(e)-(h)
is the extent of the detector.

To better appreciate this we plot the electron distribution in the detector plane,

i.e. the contribution to the (inelastic) diffraction pattern, for a few select final states
and a few select atom depths: 0 Å, 30 Å, 61 Å and 98 Å. Figures 4.5(i)-(l) show the
real space intensity of the elastic wave function at these depths for a probe initially
on the Si column (those for the probe on the C column are quite similar). These are
plotted according to their individual maxima and so the extent of the probe diffusion
is somewhat masked (see later in reference to Fig. 4.8). Nevertheless, for each given
distribution the largest concentration of electron density is still strongly centred
about the probe position. Figures 4.5(m)-(o) show, on a common intensity scale,
the contribution to the inelastic diffraction from the top surface of the specimen
with the probe situated on the Si column for transitions to \((0, 0)\), \((1, 0)\) and \((1, 1)\)
respectively. As only the latter two extend out significantly to this column, only
they show appreciable contributions. Because both these potentials are relatively
flat in the vicinity of the Si column, the diffraction patterns are nearly uniform disks
of about 50 mrad radius — very similar to the elastic diffraction pattern of the probe
itself. Fig. 4.5(p) shows the contribution for final state \((1, 1)\) from the depth of 61 Å
into the crystal. While the evolution of the probe has changed its shape somewhat,
the distribution in the diffraction pattern is still quite uniform.

Figures 4.5(q)-(s) show, on a common intensity scale, the contribution to the
inelastic diffraction from the top surface of the specimen, with the probe situated on
the C column, for transitions to \((0, 0)\), \((1, 0)\) and \((1, 1)\) respectively. The transitions
to \((0, 0)\) and \((1, 0)\) are fairly uniform, the latter being much weaker, consistent with
the relative sizes of the potentials as seen in Fig. 4.3. However for the final state
\((1, 1)\), the phase vortex in the complex transition potential combined with the rota-
tionally symmetric probe function leads to a donut-shaped diffraction pattern: very
little intensity falls on the innermost region. Fig. 4.5(t) shows the contribution for
final state \((1, 1)\) from the depth of 61 Å into the crystal. The donut is again seen, and, though wider now, it still has very little intensity within the central region. The 10 mrad detector is shown on this figure as the inner of the two dashed circles, while the outer corresponds to 50 mrad. Now we can understand the role of the detector relative to the symmetry of the states. While there may well be more C \(K\)-shell ionization events in total when the probe is closer to the C column, the distribution in the diffraction pattern of the fast electrons after causing these transitions is such that the signal on a small, on-axis detector may well be larger when the probe is displaced from the column. When we go to the 50 mrad detector, we collect most of the inelastically scattered electrons. Regions of strong signal are therefore more representative of the regions where the most ionization occurs, and as such the expected peak on the C column is regained. The large background in this case is a consequence of the delocalised potential, the density of C columns, and the elastic spreading of the probe.

Consideration of what states and in particular which atoms contribute to the signal is most easily performed by considering the extent to which the probe spreads. Figure 4.5 is deceptive in this regard: it gives the signal as a function of probe position and depth, but it does not show how the individual surrounding atoms are contributing. Figure 4.6 shows a schematic representation of the location of the atoms which contribute. Figures 4.6(a) and (b) show the location of the atoms which contribute the “first” 50 % of the total inelastic density for C \(K\)-shell ionization at the energy loss of 10 eV above threshold, with the probe on the Si and C columns respectively. To make such a reckoning we determine the inelastic density resulting from each atom, normalise so that the sum over all atoms is unity, and order from the largest contributing atom to the smallest contributing atom. “First” then refers to this ordered list. For the probe on the C column, the first 50 % contribution is provided only by atoms within that column alone, whereas for the probe on Si we find that the three nearest C columns contribute (see Fig. 4.7(e) for a depiction of the projected structure). Figures 4.6(c) and (d) show the atoms which contribute the “first” 80 % of the total inelastic density, and we see that many more states contribute.

The convergence with respect to the number of states and atoms included is very slow, a drawback of the transition potential approach, as it notably increases the calculation time. Fig. 4.7(a) shows the convergence towards the total signal as a
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Figure 4.6: Schematic depiction of the C atoms (denotes by the green disks situated at the 3D coordinates of the atom in the crystal) contributing: the first 50% of the density in the inelastic channels when the probe is on the (a) Si column and (b) C column; and the first 80% of the density in the inelastic channels when the probe is on the (c) Si column and (d) C column.
Figure 4.7: The ordered (a) cumulative and (b) individual contribution to the signal as a function of the number of states for the probes positioned on the two columns and for the two detector sizes considered. The signal strength for the (c) 10 mrad detector and (d) the 50 mrad detector, broken into contributions from select columns, with labelling corresponding to the projected structure of SiC depicted in (e).
function of the number of final states (all final states from different atoms are treated as different final states in this count). Note the logarithmic scale on the horizontal axis. Fig. 4.7(b) shows the fractional contribution of each individual state. The step-like patterns near the start show that a few states contribute significantly more than others. While those in the tail of the distribution contribute very little individually, the large number of states means their contribution cannot be neglected.

The contributions from the nearest columns, Fig. 4.7(c) and (d) show, for the 10 mrad and 50 mrad semi-angle detectors respectively, the C K-shell EELS line scan showing decompositions for specific subsets of contributing columns, labelled in accordance with the SiC structure and scan line shown in Fig. 4.7(e). In both cases, the contribution from the nearest column (col a) barely gives half the total contribution on the central Si and C probe positions. For the smaller detector, the combination of columns a, b and c gives the correct shape at the central dumbbell, but not quite the full signal. For the large detector, the significant contribution obtained from columns other than the labelled three is quite evident; the probe spreading and background contributions are significant here.

Following the approach of Dwyer and Etheridge [141] and integrating the probe intensity in radial disks about the probe position we are able to consider, in more detail, how the probe spreads inside the SiC crystal. Fig. 4.8 shows the contour plots of the radial distance from the probe axis which contains the given fraction of probe intensity, in that slice, as a function of depth. Plots are shown for the probe (a) on a Si column, (b) on a C column, (c) halfway between adjacent Si and C columns, and (d) in free space (i.e. without a specimen). It is seen that the outer contours are very similar in all cases, suggesting that the overall extent of the probe does not change much. However significant differences can be seen in the contour within which the first 20 % of the probe intensity is contained: this line spreads most slowly for the Si column, more rapidly for the C column, and more rapidly still for the case with the probe between the columns. This last scenario is almost indistinguishable from the free space plot. The cause of these differences is channelling along the columns, and the consequence is the fraction of electrons with a sufficiently high probability density in a given spot to contribute significantly to the signal. From these plots we get a hint for why the signal with the probe between the columns is lower than both that on the C and that on the Si columns (faster spreading of electron density; recall that the spacing of the Si/C dumbbell is about 1 Å), and why the signal on the Si
Figure 4.8: Contour plot showing the radial distance about the probe position axis within which the specified fraction of the probe intensity within the plane resides for the probe: (a) on the Si column, (b) on the C column, (c) halfway between the Si and C columns, and (d) in free space.
4.2 Bloch wave: rapid calculation of spectroscopic images

Allen and Josefsson [78] presented a reciprocal space method for calculating inelastic cross sections. Using the electron probability current vector and conservation of the total number of incident electrons they arrived at a cross section expression for inelastically scattered electrons,

\[ \sigma(R, t) = A t \sum_{i,j} B_{ij}(R, t) \sum_{g,h} C_{gi}^* C_{jh} \mu_{h,g}. \] (4.21)

(This can also be obtained by inserting the Bloch wave ansatz in Eq. 4.19 into Eq. 4.19.) For STEM, the cross section expression in Eq. 4.21 contains the explicit probe position dependence in the \( B_{ij} \) term which also incorporates the excitation amplitudes (see Sec. 2.3.1) and is [47, 97]

\[ B_{ij}(R, t) = \alpha_i(R) \alpha_j^*(R) e^{2\pi i (\lambda_i - \lambda_j^*) t} - \frac{1}{2\pi i (\lambda_i - \lambda_j^*) t}. \] (4.22)

4.2.1 The mixed dynamical form factor model

The inelastic scattering form factors in Eq. 4.21, \( \mu_{h,g} \), describe the effective nonlocal inelastic potential in reciprocal space and are related to the Fourier coefficients of the nonlocal potential in Eq. 4.20 \( W(r_\perp, r'_\perp) \):

\[
\mu_{h,g} = \frac{2\pi m}{\hbar^2 k_0 A} \int_A \int_A e^{-2\pi i h \cdot r_\perp} W(r_\perp, r'_\perp) e^{2\pi i g \cdot r'_\perp} dr_\perp dr'_\perp,
\]

\[
= \frac{2\pi m}{\hbar^2 k_0 A} W_{h,g}
\] (4.23)
where for a momentum transfer $Q = K - K'$,

$$W_{h,g} = \frac{2\pi m}{\hbar^2 t} F_{\text{site}} \sum_{n \neq 0} k_n \int H_{n0}^*(Q + h) H_{n0}(Q + g) \delta(k_n - k') d\Omega_{K'} dK'. \quad (4.24)$$

The site term, $F_{\text{site}}$ includes the sum over all atoms in the unit cell of species $\alpha$ at position $\tau_\alpha$ and is

$$F_{\text{site}} = \sum_{\alpha} e^{-M_{\alpha}(g-h)} e^{2\pi i(g-h) \cdot \tau_\alpha}. \quad (4.25)$$

The Fourier coefficients of the ionization potential are

$$\mu_{h,g} = \frac{N}{2\pi k V_c} F_{\text{site}} f(h, g), \quad (4.26)$$

where $N$ is the number of unit cells in the crystal, $V_c$ is the volume of the unit cell. Taking the Fourier transform of the transition matrix elements in Eq. 4.7,

$$H_{n0}(Q + g) = \frac{e^2}{4\pi^2 \epsilon_0} \frac{F_{n0}(Q + g)}{|Q + g|^2}, \quad (4.27)$$

with

$$F_{n0}(Q + h) = \int u_n^*(r') e^{-2\pi i(Q+h) \cdot r'} u_0(r') dr' \quad (4.28)$$

gives the atomic scattering form factor $f(h, g)$, which for some energy loss window $\epsilon^1$ is

$$f(h, g) = \frac{1}{2\pi^3 a_0^3} \int K' \sum_n \frac{F_n^*(Q + h, \epsilon) F_n(Q + g, \epsilon)}{|Q + h|^2 |Q + g|^2} d\Omega_{K'}. \quad (4.29)$$

We note that the atomic scattering form factors are closely related to the well known MDFFs as they appear in the numerator of Eq. 4.29, and are required for all forms of incoherent scattering. The MDFFs are defined by

$$S(Q + h, Q + g, E_{n'}) = F^*(Q + h) F(Q + g), \quad (4.30)$$

where there is a restricted sum over final state energy $E_{n'}$. The obvious distinction between the atomic scattering form factors and the MDFF is the inclusion of the

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1We have explicitly shown the $\epsilon$ dependence the transition matrix elements for the energy integration."
4.2. BLOCH WAVE: RAPID CALCULATION OF SPECTROSCOPIC IMAGES

detector geometry integration over $K'$. Discussions regarding the MDFFs and their physical significance can be found in Refs. [46, 142, 143]. As the MDFFs appear explicitly in Eq. 4.29 in this thesis we shall hereafter refer to the reciprocal space approach as the MDFF method and the real space transition potential approach as the $H_{n0}$ method.

4.2.2 A multipole expansion

The transition matrix elements in Eq. 4.28 can be expanded in powers of $r$ by Taylor expanding the exponential operator in Eq. (4.28),

$$e^{2\pi i(Q+g)\cdot r} = 1 + 2\pi i(Q+g)\cdot r + \frac{1}{2!}[2\pi i(Q+g)\cdot r]^2 + \frac{1}{3!}[2\pi i(Q+g)\cdot r]^3 + \ldots,$$

(4.31)

allowing identification of the dipole ($r$), quadrupole ($r^2$) and octupole ($r^3$) contributions to the scattering form factor. Taking a Taylor series expansion of the reciprocal space transition operator gives a power series representation in scattering angle, which should converge quickly if small angle scattering dominates. Moreover, the implied expansion of the matrix elements in powers of $r$ is effectively a multipole expansion of the Coulomb operator present in the real space representation of the transition potentials. This series is often truncated to first order: the dipole approximation. Note that a different expansion results if one seeks to make a multipole expansion of the reciprocal space operator itself (see for example Ref. [142]).

4.2.3 Efficient calculation

Using matrix notation Eq. 4.21 can be restated as the trace of a product of four matrices [97]

$$\sigma(R, t) = Tr \left( BC^{*T}UC \right),$$

(4.32)

where $B_{ij} \equiv B_{ij}(R, t) \in \mathcal{B}$, $C_{g,i} \equiv C_{g,i} \in \mathcal{C}$ and $\mu_{h,g} \in \mathcal{U}$. Using block diagonalisation allows the further reduction in computation to a sum of traces of the $n = l \times m$ sub-matrices,

$$\sigma(R, t) = \sum_{l=1}^{n} Tr \left[ B(q_l)C^{*T}(q_l)U(q_l)C(q_l) \right].$$

(4.33)

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The efficiency of this formulation is now apparent, the matrix $B$ contains all the probe and sample thickness parameters and is the only quantity that needs to calculated as a function of probe position. The matrices $C, C^{-1}$ and $U$ are only calculated once for each vector $q_l$. Using standard linear algebra software packages allows rapid computation of the inelastic cross section in STEM.

### 4.3 Computation considerations

The cross section expression in Eq. 4.21 need not be calculated using only Bloch wave. To implement this in the multislice scheme we recast Eq. 4.21 without the Bloch wave expansion

$$
\sigma(R, t) = A \int_0^t \left[ \sum_{h,g} \mu_{h,g} \Phi^*(R, h, z) \Phi(R, g, z) \right] dz. \tag{4.34}
$$

The elastic wave functions $\Phi(R, g, z)$ are now easily calculated using multislice techniques. The motivation for doing this is to more easily accommodate aperiodic objects whilst retaining the computational advantages of the nonlocal potential.

In the MDFF method, the insertion of the integration over energy loss and the sum over final states is a subtle but very useful tool. For the practical implementation of a software package this has many advantages over the real space transition potential approach in Sec. 4.1. Operationally, in the MDFF method each final state in the energy loss window is calculated once to perform the integration and is then discarded. Using this in a Bloch wave solution allows the inelastic cross section to be calculated for any number of arbitrary crystal thicknesses and probe parameters efficiently as the only quantities that need to be recalculated are the excitation amplitudes. In the real space transition potential method it is necessary to calculate and store each individual state which consumes a significant amount of computer memory. Alternatively, using a calculate and discard approach for each atom in the crystal for each final state and energy loss is also computationally expensive.

Using multislice with either the MDFFs or real space transition potentials a further computational burden is that the wave functions, both elastic and inelastic, need to be recalculated for each probe position and for every thickness inside the specimen. In STEM, the real space method must also explicitly calculate for perio-
dic specimens the contribution to the EELS signal from inelastic wave originating from each atom in the slice of the supercell. These demands are eased somewhat by considering that the STEM instrument acts as a low pass filter; it only transmits spatial frequencies smaller than the maximum momentum component permitted by the probe forming aperture. Thus using the Nyquist-Shannon sampling theorem the number of probe positions necessary in a calculation is \( N_x \times N_y = 4(X \times Y)q_{\text{max}} \) [144]. To put this in a numerical perspective, for simulations of SrTiO\(_3\) with side lengths of 3.905 Å and sufficient symmetry so that the scan area need only be 1.95 Å along the \( X \) and \( Y \) direction, a calculation modelling a typical uncorrected 300 kV STEM instrument with a 9.6 mrad probe forming aperture semi angle \( q_{\text{max}} = 0.487 \) Å\(^{-1}\) would only require \( N_x = 6 \) and \( N_y = 6 \) probe positions to sufficiently satisfy sampling requirements. It is then formally equivalent to interpolate these images onto more pixels for aesthetic purposes as it would be to calculate the image using more probe positions.

We finish with the remarks, for aperiodic samples with few atoms contributing to the EELS signal for a narrow energy loss the real space method is the most efficient simulation method. For aperiodic specimens where the EELS signal is integrated over a moderately sized energy window the MDFF multislice approach is more suitable. Finally, for periodic specimens the Bloch wave approach is usually the most efficient simulation approach.

### 4.4 Discussion and conclusions

This chapter presented three methods for calculating images based on core-loss EELS: (i) real space transition potential multislice approach, (ii) MDFF Bloch wave and (iii) MDFF multislice. The application of the real space transition potential method approach revealed insights that were not obviously clear in the MDFF methods. Coupling the multislice method which allows visualisation of wave functions with representations of the real space transition potential allows the pinning down and quantification of previously evasive concepts such as the potential delocalisation and nonlocality. Using this approach we elucidated the mechanism for the anomalous “imaging at a distance” result more clearly than had been done previously [56]. The practical limitations of this approach, most notable being the relatively
large computation demands, were discussed with alternative multislice and Bloch wave MDFF schemes presented. The Bloch wave method was shown to, under certain conditions such as when the number of beams is small, allow efficient rapid calculation of images with a only weak scaling dependence on the number of probe positions, defocus and sample thickness. The multislice MDFF method swaps the scaling dependence, weakly scaling with beams but linearly scaling with probe position, defocus and sample thickness.

The choice between the three approaches must be made on a pragmatic basis as all three are equivalent and produce the same result for the same approximations (i.e. single channelling etc.). In this thesis we shall consider both the computational burden and the clarity of interpretation when choosing an approach. Typically we calculate full two dimensional STEM images for periodic samples using Bloch wave MDFF techniques but shift to the multislice method for aperiodic samples such as impurities embedded in matrices or when we need to consider the elastic channelling of the inelastically scattered electron.
Interpreting atomic resolution spectroscopic images

The work in this chapter is based on the material presented in Refs. [57] and [145]. The experimental data was supplied by Oak Ridge National Laboratory as a result of a collaboration with M.P. Oxley. Through comparisons of theoretical simulations with experimental data we investigate the subtleties arising when interpreting spectroscopic line scans. In chapter 4, we explored the seemingly anomalous result of “imaging at a distance”, explaining and discussing the role of the detector and channelling in complicating direct interpretation of scanning transmission electron microscopy (STEM) electron energy-loss spectroscopy (EELS) images. Here we compare several STEM EELS experimental line scans taken from a specimen containing multiple atomic species, with some species containing more than one experimentally accessible EELS edge. These comparisons reveal the characteristic volcano structure [46, 73] which is observed as a consequence of thermal scattering coupled with the form of the inelastic potential. This work draws on the theory developed in chapters 2, 3 and 4, using the cross section expression in Eq. 4.19. The multipole expansion of the mixed dynamical form factor (MDFF) transition matrix elements is also examined.
CHAPTER 5. INTERPRETING ATOMIC RESOLUTION SPECTROSCOPIC IMAGES

Figure 5.1: Model structure of a LaMnO$_3$ unit cell in (a) a three dimensional perspective and (b) oriented along the [001] zone axis. The La atoms are coloured green, the Mn atoms are red and the O atoms are blue.

5.1 Experimental result LaMnO$_3$

We begin by examining the experimental result contained in Ref. [57]. The crystal structure used for investigation is the pseudocubic structure of lanthanum manganate LaMnO$_3$ as shown in Fig. 5.1. Using a hybrid of the frozen phonon algorithm to account for thermal scattering and the MDFF to model ionization, simulations were performed following the formulation outlined in Findlay et al. [132]. The frozen phonon and MDFF approaches were discussed in chapters 2 and 4 respectively. The cross section for ionization as a function of probe position and sample thickness in the frozen phonon MDFF synthesis is given by

$$
\sigma(R, t) = \frac{A}{J} \sum_{j=1}^{J} \int_{0}^{t} \left[ \sum_{h,g} \mu_{h,g} \Phi_{j}^{*}(R, h, z) \Phi_{j}(R, g, z) \right] dz ,
$$

(5.1)

where $J$ is the number of phonon configurations and $\Phi_{j}$ is the probe electron wave function in reciprocal space for the $j^{th}$ atomic configuration at a depth $z$. A STEM high angle annular dark field (HAADF) image of LaMnO$_3$ taken in the pseudocubic [001] zone axis orientation is shown in Fig. 5.2. The projected structure is indicated by the coloured circles. The yellow arrow in Fig. 5.2 indicates the generic $\langle 110 \rangle$ lattice direction. Figures 5.3(a) and (b) show the measured zero-loss peak

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5.1. EXPERIMENTAL RESULT LaMnO$_3$

![La Mn O columns diagram](image)

Figure 5.2: HAADF image of a 250 Å thick sample of LaMnO$_3$ in the [001] zone axis orientation. The ⟨110⟩ direction is indicated by the yellow arrow.

(ZLP)$^1$ and HAADF signals respectively along the ⟨110⟩ lattice direction (crosses) compared to simulation (solid line). In Figs 5.3(c) – (f) experimental integrated EELS line scans taken along the ⟨110⟩ lattice direction are compared with nonlocal simulations$^2$. Simulations assumed a probe forming aperture of 20 mrad and a spectrometer collection angle of 12 mrad. The electron probe source size, and thus spatial incoherence, was estimated to have a full-width at half-maximum (FWHM) of 1.0 Å and the beam energy was 100 keV. Typical electron optical parameters for the aberration corrected VG HB501UX STEM are: defocus $\Delta f = 62$ Å, $C_s = -0.05$ mm and $C_5 = 63$ mm. The sample thickness was estimated at 250 Å. The EELS images were formed by integrating the EELS intensities over 40 eV above the edge onset for the O $K$, La $N_{4,5}$, La $M_{4,5}$ and Mn $L_{2,3}$ absorption edges. The ZLP signal shown in Fig. 5.3(a) exhibits a reduction of intensity above the atomic columns due to high angle scattering beyond the range of the EELS detector. The HAADF signal shown in Fig. 5.3(b) has opposite contrast, exhibiting the usual $Z^{1.7}$

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$^1$We make a distinction between the ZLP and bright field STEM in chapter 3. Here the ZLP signal is considered to have a large amount of incoherent TDS due to the large collection angle and is thus only partially coherent.

$^2$The vertical scale has been set to the dimensionless quantity $\sigma/\sigma_{ave}$ to facilitate comparisons between simulation and experiment on a common scale. Whilst bright field STEM and STEM HAADF images have been placed on an absolute scale, this has yet to be attempted/achieved for STEM EELS and could explain some of the discrepancies in Fig 5.3 regarding the differences in contrast.
Figure 5.3: Experimental (110) line scans (crosses) and simulations (solid lines) for (a) the zero loss peak, (b) HAADF, (c) the O K edge, (d) the La N\textsubscript{4,5} edge, (e) the La M\textsubscript{4,5} edge and (f) the Mn L\textsubscript{2,3} edge. The positions of the atomic columns are indicated by the circles: Mn is red, La is green and O is blue.
5.1. EXPERIMENTAL RESULT LaMnO$_3$

variation of HAADF images. Since electrons scattered through high angles to the HAADF detector cannot also fall on the EELS detector, this reversal of contrast is to be expected.

Immediately striking is the shape of the line scans themselves. For the O $K$ edge line scan shown in Fig. 5.3(c) there is an obvious dip or “volcano” located above the Mn/O columns. A volcano is also clearly present in the La $N_{4,5}$ edge line scan shown in Fig. 5.3(d), with the other line scans in Figs. 5.3(e) and (f) showing a flattening of the peaks above the columns from which the signal originates. Such volcano-like structures have been noted previously in simulations but have never before been observed experimentally [46, 73]. (These will be discussed in more detail in Sec. 5.2). The O $K$ and La $N_{4,5}$ edge line scans have similar contrast and width, despite significantly different binding energies. While it has been suggested that, for the case of high resolution electron microscopy (HRTEM), EELS signals should maintain the same contrast as the ZLP signal [146], the difference in the shape and contrast of the La $M_{4,5}$ and $N_{4,5}$ suggests that the nature of the inelastic ionization potential is an essential part of inelastic image formation in STEM.

To understand why these effects are more pronounced for fine probes, Eq. 5.1 is rewritten for the case of an isolated atom whose thermal motion is ignored:

$$\sigma(R, t) \propto \sum_{h, g} f(h, g) \Phi^*(R, h) \Phi(R, g) \Delta z,$$

where $\Delta z$ is the thickness of the slice containing the atom. The range of the summation is restricted to non-zero values of $\Phi(R, g)$, determined by the probe forming aperture. In Fig. 5.4 $f_{h, g}$ are plotted for parallel reciprocal space vectors $h$ and $g$ (for ease of display). The appearance of the form factor plots for the O $K$ edge shown in Fig. 5.4(a) is similar to that of the La $M_{4,5}$ and Mn $L_{2,3}$ edge form factors shown in Figs. 5.4(c) and 5.4(d) respectively. For the La $N_{4,5}$ edge shown in Fig. 5.4(b), the structure of the form factor is somewhat different, with the central peak being far narrower with a more complex distribution of negative form factors. In all cases the aperture extends into the negative region of the form factor and the minimum value within the aperture is shown. The negative areas in the La $N_{4,5}$ edge plot cover a range of less than half that seen in the other plots. Similar behavior is found for the terms involving reciprocal vectors which are not parallel.

The contribution of negative values of the form factors to image formation is
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Figure 5.4: Inelastic atomic scattering form factors for parallel reciprocal space vectors for (a) the O \( K \) edge, (b) the La \( N_{4,5} \), (c) the La \( M_{4,5} \) edge and (d) the Mn \( L_{2,3} \) edge. The dark sections of the plots indicate negative values of \( f_{h,g} \) [147]. All form factors are normalized to have a maximum value of one (brightest region). The portion of the form factor included in the collection aperture is within the white squares in each case and the minimum value of \( f_{h,g} \) contained therein is indicated.
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illustrated in Fig. 5.5, where images of isolated atoms have been simulated. This allows the examination of the nature of the ionization interaction without the complication of channeling. The projected electron density $\rho(\mathbf{r}) = \sum_m \int |u_{0,m}(\mathbf{r})|^2 dz$ of the bound state from which the electron is ejected is shown by the solid background. The positive values of the form factors all produce “Gaussian like” images peaked on the atomic site. The negative components produce a negative contribution to image formation at the atomic site. Figure 5.5(a) shows that the O $K$ edge image, whose form factor becomes the most negative, has a distinct dip at the atomic position. The form factors for the La $M_{4,5}$ and Mn $L_{2,3}$ edges are less negative and thus do not provide as large a modifying contribution at the atomic sites and the La $M_{4,5}$ edge image shown in Fig. 5.5(c) has only a slightly flattened top. As probe forming apertures can be made larger due to aberration correction and STEM probes become correspondingly smaller, the sum in Eq. 5.2 includes more negative components of the form factor and simulations show that volcanoes will be more pronounced, albeit narrower. Increasing the collector semi-angle extends the length and magnitude of the positive valued diagonal region to larger reciprocal lattice vectors whilst simultaneously reducing the average magnitude of the negative parts of the form factor. This causes the contribution of the negative parts of the form factor sampled by the probe to be dwarfed by those of the positive form factor contributions, reducing and even eliminating the volcanoes.

An important consequence of the volcanoes is that the FWHM of the images is increased beyond that due to the positive form factor contributions. Thus, the FWHM of the La $N_{4,5}$ image is actually narrower than any of the other images despite having the lowest binding energy of 99 eV. This is contrary to classical estimates of the FWHM – see for example Ref. [148]. However, the La $N_{4,5}$ image is still nonzero at a radius of 3 Å due to its long extended “tail”.

The main difference between these single atom calculations is the bound state wave radial functions $u_{l,m_l}(r)$ used in calculating the transition matrix elements needed for $f(h, g)$ in Eq. 5.2. In Figs. 5.5(a), (c) and (d), the projected electron density of the bound states is peaked close to the atomic sites, far more so than the resulting single atom images. For La $N_{4,5}$ shown in Fig. 5.5(b) there is significant density away from the atomic site despite the fact that La $N_{4,5}$ yields the narrowest image. There is no simple relationship between the electron density of the initial state and image width. The notably different atomic images for the O $K$ and La
Figure 5.5: Single atom EELS images for (a) the O $K$ edge, (b) the La $N_{4,5}$ edge, (c) the La $M_{4,5}$ edge and (d) the Mn $L_{2,3}$ edge. The contributions to the total intensity from positive and negative $f_{h,g}$ are indicated by the dashed and dotted lines respectively. The projected electron density of each bound state is shown by a solid background.
Figure 5.6: Probe intensity as a function of depth $z$ for (a) the probe located above a La column with an intensity profile along the column shown in (d). Corresponding results for Mn/O columns are shown in (b) and (e), and O columns in (c) and (f).
$N_{4,5}$ edges in Fig. 5.5 contradicts the similarity in shape and width of the line scans seen in Figs. 5.3(c) and 5.3(d). From Eq. 5.1 it is clear that the image depends not only on the inelastic scattering, but also the channelling of the incident electrons in the sample. The role of channeling of the STEM probe through a crystalline sample is most easily described for a probe at a fixed position $\mathbf{R}$ [141, 149]. In Fig. 5.6 the probe intensity is shown as a function of depth within the crystal for the probe placed over each of the atomic columns. When the probe is positioned above La columns (Fig. 5.6(a)) the intensity peaks at $z \approx 20$ Å with a small secondary peak at $z \approx 60$ Å. The intensity variation is seen more clearly in Fig. 5.6(d) where a line scan along the column is shown. Most of the intensity has dispersed by a depth of 100 Å and the La atoms are significantly illuminated for only the first 50 Å. When the probe is located above Mn/O columns (Fig. 5.6(c) and (d)) the probe has significant penetration for the first 100 Å and the intensity remains small but nonzero for the remaining depth of the crystal. For O columns (Fig. 5.6(c) and (d)) the intensity is significant for the entire crystal thickness, with the exit surface intensity being 50 % of that at the entrance surface. Channeling of the electron probe in the sample plays an important role in image formation.

Figure 5.7 shows the evolution of the ZLP (left side) and HAADF (right side) signals as a function of specimen thickness. For a single unit cell the ZLP signal is essentially flat, with small reductions in intensity above the La and Mn/O columns. The HAADF signal has maximum intensity above the La column with lesser intensity above the Mn/O column. Consistent with the results shown in Fig. 5.6, by a depth of 61.6 Å there is a significant deficiency in the ZLP above the La columns and a correspondingly smaller volcano above the Mn/O column. Maximum intensity occurs on the O columns where the probe continues to have significant intensity as seen in Fig. 5.6(f). The peak above the Mn/O column in the HAADF signal has increased slightly compared to that above the La columns, due to the higher incident electron density about this column at this depth. By the time the probe has channeled through 123.2 Å, there is only significant probe intensity remaining on the O columns. This is reflected in the ZLP signal, where the image is peaked above the O columns. The fact that the probe has significant intensity on the Mn/O column for approximately twice the depth that it does on the La column has led to an increase in the HAADF signal above the Mn/O column relative to the signal above the La column such that the two are now similar in magnitude. Since there is no further
Figure 5.7: ZLP (left) and HAADF (right) intensities as a function of specimen thickness. These simulations do not include convolution with a source size term in order to emphasize the mechanisms underlying image formation. The black lines indicate the \( \langle 110 \rangle \) scan direction.
significant probe intensity on either the La or Mn/O columns after this depth, there is little change in the relative HAADF signals for thicker samples.

In Fig. 5.8 the evolution of the images based on the measured edges as a function of crystal thickness across the whole unit cell is shown. The simulated images for a “crystal” one unit cell thick gives the “atomic” images without the complication of channeling. The contribution to the image from each O column is identical at this stage. The O columns are only 1.93 Å apart and this results in considerable overlap between the images formed by each atomic column. (The blue circles represent the position where the volcanoes would occur if only individual atoms where considered.) This makes the interpretation of a single line scan difficult. As specimen thickness increases the intensity above the central column in the unit cell shows a significant reduction. This column contains the heavier Mn atoms, which generate
significant TDS (as evident from the large HAADF signal) and reduce the intensity on the column. By the time the sample is 64 unit cells thick, approximately the estimated thickness of the experimental specimen, this reduction in intensity has become substantial. A line scan taken in the \( \langle 010 \rangle \) direction across alternating O/MnO/O columns would show a significant deficiency on the Mn/O column, possibly leading to the erroneous conclusion that there were fewer O atoms in the central column.

The La \( N_{4,5} \) image for single unit cell thickness is more straightforward, with a peak on each atomic column. There is however considerable intensity away from the columns, with the minimum at the center of the unit cell being almost 40% of the on column intensity. As the sample becomes thicker a volcano develops. With significant absorption due to TDS occurring when the probe is positioned above the La or Mn/O columns, there is less contribution to the image than when the probe is positioned above the O columns and interacting with the 40% “background”. The small peaks above the O columns for 246.4 Å reflects the peaks in the ZLP seen in Fig. 5.6. This again leads to an image that is difficult to interpret without comparison to simulation. For the simulation at the greatest thickness there are peaks on the O columns and relatively little intensity on the La columns.

It is interesting to compare the La \( M_{4,5} \) edge image to that formed by the La \( N_{4,5} \) edge. Because the signals originate from the same atoms, channeling and TDS is identical in both cases. The La \( M_{4,5} \) image is however significantly localised about the La columns, with little overlap between columns even for the simulation for the greatest thickness shown here. The drastically different shape and distribution of these two cross sections illustrates clearly the importance of the inelastic scattering potential. While it has been shown that for HRTEM low-loss EELS, “most inelastic scattering processes in crystals preserve image contrast to a first approximation” [146], clearly for core-loss EELS, at least in the case of atomic resolution STEM, this approximation is poor.

The image formed by the Mn \( L_{2,3} \) edge is largely contained within the unit cell, consistent with previous results supporting column by column spectroscopy [45]. However a significant deficiency in the edge intensity occurs above the column for increasing thickness due to TDS.
5.2 The volcano structure and multipole contributions

The striking differences in the shape and widths of the experimental EELS images in Fig. 5.3 was attributed to the characteristic volcano structure and warrants further investigation into its origin and more specifically the subtleties of the inelastic scattering potential. In this section we shall elucidate the mechanism behind the volcano formation. We shall consider the test case of isolated Ti atoms and the spectroscopic image formed when integrating up the $L_1$ and $L_{2,3}$ edges. Choosing Ti allows us to attempt to isolate the influence that the bound state wave function has on the image as the binding energy of the $L_1$ and $L_{2,3}$ shell electrons is similar. We begin by considering the dipole approximation and consider the effect of the higher order terms in Eq. 4.31. Modelling inner-shell ionization using the dipole approximation, Kohl and Rose [46] presented single atom EELS images. Using a HRTEM geometry they separated contributions from the parallel to the incident beam and perpendicular to the incident beam dipole excitations to show the dependence of each component’s weighting on the incident probe energy loss (cf. Eq. (58) in Ref. [46]). Muller and Silcox [150] derived equivalent expressions for STEM. Large energy losses cause the parallel excitation weighting, which peaks at the atom location $R = 0$, to dominate over the perpendicular contributions which is identically zero at the atom location $R = 0$. As the energy loss decreases, the perpendicular excitations, which have the characteristic volcano shape, begin to dominate. The balance between parallel and perpendicular excitations determines the extent of the image’s volcano structure. The parallel and perpendicular components, in the dipole approximation for crystals with low symmetry, can easily be obtained using

$$f_{\text{dipole}}(\mathbf{h}, \mathbf{g}) = \int \int C(\epsilon) \frac{(Q + h) \cdot (Q + g)}{|Q + h|^2 |Q + g|^2} d\Omega_{K'} d\epsilon$$

$$= \int C(\epsilon) \int \frac{(k\theta_E)^2}{|Q + h|^2 |Q + g|^2} + \frac{(h - K'_\perp) \cdot (g - K'_\perp)}{|Q + h|^2 |Q + g|^2} d\Omega_{K'_\perp} d\epsilon,$$

(5.3)

where the function $C(\epsilon)$ absorbs all the constants for a given energy loss within the energy window, and $\theta_E$ is the characteristic scattering angle as defined by $\theta_E = \Delta E/(2E_0)$ [148], which for plane wave incidence links the half width of the scattered electron angular distribution $\theta_E$ with the energy loss $\Delta E$ and the accelerating
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voltage $E_0$. This allows for the separate calculation of the parallel and perpendicular components (relative to the incident electron’s wave vector), the contributions arising from the first and second terms of the integral respectively. Considering a single energy loss within the energy window reduces $C(\epsilon)$ to a constant scaling factor. The usefulness of the dipole expression is its direct relationship to STEM scattering geometry: the fine details of the bound and continuum state wave functions contained in $C(\epsilon)$ only scale the image, they do not change its shape.

5.2.1 Single atom images

For our case study of the features of STEM EELS images arising at the level of a single atom we consider an isolated Ti atom. We assume a 100 keV probe, with a 37.5 mrad probe-forming aperture semi-angle (giving a probe full width at half maximum of around 0.5 Å, the resolution goal of the TEAM project [151]), and an EELS detector collection semi-angle of 10 mrad. It must be remembered that using a collection angle smaller than the probe forming aperture does not make the best use of the available signal. However, for our theoretical simulations this is not a primary concern and demonstrates physical principals more clearly. Figures 5.9(a) and (b) show STEM EELS images for the $L_1$ and $L_{2,3}$ edges respectively in Ti, simulated using the dipole approximation (Eq. (5.3)), and the decomposition of these signals into parallel and perpendicular contributions. Due to the relatively similar binding energies of the $L_1$ and $L_{2,3}$ edges, the dipole approximation predicts similar shape images for both edges (albeit scaled). For the simulated probe parameters and energy losses the perpendicular excitations dominate over the parallel and the characteristic volcano structure is seen. Whilst the $L_1$ edge is not easily accessible experimentally, its inclusion here allows for comparison with previous work [152]. Figures 5.9(c) and (d) show the corrections introduced by going to successively higher order expansions of the exponential operator (Eq. (4.31)). The quadrupole correction is obtained by taking the difference between simulations with the series in Eq. (4.31) truncated to quadrupole order and simulations with the series truncated to dipole order. Likewise, the octupole correction is obtained from the difference between simulations truncated to octupole order and those truncated to quadrupole order. As such these “corrections” may be negative, but the important feature is their magnitude, which is indicative of whether or not the series is adequately converged.
Figure 5.9: Single Ti atom EELS line scans as a function of probe position and the relative contributions of perpendicular and parallel excitations to the total dipole cross section are shown for the (a) $L_1$ and (b) $L_{2,3}$ edges. The corrections introduced by extending the exponential series (Eq. (4.31)) to quadrupole and octupole orders are shown for the (c) $L_1$ and (d) $L_{2,3}$ edges. The collection semi-angle was 10 mrad. The intensity was integrated up 40 eV above the ionization threshold. The 100 keV probe was aberration-free with a probe forming aperture semi-angle of 37.5 mrad. The Ti atom is located at 0 Å.
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The $L_1$ image has a quadrupole correction that has a similar magnitude to its dipole contribution. Both edges have a significant octupole correction which reduces the prominence of the dipole volcano. The strength of the quadrupole correction (and to a lesser extent the octupole correction) in the $L_1$ image totally removes the volcano, leaving a large peak on column. This does not occur to the same extent in the $L_{2,3}$ image. The relative difference in the strength of these corrections has caused the shape of the images to differ markedly from one another.

Examining the real space transition potentials for the $L_1$ and $L_{2,3}$ edges plotted in Figs. 5.10(a) and (b) respectively, calculated using Eq. 4.14, we see that the dipole allowed $l' = 1, m' = 0$ transition is significantly more delocalised than the quadrupole allowed $l' = 0, m' = 0$ transition. Overlaid on Fig. 5.10(a) is the probe intensity profile for a probe formed using a 37.5 mrad aperture semi-angle. As such, the overlap of the probe intensity and the $l' = 0, m' = 0$ transition potential is greater than the $l' = 1, m' = 0$ dipole overlap.

Saldin and Ueda [152] calculated the dipole approximation validity analytically for both the $L_1$ and $L_{2,3}$ edges assuming plane wave incidence. They found the maximum momentum transfer permissible before higher order multipole contributions become significant was larger in the $L_1$ edge than in the $L_{2,3}$ edge. However Fig. 5.9 indicates that the non-dipole corrections are larger for the $L_1$ edge than for the $L_{2,3}$, and thus in STEM, where the electron probe is a coherent sum of plane waves and interference between waves is possible, the results of Saldin and Ueda appear not to hold. We can gain insight into why non-dipole allowed transitions are more important for STEM by considering Fig. 5.10. Supposing the “probe” is a plane wave, the overlap between the plane wave and the $l' = 1, m' = 0$ dipole allowed transition dominates. But for a STEM probe positioned directly above the atomic site, there is a large overlap with the peaked quadrupole potential: it has a greater interaction strength and consequently dominates, provided that the dipole state is sufficiently delocalised. This is consistent with the analysis of Muller and Silcox [150], who showed that the dipole approximation would dominate unless the impact parameters were the same size as the dipole matrix elements. As Fig. 5.10(a) indicates, the latter situation will be realised in current and next generation scanning transmission electron microscopes.

It is important to recognise the distinction between the dipole approximation –truncating Eq. 4.31 to first order – and considering dipole allowed transitions. Fi-
Figure 5.10: (a) Transition potentials for exciting a Ti $L_1$ ($l = 0, m = 0$) electron to final states ($l' = 1, m' = 0$) and ($l' = 0, m' = 0$) at 1 eV above threshold (left axis) and the probe intensity profile for a 37.5 mrad probe forming aperture semi-angle (right axis). (b) The transition potentials for exciting a Ti $L_{2,3}$ ($l = 1, m = 0$) electron to final states ($l' = 2, m' = 0$) and ($l' = 1, m' = 1$), and a Ti $L_{2,3}$ ($l = 1, m = 1$) electron to final states ($l' = 2, m' = 1$) and ($l' = 2, m' = 2$) at 1 eV above threshold. (c) and (d) STEM EELS probe line scans across an isolated Ti atom for the $L_1$ and $L_{2,3}$ edges respectively at 1 eV above threshold, for an electron detector collection semi-angle of 10 mrad and a 100 keV probe formed with an aperture semi-angle of 37.5 mrad. In (c) and (d) contributions are shown separately for transition to final states $l' = 0, l' = 1, l' = 2$, and the total of these three (legend in (d)).
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gures 5.10(c) and (d) show the contributions to the Ti $L_1$ and $L_{2,3}$ edges arising from transitions to final states with specific orbital angular momentum quantum numbers $l'$. (Unlike the “correction” terms in Fig. 5.9, these contributions have physical meaning in their own right, and as such the image from each is strictly positive.) The contribution from the dipole allowed transition in Fig. 5.10 is different to the dipole approximation signal in Fig. 5.9, because, though the number of final states is restricted, all orders in the Taylor expansion are retained. The dipole allowed transitions effectively include the significant octupole corrections seen in Fig. 5.10. The total signal in Fig. 5.10 differs slightly to that in Fig. 5.9 and is the more converged calculation.

Fig. 5.9 showed the importance of including higher order contributions, though the differences were more quantitative than qualitative for the $L_{2,3}$ edge. Including all orders of the Taylor expansion (as we do from this point onward), the STEM image of the isolated Ti atom is presented in Fig. 5.11 as a function of probe position and probe forming aperture semi-angle. Small probe-forming aperture semi-angles are seen to produce smaller volcanoes in the Ti $L_1$ image than in the $L_{2,3}$ image. Increasing the aperture semi-angle causes the $L_1$ image to fill the volcano, eventually peaking sharply on column. This is attributed to the increasing significance of the quadrupole allowed transition. In contrast the $L_{2,3}$ image has larger volcanoes that increase slightly in depth with larger aperture semi-angles.

Having considered the dependence of single atom images on probe size, it is worth making some observations on the role of the detector size. Rather than considering the fractional intensity as a function of detector collection angle, we consider its derivative with respect to the detector collection angle. This differential fractional intensity, shown in Figs. 5.12 and 5.13, can be thought of as the signal in a very narrow annular detector with the mean collection angle as shown. The figures in the left hand column correspond to a probe with probe-forming aperture semi-angle of 25 mrad, those on the right to a probe-forming aperture semi-angle of 37.5 mrad. Figs. 5.12(a) and (b) show this differential fractional intensity as a function of probe position and detector acceptance angle for the $L_1$ edge, and Figs. 5.12(c) and (d) show the same for the $L_{2,3}$ edge. The outermost detector angles (think annular detectors) register no volcanoes, whereas the smaller angles do. As the probe moves away from the atomic site beyond a Bohr radius (i.e. the probe is no longer directly above the atom) the quantity of large angle scattering decreases until
eventually it is surpassed by small angle scattering. The signal FWHM for the outer annular detectors is much smaller than for the inner detectors. This is consistent with previous work [150, 153], showing an increase in signal localization by using displaced detectors. The resolvability of single atom images could be improved by using annular detectors.

Figures 5.13(a) and (b) show extracts from the plots in Fig. 5.12 for two fixed probe positions: above the atom and 0.55 Å off the atom (solid and dashed lines respectively). Both Ti $L_1$ (gray lines) and $L_{2,3}$ (black lines) edges are shown. For the probe above the atom, the signal increases with scattering angle up to the angle of the probe-forming aperture, suggesting a fairly uniform intensity distribution such that the signal increases with the circumference of the annular detector. The signal drops off for higher scattering angles, with that for the $L_1$ orbital falling off more slowly than the $L_{2,3}$ orbital. For the $L_{2,3}$ edge, the amount of inelastic scattering from the displaced probe increases in the forwards direction, out to about 15 mrad with the 25 mrad probe and 22 mrad for the 37.5 mrad probe. Beyond this, the amount of scattering is reduced. Thus the total inelastic scattering is less for the displaced probe but it is more forward focused, creating the volcano ridge. A subtle change in the scattering distribution with increasing probe forming aperture semi-
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Figure 5.12: The differential EELS signal with respect to detector collection angle as a function of detector angle and probe position for the Ti $L_1$ edge, (a) and (b), and the $L_{2,3}$ edge, (c) and (d). The differential fractional intensity can be thought of as the signal in a very narrow annular detector with the mean collection angle as shown. The 100 keV probe was aberration-free with probe forming aperture of 25 mrad in (a) and (c), and 37.5 mrad in (b) and (d). The figures were calculated for a single energy loss 1 eV above ionization threshold.
Figure 5.13: The differential EELS signal with respect to detector collection angle as a function of detector angle at fixed probe positions above the atom (solid) and 0.55 Å off the atom (dashed), extracted from Fig. 5.12 for the Ti $L_1$ edge (grey line) and the $L_{2,3}$ edge (black line) is shown in (a) and (b). (c) and (d) are the integrated intensity plots of (a) and (b) respectively. The 100 keV probe was aberration-free with a probe forming aperture of 25 mrad in (a) and (c), and 37.5 mrad in (b) and (d). The figures were calculated for a single energy loss 1 eV above ionization threshold.
angle is seen in Fig. 5.13(b) for a probe forming semi-angle of 37.5 mrad. The $L_1$ edge maintains a larger signal on top of the atom than off the atom whereas the $L_{2,3}$ edge does not. This change in scattering distribution serves to ‘fill’ in the volcano, as was seen in Fig. 5.11(a). The $L_1$ orbital has a bound state radial wave function that has a single radial crossing but the $L_{2,3}$ orbital does not. This affects the shape of the transition potential and consequently the details of the scattering distribution.

Figs. 5.13(c) and (d) show the integrated signals corresponding to the plots in Figs. 5.13(a) and (b). The cross-over at small scattering angles which is indicative of the volcano can again be seen. Additionally, the volcano feature is clearly suppressed for larger collection angles.

5.3 Discussion and conclusions

This section compares EELS channelling theory with experimental results revealing subtleties in the underlying interaction which makes images difficult to interpret. Delocalisation gives an extended tail to atomic images, which reduces contrast but does not preclude atomic resolution. In such cases dechannelling from columns may lead to a volcano-like contrast at high thickness. The geometrical considerations which have been used to interpret EELS images must be applied cautiously. The expansion of the exponential into its multipole form reveals that for accurate quantitative simulations it is not possible to discard the final states beyond the dipole transitions. Qualitative interpretations may be made using dipole transitions provided that the bound state radial wave function is strictly positive (i.e. no radial crossings) but is nevertheless not straightforward due to the significant octupole induced correction. The volcano structure seen in both simulation and experiment is a result of the balance between three distinct influences: the inelastic scattering potential, scattering geometry and the probe evolution in the specimen.
Two-dimensional chemical mapping

As was shown in the previous chapter, the interpretation of EELS lines scans in scanning transmission electron microscopy (STEM) based on core-loss electron energy-loss spectroscopy (EELS) requires a more than superficial understanding of the probe, its channelling and dechannelling and its interaction with a delocalised ionization potential. This chapter discusses chemical mapping in two dimensions and is based on the work in Refs. [58, 60, 154]. The first section compares theory and experiment for two dimensional EELS maps of a sample of Bi$_{0.5}$Sr$_{0.5}$MnO$_3$. The experimental data was provided by M. Bosman from a collaboration between the University of Sydney, The University of Newcastle, Universitari de Bellaterra and the University of Melbourne. The experimental data for the contrast reversal in a Si sample was taken by P. Wang in collaboration with the SuperSTEM laboratory in Daresbury. The energy dispersive x-ray spectroscopy data was provided by B. Freitag from FEI.

The correlation of structure, composition, and physical properties using high-resolution STEM has predominantly been achieved by using the high angle annular dark field (HAADF) image as a probe position reference to record energy-loss spectra at select, structurally significant points [42, 43]. With the latest generation of aberration corrected microscopes [53], recording energy-loss scans along a contiguous sequence of points is possible [45, 155], although it is not routine. Overcoming the restriction of EELS studies to predetermined regions of interest enables a broader investigation of structure-composition-property relations. As shown in the previous chapter, implementing this is complicated as high-resolution STEM
images, both HAADF and EELS images, do not always admit direct, visual interpretation [43, 56, 108, 132, 141, 156, 157].

The three inter-related reasons discussed in chapter 4, channelling, inelastic phonon scattering and the long range nature of the coulomb interaction can lead to a non-intuitive link between the probe density in the sample and the magnitude of the recorded signal. These complications are particularly difficult to identify if only point or line scan data is available [57]. EELS mapping in two dimensions, as demonstrated here, allows more convincing comparisons with simulations based on shape than is possible for line scans and will help our understanding of these processes.

The restriction to EELS line scans at atomic resolution arises because the scattering cross section for inner-shell ionization processes is relatively low. Adequate counting statistics for HAADF images are obtained with millisecond dwell times, whereas dwell times for electron energy-loss spectra need to be of the order of tenths of a second, comparable to the time scale on which beam damage, specimen drift and other mechanical instabilities manifest themselves.

6.1 Two-dimensional mapping of $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$

The construction of highly stable microscope environments and the ongoing developments in aberration correction (which enable an increase in beam current) have made possible and are actively improving full two dimensional mapping. It is now possible to obtain two dimensional compositional maps at atomic resolution. The specimen used for the present study was $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, a new material that shows colossal magnetoresistant behavior [158]. It is also one of the few materials that shows “charge ordering” at room temperature [159, 160]. Neutron and x-ray powder diffraction showed that the material is not an ideal perovskite, but possesses lattice distortions that are most evident in the inclination of the O octahedra about the Mn sites. The Bi and Sr cations are evenly distributed at equivalent lattice sites in a random manner throughout the compound. A model of the unit cell is shown in Fig. 6.1.

The specimen was imaged along the three zone axes $\langle 001 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ (where the labelling is based on the approximate cubic perovskite structure). The
6.1. TWO-DIMENSIONAL MAPPING OF Bi$_{0.5}$Sr$_{0.5}$MnO$_3$

Figure 6.1: Model structure of a Bi$_{0.5}$Sr$_{0.5}$MnO$_3$ unit cell in (a) a three dimensional perspective and (b) oriented along the ⟨001⟩ zone axis and (c) oriented along the ⟨010⟩ zone axis. The Bi/Sr cations locations are indicated in green, the Mn atoms are purple and the O atoms are red. The apparent asymmetry in (b) and (c) is due to the distorted structure having Bi/Sr atoms just outside the unit cell bounds.

Data were acquired using the VG HB501 dedicated STEM at the SuperSTEM facility in Daresbury, UK. The probe-forming semi-angle and EELS detector collection semi-angle were both around 24 mrad.

Figure 6.2 shows a typical example of an EELS spectrum after alignment and dark current subtraction. The spectral features of interest, the O K edge and the Mn $L_{2,3}$ edge, are situated on a sloping background signal that should be removed to obtain the accurate O or Mn intensities.

As shown in Fig. 6.2, power-law fits were applied to the pre-edge intensities of the principal component analysis reconstructed spectra and these background signals were subtracted from the original spectra. This routine was applied to extract both the O signal and the Mn signal. The background-subtracted O and Mn intensity for all spectra were integrated over a 30 eV window above their respective thresholds to produce EELS maps. This energy range avoids major multiple scattering effects, which are strongest at higher energy losses. Figures 6.3, 6.4 and 6.5 show experimental and simulated HAADF images, together with EELS maps of the O and Mn signal for the three orientations. The acquisition parameters were identical for the HAADF and EELS measurements. The specimen thicknesses, determined using low-loss spectra from the same area, were estimated as 313 – 358 Å,
Figure 6.2: An example of a single EELS spectrum, taken from the left-hand corner of the EELS data set in Fig. 6.3. The circles show the raw spectrum after subtracting the dark current. The thick grey line is the principal component analysis (PCA) reconstruction of the raw spectrum, as calculated from the first three principal components of the whole EELS data set of Fig. 6.3. The thin grey line is a power-law fit to the reconstructed spectrum, using a 20 eV wide window before the O K edge. The thin black line shows the background-subtracted raw spectrum, which is used for further analysis.
120 – 125 Å, and 350 – 450 Å for the \( \langle 001 \rangle \), \( \langle 110 \rangle \), and \( \langle 111 \rangle \) oriented samples respectively – the large spread in the last being attributed to beam damage as will be discussed later.

The “orth 1” atomic structure at 300 K given in Ref. [161] is used as input to the direct simulations. These are Bloch wave simulations based on effective inelastic scattering potentials calculated using the method described in Sec. 4.2, accounting for the Bi/Sr columns using fractional occupancy. The aberration-balanced system is modelled as aberration-free within the 24 mrad probe-forming aperture—an assumption which may account for some of the discrepancy between measured and simulated resolutions. The HAADF images were simulated for a 60–160 mrad annular dark field detector. The EELS images were simulated with a 24 mrad detector semi-angle and the effect of the crystal potential on the ejected atomic electron was ignored as the spectrum was integrated over a 30 eV energy window above the ionization threshold averaging over the associated fine structure. For the present experiment, the demagnification of the effective electron source was slightly lower than that for optimal resolution to enhance the current in the probe for better EELS counting statistics. To account for this finite width of the effective source, all simulated images were convolved with a Gaussian of full-width at half-maximum (FWHM) of 1.2 Å [127]. This number, obtained by best visual comparison with the experimental data, still permits the imaging of the 1.4 Å dumbbell structure in Si along the \( \langle 110 \rangle \) zone axis, consistent with results obtained from this scanning transmission electron microscope under similar operating conditions.

In the simulated O image in Fig. 6.3(b), the signal on the Mn/O column is smaller than that on the pure O columns, despite the identical O densities. This is a consequence of the different scattering and absorption caused by the presence of Mn. However, the difference is too small to be evident in the experimental image. More pronounced dechanelling effects can be seen in the O map of Fig. 6.4(b), where the signal is smallest on the Bi/Sr/O column, though admittedly in this orientation the O density on these columns is half that on the clearly visible pure O columns. More intriguingly in this image, the simulations show evidence of the inclination of the MnO\(_6\) octahedra through the alternating displacements in O position when looking along horizontal rows in the figure. A hint of this behaviour is also seen in the experimental data.

Specimen damage was only observed in the \( \langle 111 \rangle \) orientation. The experiemen-
Figure 6.3: Comparison between experiments (tilted images) and simulations of \( \text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3 \) oriented along the \( \langle 001 \rangle \) zone axis. (a) HAADF, (b) O \( K \) edge and (c) Mn \( L_{2,3} \) edge STEM images. The atomic structure is indicated. The EELS maps were generated by integrating the EELS spectra over a 30 eV window above the respective ionization threshold. This is shown in grey shading on the spectra to the right, which are summations of all the spectra in the adjacent EELS maps. The HAADF image is the summation of three cross-correlated single images, taken from the same area, with the same experimental settings as the EELS maps. The simulations assume a 330 Å thick sample.
6.1. TWO-DIMENSIONAL MAPPING OF Bi$_{0.5}$Sr$_{0.5}$MnO$_3$

Figure 6.4: As Fig. 6.3 but with the Bi$_{0.5}$Sr$_{0.5}$MnO$_3$ specimen oriented along the $\langle 110 \rangle$ zone axis. (a) HAADF, (b) O K edge and (c) Mn $L_{2,3}$ edge STEM images. The zig-zag pattern of the O columns is most noticeable in this specimen orientation and is caused by the tilted MnO$_6$ octahedra. The simulations assume a 120 Å thick sample.
Figure 6.5: As Figs. 6.3 and 6.4 but with the Bi$_{0.5}$Sr$_{0.5}$MnO$_3$ specimen oriented along the ⟨111⟩ zone axis. (a) HAADF, (b) O $K$ edge and (c) Mn $L_{2,3}$ edge STEM images. The shoulder on the low-energy side of the Mn $L_3$ edge (inset) becomes more pronounced from top to bottom in the EELS data, indicating a reduction of the Mn cations during data acquisition. The simulations assume a 400 Å thick sample.
tal O map in Fig. 6.5(b) has less intensity in the lower part, towards the end of the EELS acquisition, indicating a decrease of O content. The Mn map is more uniform. However, a shoulder on the low-energy side of the Mn L\textsubscript{3} edge becomes more pronounced for spectra in the lower part of the data set. Systematic studies \cite{162, 163} in combination with the O map indicate the partial reduction of the Mn cations due to electron beam-induced specimen damage. This effect necessitated the selection of a relatively thick area for the \langle 111 \rangle measurements of Fig. 6.5. Of all three Figs. 6.3–6.5, the \langle 111 \rangle orientation with its 350–450 Å thickness gives the least intuitive EELS maps. The O image, Fig. 6.5(b), has high intensity on the O columns, as might be expected. However, the experimental O map exhibits a low contrast (Michelson visibility of 0.13) which makes direct comparisons with simulation somewhat problematic. Propagation effects are of secondary significance to this image; a similar spatial distribution is observed in simulations for a single cell thickness. In Fig. 6.5(c), however, the Mn signal is smallest on the Bi/Sr/Mn columns, the only columns containing Mn. The greyscale images, plotting minimum to maximum as black to white, obscure the relatively low contrast variation which is more obvious in the experimental than the simulated data. The dip at the Bi/Sr/Mn columns is a consequence of the strong absorption by that column; the stronger signal between these columns is a consequence of probe spreading towards the Mn-containing columns. The brighter ring about the Bi/Sr/Mn columns indicates the range of significant interaction with the delocalised ionization potential.

### 6.2 Silicon, delocalised interaction potentials and contrast reversals

The consequence of the delocalised potential was hinted at with the anomalous result shown in Fig. 6.5(c) in Sec. 6.1. However, for another perspective on the significance of the delocalised potential and how taking full two-dimensional maps aids interpretation of spectroscopic data, we shall investigate the EELS images obtained from a sample of Si viewed along the \langle 011 \rangle zone axis. The Si unit cell is shown in Fig. 6.6. The \langle 011 \rangle Si specimen was estimated to be 910 Å thick. The convergence semi-angle of the 100 kV Nion UltraSTEM was 24 mrad. The simultaneous HAADF image, Fig. 6.7(a), was obtained using a 105–300 mrad annular
Figure 6.6: Model structure of a Si unit cell in (a) a three dimensional perspective, (b) oriented along the \(\langle 001 \rangle\) zone axis and (c) oriented along the \(\langle 011 \rangle\) zone axis.

collection range. The Nion UltraSTEM was equipped with a Gatan Enfina electron energy loss spectrometer that has a collection semi-angle of 67 mrad in the spectrometer’s energy dispersive direction and 22 mrad in the non-energy dispersive direction. A dispersion of 0.5 eV/channel was selected and the dwell time was set to 5 msec/spectrum. The charge on the CCD detector was binned from 100 into 20 channels in the non-energy dispersive direction. The entire spectrum image of \(20 \times 20\) pixels was recorded in 17 seconds with dark current and gain normalization. A \(20 \times 16\) pixel subset is show in Figs. 6.7(b) and (c) for energy loss windows of 143–163 eV and 280–300 eV subsequent to background subtraction. The power-law background fitting was sampled within a 20 eV window before the edge onset of the Si \(L_{2,3}\) edge. A typical example of the energy loss spectrum, depicting the background subtraction and the selected energy windows, is shown in Fig. 6.7(d).

Theoretical calculations were again carried out using the Bloch wave method in Sec. 4.2 due to its computational efficiency. The effect of the crystal potential on the ejected electron was ignored as we integrate over a 20 eV energy window. Calculations predict that the contribution of electrons that eject an electron from the \(L_1\) orbital is over an order of magnitude smaller than those that eject an electron from the \(L_{2,3}\) orbitals, and so the former are neglected. The 24 mrad probe forming aperture was modelled as being aberration free. The effective source size (and thus
Figure 6.7: Comparison between experimental (underlay) and simulated (overlay) images of ⟨011⟩ Si. (a) HAADF, (b) 143–163 eV EELS and (c) 280–300 eV EELS images. (d) A typical acquired Si EELS spectrum showing the background fit curve subtraction. The energy windows are colour coded with the indicated atomic structures on the corresponding images. All images were acquired simultaneously.
spatial incoherence) was accounted for by convolving with a Gaussian of FWHM 1.6 Å. This source size no longer allows for resolution of the 1.4 Å Si dumbbell spacing for the ⟨011⟩ projection in the simulated HAADF image, in agreement with the experimental results. As used previously, an Einstein model for thermal scattering was used to calculate the scattering into the HAADF detector and also to model the absorptive effect on the elastic probe, see Sec. 2.3.5.

The projected dumbbell structure formed by adjacent columns of Si atoms is correctly shown by the experimental (underlay) and simulated (overlay) HAADF images in Fig. 6.7(a). The \( L_{2,3} \)-shell EELS images for the energy windows 143–163 eV and 280–300 eV in Figs. 6.7(b) and (c) are obtained simultaneously with the HAADF image, and thus the electron probe experiences identical scattering and absorption conditions. We note that while the columns for the 280–300 eV energy window image are in register with the HAADF image, correctly reflecting the known structure, in the 143–163 eV energy window image the columns have apparently been translated. Since the evolution of the electron probe through the specimen is identical in both images, the difference must arise from the variation of the ionization interaction with energy loss. This was hinted at earlier with the \( ⟨111⟩ \) \( \text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3 \) result, Fig. 6.5. The ionization probability is known to become increasingly localised with increasing energy loss [148]. Using experimental data for this same edge, though in a thinner \( \text{Si}_3\text{N}_4 \) specimen, Kimoto et al. [52] recently demonstrated this effect in 2D EELS images. We can assess the variation in localisation directly and quantitatively by exploring the dependence of the localisation of the inelastic transition potential on energy loss [48]. The inelastic wave function is proportional to the product of the transition potential and the elastic wave function, so the modulus squared of the transition potentials measures the strength of the transfer of electron density into the inelastic channels. Fig. 6.8(a) shows the modulus squared of the inelastic transition potentials from an initial state with quantum numbers \( l = 1, m_l = 0 \) to a final state with quantum numbers \( l' = 2, m_{l'} = 0 \) as a function of energy loss for the Si \( L_{2,3} \) edge. While the width of the potential over the 280–300 eV window is comparable to the inter-dumbbell spacing, over the 143–163 eV window the potential is much more delocalised. The manner in which this variation affects the STEM EELS images depends on how the widths of these potentials compares with the distribution of the probe wave function at the various energies. For the fine probe and relatively thick but weakly scattering specimen,
6.2. SILICON, DELOCALISED INTERACTION POTENTIALS AND CONTRAST REVERSALS

Figure 6.8: (a) Modulus squared of the transition potentials, normalized to unity at the origin for a clear comparison of the change in shape, from initial state $l = 1$, $m_l = 0$ to final state $l' = 2$, $m_{l'} = 0$ as a function of energy loss for an isolated Si atom. The 143–163 eV and 280–300 eV energy windows are indicated. Circles show the locations of columns along [100]. (b) Proportion of the electron probe intensity as a function of radial distance from the probe origin when the probe is placed at $(x, y) = 4.07, 0.00$ Å (off column). Cumulative contribution to the Si L$_{2,3}$-shell EELS signal for Si ⟨011⟩ scanning along the [100] direction for energy-loss windows of (c) 143–163 eV and (d) 280–300 eV.
probe spreading is significant. This is illustrated by the radially integrated probe intensity shown in Fig. 6.8(b), where the intensity distribution for the probe placed on an open channel is seen to spread quite rapidly.

The consequences of this probe diffusion on the images is shown in Figs. 6.8(c) and (d), where we plot the EELS line scan along the axis of the Si dumbbells as a function of thickness for the two different energy loss windows. Spatial incoherence has been omitted here to concentrate solely on the channelling and delocalisation aspects. The first point to note is that the contrast is quite low for a wide range of thickness values, a consequence of the significant delocalisation of the potential. Kimoto et al. [52] suggested that such delocalisation might prevent atomic resolution imaging. As seen in Fig. 6.7 and for certain depths in Figs. 6.8(c) and (d), atomic scale features can sometimes be seen clearly above the “delocalised background”. Moreover, we find cases where the correspondence between atomic scale features and the true atomic structure changes depending on the delocalisation. The change in the EELS image contrast is a subtle competition between the elastic and inelastic scattering as a function of the probe position. General principles for how the balance between these aspects plays out remain elusive, making simulation an often essential part of atomic resolution EELS chemical mapping.

The usual approach to EELS imaging uses a large energy window directly above the ionization threshold. The large width maximises the signal while proximity to the edge makes the background subtraction, based on extrapolation of the pre-edge, as reliable as possible. Figure 6.9 shows the integration of the modulus squared of the $l = 1, m_l = 0$ to $l' = 2, m'_l = 0$ transition potentials as a function of radial distance over energy windows of width 10 eV and 40 eV and starting at three different initial values of energy loss. The integrated potential becomes notably more localised for increasing energy loss. The energy window near threshold encompasses the most delocalised potentials and so gives the least resolvable images. With respect to localisation, one should place the energy window as far above threshold as the background subtraction procedure justifiably allows. Kimoto et al. reached the same conclusion [52]. The main effect on the localisation of the long range behavior of the potential is the energy loss rather than the specific atomic states involved in the transition [150]: the effect is strongly pronounced here because the ionization threshold energy is low. For an element and shell with a much higher ionization threshold, the variation in localisation with energy loss will be much weaker. It is
6.2. SILICON, DELocalised Interaction Potentials and Contrast Reversals

Figure 6.9: Integrated modulus squared of the transition potentials for the $l = 1$, $m_l = 0$ to $l' = 2$, $m_{l'} = 0$ transition as a function of radial distance for energy windows of width 10 eV (solid lines) and 40 eV (dashed lines), starting at three different initial values of energy. The top two (blue) lines are for windows starting at the ionization edge, 100 eV, the next two lines (red) are for windows starting at 143 eV and the bottom two (green) are for an initial energy value of 280 eV. The results are all normalized to unity at the origin to better observe the variation in shape.

clear from Fig. 6.8(a) and 6.9 that the size of the energy-loss window only affects the localisation if strong variation in the localisation of the potential occurs on a smaller energy scale.

Two further points are needed to fully appreciate what is occurring with this data set. First, if the effect of inelastic thermal scattering on the evolution of the elastic wave function is neglected then the simulations do not show a contrast reversal. This suggests that thermal scattering in this thicker specimen appreciably modifies the evolution of the probe wave function, despite the generally weak scattering power of Si atoms, and that the absorption effect (i.e. thermal scattering prior to the excitation of ionization events) may in part be contributing to the reduction of the signal on column [58]. That this might lead to a contrast reversal depending on the energy loss has been predicted previously (albeit for different edges) [132], but has not hitherto been seen experimentally. Second, attributing the contrast reversal to probe spreading depends on the excitation of atoms in multiple columns, which has previously been dubbed cross-talk (see, for instance, Refs. [47, 141]). We can elucidate this by a trial calculation in which only Si atoms in a single column are allowed to undergo ionization. Such an approach retains the physically correct evo-
Figure 6.10: The cumulative contribution from a single column located at \( x = 0.0 \) Å using (a) 143–163 eV and (b) 280–300 eV integration windows for a line scan through the Si dumbbells.

olution of the wave function, while analysing the contribution to the EELS signal from only a subset of atoms. This dissection is physically meaningful because core-loss ionization of different atoms is incoherent. The resultant signal as a function of specimen thickness is given in Figs. 6.10(a) and (b). For both energy loss ranges the ionization signal from that single column is a maximum when the probe is on that column. As the line scans shown in Fig. 6.8(c) and (d) result from the superposition of such single column signals, the addition of the inter-columnar contribution from adjacent columns reduces the overall contrast and is directly responsible for the observed contrast reversal.

6.3 Energy dispersive x-ray spectroscopy

We have seen that the implementation of aberration correction in the electron optics has allowed probe sizes to approach less than 1 Å and this, coupled to increases in EELS detector efficiency, has allowed EELS chemical mapping of crystals in two dimensions. The interpretability of these images is not always direct. Muller and co-workers suggested that direct interpretability would be ensured provided a large EELS collection aperture was used, as was the case in their experiment using a new Nion UltraSTEM system in which a detector collection semi-angle of up to 60 mrad was used [59]. As was shown in Sec. 6.2, using a similar EELS collection angle we observed and explained a contrast reversal from images constructed with different regions of the energy loss spectra. In principle, the difficulties of interpreting
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such anomalous results are offset somewhat by simultaneously acquiring HAADF images to correlate the crystal structure with the corresponding EELS images. However, for crystals containing light elements or species of similar atomic number, atom discrimination based on HAADF image contrast is difficult. A novel alternative approach to EELS chemical mapping that offers the direct visual interpretability of HAADF imaging, whilst simultaneously unambiguously identifying the atoms, is energy dispersive x-ray spectroscopy (EDS).

EDS in STEM has been used to map regions containing a particular species of atom in nanostructures [164–166]. In this method a coherent focused probe is raster scanned across the specimen and at each probe position the resultant x-ray emission spectrum is recorded. This spectrum is then used to construct an elemental map. Two advantages that STEM EDS has are that the inelastic interaction is always effectively local, like that in HAADF, and that the inner-shell ionization potential is as localized as possible for a given ionization edge. Consequently, the resultant incoherent image can be directly interpreted.

The experiment that this section is based upon used a test sample of \(\langle 001\rangle\) \(\text{SrTiO}_3\) that was electro-polished and chemically etched, creating an ultra clean surface. This was essential as it was observed that even a small amount of surface amorphization had a negative impact on the quality of the result. A model of the \(\text{SrTiO}_3\) unit cell is shown in Fig. 3.2. The sample thickness was estimated to be 1000 Å and a specimen of this thickness was needed to ensure sufficient x-ray counting statistics. The 300 keV probe had a third order spherical aberration coefficient \(C_s = 1.2\) mm. The probe forming aperture semi-angle was 9.6 mrad and the probe was under-focused by 560 Å into the specimen. The probe size was estimated at 1.4 Å and the beam current to be 10-20 pA. The EDS detector subtended a collection angle of 0.13 sr and the acquisition time for a single x-ray spectrum was 500 ms (corrected for dead time).

Two dimensional EDS chemical maps are shown in Fig. 6.11. That for the Ti sub-lattice is shown in Fig. 6.11(a), and for the Sr sub-lattice in Fig. 6.11(b). Shown in Fig. 6.11(c) is the simultaneously acquired STEM HAADF image. In each case the experimental EDS maps and the HAADF image have the simulations overlayed. Good qualitative agreement is seen and there is a one-to-one correspondence between the known projected structure, the EDS maps and the HAADF image. The simulations will be discussed in more detail shortly.
Figure 6.11: Experimental and simulated results (overlay) for SrTiO$_3$ chemical maps for (a) Ti (red) and (b) Sr (blue) and in (c) the corresponding STEM HAADF image. The sample was estimated to be 1000 Å thick. The projected structure along the ⟨001⟩ direction is indicated on each map.
Figure 6.12(a) shows a HAADF line scan along \( \langle 110 \rangle \) and Fig. 6.12(b) shows the simultaneously recorded EDS line scans. The EDS line scans shown in Fig. 6.12(b) are consistent with the HAADF image in Fig. 6.12(a). These were extracted from the two-dimensional maps in Fig. 6.11. The Sr signal follows the reference HAADF line scan and this is to be expected as the HAADF contrast should be dominated by the Sr columns. The Sr line scan in Fig. 6.12(b) was constructed from the sum of the Sr \( K \)- and \( L \)-shell ionization events. The corresponding Ti line scan only uses the Ti \( K \)-shell. The alternating Sr-Ti-Sr structure is clearly seen in the two line scans in Fig. 6.12(b).

A typical EDS spectrum is shown in Fig. 6.12(c) and it is instructive to notice that whilst the count rates are quite low, so is the accompanying background. Whilst the x-ray detector count statistics may be considered low, the peak-to-background (P/B) ratio is high. Next generation detectors will have count rates an order of magnitude larger than that used here, thus improving signal to noise ratios. [167] This is in contrast to EELS where low P/B ratios often demand the use of principal component analysis in conjunction with conventional power law background subtraction to remove spectral noise and obtain usable spectra. [58, 168] Typical P/B ratios in EELS are around 1:1 and can become even worse in composite materials with many different atomic species, where edges of the different elements contribute to background of the characteristic edges following at higher energy losses. For state-of-the-art EDS detectors P/B ratios of between 60:1 and 100:1 are possible depending on the energy loss of the characteristic absorption edge in the EDS spectrum. It must be stressed that all of the data was obtained on a machine with no \( Cs \) aberration correction. Using aberration correctors will allow the illumination aperture to be increased, decreasing the probe spot size whilst simultaneously increasing the beam current. This would increase the beam density and in turn improve the x-ray yield per pixel and thus improve the quality of the EDS chemical maps [169].

As the specimen was so thick, to adequately handle probe spreading and the contribution from the diffuse background, simulations were performed using the frozen phonon mixed dynamical form factor (MDFF) hybrid (see Sec. 5.1). The effect of demagnifying the source to improve beam current and thus increasing the spatial incoherence of the probe has not been accounted for in any of the simulations. This may account for some discrepancy between the simulated and experi-
mental images but this does not affect any conclusions. The HAADF simulation in Fig. 6.11(c) was performed using the standard frozen phonon algorithm in Sec. 2.3.5 for a HAADF collection range of 60-160 mrad. To simulate the EDS maps, the assumption is made that the total cross section for all x-ray emission events corresponding to filling a hole in the K- or L-shell is proportional to the total cross section for K- or L-shell ionization respectively. For EELS imaging the angular range of the scattered electron integration $d\Omega_{K'} = \sin \theta d\theta d\phi$ in Eq. 4.24 would be limited to the physical dimensions of the EELS collection aperture. However, for EDS the integration extends over the full solid angle since electrons with all possible ionization scattering kinematics contribute to the signal. This in effect reduces the nonlocal potential in Eq. 4.24 to the local approximation in Sec. 2.2 (with transition matrix elements pertinent to ionization) so that the potential is

$$W(r_\perp, r_\perp') \approx 2V(r_\perp)\delta(r_\perp - r_\perp').$$  

(6.1)

Thus the $\mu_{h,g}$ in Eq. 4.23 are now,

$$\mu_{g,h} = \frac{4\pi m}{\hbar^2 k_0} \int_A e^{-2\pi i \mathbf{h} \cdot \mathbf{r}_\perp} V(r_\perp) e^{2\pi i \mathbf{g} \cdot \mathbf{r}_\perp} d\mathbf{r}_\perp = \mu_{h-g,0}.$$  

(6.2)

Using the fact that the scattering coefficients reduce to the form $\mu_{h,0}$, Eq. 5.1 can be shown to reduce to

$$\sigma(R, t) = \frac{A}{J} \sum_{j=1}^{J} \left[ \sum_{h} \mu_{h,0} \int_A \int_0^t |\psi_j(R, r_\perp, z)|^2 dz \right] e^{2\pi i \mathbf{h} \cdot \mathbf{r}_\perp} d\mathbf{r}_\perp.$$  

(6.3)

(see appendix B in Ref. [47]). Understanding that the $\mu_{h,0}$ can be thought of as the Fourier coefficients of a local effective scattering potential $V(r_\perp)$ and that Eq. 6.3 contains the Fourier transform of the depth integrated elastic wave function intensity, Eq. 6.3 can be recast as

$$\sigma(R, t) = \frac{A}{J} \sum_{j=1}^{J} \int_0^t \int_A |\psi_j(R, r_\perp, z)|^2 V(r_\perp) d\mathbf{r}_\perp.$$  

(6.4)

The form of Eq. 6.4 shows that EDS is an incoherent imaging mode. The lo-
Figure 6.12: (a) Reference HAADF line scan of the SrTiO$_3$ sample along the $\langle 110 \rangle$ direction. The corresponding EDS line scans shown in (b) are for Ti (red) and Sr (blue) and were constructed from the integrated shaded region of the x-ray spectrum indicated in (c), where a typical EDS spectrum is shown. The spectrum in (c) corresponds to the position indicated by the pink dashed lines in (a) and (b).
CHAPTER 6. TWO-DIMENSIONAL CHEMICAL MAPPING

Figure 6.13: The effective scattering potential for HAADF for a detector spanning 60-160 mrad (black) and for EDS Ti $K$-shell x-ray emission (red) and the sum of the Sr $K$- and $L$-shell potentials for x-ray emission (blue). The scattering potential is for the ⟨110⟩ direction for a single unit cell of SrTiO$_3$. The Sr and Ti sites are indicated by the blue and red circles respectively. For ease of comparison, each line plot has its maximum value normalized to one.

The effective scattering potential $V(r_\perp)$ in Eq. 6.4 contains an integration over all possible final states (energies) of the ejected electron (see Eq. 2.15). These transition potentials become more localized as the energy of the ejected electron increases, i.e. for greater energy losses of the incident electron. The effective scattering potentials in Eq. 6.4 for HAADF (black), Ti $K$-shell x-ray emission for EDS (red) and Sr $K$- plus $L$-shell x-ray emission (blue) are shown in Fig. 6.13. The HAADF potential is the most peaked and corresponds closely to the projected structure. It is more peaked around the Sr columns than on the Ti columns. The EDS potentials are also quite peaked and have a localisation comparable to the HAADF potential. These potentials of course are pertinent to a particular atomic species in a sub-lattice. Examining Figs. 6.11(a) and (b) it is clearly evident that the Ti map is significantly more localised than the Sr map. This is a consequence of using the single tightly bound Ti $K$-shell (threshold energy approximately 4,965 eV), as opposed to the sum of the relatively delocalised Sr $L$-shell (threshold energy approximately 2,007 eV) with the Sr $K$-shell (threshold energy approximately 16,206 eV). The relative FWHM of the respective EDS potentials are 0.22 Å and 0.33 Å respectively. The restriction to the Ti $K$-shell is due to the relatively low energy resolution of the EDS detector and its inability to separately resolve the O $K$- and Ti $L$-shell events (as can be seen in Fig. 6.12(c)).
6.4. DISCUSSION AND CONCLUSIONS

In EELS chemical mapping a power law subtraction is needed to remove an often substantial background from the ionization edge under consideration. Kimoto et al. [52] used the background extrapolation technique to extract spectra far from the edge onset to improve the spatial resolution of experimental EELS images, as it is well known that the degree of localisation increases with increasing energy loss [60, 148]. However, the further from the edge onset the more the accuracy of the extrapolation is tested. By contrast, in EDS all energy losses above the edge contribute to the signal whilst at the same time there is no substantial background subtraction to complicate the integration of the signal.

As a final comment we highlight some pertinent issues regarding STEM EDS and the disadvantages of the technique. At low ionization energies the x-ray fluorescent yields are much lower than unity, thus the product of the ionization cross section with the x-ray fluorescence yield is roughly constant and is small. Coupling the small fluorescence yield to the increased absorption of low energy x-ray photons both in the x-ray detector, before its active region, and inside the specimen implies that an already small signal is reduced even further. Full use of these small signals will be enhanced, just like in EELS, by combining advanced theoretical simulations with experiment. In the present study, we note that the calculations can be further refined by taking into account x-ray fluorescence yields and x-ray absorption in the specimen but neither are crucial for the qualitative comparisons presented here. However, as experimental results improve better comparisons between theory and experiment will necessitate the inclusion of these effects.

6.4  Discussion and conclusions

In summary, the Bi$_{0.5}$Sr$_{0.5}$MnO$_3$ results in this chapter have shown that the ability to record two dimensional EELS chemical mapping greatly aids the interpretation of compositional information in terms of the chemical structure of the specimen. The direct interpretation of these images is not always straight forward. For a sample of Si, using electrons from different regions of the Si core-loss spectrum produced an unexpected contrast reversal from within the same ionization edge. This result highlighted the importance of properly accounting for the dynamical scattering of the probe, hinted at but not fully appreciated from the Bi$_{0.5}$Sr$_{0.5}$MnO$_3$ result. This
result arises because probe spreading from an open channel ultimately allows for more interaction with the delocalised transition potentials of more Si atoms than when it is placed upon a column. Whilst the reversal is observed in an area of the sample that was relatively thick, good HAADF images and EELS spectra were obtained; whilst the contrast is low, reliable signal variation is seen. For the most delocalised potentials atomic scale features do not always reliably represent the atomic scale structure, making simulation a necessary adjunct to experiment.

We then discussed a demonstration of two-dimensional atomic resolution EDS maps and showed why the maps should be directly interpretable (at least in the same way that STEM HAADF is). The combination of simultaneous STEM EELS, HAADF and EDS provides a powerful approach to investigate structural chemical and functional information in real space at atomic resolution. These technique developments coupled with ever increasing probe forming apertures, beam currents and stable microscope environments in conjunction with accurate theoretical simulations are beginning to facilitate attempts at three-dimensional structure retrieval.
Three dimensional mapping using depth sectioning in scanning transmission electron microscopy

The work in this chapter is based on Ref. [170], using the tools and ideas from earlier chapters to explore the use of core-loss electron energy loss spectroscopy (EELS) to depth section zone axis aligned crystals in scanning transmission electron microscopy (STEM). The localisation of individual atoms in three dimensions by a direct imaging technique is the focus of this chapter, specifically depth sectioning in STEM using core-loss EELS.

Conventional tilt series tomography [63, 64] is capable of 1 nm² volume resolution [61]. However, this impressive resolution is only attainable if the recorded signal is a monotonic function of thickness, otherwise known as the projection requirement. The projection requirement is most readily satisfied in materials science using incoherent imaging in STEM but may become more difficult to satisfy for larger probe forming aperture semi-angles due to the associated probe spreading [141, 156, 171]. Although it is not envisaged that STEM will necessarily directly compete with tomography for depth resolution, its ability to probe specific depths in a sample, and obtain data without the need for lengthy data reconstruction, will mean that it is useful for many applications.

The development of aberration-correcting electron optics has increased the angular range of incident electrons that can be used to form a diffraction-limited
Figure 7.1: The STEM depth sectioning scheme. Varying the probe defocus $\Delta f$ in addition to conventional lateral scanning enables the probe to be raster scanned throughout the sample in the three dimensions $X, Y, Z$.

probe, facilitating an increase in probe-defining aperture size and resulting in sub-Ångström probes [53, 55]. Smaller probe size has increased the transverse resolution of the STEM while simultaneously producing a reduced depth of focus. This reduction in the depth of focus coupled with atomic resolution STEM imaging offers the possibility to depth section samples.

In STEM depth sectioning a three-dimensional model is obtained from the reconstruction of a through focal series of images. The electron beam is raster scanned throughout the sample using defocus to probe different depths inside the specimen. The depth sectioning scheme proposed is shown in Fig. 7.1 with the narrow depth of focus in Fig. 7.1 corresponding to there being a significant proportion of the electron intensity located at the focal position. The recorded signal is then used to extract three dimensional atomic locations [65–67]. It is proposed that STEM depth sectioning has similar experimental probe constraints to confocal scanning optical microscopy (CSOM)); STEM depth sectioning demands the electron probe has a narrow depth of focus with the STEM probe and detector sizes ultimately determine the feasibility of three-dimensional structure determination.
7.1 Electron probes

Starting from Eq. 2.21 a diffraction-limited electron probe may be described in free space using Eq. 2.24. Recasting this as a continuous quantity we have

\[
\psi(R, r_\perp, z) = \int A(q) e^{-i\pi \lambda q^2(\Delta f + z)} e^{2\pi i q (r_\perp - R)} dq. \tag{7.1}
\]

As the probe intensity distribution is axially symmetric, a cross section of the distribution suffices to describe the full three dimensional electron density profile. Figure 7.2 illustrates how the electron intensity distribution changes as one increases the maximum allowed transverse momentum \( q_{\text{max}} \). The electron intensity in Fig. 7.2 is well localised on the optical axis. The intensity distribution along the axis describes what we will refer to as the depth of focus and is fairly broad. As the probe forming aperture increases, going from Fig. 7.2(a) to Fig. 7.2(b), note how the depth of focus decreases. However, even in the case of a 37.5 mrad probe (Fig. 7.2), the intensity is still very elongated in the \( z \) direction. Evaluating the probe function in Eq. 7.1, for zero STEM probe displacement (\( R = 0 \)) and zero defocus (\( \Delta f = 0 \) Å), gives [172]

\[
\psi(r_\perp, z) = 2\pi \int_0^{q_{\text{max}}} q \exp(-\pi i \lambda q^2) J_0(2\pi qr_\perp) dq. \tag{7.2}
\]

Figure 7.2: Free space intensity profiles for a diffraction-limited 200 keV probe with probe forming aperture semi-angles (a) \( \alpha = 17 \) mrad and (b) \( \alpha = 37.5 \) mrad. Note the different scales on the radial and defocus axes.
Evaluating the intensity profiles in the transverse and axial directions we have

\[ I(r_\perp) = |\psi(r_\perp, z = 0)|^2 = \left[ q_{\text{max}} J_1\left(\frac{2\pi q_{\text{max}} r_\perp}{r_\perp}\right)\right]^2 \] (7.3)

and

\[ I(z) = |\psi(r_\perp = 0, z)|^2 = \left[ \pi q_{\text{max}}^2 \text{sinc}\left(\frac{\pi \lambda q_{\text{max}}^2 z}{2}\right)\right]^2. \] (7.4)

It readily follows that the full-width at half-maximum (FWHM) values of the probe transverse spot size and depth of focus are

\[ r_{\text{FWHM}} = 0.5145 \frac{q_{\text{max}}}{\lambda} \approx 0.5145 \frac{\alpha}{\lambda}, \]

\[ z_{\text{FWHM}} = 1.772 \frac{\lambda q_{\text{max}}^2}{\alpha^2} \approx 1.772 \frac{\lambda}{\alpha^2}. \] (7.5)

The implication of Eq. 7.5 for the free space probe is that the depth of focus \( z_{\text{FWHM}} \) decreases more rapidly than the transverse spot size \( r_{\text{FWHM}} \) for larger probe forming aperture semi-angles \( \alpha \). From Eq. 7.5 it is noted that currently available probe forming apertures can produce probes which have sub-Ångström transverse spot size and depth of focus approaching 30 Å. In many materials the vertical unit cell sizes are typically of the order 5 Å and having a depth of focus of 30 Å appears to make ultra high resolution depth sectioning impossible. It must be appreciated however that reliable qualitative depth interpretation is not simply dependent upon probe depth resolution. There is a clear distinction between the precision to which one can determine dopant depth and the depth resolution of a probe. In the former, we require some signature feature to verify a dopant’s position as opposed to the latter which implies a reconstructed image. Accurate theoretical simulations of experimental images can enable precise structure determination from probes having relatively poor depth resolution [66]. Depth sectioning reconstruction techniques similar to conventional tilt tomography using prior knowledge about the sample, although not a direct form of structure determination, have also been explored [173].
7.2 Coherent, partially coherent and incoherent depth sectioning

The depth sectioning approach depicted in Fig. 7.1 requires the image signal to be dominated by the contribution from the three dimensional position of the beam waist. This is satisfied if we are operating in an incoherent imaging mode, see Eq. 6.4. Using the projected potential approximation allows the inelastic scattering potential \( V_{\text{inel}}(r_{\perp}, z) \) to fit within a multislice framework. This framework facilitates discussion about the contributions to images from particular slices, specifically those contributions from slices containing impurities as we can modify the slice potential to accommodate the impurity. In EELS incoherence between slices is enforced by assuming that the ionization of one atom is independent of all other crystal atoms. Furthermore each atomic transition is incoherent with respect to other atomic transitions. In chapter 4 we saw that as each wave is coherent with respect to itself and as the transition potential can be quite delocalised the interference of the inelastic wave can manifest itself in core-loss EELS images producing somewhat anomalous results. Under certain conditions where the EELS detector collection angle is appreciably larger than the probe forming aperture the local approximation (incoherent imaging) is more likely to be valid. In this case the recorded signal is proportional to the intensity and the correlation of the signal with defocus is directly dependent on the probe channelling. For situations where the local approximation is not valid and the effective nonlocal potential is quite delocalised it is difficult to know if the correlation between defocus and the impurity location can be easily determined. Nevertheless, is it still somewhat useful to examine how the strong channelling conditions of a zone axis aligned crystal impacts on the depth sectioning procedure.

7.3 Case study: Al\(_x\)Ga\(_{1-x}\)As and Sb in Si

Consider two test scenarios: Al in a GaAs crystal and Sb in a Si crystal. As a member of the group III-V semiconductor family, the Al\(_x\)Ga\(_{1-x}\)As heterostructure has received much scientific attention making it an excellent candidate for exploratory study. High angle annular dark field (HAADF) is unable to resolve a single substi-
Figure 7.3: Model structure of a GaAs unit cell in (a) a three dimensional perspective, (b) oriented along the \langle001\rangle zone axis and (c) oriented along the \langle110\rangle zone axis. The Ga atoms are coloured yellow and the Ga atoms are black.

Institutional Al dopant as it has a significantly smaller atomic mass than the supporting GaAs crystal. The Al \textit{K}-shell ionization edge lies at 1560 eV [148] and is a suitable candidate to demonstrate the principles of EELS depth sectioning. From a practical perspective detecting and quantifying the Al \textit{K} edge in AlGa is somewhat difficult because of the high background due to the low lying Ga and As \textit{L}_{2,3} edges. Simulations for the \textit{L}-shell, which is experimentally more accessible, have the same general features but are more adversely affected by the delocalised nature of the interaction and so are not shown in this chapter, later in chapter 9 we shall see the effect of a significantly delocalised ionization potential. The simulations presented involved substituting an Al atom for a Ga atom at various depths into a Ga column.

Whilst HAADF Sb in Si crystal simulations have been reported [174], we present a set of complementary Sb EELS results showing the spectroscopic identification of the dopant Sb within the Si bulk. The Sb edge considered was the \textit{M}_{4,5} edge at 528 eV [148]. The Sb in Si crystal simulations also involved artificially replacing a single Si atom with a Sb dopant on column. Once again from a practical perspective, preventing Si from oxidising in air is quite challenging. As the Sb \textit{M}_{4,5}
7.3. CASE STUDY: Al\textsubscript{x}Ga\textsubscript{1−x}As AND Sb IN Si

edge has a similar threshold energy to O it may be difficult to resolve that corresponding to Sb impurities and that from the oxidised Si. The GaAs and Si crystals were both aligned along the ⟨001⟩ zone axis. The GaAs unit cell is shown in Fig. 7.3 and the Si unit cell was shown in chapter 6 Fig. 6.6. The simulations assume a 200 keV diffraction-limited probe with user-variable defocus. The EELS signal was integrated up over a 40 eV energy window above ionization threshold. (This energy window may be too small to collect much signal in practice from the delayed Sb M\textsubscript{4,5} edge but it does not exclude exploratory simulations.) The HAADF images, using a local approximation, and EELS results, using the nonlocal potential in Eq. 4.24, were calculated via absorptive multislice techniques as described in chapters 2 and 4.

7.3.1 Channelling considerations

Large probe forming aperture semi-angles result in finer probes that should focus inside the specimen without significant distortions introduced by the crystal surrounding a column. This is pertinent to depth sectioning as the scheme relies upon a narrow beam waist whose location can be adjusted by varying the defocus $\Delta f$. Wolf produced contour plots detailing the fractional intensity present on circular discs for perfectly spherical waves emanating from a circular aperture [175]. Here we present the analogous STEM case. The radial integration of the electron probe intensity surrounding a column at different depths within the crystal shows the evolution of the probe and the effect of the crystal on the electron intensity distribution. Electron probe intensity calculations for free space and the two test cases are presented in Fig. 7.4. The free space situation represents the ideal case where the probe does not interact with its surroundings. The narrow beam waist is illustrated by the localisation of electron intensity at $z = 60$ Å in Figs. 7.4(a) and (b). The Si crystal electron intensity plots shown in Figs. 7.4(c) and (d) are considerably more symmetrical and contain a sharper beam waist than those of the GaAs crystal, Figs. 7.4(e) and (f). The sharper beam waist is indicated by the tighter cluster of contour lines in the region $z \approx 60$ Å. For heavier crystals the probes intensity not only spreads but also shifts the location of the waist along the column away from the set probe defocus. The shifting of the beam waist toward the incident surface shows the influence of the crystal and specifically the atomic focusing of the probe.
The narrow beam waist reflecting the desired operating regime presented in Fig. 7.1 can only be achieved with large probe forming apertures.

Figure 7.5 shows the effect of varying the electron detector collection semi-angle $\beta$ on the image line scans along $\langle 001 \rangle$. Within Fig. 7.5 the dopant Sb was placed on a Si column at $x = 0$ Å and at a depth of 65 Å. The negative defocus corresponds to the beam waist being located inside the crystal. In the z-direction, increasing the detector collection semi-angle serves to shift the maximum intensity recorded from the surface ($\Delta f = 0$ Å) of the crystal to the region inside the crystal near the dopant site ($\Delta f \approx -70$ Å). The appearance of volcano-like behaviour in the image when the defocus approximately equals the dopant depth is shown explicitly in Fig. 7.6(a) and is removed with the inclusion of larger collection semi-angles, Fig. 7.6(b). It would be convenient to be able to define a pseudo-FWHM for the depth response relating the recorded intensity as a function of probe defocus. However when $\alpha = 25$ mrad the emergence of double peaks and volcanoes complicates the interpretation of conventional z-direction FWHM values.

In Fig. 7.7 the Al dopant was placed on a Ga column at $x = 0$ Å and at a depth of 62 Å. The image detector collection angle dependence is explicitly shown in Fig. 7.7. Qualitative interpretation of the image when using a detector collection semi-angle $\beta = 10$ mrad suggests that the dopant is located on the surface of the crystal which is clearly an incorrect interpretation. The larger detector collection semi-angle $\beta = 30$ mrad has a smeared peak intensity that encompasses the entire defocus range. Finally, when the detector collection semi-angle $\beta = 50$ mrad the majority of the signal intensity is localised at $\Delta f$ approximately equal to the dopant depth. The peak intensity corresponding to dopant depth in Fig. 7.7(c) shows the over-focusing effect of the column. The peak intensity occurs for probes focused further into the crystal than the depth at which the dopant is located.

### 7.3.2 Detector considerations

As discussed previously and illustrated in chapter 4, the degree of validity that a local ionization potential and thus the likelihood that an experiment satisfies incoherent imaging conditions is dependent on the detector collection angle $\beta$ with respect to the probe illumination angle $\alpha$. Shown in Fig. 7.8 is the precision to which a dopant Al atom could be located inside a GaAs crystal as a function of the
Figure 7.4: Proportion of the electron probe intensity as a function of radial distance from the column for a 200 keV probe with defocus $\Delta f = -60 \text{ Å}$. The free space (non-interacting) scenario is shown with probe forming aperture semi-angles (a) $\alpha = 25 \text{ mrad}$ and (b) $\alpha = 37.5 \text{ mrad}$. Situating the probe above a Si column in a Si crystal oriented along $\langle 100 \rangle$ is shown with probe forming apertures (c) $\alpha = 25 \text{ mrad}$ and (d) $\alpha = 37.5 \text{ mrad}$. Finally, the probe intensity in a GaAs crystal oriented along $\langle 100 \rangle$ when the probe is placed above the Ga column is presented with probe forming aperture semi-angles (e) $\alpha = 25 \text{ mrad}$ and (f) $\alpha = 37.5 \text{ mrad}$.
Figure 7.5: Sb $M$-shell EELS probe line scan simulations along $\langle 001 \rangle$. The Sb atom is embedded 65 Å deep on a Si column at $x = 0$ Å in a Si crystal oriented along the $\langle 100 \rangle$ zone axis. The consequence of increasing EELS detector collection semi-angles, (a) $\beta = 10$ mrad, (b) $\beta = 30$ mrad and (c) $\beta = 50$ mrad, is shown. The 200 keV probe had a 25 mrad probe forming aperture semi-angle.
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![Figure 7.6: Sb M-shell EELS probe line scans for Sb in Si (100) crystal. Extracts from Fig. 7.5 with $\Delta f = -70$ Å using (a) $\beta = 10$ mrad and (b) $\beta = 50$ mrad electron collection semi-angles.](image)

probe aperture parameter.

In Fig. 7.8(a), when the probe forming aperture is less than $\alpha = 20$ mrad the intensity is almost uniform as a function of defocus for all three dopant depths. Figure 7.8 suggests a minimum probe forming aperture of $\alpha = 35$ mrad is required for the Al$_x$Ga$_{1-x}$As structure for an EELS detector subtending $\beta = 50$ mrad. At a probe forming aperture above $\alpha = 35$ mrad the intensity as a function defocus is localised around the dopant depth. It is interesting to note the false peak clearly evident in Fig. 7.8(c) at $\Delta f = 0$ Å when the probe forming aperture is less than $\alpha = 25$ mrad. The false peak is comparable to the true peak ($\Delta f \approx -110$ Å) in magnitude, implying the possibility of falsely assuming that two dopants are present in the column. One possible mechanism by which this arises could be attributed to channelling along a column. In high resolution transmission electron microscopy (HRTEM), channelling is often described using an $s$-state model. Bloch states localised around the column may be labelled in analogy to bound atomic orbitals [176]. As the Bloch states are eigenstates of the system, if one neglects absorption, the portion of the incident wave which couples to the $s$-state will propagate along the column to the exit surface. As STEM is just the coherent superposition of many incident electron tilts this should also be true in STEM. The origins of the false peak can be explained with examination of Fig. 7.9 which shows the fraction of the probe which couples to the $s$-like column state for the probe positioned above the Ga column (calculated following Ref. [177]). The maximum coupling
Figure 7.7: Al $K$-shell EELS probe line scan simulations along $(001)$. The Al atom is embedded 62 Å deep on a Ga column at $x = 0$ Å in a GaAs crystal oriented along the $(100)$ zone axis. The consequence of increasing EELS detector collection semi-angles, (a) $\beta = 10$ mrad, (b) $\beta = 30$ mrad and (c) $\beta = 50$ mrad, is shown. Simulations used a 200 keV probe with a probe forming aperture semi-angle of $\alpha = 25$ mrad.
Figure 7.8: Plots for various Al dopant depths, (a) 28 Å, (b) 62 Å and (c) 90 Å, relating the increase in aperture semi-angle $\alpha$ to the EELS intensity recorded. The GaAs crystal is oriented along the $\langle 100 \rangle$ zone axis. The 200 keV probe is located directly above the Ga column containing a single Al dopant atom. The detector collection semi-angle is $\beta = 50$ mrad. The intensity scales are independent to emphasise the local maxima occurring at $\Delta f \approx 0$ Å.
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Figure 7.9: The fraction of the 200 keV probe that is coupled to the Ga column s-like states for varying probe defocus and aperture sizes $\alpha$.

of the probe to these states is achieved for a probe positioned on the surface when the width of the probe is commensurate with the width of the column s-like state. When the probe is focused onto the surface and couples to the column s-like state, the subsequent electron channelling along the column generates ionization events at the dopant depth. This registers significant counts onto the detector for a defocus which does not correlate to the dopant depth. As a final note we remind the reader that the extent of probe coupling is dependent on the material and incident electron energy in conjunction with the size of the probe forming aperture.

Provided that the probe lens system can produce sufficiently fine probes, Fig. 7.10 shows the results depth sectioning could provide for increasing collector sizes. When the probe forming aperture is large ($\alpha = 37.5$ mrad) and the collection semi-angle small ($\beta = 10$ mrad) the relative probe and detector sizes couple with a strongly absorbing Ga column to increase the effect of volcanoes (see Fig. 7.10(a)). Reversing the relative size difference and making the detector collection semi-angle $\beta = 50$ mrad (i.e. $\beta \geq \alpha$) returns results agreeing with a local model and suggests that qualitative dopant depth interpretation will be achievable (see Fig. 7.10(c)). We have seen that, for an isolated impurity, a number of factors affect the interpretation of depth sectioning based on EELS. For too small a probe forming aperture, there is strong coupling of the s-like state to the atomic column, resulting in a large artificial peak in the integrated EELS intensity when the probe is focused near the specimen’s entrance surface. Figure 7.8 demonstrates that there can be a significant
Figure 7.10: Al K-shell EELS probe line scan simulations along $\langle 001 \rangle$. The Al atom is embedded on a Ga column 62 Å deep at $x = 0$ Å in a GaAs crystal oriented along the $\langle 100 \rangle$ zone axis. The consequence of increasing EELS detector collection semi-angles, (a) $\beta = 10$ mrad, (b) $\beta = 30$ mrad and (c) $\beta = 50$ mrad, is shown. Simulations used a 200 keV probe with probe forming aperture $\alpha = 37.5$ mrad.
s-like state contribution even for impurities located at significant depths. In addition the overfocusing of the electron probe due to the atomic column results in a shifting of the observed maximum signal away from the depth of the impurity.

In Fig. 7.11 we consider the case of two Al impurity atoms located in a Ga column in ⟨100⟩ zone axis oriented GaAs. These substitutional impurities are located at depths of 62 Å and 130 Å. The variation in intensity is shown as a function of defocus for probe forming apertures of 25 and 37.5 mrad in Figs. 7.11(a) and (b) respectively. For \( \alpha = 25 \) mrad we see a large contribution to the intensity from s-like state coupling for the probe focused near the entrance surface. For the remainder of the focal range there is a smeared out peak centered between the dopants. This intensity distribution can be understood by examining Fig. 7.11(c) which shows the intensity on the Ga column as a function of defocus as well as the contributions from each dopant individually, which may be added to produce the total signal. Both impurities result in a strong signal due to s-like state coupling for the probe focus near the surface adding to produce the maximum signal. The impurity at 62 Å produces a peak around a defocus of \(-80\) Å which is significantly larger than its zero defocus contribution. The impurity at 130 Å however produces a peak at a defocus value of \(-160\) Å with less than half this intensity. Because of the large depth of field there is significant overlap of these peaks and the individual impurities are not resolved. For the smaller probe used in Fig. 7.11(b) there are three clearly resolved peaks in intensity as a function of defocus. As seen in Fig. 7.11(d), the first is again due to the addition of the coupled s-like states from each impurity. Both impurities produce delayed intensity peaks with magnitudes greater than the s-like states and the decreased depth of field means that the individual peaks are clearly resolved.

### 7.4 Discussion and conclusions

It has been shown that depth sectioning within STEM using EELS signals is possible for point like objects. Provided that aberration correctors continue to allow increases in probe convergence angles, depth sectioning will be possible on the nanometer scale due to a further reduced depth of focus. All the peculiarities and subtleties for two dimensional images manifest themselves quite strongly in the
7.4. DISCUSSION AND CONCLUSIONS

Figure 7.11: Simulated Al K-shell EELS line scans as a function of defocus formed by a 200 keV probe with (a) $\alpha = 25$ mrad and (b) $\alpha = 37.5$ mrad, for Al impurities in $\langle 100 \rangle$ zone axis oriented GaAs. The substitutional Al impurities are located in the Ga column positioned at $x = 0$ Å at depths of 62 Å and 130 Å. An EELS detector semi-angle of 50 mrad and energy window of 40 eV above threshold was used. Line scans as a function of defocus for $x = 0$ Å are shown in (c) and (d) for probe apertures corresponding to (a) and (b) respectively. The total intensities are indicated by the solid lines, with signals due to the dopants at 62 Å and 130 Å indicated by the dotted and dashed lines respectively.
depth sectioning procedure. Interpretation of delocalised images should be aided somewhat with full two dimensional focal series, but is still somewhat difficult experimentally. Probe coupling to the $s$-like state of the atomic column is a limiting concern which was demonstrated to place strict requirements on STEM probes. Furthermore, this chapter did not address the elongation issue pertinent to extended objects (i.e. embedded nanostructures, etc.). Imaging extended objects places even more stringent demands on the probe. One approach to circumvent both the probe coupling to columns and the elongation problem is to perform scanning confocal electron microscopy.
Scanning confocal electron microscopy

Depth sectioning in scanning transmission electron microscopy (STEM) using high angle annular dark field (HAADF) has been shown to reveal the three dimensional location of impurity atoms embedded in the bulk [65, 66, 178]. In the previous chapter we explored and confirmed the feasibility of using STEM electron energy-loss spectroscopy (EELS) to depth section samples. It was noted that the reconstructed image was elongated in the depth direction relative to the atoms actual size. For objects larger than isolated impurity atoms there have been some successful experiments mapping the distribution of metal nanoparticles on a substrate in three dimensions [67, 179]. In these experiments there was a pronounced elongation of the reconstructed particle along the optical axis. The elongation problem in STEM HAADF shown in Refs. [67, 179, 180] and discussed more fully in chapter 9 is symptomatic of the inability to exclude image contributions originating from atomic planes not at the focal point.

The desire to limit the out of plane contribution in optical microscopy motivated the development of confocal scanning optical microscopy (CSOM) [181]. The electron microscopy analogue of CSOM is known as scanning confocal electron microscopy (SCEM) [182]. A schematic of the SCEM geometry is shown in Fig. 8.1. In SCEM, a STEM probe is transmitted through a sample where the exit surface wave function is then imaged by post-specimen electron optics. The probe is raster scanned across the specimen and by recording the intensity at a point in the image plane as a function of defocus and probe position an image is constructed. Frigo et al. [12] demonstrated the first experimental results by imaging buried structures
at the micrometer resolution scale. The improved image contrast also facilitated the imaging of thicker specimens than would normally be possible in transmission electron microscopy.

SCEM imaging at higher resolution requires the use of aberration correctors. The first successful implementation of the confocal geometry with aberration correction on both the pre- and post-specimen electron optics was demonstrated by Nellist et al. [71]. Sub-nanometer elastic SCEM imaging was demonstrated recently by Takeguchi et al. [183] with the observation of the ⟨111⟩ lattice fringes in gold nanoparticles for a range of probe defocus values. More recently, Zaluzec et al. [184] used an aberration corrected confocal arrangement to obtain a through focal series of a cluster of 6 nm diameter core-shell Au/Pt nanoparticles.

Theoretical development has progressed alongside these technical advances. Einspahr and Voyles [185] used linear imaging theory to suggest optimal imaging conditions for SCEM. Multislice simulations of a spherical Au crystal embedded in amorphous carbon were also presented showing a non-linear relationship between image contrast and probe defocus. Mitsuishi et al. [186] developed a Bloch wave theory for elastic SCEM and produced accompanying simulations for a range of atomic elements in buried layers. Using a wave function formulation Nellist et al. [187] showed that the image contrast in elastic SCEM contained no first order phase contrast term. The fundamental equation for elastic SCEM in both approaches was, unsurprisingly, equivalent.

The work presented in this chapter and the next is primarily the result of a collaboration between the groups of P. D. Nellist in Oxford and L. J. Allen in Melbourne, initiated by a three-month visit by E.C. Cosgriff to Melbourne. The theoretical framework for both elastic scattering described in this chapter and inelastic scattering described in chapter 9 was developed in detail during that visit by L. J. Allen, S. D. Findlay, E.C. Cosgriff, P. D. Nellist and the author by building on previous work from both groups and appears in Refs. [188] and [189].

8.1 A note on the confocal condition

Before commencing the theoretical description of elastic SCEM we pause to clarify what is meant by the term the confocal condition. A schematic of the SCEM geo-
8.1. A NOTE ON THE CONFOCAL CONDITION

**Figure 8.1:** The scanning confocal electron microscope configuration. The pre-specimen lens is defocused by an amount $\Delta f_1$ and the post-specimen lens is defocused by an amount $\Delta f_2$ into a specimen of thickness $t$. Underfocus is negative and corresponds to a focal plane within the specimen.
metry is shown in Fig. 8.1. Consider a specimen of thickness \( t \) and an aperture-free lens system (i.e. \( A(q_{\perp}) = 1 \) everywhere) with no coherent aberrations other than defocus. For a point source in real space (in reciprocal space \( \Psi(q_{\perp}) = 1 \)) the wave function at the entrance surface of the specimen after the action of the pre-specimen lens transfer function is

\[
\Psi(q_{\perp}) = T_1(q_{\perp}) = e^{-\pi i \lambda \Delta f_1 q^2}.
\]

(8.1)

Ignoring the channelling effect of the specimen and propagating the wave function through the distance \( t \) the exit surface wave function is now

\[
\Psi(q_{\perp}) = T_1(q_{\perp}) P(q_{\perp}) = e^{-\pi i \lambda \Delta f_1 q^2} e^{-i \pi \lambda t q^2}.
\]

(8.2)

Applying the transfer function of the second imaging lens the representation of the point source is now,

\[
\Psi(q_{\perp}) = T_2(q_{\perp}) P(q_{\perp}) T_1(q_{\perp})
\]

(8.3)

or we may write

\[
1 = e^{-i \pi \lambda (\Delta f_1 + t + \Delta f_2)}.
\]

(8.4)

So the confocal condition is

\[
0 = \Delta f_1 + t + \Delta f_2
\]

(8.5)

or for a given incident probe defocus the confocal condition is obtained for an imaging lens defocused

\[
\Delta f_2 = -t - \Delta f_1.
\]

(8.6)

A perfectly in focus lens would image the specimen surface closest to that imaging system i.e. pre-specimen lens has zero defocus at the entrance surface and the post-specimen lens has zero defocus at the exit surface. Underfocus into the specimen in both cases implies a negative defocus.
8.2 Coherent imaging theory

In this section we shall derive the fundamental equation describing the coherent imaging theory for elastic SCEM. Following the derivation given in Ref. [187], but using the notation developed so far, we begin with an expression for the illuminating probe wave function in real space given in Eq. 7.1:

$$\psi_1(r_{\perp}, R_{1\perp}, \Delta f_1) = \int A_1(q_{1\perp}) e^{-2\pi i q_{1\perp} \cdot R_{1\perp}} e^{-i \chi_1(q_{1\perp})} e^{2\pi i q_{1\perp} \cdot r_{\perp}} d q_{1\perp}, \quad (8.7)$$

where $q_{1\perp}$ and $R_1$ denotes the transverse momentum components in the probe wave function and the probe position respectively. The subscript 1 identifies the probe wave function associated with the pre-specimen electron optics. For convenience we only consider the defocus aberration such that the aberration function in Eq. 2.22, $\chi_1(q_{1\perp})$, describes the aberration associated with defocus $\Delta f_1$ (positive for overfocus) and is

$$\chi_1(q_{1\perp}) = \pi \lambda \Delta f_1 q_{1\perp}^2. \quad (8.8)$$

In Eq. 8.8 we have multiplied Eq. 2.22 by a factor of $2\pi/\lambda$ to simplify the subsequent analysis. We describe the scattering from a single isolated atom by the transmission function $q(r_{\perp})$ such that the wave function in the back focal plane of the post-specimen lens, indicated by the subscript 2, is

$$\Psi(q_{2\perp}, R_{1\perp}, \Delta f_1) = \int A_1(q_{1\perp}) e^{-2\pi i q_{1\perp} \cdot r_{\perp}} e^{-i \chi_1(q_{1\perp})} q(r_{\perp})$$

$$\times e^{2\pi i(q_{1\perp} - q_{2\perp}) \cdot r_{\perp}} d q_{1\perp} d r_{\perp}. \quad (8.9)$$

Performing the explicit Fourier transform with respect to the coordinate $r_{\perp}$ we obtain,

$$\Psi(q_{2\perp}, R_{1\perp}, \Delta f_1) = \int A_1(q_{1\perp}) e^{-2\pi i q_{1\perp} \cdot R_{1\perp}} e^{-i \chi(q_{1\perp})} Q(q_{2\perp} - q_{1\perp}) d q_{1\perp}, \quad (8.10)$$

which describes the scattering of the incident wave vector $q_{1\perp}$ into the wave vector $q_{2\perp}$. The scattered wave is then imaged by the post-specimen lens, indicated by the subscript 2, that is defocused by an amount $\Delta f_2$. At the point $R_{2\perp}$ the wave
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function is,

\[ \psi(R_{1\perp}, \Delta f_1, R_{2\perp}, \Delta f_2) = \int \int A_1(q_{1\perp}) e^{-2\pi i q_{1\perp} \cdot R_{1\perp}} e^{-i \chi_1(q_{1\perp})} Q(q_{2\perp} - q_{1\perp}) \times A_2(q_{2\perp}) e^{2\pi i q_{2\perp} \cdot R_{2\perp}} e^{-i \chi_2(q_{2\perp})} dq_{2\perp} dq_{1\perp}. \]  

(8.11)

Taking the Fourier transform of the transmission function and separating the integrals over \( q_{1\perp} \) and \( q_{2\perp} \) reveals,

\[ \psi(r_{1\perp}, \Delta f_1, R_{2\perp}, \Delta f_2) = \int q(r_{\perp}) \int A_1(q_{1\perp}) e^{-i \chi_1(q_{1\perp})} e^{-2\pi i (r_{\perp} - R_{1\perp}) \cdot q_{1\perp}} \times \int A_2(q_{2\perp}) e^{-i \chi_2(q_{2\perp})} e^{2\pi i (R_{2\perp} - r_{\perp}) \cdot q_{2\perp}} dq_{2\perp} dq_{1\perp} dr_{\perp}. \]  

(8.12)

Identifying the complex point spread functions\(^1\) of the pre- and post-specimen optics as \( P_{1\perp} \) and \( P_{2\perp} \) respectively Eq. 8.12 gives

\[ \psi(R_{1\perp}, \Delta f_1, R_{2\perp}, \Delta f_2) = \int q(r_{\perp}) P_1(r_{\perp} - R_{1\perp}, \Delta f_1) \times P_2(R_{2\perp} - r_{\perp}, \Delta f_2) dr_{\perp}. \]  

(8.13)

In the confocal mode of operation \( R_{1\perp} = R_{2\perp} \equiv R_{\perp} \) such that Eq. 8.13 is,

\[ \psi(R_{\perp}, \Delta f_{1\perp}, \Delta f_{2\perp}) = q(R_{\perp}) \ast [P_1(-R_{\perp}, \Delta f_1) P_2(R_{\perp}, \Delta f_2)]. \]  

(8.14)

The intensity at the confocal point \( R_{\perp} \) in the image plane is then

\[ I(R_{\perp}, \Delta f_{1\perp}, \Delta f_{2\perp}) = |q(R_{\perp}) \ast [P_1(-R_{\perp}, \Delta f_1) P_2(R_{\perp}, \Delta f_2)]|^2. \]  

(8.15)

In depth sectioning the confocal point \( R_{\perp} \), the pinhole detector in Fig. 8.1, is raster scanned across the sample for each defocus value. The convolution over all space in Eq. 8.15 between the scattering potential and the probe wave function preserves the dependence of the phase of the potential and the wave function on the image contrast. Thus the form of the expression in Eq. 8.15 indicates the coherent nature of SCEM.

\(^1\)The usual usage of the term point spread function implies the intensity of the impulse response of the lens system. Here the use of the complex qualifier signifies that we have not taken the intensity.
The phase contrast dependence of scanning confocal electron microscopy

In this section we shall establish the phase contrast dependence of elastic SCEM. We begin by making the weak phase approximation for the transmission function, \( q(\mathbf{r}_\perp) \) in Eq. 8.9, setting \( R_{1\perp} = R_{2\perp} = 0 \) and taking the Fourier transform we have

\[
q(\mathbf{r}_\perp) = e^{i\sigma V(\mathbf{r}_\perp)} \approx 1 + i\sigma V(\mathbf{r}_\perp) \tag{8.16}
\]

where \( \sigma \) is the interaction constant and

\[
Q(\mathbf{q}_\perp) = \delta(\mathbf{q}_\perp) + i\sigma \bar{V}(\mathbf{q}_\perp), \tag{8.17}
\]

such that the fast electron wave function after the action of the second lens in reciprocal space is

\[
\Psi(\mathbf{R}, \mathbf{q}_{2\perp}) = A_2(\mathbf{q}_{2\perp}) e^{-i\chi_2(\mathbf{q}_{2\perp})} \int A_1(\mathbf{q}_{1\perp}) e^{-i\chi_1(\mathbf{q}_{1\perp})} \left[ \delta(\mathbf{q}_{2\perp} - \mathbf{q}_{1\perp}) + i\sigma \bar{V}(\mathbf{q}_{2\perp} - \mathbf{q}_{1\perp}) \right] d\mathbf{q}_{1\perp}. \tag{8.18}
\]

Expanding Eq. 8.18 then the intensity at the pinhole detector in the image plane is,

\[
I(0) = \left| \int A_2(\mathbf{q}_{2\perp}) A_1(\mathbf{q}_{2\perp}) e^{-i[\chi_2(\mathbf{q}_{2\perp})+\chi_1(\mathbf{q}_{1\perp})]} d\mathbf{q}_{2\perp} 
+ i\sigma \int A_2(\mathbf{q}_{2\perp}) A_1(\mathbf{q}_{1\perp}) \bar{V}(\mathbf{q}_{2\perp} - \mathbf{q}_{1\perp}) e^{-i[\chi_2(\mathbf{q}_{2\perp})+\chi_1(\mathbf{q}_{1\perp})]} d\mathbf{q}_{2\perp} d\mathbf{q}_{1\perp} \right|^2. \tag{8.19}
\]

In the confocal arrangement the aberrations in both lenses would, ideally, be equal and opposite, \( \chi_1 = -\chi_2 \), and as such the first term in Eq. 8.19 is purely real. Phase contrast would require that the imaginary second term in Eq. 8.19 causes changes in the intensity. This would imply that, to first order, the phase contrast function is non-zero over all the momentum components present in each aperture. The complex conjugate of the double integral in Eq. 8.19 is

\[
c.c. = \int A_2(\mathbf{q}_{2\perp}) A_1(\mathbf{q}_{1\perp}) \bar{V}^*(\mathbf{q}_{2\perp} - \mathbf{q}_{1\perp}) e^{+i[\chi_2(\mathbf{q}_{2\perp})+\chi_1(\mathbf{q}_{1\perp})]} d\mathbf{q}_{2\perp} d\mathbf{q}_{1\perp}. \tag{8.20}
\]
Finally, as the scattering potential is real, \( \bar{V}^*(\mathbf{q}_{2\perp}-\mathbf{q}_{1\perp}) = \bar{V}(\mathbf{q}_{1\perp}-\mathbf{q}_{2\perp}) \), \( A_1 = A_2 \) and the integrals are over all of reciprocal space we can swap \( \mathbf{q}_{1\perp} \leftrightarrow \mathbf{q}_{2\perp} \). Then

\[
\text{c.c.} = \iiint A_1(\mathbf{q}_{2\perp}) A_1(\mathbf{q}_{1\perp}) \bar{V}(\mathbf{q}_{2\perp}-\mathbf{q}_{1\perp}) e^{+i[\chi_1(\mathbf{q}_{2\perp})-\chi_1(\mathbf{q}_{1\perp})]} d\mathbf{q}_{2\perp} d\mathbf{q}_{1\perp}. \tag{8.21}
\]

As the expression in Eq. 8.19 is the same as Eq. 8.20 it is real, and there is no contrast in the image due to the phase shift induced by the atomic potential to first order. Contrast in SCEM must be produced by the higher order terms which, for an atomic potential will be small. Consequently the contrast in atomic resolution elastic SCEM images will be low. Shown in Fig. 8.2 is the elastic signal for a single isolated atom of In and Al. The calculations do not contain a thermally smeared potential (i.e. the Debye-Waller factor is zero) and were performed on a 1024 x 1024 grid of dimensions 40 Å x 40 Å. The atomic potential was projected over 4 Å into a single phase grating slice. The simulations modelled the Oxford Jeol 2200FS machine with the pre- and post-specimen lenses aberration corrected up to 5\(^{th}\) order, allowing apertures of 30 mrad and an incident energy of 200 keV. As might be expected in bright field imaging (of a single atom) the recorded intensity decreases when the incident probe is focused at the atomic site. This decrease in the intensity is due to elastic scattering outside the aperture of the second imaging lens. The low contrast in the image can be attributed to the lack of first order phase contrast present for elastic SCEM. The full-width at half-maximum (FWHM) depth response is approximately 80 Å and 60 Å for the Al and In atoms respectively. The shallow peak occurring in the plane of the atom, which becomes more pronounced for larger aperture sizes, is a result of the atomic focusing of the incident electron [190].

### 8.3 Depth sectioning zone axis aligned crystals using elastic SCEM

It is anticipated that the higher order terms present in the Taylor expansion of Eq. 8.17 will increase in significance for thicker specimens. Furthermore thermal scattering processes typically involve a broad range of momentum transfers which may be scattered outside the post-specimen objective aperture leading to a reduction
in the recorded signal intensity and therefore affecting the image contrast. To investigate the dynamical scattering effects a GaAs sample of thickness 300 Å oriented along the $\langle 110 \rangle$ zone axis was investigated. A model of a unit cell of this structure rotated appropriately was shown in chapter 7 in Fig. 7.3. Embedded within this sample was an InAs layer that was assumed to have same lattice parameter as the GaAs. Simulations once again modelled the Oxford Jeol 2200FS machine with the pre- and post-specimen lens apertures of 30 mrad and an incident energy of 200 keV. A Debye-Waller factor smeared elastic potential was used with TDS being modelled using an absorptive multislice model.

Figure 8.3 shows the recorded intensity at the pinhole for a 100 Å thick InAs layer in $\langle 110 \rangle$ GaAs as the confocal plane is depth scanned through the sample. Specifically, Fig. 8.3(a) shows the profile for an InAs layer located with its upper surface at depths of 10 Å and 190 Å within the GaAs matrix (plotted together as in both cases the layer is 10 Å from a specimen surface). The layer causes a breaking in the symmetry of the profile about the midplane of the crystal, compared to the pure GaAs sample, and as the layer is moved deeper into the crystal the shape of the profile changes. Comparing two equivalent calculations that have a single impurity layer placed at the same distance from the entrance and the exit surface (the dotted
Figure 8.3: Intensity as a function of probe defocus for 300 Å ⟨110⟩ GaAs (solid line) and 300 Å ⟨110⟩ GaAs with a 100 Å InAs layer at different depths for a confocal system with 30 mrad lens apertures. Results are shown for a 100 Å thick InAs layer starting at depths of (a) 10 Å and 190 Å, (b) 50 Å and 150 Å, and (c) 100 Å. The probe is located above a Ga(In) column in all cases.
8.4. DISCUSSION AND CONCLUSIONS

and dashed line pairs in Figs. 8.3(a) and (b)) we see the same confocal profile albeit reflected about the midplane. This is an expected result when reciprocity is taken into account. As the layer is moved closer to the midplane of the specimen, Fig. 8.3(b) and (c), the shape of the confocal profile changes with the mirror symmetry about the midplane being maintained. This demonstrates sensitivity to the depth of the layer although the fine features do not correspond directly to the layer surfaces. Without performing accompanying simulations it would be challenging to infer the depth of a layer within a specimen from an experimental data set. Figure 8.3(c) shows the layer centred about the midplane of the GaAs crystal. This restores the symmetry of the profile, although the difference in signal and shape is minimal compared to the calculation without the buried layer.

A consistent feature present in the Fig. 8.3 is the reduction in the recorded intensity when the confocal plane is located at both the entrance and exit surfaces. For the probe focused at the entrance surface, there is usually a not insignificant degree of coupling to the $s$-states of the column (see Fig. 7.9). For probe forming aperture sizes around 30 mrad, this amounts to a significant proportion of the probe coupling to the $s$-states of the column and transmitted to the exit surface. The imaging lens, which is focused at the entrance surface, would focus these electrons as if they originated at the exit surface and thus would appear out of focus causing a drop in the recorded intensity. By reciprocity this same process would occur at the exit surface. The determination of the entrance and exit surfaces of the sample would allow for an accurate estimation of the sample thickness.

8.4 Discussion and conclusions

This chapter presented the theory for coherent SCEM. It examined the contrast mechanisms for SCEM using elastically scattered electrons. Even when the confocal plane is defocused away from an atom, it was shown that there is no first-order phase contrast, and hence that the image contrast is weak. The calculated contrast arising from a single atom has been explained by considering the atom as an atomic focuser. For thicker samples, where electron channelling becomes important, we have shown that the confocal mode allows accurate measurement of sample height and thickness. The ability to directly measure sample thickness provides a useful al-
ternative to existing methods using inelastic scattering measurements or convergent beam electron diffraction [148, 191, 192]. Furthermore, this strong entrance surface dependence may help in mapping particle distributions and location in height. The low contrast variation with atomic number for single atoms is shown to translate to low contrast variation for buried impurity layers that are several unit cells thick. The low contrast variation is seen to be the largest obstacle in the ability to detect buried impurity layers. Novel experiments using thermally scattered electrons may improve layer determination in SCEM somewhat [193].
Three dimensional imaging in energy filtered scanning confocal electron microscopy

Initial investigations suggested that inelastic scanning transmission electron microscopy (STEM) is capable of optically slicing samples for the purpose of imaging single atom impurities provided that the probe dimensions are sufficiently small [66, 69, 170]. For an incoherent signal originating from a point scatterer the intensity of the illuminating probe (or point spread function (PSF)) in STEM as a function of defocus gives an estimate of the depth resolution. The motivation of elastic scanning confocal electron microscopy (SCEM) was to avoid the pronounced elongation of reconstructed nanoparticles along the optical axis that had plagued STEM depth sectioning experiments [67, 70, 179, 180]. The investigation of STEM depth sectioning in chapter 7 did not address the issue of extended objects such as embedded nanostructures or nanoparticles. In this chapter we address the elongation problem for the reconstruction of extended objects. We begin by considering the electron microscopy equivalent of the optical microscopy optical transfer function (OTF) [194, 195]. To distinguish between the optical microscopy and electron microscopy cases we define the Fourier transform of the STEM illuminating probe PSF as the contrast transfer function (CTF) (although mathematically they are defined in the same way). The incoherent STEM CTF was considered in considerable detail by Intaraprasonk et al. [196]. Voyles and Einsphar [185] investigated...
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the CTF of SCEM to evaluate optimum imaging conditions for elastic SCEM. The work in this chapter is based on the work of D’Alfonso et al. [189] which compared the CTF of incoherent STEM and SCEM as well as the first calculations of energy filtered scanning confocal electron microscopy (EFSCM). More recently, Xin et al. [70] provided a comprehensive survey of the pertinent CTFs of high resolution transmission electron microscopy (HRTEM), STEM high angle annular dark field (HAADF), bright field STEM (BFSTEM), elastic SCEM and inelastic SCEM. This chapter presents the theory describing EFSCM and then goes on to present and discuss depth sectioning calculations of EFSCM. Firstly we consider the depth response of single isolated atoms. This is then extended to isolated impurity atoms in a crystalline support and finally to a cluster of impurities in a support.

9.1 Contrast transfer functions

In this section we derive and discuss some of the CTF’s for STEM and SCEM. The CTF of a microscopy system quantifies the extent of information transfer which is possible in a given experiment. We begin by deriving and discussing the incoherent STEM CTF. As the goal of this chapter is to theoretically evaluate and compare EFSCM to STEM electron energy energy-loss spectroscopy (EELS) we then derive and discuss the incoherent EFSCM CTF and the partially coherent STEM CTF.

9.1.1 The incoherent scanning transmission electron microscopy contrast transfer function

We begin by taking a three dimensional Fourier transform, for reciprocal space variable \( p \), of the recorded STEM image as a function of probe position \( R_{\perp} \) and defocus \( \Delta f_1 \)

\[
\tilde{I}_{\text{STEM}}(p) = \int \int I_{\text{STEM}}(R_{\perp}, \Delta f_1) e^{-2\pi i p \cdot R_{\perp}} e^{2\pi i p_z \Delta f_1} dR_{\perp} d(\Delta f_1), \quad (9.1)
\]

Using the conventional incoherent STEM image description (i.e. scattering from an effective local potential Eq. 6.4)

\[
I_{\text{STEM}}(R_{\perp}, \Delta f_1) = |\psi_1(R_{\perp}, \Delta f_1)|^2 \ast V_{\text{eff}}(R_{\perp}), \quad (9.2)
\]
9.1. CONTRAST TRANSFER FUNCTIONS

in Eq. 9.1 and making the approximation that the free space STEM probe evolution given by Eq. 8.7 sufficiently describes the probe within the specimen gives

\[
\tilde{I}_{\text{STEM}}(\mathbf{p}) = \iint \left\{ \int \langle \mathbf{q}_{1\perp} \rangle e^{-i\pi \lambda q_{1\perp}^2 (\Delta f_1 + z)} e^{2\pi i q_{1\perp} \cdot (\mathbf{r}_\perp - \mathbf{R}_{1\perp})} d\mathbf{q}_{1\perp} \right\}
\times \left\{ \int \langle \mathbf{q}'_{1\perp} \rangle e^{i\pi \lambda q_{1\perp}^2 (\Delta f_1 + z)} e^{-2\pi i q_{1\perp} \cdot (\mathbf{r}_\perp - \mathbf{R}_{1\perp})} d\mathbf{q}'_{1\perp} \right\}
\times V_{\text{eff}}(\mathbf{r}_\perp, z) d\mathbf{r}_\perp d\Delta f_1
\]

\[
= \iint T(\mathbf{q}_{1\perp}) T(\mathbf{q}'_{1\perp}) \left[ \iint e^{2\pi i (\mathbf{q}_{1\perp} - \mathbf{q}'_{1\perp}) \cdot \mathbf{r}_\perp} e^{-i\pi \lambda (q_{1\perp}^2 - q_{1\perp}^2)} d\mathbf{r}_\perp \Delta f_1 \right]
\times \left[ \iint e^{-2\pi i (\mathbf{q}_{1\perp} - \mathbf{q}'_{1\perp}) \cdot \mathbf{R}_{1\perp}} d\mathbf{R}_{1\perp} \right] d\mathbf{q}_{1\perp} d\mathbf{q}'_{1\perp}
\]

\[
= \iint T(\mathbf{q}_{1\perp}) T(\mathbf{q}'_{1\perp}) \left[ \int e^{-i\pi \lambda (q_{1\perp}^2 - q_{1\perp}^2)} V_{\text{eff}}(\mathbf{q}'_{1\perp} - \mathbf{q}_{1\perp}, z) d\mathbf{z} \right]
\times \delta \left[ p_z - \frac{\lambda}{2} (q_{1\perp}^2 - q_{1\perp}^2) \right] \delta \left( \mathbf{q}_{1\perp} - \mathbf{q}'_{1\perp} + \mathbf{p}_\perp \right) d\mathbf{q}_{1\perp} d\mathbf{q}'_{1\perp}
\]

\[
= \int T(\mathbf{q}_{1\perp}) T(\mathbf{q}_{1\perp} + \mathbf{p}_\perp) \left[ \int e^{-2\pi i p_z z} V_{\text{eff}}(\mathbf{p}_\perp, z) d\mathbf{r}_\perp d\mathbf{z} \right]
\times \delta \left[ p_z + \frac{\lambda}{2} (\mathbf{2q}_{1\perp} \cdot \mathbf{p}_\perp + p_{z\perp}^2) \right] d\mathbf{q}_{1\perp}
\]

\[
= \tilde{V}_{\text{eff}}(\mathbf{p}) \int T(\mathbf{q}_{1\perp}) T(\mathbf{q}_{1\perp} + \mathbf{p}_\perp) \delta \left[ p_z + \frac{\lambda}{2} (\mathbf{2q}_{1\perp} \cdot \mathbf{p}_\perp + p_{z\perp}^2) \right] d\mathbf{q}_{1\perp}.
\]

(9.3)

Equation 9.3 is the incoherent STEM CTF and tells us the degree of information transfer of \( V_{\text{eff}} \). The arguments of the \( \delta \) function, that is for any given value of \( (\mathbf{p}, p_z) \), combined with the limits imposed by the probe forming aperture determines whether or not \( \tilde{I}_{\text{STEM}}(\mathbf{p}) \) is non-zero, and thus whether or not any information about \( V_{\text{eff}} \) is contained in the three-dimensional STEM through focal series. To enable a graphical representation illustrating the consequence of these bounds, consider \( \mathbf{p}_\perp = (p_x, 0) \). Then \( \tilde{I}(p_x, 0, p_z) \) will only be non-zero if there exists a \( q_x \) for which

\[
p_z = -\frac{\lambda}{2} (2q_x p_x + p_{z\perp}^2)
\]

(9.4)
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Figure 9.1: Numerically calculated CTF for (a) STEM and (b) SCEM. The 200 keV probe has a probe forming aperture of 30 mrad. The SCEM image forming lens aperture subtends a 30 mrad semi-angle. The image forming and lens forming apertures are both aberration free. The thick black lines superimposed onto the plots are the analytically derived bounds for the respective geometries.

and for which the equalities

\[-q_{\text{max}} \leq q_x + p_x \leq q_{\text{max}} \quad \text{and} \quad -q_{\text{max}} \leq q_z \leq q_{\text{max}} \quad (9.5)\]

are satisfied. If \( p_x = 0 \) then Eq. 9.4 demands that \( p_z = 0 \). If \( p_x \neq 0 \) then Eqs. 9.4 and 9.5 yield four analytic bounds for the limits of the CTF. Spatial frequencies in the object which lie outside these bounds are not retained in the image. Fig. 9.1(a) shows the numeric CTF of STEM with the analytic bounds of Eqs. 9.4 and 9.5 superimposed, calculated for a 200 keV probe with a probe forming aperture of 30 mrad, in which the “missing cone” of information inherent in STEM depth sectioning is evident. In Fig. 9.1(a) the maximum transferred longitudinal spatial frequency \( p_z \) is given by the turning point of the analytic bounds which occurs at \( p_x = q_{\text{max}} \). To reach this maximum longitudinal resolution, therefore, requires an object containing spatial frequencies at \( p_x = q_{\text{max}} \). However, in many cases the STEM image contains much lower lateral spatial frequencies, for example when imaging metal particles in a homogeneous catalyst that are not aligned to a zone axis. The bound makes an angle of \( \lambda q_{\text{max}} \) with the \( p_x \) axis at the origin, identical to \( \alpha \), the semi-angle of convergence of the illuminating probe. For low la-
teral spatial frequencies, where the bounds can be approximated to being linear, only longitudinal spatial frequencies up to $\alpha p_\perp$ will be transferred. This shows that the depth resolution of an object with characteristic lateral length scale, $d$, is $d/\alpha$. Unlike optical microscopy, $\alpha$ in an electron microscope is very small; even in an aberration-corrected instrument $\alpha$ may only be around 35 mrad. This means that the depth resolution of a 50 Å particle may be around 2000 Å, much worse than the full-width at half-maximum (FWHM) depth of the probe intensity and this effect is readily observed in experimental data [67, 70, 179, 180].

It must be pointed out, however, for objects in one or two dimensions (i.e. atomic planes or isolated impurities) these bounds are not as restrictive. If the object is smaller than the dimensions of the probe, then the Fourier bound on the object effectively collapse to a projection which fills the CTF missing cone.

### 9.1.2 The incoherent scanning confocal electron microscopy contrast transfer function

In SCEM it is unclear under what conditions the incoherent imaging approximation would be valid. Nevertheless, using analogous reasoning applied to incoherent fluorescent confocal scanning optical microscopy [197–199], we consider the SCEM image to be

$$I_{SCEM}(R_\perp) = V_{\text{eff}}(R_\perp) * |P_1(r_\perp, z)|^2 |P_2(R_\perp, t - z)|^2.$$  \hspace{1cm} (9.6)

Thus in the confocal geometry it is possible to consider the PSF as being the product of two STEM probe intensities, one arising from the pre-specimen optics and the other from the post-specimen optics. If the optical system is symmetric, then both probes have the same form. The CTF is the Fourier transform of this PSF and it follows that the SCEM CTF is the autocorrelation of the STEM CTF. The SCEM CTF is shown in Fig. 9.1(b). The shape of the bounds of the CTF can be visualised by translating the donut-shaped STEM CTF around another with their surfaces touching. Clearly the CTF has limits in the perpendicular and parallel directions that are twice as large as the STEM case. More importantly, there is no missing cone of information and the maximum longitudinal resolution can still be achieved for extended objects.
Having emphasized the behaviour of the bounds for information transfer in STEM and SCEM, as indicated by the solid lines in Figs. 9.1(a) and (b), it must be appreciated that the plotted transfer functions show the region of significant information transfer to be significantly smaller than these bounds. That said, Figs. 9.1(a) and (b) make it clear that the useful frequency transfer in all directions is better in SCEM than STEM and that SCEM fills in the missing cone within the region of significant transfer.

Discussion

The previous reciprocal space analysis, though giving the necessary quantitative results, is somewhat abstract. Hence we also provide a real space explanation for the relatively poor depth of focus anticipated for STEM depth sectioning of extended objects. The local STEM expression of Eq. 9.2 shows that, for a given probe position and defocus, the signal is the convolution the probe intensity and the effective scattering potential. It is a direct consequence of the conservation of electrons that the integrated intensity is the same in all planes perpendicular to the beam axis. For a point-like object this was irrelevant, because the convolution was only sensitive to the intensity of the probe in one place. In contrast, an extended object includes contributions from a range of points in the plane. Thus, for an extended object the contribution from out-of-focus planes can be very similar to that from the in-focus plane this is because although the wave function density will be less, more scatterers will be encountered. If the in-focus plane does not contribute the dominant part of the signal, then the depth sectioning concept fails. Thus STEM depth sectioning has poor sensitivity in the $z$-direction for extended objects whereas the SCEM geometry is not subject to this restriction. The form of the imaging expression, Eq. 9.6, shows that the signal is not governed by just the intensity flux through the plane, and signal transfer from regions of the beam waist dominate the image.

9.1.3 The partially coherent scanning transmission electron microscopy contrast transfer function

The analysis in Sec. 9.1.1 is based on an incoherent imaging approximation. This may not always hold for STEM and it seems less likely to hold for SCEM. The
Fourier analysis of Eq. 9.1 can however be applied to the nonlocal case. For the nonlocal analysis, we restate Eq. 4.19:

\[
I(R) = \frac{2\pi}{hv} \int_0^t \int \int \phi_0(r_\perp, z) W(r_\perp, r_\perp', z) \phi_0(r_\perp, z) \, dr_\perp \, dr_\perp' \, dz. \tag{9.7}
\]

Neglecting elastic scattering and Substituting Eq. 9.7 into Eq. 9.1 gives

\[
\tilde{I}_{\text{STEM}}(p) = \int \int \int \left\{ \int A(q_{1\perp}) e^{-i\pi \lambda_{q}^2 (\Delta f_1 + z)} e^{2\pi i q_{1\perp} \cdot (r_\perp - R_{1\perp})} \, dq_{1\perp} \right\}
\times \left\{ \int A(q_{1\perp}') e^{i\pi \lambda_{q}^2 (\Delta f_1 + z)} e^{-2\pi i q_{1\perp}' \cdot (r_\perp' - R_{1\perp})} \, dq_{1\perp}' \right\}
\times W_{\text{eff}}(r_\perp, r_\perp', z) \, dr_\perp \, dr_\perp' \, dz \, e^{-2\pi i p_\perp \cdot R_{1\perp} e^{2\pi i p_\perp \cdot \Delta f_1} dR_{1\perp}} d(\Delta f_1)
= \int \int \int \int e^{2\pi i (q_{1\perp} - q_{1\perp}') \cdot r_\perp} e^{-i\pi \lambda (q_{1\perp}^2 - q_{1\perp}'^2) z} W_{\text{eff}}(r_\perp, r_\perp', z) \, dr_\perp \, dr_\perp' \, dz
\times \left[ \int e^{2\pi i [q_{1\perp} - q_{1\perp}'] \cdot [q_{1\perp} - q_{1\perp}']}] \Delta f_1 d(\Delta f_1) \right]
\times \left[ \int e^{-2\pi i (q_{1\perp} - q_{1\perp}') \cdot p_{\perp} \cdot R_{1\perp}} dR_{1\perp} \right] dq_{1\perp} \, dq_{1\perp}'
= \int \int A(q_{1\perp}) A(q_{1\perp}') \left[ \int e^{-i\pi \lambda (q_{1\perp}^2 - q_{1\perp}'^2) z} \tilde{W}_{\text{eff}}(q_{1\perp}, q_{1\perp}', z) \, dz \right]
\times \delta \left[ p_{z} - \frac{\lambda}{2} (q_{1\perp}^2 - q_{1\perp}'^2) \right] \delta (q_{1\perp} - q_{1\perp}') \, dq_{1\perp} \, dq_{1\perp}'
= \int A(q_{1\perp}) A(q_{1\perp} + p_{\perp}) \tilde{W}_{\text{eff}}(q_{1\perp}, q_{1\perp} + p_{\perp}, p_{z})
\times \delta \left[ p_{z} + \frac{\lambda}{2} (2q_{1\perp} \cdot p_{\perp} + p_{\perp}^2) \right] \, dq_{1\perp} , \tag{9.8}
\]

where the object and detector information is contained in the quantity \( \tilde{W}_{\text{eff}}(r_\perp, r_\perp', z) \). The bounds on the non-zero values of \( \tilde{I}_{\text{STEM}}(p) \) are seen to be identical whether the local or nonlocal model is used. This follows from the dependence on the probe position and defocus; the STEM image coordinates used in this Fourier analysis are the same in both cases. The same is true for the SCEM analysis; the bounds on the non-zero values of \( \tilde{I}_{\text{SCEM}}(p) \) are the same for both the local or nonlocal models. What differs is that the effective potential containing the information about
the object can no longer be factorized out of the expression. It is possible, therefore, to get object frequencies beyond these limits transferred to frequencies in the STEM/SCEM images within these limits (although Eq. 9.8 imposes a restriction on the extent of this). However, given the convoluted manner of this transfer, it is unclear that any higher resolution information could be gained without considerable numerical analysis, and thus the local model bounds provide a good indication of the relative merits of STEM and SCEM with respect to depth sectioning.

### 9.2 Theory of energy filtered scanning confocal electron microscopy

The analysis in the preceding section refines and provides an insight into the elongation problem. An incoherent form of aberration corrected SCEM would effectively fill the missing cone and allow through focal depth sectioning at sub nanometer resolution. A candidate for this incoherent signal is core shell ionization, and thus combining the tools in chapters 2, 3, 4 and 8 we will construct a framework for calculating EFSCEM images. We begin from Eq. 8.7 describing the probe incident onto the specimen, restated

$$T_1(q_{1\perp}) \equiv A_1(q_{1\perp})e^{-\pi i \Delta f q_{1\perp}^2}. \quad (9.9)$$

Using the $S$ matrix notation introduced in chapter 2, the elastic wave function at a depth $z$ within the crystal is,

$$\Phi_1(q_{\perp}, z_\alpha, R_{1\perp}) = \sum_{q_{1\perp}} S_{q_{\perp},q_{1\perp}}(z_\alpha) T_1(q_{1\perp}) e^{-2\pi i q_{1\perp} \cdot R_{1\perp}} e^{2\pi i q_{\perp} \cdot r_{\perp}}. \quad (9.10)$$

in reciprocal space and

$$\phi_1(r_{\perp}, z_\alpha, R_{1\perp}) = \sum_{q_{\perp}} \sum_{q_{1\perp}} S_{q_{\perp},q_{1\perp}}(z_\alpha) T_1(q_{1\perp}) e^{-2\pi i q_{1\perp} \cdot R_{1\perp}} e^{2\pi i q_{\perp} \cdot r_{\perp}}. \quad (9.11)$$

in real space. The reciprocal space form is obtained simply by the action of the scattering matrix $S_{q_{\perp},q_{1\perp}}(z_\alpha)$ on the incident surface (reciprocal space) wave function $T_1(q_{1\perp}) e^{-2\pi i q_{1\perp} \cdot R_{1\perp}}$ which effects propagation, including absorption, through
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the distance \( z_\alpha \). At the distance \( z_\alpha \) an ionization event occurs such that an inelastic wave is generated (see Sec. 4.1.1). Eq. 4.6 may be written in discrete reciprocal space form as

\[
\Phi_n(q'_\perp, z_\alpha, R_{1\perp}) = -\frac{2m\Lambda n}{\hbar^2} \sum_{q_\perp} \Phi_1(q_\perp, z_\alpha, R_{1\perp}) \sum_{q'_\perp} S_{q_\perp, q'_\perp}(t - z_\alpha) \sum_{q_1\perp} S_{q_1\perp, q'_1\perp}(z_\alpha) T_1(q_1\perp) \sum_{q_2\perp} \Phi_2(q_2\perp, R_{2\perp} = R_{1\perp}) \sum_{q'_2\perp} S_{q_2\perp, q'_2\perp} e^{2\pi i q_2\perp \cdot R_{2\perp}}. 
\] (9.12)

where the superscript \( \alpha \) indicates the three-dimensional location of the atom at which the ionization and hence energy loss took place, \( \Phi_1 \) is the reciprocal space form of the elastic wave function incident upon this atom and the subscript label indicates association with the pre-specimen optics. The inelastic wave function \( \Phi_n(q'_\perp, z_\alpha, R_{1\perp}) \) given in Eq. 9.12 may be propagated to the exit face of the specimen and the transmission function of the post-specimen lens applied:

\[
\Phi_n(q_{2\perp}, z_\alpha, R_{1\perp}) = \sum_{q'_2\perp} S_{q_{2\perp}, q'_2\perp}(t - z_\alpha) \Phi_n(q'_\perp, z_\alpha, R_{1\perp}). 
\] (9.13)

Combining Eqs. 9.11, 9.12 and 9.13, and taking the Fourier sum, yields the wave function in the SCEM detector plane:

\[
\phi_n(R_{2\perp}, t, R_{1\perp}) = -\frac{2m\Lambda n}{\hbar^2} \sum_{q_{2\perp}} e^{2\pi i q_{2\perp} \cdot R_{2\perp}} T_2(q_{2\perp}) \sum_{q'_2\perp} S_{q_{2\perp}, q'_2\perp}(t - z_\alpha) \sum_{q_{1\perp}} \sum_{q_{1\perp}} S_{q_{1\perp}, q'_1\perp}(z_\alpha) T_1(q_{1\perp}) e^{-2\pi i q_{1\perp} \cdot R_{1\perp}}. 
\] (9.14)

For an image plane pinhole detector located directly at the center of the probe image \( R_{2\perp} = R_{1\perp} \) the SCEM image intensity is

\[
I_{SCEM}(R_{1\perp}, \Delta f_1) = \left| -\frac{2m\Lambda n}{\hbar^2} \sum_{q_{2\perp}} e^{2\pi i q_{2\perp} \cdot R_{1\perp}} T_2(q_{2\perp}) \sum_{q'_2\perp} S_{q_{2\perp}, q'_2\perp}(t - z_\alpha) \sum_{q_{1\perp}} \sum_{q_{1\perp}} S_{q_{1\perp}, q'_1\perp}(z_\alpha) T_1(q_{1\perp}) e^{-2\pi i q_{1\perp} \cdot R_{1\perp}} \right|^2, 
\] (9.15)

where we have reintroduced the explicit defocus dependence on the left (but not the right) having assumed the confocal condition \( \Delta f_2 = -\Delta f_1 - t \). Equation 9.15 is the
equation for the calculation of an inelastic SCEM image from a single transition after ionizing a single atom. The method of evaluating Eq. 9.15 need not be restricted to scattering matrices. As was noted in chapter 4, by using the multislice method it is possible to efficiently calculate EFSCEM images for aperiodic specimens.

Up to this point, we have only considered the SCEM image contribution from a single atom excited to a single final state \( n \). Introducing the incoherent sum over all possible final states for each atom of the pertinent species in a crystal, summing over the slice depth \( z_\alpha \) and the location in the plane \( r_{\alpha \perp} \) in Eq. 9.24 gives

\[
I_{\text{SCEM}}(R_{1\perp}, \Delta f_1) = \sum_{z_\alpha, r_{\alpha \perp}, n} \left| \frac{2mA_n}{\hbar^2} \int_0^\infty \phi_2(r_{\perp}, t - z_\alpha, R_{1\perp}) \right|^2 \times H_{n0}^\alpha(r_{\perp}) \phi_1(r_{\perp}, z_\alpha, R_{1\perp}) \Gamma(r_{\perp}, r'_{\perp}, z) \times \phi_1^*(r_{\perp}, z, R_{1\perp}) \phi_2(r'_{\perp}, z, R_{1\perp}) dr_{\perp} dr'_{\perp} dz ,
\]

(9.16)

where

\[
\Gamma(r_{\perp}, r'_{\perp}, z) \equiv \frac{1}{\Delta z} \sum_{r_{\alpha \perp}, n} \left| \frac{2mA_n}{\hbar^2} \right|^2 H_{n0}^\alpha(r_{\perp}) H_{n0}^\alpha(r'_{\perp}) .
\]

(9.17)

On the right hand side of the Eq. 9.17 it is understood that only atoms, \( \alpha \) which are pertinent to the interval \( z + \Delta z \) for the implementation of the \( z \)-integration are used to evaluate \( \Gamma(r_{\perp}, r'_{\perp}, z) \) in that interval.

Equation 9.16, which might be considered to be the fundamental equation describing partially coherent inelastic imaging in SCEM, suppresses the explicit sum over incoherent final states at the expense of introducing a nonlocal form.

9.2.1 Rapid method for image simulation

Equation 9.15 describes the intensity at the pinhole detector from a single atom that has been ionized to a final state. Realistic calculations must incoherently sum the contribution from all possible final states \( n \) from all atoms of the pertinent species \( \alpha \) at the depth \( z_\alpha \) inside the crystal, as done in Eq. 9.16. Consequently, the incoherent sum required of Eq. 9.15 is a computationally expensive quantity to calculate (albeit still within the realms of possibility). For a more computationally efficient method
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useful for image simulation we define the quantity

\[ \phi_2(r_\perp, t - z_\alpha, R_{2\perp}) = \sum_{q_2\perp} \left[ \sum_{q_2\perp} S_{q_2\perp, q_2\perp} (t - z_\alpha) T_2(q_2\perp) e^{-2\pi i q_2\perp \cdot R_{2\perp}} \right] e^{2\pi i q_2\perp \cdot R_\perp}. \]  

(9.18)

Guided by reciprocity, we now anticipate that the overlap integral between the inelastic wave in the slice of the ionized atom and a virtual probe created by a virtual point source in the image plane propagated backward through a distance \( t - z_\alpha \) from the exit surface to the slice of the ionized atom is related to the observed intensity at the pinhole detector,

\[ \frac{1}{A} \int \phi_2(r_\perp, t - z_\alpha, R_{1\perp}) H_{n0}^\alpha(r_\perp) \phi_1(r_\perp, z_\alpha, R_{1\perp}) dr_\perp. \]  

(9.19)

Substituting Eqs. 9.11 and 9.18 into 9.19 we obtain

\[ \frac{1}{A} \int \phi_2(r_\perp, t - z_\alpha, R_{1\perp}) H_{n0}^\alpha(r_\perp) \phi_1(r_\perp, z_\alpha, R_{1\perp}) dr_\perp = \sum_{q_1\perp} \left[ \sum_{q_1\perp} S_{q_1\perp, q_1\perp} (z_\alpha) T_1(q_1\perp) e^{-2\pi i q_1\perp \cdot R_{1\perp}} \right] \times \frac{1}{A} \int H_{n0}^\alpha(r_\perp) e^{2\pi i (q_1\perp + q_2\perp) \cdot r_\perp} dr_\perp \]  

(9.20)

Relabelling the dummy indices \( q_2\perp \rightarrow -q_2\perp \) and \( q_2' \rightarrow -q_2' \) and assuming that the second lens is rotationally symmetric \( (T_2(q_2\perp) = T_2(-q_2\perp)) \), the right hand side of Eq. 9.20 becomes

\[ \sum_{q_2\perp} T_2(q_2\perp) e^{2\pi i q_2\perp \cdot R_{1\perp}} \sum_{q_2'\perp} S_{-q_2', -q_2\perp} (t - z_\alpha) \times \sum_{q_1\perp} H_{n0}^\alpha(q_1' - q_1\perp) \sum_{q_1\perp} S_{q_1\perp, q_1\perp} (z_\alpha) T_1(q_1\perp) e^{-2\pi i q_1\perp \cdot R_{1\perp}}. \]  

(9.21)

Using the anti-diagonal symmetry of the \( S \) matrix \( (S_{-q_2', -q_1\perp} = S_{q_2\perp, q_1\perp}) \) [95]
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Eq. 9.20 reduces to

\[
\frac{1}{A} \int \phi_2(r_\perp, t - z_\alpha, R_{1\perp}) H_{n_0}^{\alpha}(r_\perp) \phi_1(r_\perp, z_\alpha, R_{1\perp}) dr_\perp \\
\times \sum_{q_{2\perp}} T_2(q_{2\perp}) e^{2\pi i q_{2\perp} \cdot R_{1\perp}} \sum_{q'_{\perp}} S_{q_{2\perp}, q'_{\perp}} (t - z_\alpha) \\
\times \sum_{q_{\perp}} H_{n_0}^{\alpha}(q'_{\perp} - q_{\perp}) \sum_{q_{1\perp}} S_{q_{\perp}, q_{1\perp} (z_\alpha)} T_1(q_{1\perp}) e^{-2\pi i q_{1\perp} \cdot R_{1\perp}}. \tag{9.22}
\]

In Eq. 9.21, had the lens not been rotationally symmetric then the appropriate ansatz for Eq. 9.18 would have contained \( T_2(-q_{2\perp}) \) instead, which would not have had the usual form of an incident wave function but would still have allowed for rapid calculation. Thus

\[
\frac{1}{A} \int \phi_2(r_\perp, t - z_\alpha, R_{1\perp}) H_{n_0}^{\alpha}(r_\perp) \phi_1(r_\perp, z_\alpha, R_{1\perp}) dr_\perp \\
= \sum_{q_{2\perp}} T_2(q_{2\perp}) e^{2\pi i q_{2\perp} \cdot R_{1\perp}} \sum_{q'_{\perp}} S_{q_{2\perp}, q'_{\perp}} (t - z_\alpha) \sum_{q_{\perp}} H_{n_0}^{\alpha}(q'_{\perp} - q_{\perp}) \\
\times \sum_{q_{1\perp}} S_{q_{\perp}, q_{1\perp} (z_\alpha)} T_1(q_{1\perp}) e^{-2\pi i q_{1\perp} \cdot R_{1\perp}}, \tag{9.23}
\]

where, up to constant factors, the right hand side is precisely the quantity we wished to calculate in Eqs. 9.14 and 9.15. Thus, the SCEM image intensity can also be written as

\[
I_{\text{SCEM}}(R_{1\perp}, \Delta f_1) = \left| \frac{2m\Lambda_\alpha}{\hbar^2} \frac{1}{A} \int \phi_2(r_\perp, t - z_\alpha, R_{1\perp}) H_{n_0}^{\alpha}(r_\perp) \phi_1(r_\perp, z_\alpha, R_{1\perp}) dr_\perp \right|^2. \tag{9.24}
\]

The quantity defined in Eq. 9.18 has the same form as Eq. 9.11, both represent forwards propagation through a given thickness of crystal of a given “incident” wave function. Equation 9.11 would more normally be evaluated via multislice methods, and therefore Eq. 9.18 can also be evaluated the same way. We note that absorption is correctly included in both propagation stages. This expression reveals that rather than carrying out forward calculations separately for all final states (which is computationally expensive when the sample thickness and the number of final states is
large), it suffices to calculate only two elastic wave functions for all final states of all the atoms at a particular depth per probe position. However, this approach is only effective if we assume an ideal point detector, and loses its efficiency when a finite detector size is taken into account.

We can make the identification in SCEM that the second wave $\phi_2(r_{\perp}, t-z_\alpha, R_{2\perp})$ describes an elastic wave which would be formed by the post specimen optics and an on-axis point source in the image plane; a possibility suggested by the reciprocity apparent in the SCEM geometry. However, it must be stressed that the identification of a virtual probe is just a construct to hasten calculations and aid interpretation. In reality the post specimen optics merely image the exit surface wave to the detector plane.

Using the scanning confocal electron microscopy equations to obtain the scanning transmission electron microscopy equations

In the next section we shall directly compare STEM EELS and EFSCEM depth sectioning techniques. In this section we show how to extract STEM EELS results from the EFSCEM calculation. We then proceed to make the single channelling approximation and obtain the conventional STEM EELS cross section equation (Eq. 4.19). Using Parseval’s theorem (or conservation of electrons) the signal obtained by integrating the SCEM image plane intensity, as a function of probe position, gives the STEM result for a collection angle equal to the SCEM post specimen lens. Generalising Eq. 9.16 such that the point detector at $R_{2\perp}$ is not fixed at $R_{1\perp}$ we have,

$$I_{\text{SCEM}}(R_{1\perp}, R_{2\perp}, \Delta f) = \iiint \phi_2^*(r_{\perp}, t-z, R_{2\perp}) \phi_2(r'_{\perp}, t-z, R_{2\perp}) \Gamma(r_{\perp}, r'_{\perp}, z)$$

$$\times \phi_1^*(r_{\perp}, z, R_{1\perp}) \phi_1(r'_{\perp}, z, R_{1\perp}) dr_{\perp} dr'_{\perp} dz . \quad (9.25)$$

Assuming a single channelling approximation\(^1\), where by the scattering matrix pertaining to the inelastic wave function in Eq. 9.18 is replaced by a Kronecker delta

---

\(^1\)For the relatively large aberration corrected post specimen lens in SCEM the equivalent collection angle in STEM is considered sufficiently large to make this approximation [133, 137].
multiplied by a propagating phase factor, such that

\[ \phi_2(r_\perp, t - z_\alpha, R_\perp) = \sum_{q_\perp} T_2(q_\perp) e^{-\pi i q_\perp^2 (t - z_\alpha)} e^{2\pi i q_\perp (r_\perp - R_\perp)}. \] (9.26)

Substituting in Eq. 9.25 and integrating over \( R_\perp \) gives

\[ I_{\text{STEM}}(R_\perp, \Delta f_1) = \int \int \int \left[ \sum_{q_\perp} |T_2(q_\perp)|^2 e^{-2\pi i q_\perp (r_\perp - r'_\perp)} \right] \Gamma(r_\perp, r'_\perp, z) \times \phi_1^*(r_\perp, z, R_\perp) \phi_1(r'_\perp, z, R_\perp) dr_\perp dr'_\perp dz, \] (9.27)

where we have identified the detector function \( D(r_\perp - r'_\perp) \). This has the same form as Eq. 4.19, the standard nonlocal inelastic cross section expression for STEM with a detector function wrapped into the nonlocal potential \( W(r_\perp, r'_\perp) \).

### 9.3 Energy filtered scanning confocal electron microscopy case study: impurities in a zone axis aligned crystal

Using the theoretical framework described above, but performing the elastic propagation using conventional multislice techniques (see Sec. 2.3.3) we now consider the imaging of two different types of impurities added to a GaAs crystal aligned along a \( \langle 110 \rangle \) zone axis A model of this structure rotated appropriately is shown in Fig. 7.3. These impurities are Al and C atoms, which substitutionally displace a Ga atom at a range of depths in the column. The characteristic energy losses for ionizing a \( K \)-shell electron of both impurities were used to generate energy-filtered images. All simulations account for the attenuation of the elastic wave function by thermal diffuse scattering using an Einstein model and were performed on a 22.6 \( \AA \times 20.0 \AA \) supercell. The microscope geometry was simulated with equivalent pre- and post-specimen lens aperture semi-angles of \( \alpha = 30 \) mrad. The electron
probe energy is 200 keV, with no lens aberrations present other than user-variable defocus. The image plane SCEM point detector is aligned along the optical axis of the microscope and is a single pixel. The STEM detector, used for comparison with the SCEM image, subtends a collection semi-angle of $\beta = 30$ mrad and is also aligned along the optical axis. All STEM simulations included elastic scattering to all orders for the fast electron pre- and post-ionization.

### 9.3.1 Single isolated atoms

To begin the investigation of inelastic SCEM depth sectioning we consider the probe defocus response of single isolated C and Al atoms before introducing the supporting GaAs crystal.

Figure 9.2 shows the isolated C $K$-edge line scan as a function of defocus for (a) SCEM and (b) STEM. The C atom is located at a position of 0 Å. The SCEM and STEM images as a function of lateral probe position at zero defocus have significantly different shapes: the SCEM image has a "volcano structure" whereas the STEM image resembles a Gaussian. The origin of these features lies in the shape of the projected transition potentials. In the STEM geometry the fine manifestations of these transition potentials are integrated over the post specimen detector. However, in the case of SCEM the inelastic wave function is re-interfered by the coherent post specimen optics and the fine details of the transition potentials generating these waves manifest themselves more strongly. The increased depth resolution of SCEM compared to STEM is clearly evident when comparing Figs. 9.2 (a) and (b). The equivalent Al images are shown in Figs. 9.2(c) and (d). Comparing the C and Al STEM simulations, the effect of the interaction delocalisation on both the SCEM and STEM images is clear, with the more tightly bound Al $K$-edge (and therefore less delocalised potential) images appearing more localised than the broader C $K$-edge images. This is particularly evident in the STEM case. Overall, comparison between Al and C images implies that the interaction delocalisation is a significant factor influencing the image depth of focus. The more tightly bound Al $K$ shell has a much lower cross section than the C $K$ shell and consequently has a much lower intensity SCEM image.
Figure 9.2: C K-shell EELS line scan images as a function of defocus ($\Delta f_1$) for (a) SCEM and (b) STEM geometries. Al K-shell EELS line scan images as a function of defocus ($\Delta f_1$) for (c) SCEM and (d) STEM geometries. The SCEM simulation used equivalent pre- and post-specimen lens aperture semi-angles of $\alpha = 30$ mrad. The STEM simulations used equivalent probe forming and electron collection aperture semi-angles of $\alpha = \beta = 30$ mrad. The electron probe energy was 200 keV, with no lens aberrations present other than user-variable defocus.
9.3.2 Depth sectioning under channelling conditions

We now consider the effect of the crystalline matrix, and the associated dynamical scattering of the incident and inelastic waves. Substitutionally displacing a Ga atom in the column with a C or Al impurity at a depth of 152 Å within a 308 Å thick GaAs crystal oriented along a \(<110>\) zone axis and depth sectioning shows how the recorded crystal image (Fig. 9.3) changes from the previous single atom calculations.

Figures 9.3(a) and (b) show the C K-edge and Figs. 9.3(c) and (d) the Al K-edge SCEM and STEM images. The extent of the C K-edge delocalisation is more apparent when the atom is included in a crystal containing a strongly scattering As column close to the impurity column. In Figs. 9.3(a) and (b) both the SCEM and STEM images show an offset in the image intensity peak towards the As column and the increased resolution of SCEM makes this image delocalisation much more pronounced. As seen in the single atom case the Al K-shell transition potential is significantly more localised than the C K-shell and consequently the Al images (Figs. 9.3(c) and (d)) do not show as pronounced a shift toward the As column. In both STEM images an intensity peak around the region of \(\Delta f_1 = 0\) Å is observed. This peak is most likely a consequence of the probe coupling to the \(s\)-like state of the Ga column (refer to Sec. 7.3.2). When the probe is focused onto the specimen surface and couples to the \(s\)-like state, the subsequent electron channelling along the column generates ionization events at the depth of the dopant. The SCEM geometry ensures that any inelastically scattered electrons which do not originate from the focal plane of the electron optics are not focused onto the detector. This is demonstrated by the lack of intensity in the peak at zero defocus. As expected, the defocus FWHM is smaller for the SCEM geometry than the STEM geometry. In the STEM geometry the extent of the interaction delocalisation increases the intensity defocus FWHM significantly. This increase also occurs in SCEM, but to a lesser extent relative to STEM.

To gauge the extent to which the energy filtered image represents the specimen structure when the probe is focused into the crystal we examine Figs. 9.4(a) and (b) which show 2D SCEM EELS raster scans for a probe with a defocus of \(\Delta f = -150\) Å. The C K-edge energy filtered SCEM image in Fig. 9.4(a) is quite delocalised whereas the equivalent Al K-edge image in Fig. 9.4(b) is considerably less deloca-
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Figure 9.3: C $K$-edge line scans for (a) SCEM and (b) STEM geometries. Al $K$-edge line scans for (c) SCEM and (d) STEM geometries. The impurities are embedded 152 Å deep, substitutionally displacing a Ga atom on column, for a 308 Å thick GaAs crystal that is oriented along a $\langle 110 \rangle$ zone axis. The Ga and As columns are indicated by the thin and thick rimmed circles respectively. The SCEM simulation used equivalent pre- and post-specimen lens aperture semi-angles of $\alpha = 30$ mrad. The STEM simulations used equivalent probe forming and electron collection aperture semi-angles of $\alpha = \beta = 30$ mrad. The electron probe energy was 200 keV, with no lens aberrations present other than user-variable defocus.
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It is tempting to conclude that the drop in the intensity directly above the Ga column in the C K-edge image is a result of TDS absorption, but this is not the only possible mechanism as the Al K-edge image has a significantly smaller reduction in intensity above the same column despite the elastic wave functions incident upon the impurities being identical in both cases.

These somewhat counter-intuitive results from the 2D images for the lower lying edges may necessitate the simultaneous acquisition of a structural reference image to align the energy filtered images. This would allow the location of the dopant in relation to the lattice to be accurately determined while its depth is obtained from the sectioning procedure. In STEM the simultaneous recording of HAADF images with EELS maps is usually used to provide this structural reference [43, 58, 60]. Hence, one possible experimental protocol to provide a structural reference might be to switch from SCEM to STEM mode, acquire a HAADF image, and then return to SCEM mode. Figure 9.4 shows STEM HAADF images corresponding to the Al case, in Figs. 9.4(c) and (d), for two different defocus values, demonstrating that, as expected, this approach would provide an adequate lattice reference image over a wide range of defocus values.

In STEM, the depth at which a dopant is located changes the form of the inelastic wave function that is generated at the atomic site. The subsequent channelling experienced by the fast electron post interaction further changes the exit surface wave, altering the diffraction pattern (or image). Although the process of integrating up over some angular detector in STEM ameliorates some of the complications due to dynamical propagation in the image interpretation, dynamical effects are made more pronounced in SCEM due to the coherent re-interference of the wave function by the post specimen lens and the use of a point detector aperture. Previously, by considering both the situation where the dopant is located in the mid-plane of a specimen, and the overlap integral method for image simulation given in Sec.9.2, it is clear that there is a significant degree of symmetry in the wave functions used to generate Fig. 9.3. Figure 9.5 shows a simulation where the depth symmetry of the impurity position is broken: the impurity is again placed at a depth of 152 Å, substitutionally displacing a Ga atom on the column, but now the crystal is only 256 Å thick. This implies that the inelastically scattered electron will channel through only 104 Å of GaAs crystal post interaction, rather than the 156 Å in the previous simulations (especially Fig. 9.3). Comparing the symmetric case in Fig. 9.3 to
Figure 9.4: 2D SCEM energy filtered inelastic (a) C K-edge and (b) Al K-edge images produced by a probe with $\Delta f_1 = -150$ Å. The impurities are embedded 152 Å deep, substitutionally displacing a Ga atom on column, for a 308 Å thick GaAs crystal that is oriented along a $\langle 110 \rangle$ zone axis. The Ga and As columns are indicated by the thin and thick rimmed circles respectively. The SCEM simulation used equivalent pre- and post-specimen lens aperture semi-angles of $\alpha = 30$ mrad. The STEM simulations used an equivalent probe forming aperture semi-angle of $\alpha = \beta = 30$ mrad. The electron probe energy was 200 keV, with no lens aberrations present other than user-variable defocus. Also shown are STEM HAADF images for the Al case for a probe with (c) $\Delta f_1 = -150$ Å and (d) $\Delta f_1 = 0$ Å. The HAADF detector subtends 60-160 mrad. An incident probe energy of 200 keV was used for the simulations.
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Figure 9.5: C K-edge line scans for (a) SCEM and (b) STEM geometries. Al K-edge line scans for (c) SCEM and (d) STEM geometries. The impurities are embedded 152 Å deep substitutionally displacing a Ga atom on column for a 256 Å thick GaAs crystal that is oriented along a \langle110\rangle zone axis. The SCEM simulation used equivalent pre- and post-specimen lens aperture semi-angles of $\alpha = 30$ mrad. The STEM simulations used equivalent probe forming and electron collection aperture semi-angles of $\alpha = \beta = 30$ mrad. The electron probe energy was 200 keV, with no lens aberrations present other than user-variable defocus.
the asymmetric case in Fig. 9.5 shows that the STEM image has not changed significantly in a qualitative manner; all of the image anomalies that were present in the symmetric 308 Å simulations still persist for the asymmetric 256 Å simulation. This is consistent with a single channelling approach used in chapter 7, an approach which would produce identical images for the symmetric and asymmetric case. Conversely, the SCEM image has changed in a qualitative fashion such that there is a visible skew in the defocus of the intensity peak towards the exit surface of the crystal.

If depth determination is the prime motivation for the experiment then by integrating the SCEM and STEM raster scan for each probe defocus point it is possible to avoid most of the complications due to image delocalisation. Fig. 9.6 shows the result of integrating a 6 × 6 point raster scan as a function of probe defocus for both STEM and SCEM. Each raster scan was performed over a 1.4 Å × 1.0 Å rectangle centered above the Ga column. The GaAs crystal was 308 Å thick. For all of the depths at which the impurity was placed the peak intensity recorded occurs at a defocus corresponding to the depth of the impurity. The STEM integrated raster allows depth determination but the depth resolution is poorer than the SCEM integrated raster scans. Moreover, the degree of defocus asymmetry in the intensity signal is small for both edges in both geometries.

9.3.3 Pinhole effects

The scale in Fig. 9.6 reveals a key point somewhat neglected in the current discussion. The fractional intensity in EF-SCEM is considerably lower than that for STEM EELS. The pinhole detector which limits the out-of-plane contribution to the EF-SCEM image also reduces the intensity in the rastered image. Thus, a key point to consider is how the transition from SCEM to STEM occurs. Shown in Fig. 9.7 is a series of simulated depth sectioning experiments for increasing pinhole radii: (a) perfect pinhole, (b) 0.5 Å, (c) 1.0 Å, (d) 1.5 Å, (e) 2.0 Å, and (f) STEM and printed on these images is the maximum and minimum intensity. Immediately obvious is the smooth transition from the depth localised pinhole EF-SCEM image in 9.7(a) to the more delocalised STEM EELS image in Fig. 9.7(f). The characteristic

\[^2\]In practice the physical dimensions of the pinhole is limited to the calculation pixel size and here it is 0.04 Å × 0.04 Å.
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Figure 9.6: Integrated signal for a raster scan as a function of impurity depth and probe defocus for the SCEM (a) C $K$-edge and (b) Al $K$-edge, and STEM (c) C $K$-edge and (d) Al $K$-edge. Each magnified raster scan of $6 \times 6$ pixels is performed on a $1.4 \, \text{Å} \times 1.0 \, \text{Å}$ rectangle above the Ga column. Each integrated scan has a single impurity substitutionally displacing a Ga atom on the column in a $308 \, \text{Å}$ thick GaAs crystal oriented along a $(110)$ zone axis. The SCEM simulation used equivalent pre- and post-specimen lens aperture semi-angles of $\alpha = 30 \, \text{mrad}$. The STEM simulations used equivalent probe forming and electron collection aperture semi-angles of $\alpha = \beta = 30 \, \text{mrad}$. The electron probe energy was 200 keV, with no lens aberrations present other than user-variable defocus.
Figure 9.7: Al K-edge line scans for SCEM image plane detectors with radius: (a) perfect pinhole, (b) 0.5 Å, (c) 1.0 Å, (d) 1.5 Å, (e) 2.0 Å and (f) STEM. The impurities are embedded 152 Å deep, substitutionally displacing a Ga atom on column, for a 308 Å thick GaAs crystal that is oriented along a ⟨110⟩ zone axis. The Ga and As columns are indicated by the thin and thick rimmed circles respectively. The SCEM simulation used equivalent pre- and post-specimen lens aperture semi-angles of $\alpha = 30$ mrad. The STEM simulations used equivalent probe forming and electron collection aperture semi-angles of $\alpha = \beta = 30$ mrad. The electron probe energy was 200 keV, with no lens aberrations present other than user-variable defocus.
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$s$-state peak (occurring at $\Delta f = 0$ Å) begins to appear as the detector pinhole size is increased. The detector pinhole area ratio of that in Fig. 9.7(a) to that in Fig. 9.7(b) is approximately 1:500 and is largely responsible for the increased intensity. Two pertinent remarks regarding the optimal balance between maximising the signal intensity and reducing the signal delocalisation in depth as a consequence of increasing pinhole size can be made from inspection of Fig. 9.7. Firstly, a perfect STEM probe with a probe forming aperture semi-angle of 30 mrad has a FWHM of approximately (cf. Eq. 7.5(a)) 0.43 Å, by opening up the pinhole just beyond this number as in Fig. 9.7(b), the signal localisation in depth is maintained, and the intensity is maximised when compared to the perfect pinhole in Fig. 9.7(a). Secondly, the pinhole detector itself acts as a natural energy filter. Only electrons that have lost a particular amount of energy are brought to a focus at the pinhole. Increasing the pinhole size effectively increases the energy window, further increasing the intensity. However, increasing the pinhole also simultaneously increases the out-of-plane contributions and so must be done cautiously.

9.3.4 Fe in graphite: multiple dopants

To demonstrate the full potential of EFSCEM in an arguably more realistic, albeit somewhat ambitious scenario, Fig. 9.8 shows the EFSCEM through focal series map for multiple Fe impurities embedded inside a thin graphite matrix. The specimen was only 34 Å thick and this, in conjunction with the impurities being clustered so close to one another, would render STEM depth sectioning with its poor depth resolution somewhat difficult. Furthermore, the delocalisation of the STEM EELS image as a function of defocus and probe position, as was demonstrated for the single isolated impurity in Figs. 9.3 and 9.5, would make STEM depth sectioning results somewhat inconclusive. The EFSCEM simulation includes all dipole allowed transitions for the Fe $L_{2,3}$ edge. The focal series in Fig. 9.8 clearly shows impurities coming in and out of focus as the probe is focused further into the sample. Quantitatively, Fig. 9.9 shows the determined location of the dopant atoms for the cluster, with dopant atoms in the columns labelled $\delta, \gamma$ and $\epsilon$. Dopant depth determination obtained by locating the maximum intensity contained in the pink disc in Fig. 9.9(b) as a function of defocus. The striking feature is that the peak intensity of each column is located precisely at the depth of the dopant. The relatively close
proximity of the neighbouring dopants is found to have little effect on the depth response.

9.4 Discussion and conclusions

This chapter has investigated future prospects for depth sectioning extended objects in inelastic STEM and EFSCEM. It is found that due to the missing cone of information present in the STEM CTF and the associated elongation problem, depth sectioning in STEM will always remain a somewhat dubious and difficult proposition for nanoparticles. The low contrast present in elastic SCEM prohibits sectioning using that technique. However, as was shown, the CTF for incoherent SCEM does not contain a missing cone of information and hence is capable of depth sectioning without elongation of the reconstructed focal series. Modelling EFSCEM as a partially incoherent form of imaging in the electron microscope it is shown that depth sectioning should produce interpretable results. This chapter described the theoretical framework that was necessary to simulate EFSCEM images, culminating with Eq. 9.16 which is the fundamental equation describing imaging in confocal electron microscopy using inner shell ionization. We have demonstrated a computationally efficient method for image simulation by identifying the “backward” propagating probe. Finally, we have seen how the delocalised nature of the transition potential for lower lying ionization edges influences SCEM images in a subtle and complicated manner which necessitates the use of accurate theoretical simulations. A significant result of this thesis is contained in this chapter, it is the demonstration that EFSCEM depth sectioning will allow three-dimensional structure determination.
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Δf = 20.0 Å
Δf = 16.5 Å
Δf = 13.0 Å
Δf = 9.5 Å
Δf = 6.0 Å
Δf = 2.5 Å
Δf = -1.0 Å
Δf = -4.5 Å
Δf = -8.0 Å
Δf = -11.5 Å
Δf = -15.0 Å
Δf = -18.5 Å
Δf = -22.0 Å
Δf = -25.5 Å
Δf = -29.0 Å
Δf = -32.5 Å
Δf = -36.0 Å
Δf = -39.5 Å
Δf = -43.0 Å
Δf = -46.5 Å

Figure 9.8: Through-focal series of Fe $L_{2,3}$ edge SCEM EELS images (overfocus, positive defocus) for Fe impurity atoms in 34 Å of graphite [001]. The schematic in the lower left shows the projected structure, with the depth of the substitutional Fe atoms (in Ångström) given above each site. The 200 keV probe is assumed to be aberration-free. Both the pre- and post-specimen lens apertures have a semi-angle of 30 mrad.
Figure 9.9: (a) The integrated EFSCEM Fe $L_{2,3}$ signal as a function of probe defocus for the columns labelled $\delta$ (green), $\epsilon$ (red) and $\gamma$ (black) in the projected structure shown in (b). The inset on (b) shows a single through focal series image and the pink disc indicates the area that was integrated to form the line plot. The Fe impurity atoms are embedded in 34 Å of graphite [001]. The 200 keV probe is assumed to be aberration-free. Both the pre- and post-specimen lens apertures have a semi-angle of 30 mrad.
Conclusion

The electron microscope is one of the most powerful tools capable of imaging at the atomic scale. The value and importance of the electron microscope to many scientists in numerous fields is immeasurable. It is an understanding of the physical processes occurring inside the microscope that allows the instrument measurements to be fully exploited. As a general overarching theme this was the topic and motivation of this thesis, simulating and interpreting scanning transmission electron microscopy (STEM) and scanning confocal electron microscopy (SCEM).

This thesis investigated coherent, partially coherent and incoherent imaging modes in STEM and SCEM. We began by demonstrating quantitative agreement between theory and experiment in bright field scanning transmission electron microscopy (BFSTEM). Using the principle of reciprocity and reasoning that the physical processes in both STEM and high resolution transmission electron microscopy (HRTEM) are identical we were able to make informed speculations on the origin of the HRTEM Stobbs factor problem. The quantitative agreement in BFSTEM, coupled to the previously demonstrated quantitative agreement in STEM high angle annular dark field (HAADF) [30], validates current theories for the scattering of a fast electron within a specimen of condensed matter. Furthermore, this agreement elucidates the Stobbs factor problem [17], ruling out the specimen electron interaction as a mechanism for the prevailing contrast mismatch in HRTEM. This points microscope users in the direction of characterising and understanding their imaging apparatus, as well as compelling theoreticians to more closely model the experimental setup. This quantitative agreement of coherent BFSTEM simulations
with experiment, which by reciprocity is equivalent conventional coherent HRTEM, raises the tantalising prospect of the post specimen retrieval of a wave function that would be equivalent to HRTEM but not affected by a Stobbs type factor.

By using the real space transition potential approach of Coene and VanDyck [131] we delved deeper into understanding and interpreting STEM electron energy-loss spectroscopy (EELS) images. Using this approach exposed the physical processes causing seemingly anomalous images. Applying this approach helped to clarify the previously elusive concept of nonlocality. Solving the Yoshioka equations using the real space transition potential approach in a multislice framework, in conjunction with the mixed dynamical form factor (MDFF) Bloch wave solution, we were able to explore and test our predictions with experimental STEM EELS results. The good agreement between the simulations and experiments validated current inelastic scattering theories. It was demonstrated that the differences in the shapes and widths of the effective ionization potential had more than a superficial dependence on the binding energy of the target electron and this manifested itself strongly in the recorded experimental images.

Due to the focused coherent nature of the STEM probe we showed that the transition matrix elements pertinent to inelastic scattering need to be calculated to orders greater than the dipole approximation. Thus we have demonstrated that any calculations attempting to calculate electron energy-loss spectra in aberration corrected STEM must calculate the pertinent transition matrix elements with appropriate final state wave functions to all orders in $r$ in conjunction with accurate electron channelling calculations.

We then demonstrated the first published chemical mapping in two-dimensions at atomic resolution for a sample of Bi$_{0.5}$Sr$_{0.5}$MnO$_3$ for a range of zone axis orientations. As the energy-loss spectrum was integrated up over in these experiments the tools developed in the earlier chapters were particularly successful: they produced qualitatively identical simulations to the experimental images. Our two-dimensional images facilitated more convincing comparisons than typical line scans permitted.

The ability to perform two-dimensional comparisons between theory and experiment proved essential to explain experimental results. The importance of accurate theoretical modelling was highlighted even further for the chemical mapping of Si. Thermal scattering coupled with the delocalised long range ionization potential and the dynamical spreading of the electron probe was seen to cause a complete
contrast reversal for images constructed from different regions of the energy loss spectrum. These seemingly anomalous results, unexplainable when considered in isolation, were understood using the tools presented in this thesis. The experimental advances allowing full two-dimensional maps facilitated these tests and demonstrated the usefulness of STEM EELS.

The feasibility of chemically mapping samples using STEM energy dispersive x-ray spectroscopy (EDS) was investigated with the experimental results being encouraging. The demonstrated incoherent nature of EDS imaging coupled to the excellent agreement between the predicted image and the experimental result and the associated interpretations, highlight that STEM EDS will become a valuable tool in the future.

This thesis then investigated extending STEM EELS to chemical mapping in three dimensions. This was performed by adjusting the incident probe’s defocus, optically slicing a sample and monitoring the STEM EELS signal as a function of defocus, effectively performing a probe raster scan in three dimensions. As the STEM contrast transfer function (CTF) was found to have the characteristic parabolic information transfer limits in the depth direction, investigations were limited to locating point impurities within zone axis aligned crystals to avoid the elongation problem due to the CTF. We demonstrated a method to locate, with a high degree of precision, a light atom in a relatively heavy supporting matrix provided the experimental setup meets certain constraints. Whilst the depth resolution of the STEM coupled with the elongation problem complicates matters somewhat, it was seen that combining simulation with experiment does ameliorate these issues. The natural extension of this work is combining the depth sectioning data from more than one zone axis orientation to perform a hybrid of tilt series tomography and depth sectioning.

The novel experiments of Frigo et al. [12] served as a catalyst in this thesis to develop a theoretical description of SCEM. In this thesis we presented the fundamental equations describing coherent elastic SCEM. We demonstrated that due to the lack of first order phase contrast in elastic SCEM the image contrast is low for atomic resolution images. Through simulation it was shown that whilst elastic SCEM may have difficulty in locating buried impurity layers it is excellent in locating the entrance and exit surface of a specimen and should be capable of mapping the shape and height of nanoparticles. The fundamental equation modelling energy
CHAPTER 10. CONCLUSION

filtered SCEM (EFSCEM) was derived and accompanying simulations demonstrated the capability and potential of EFSCEM to depth section samples. EFSCEM does not suffer from either a lack of first order phase contrast or the STEM elongation problem. It is a promising technique still in its formative stages. Guided by the principle of reciprocity we described an efficient method to simulate EFSCEM images in the multislice framework.

In summary, this thesis demonstrated that theory is a necessary adjunct to experiment. When careful theoretical simulations are used in conjunction with sophisticated experiments the amount of information that can be extracted from a dataset is increased greatly. This aids our understanding of the materials we image and goes a long way towards answering Richard P. Feynman’s challenge of making the electron microscope more powerful.
Bibliography


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Title: Atomic resolution imaging in two and three dimensions

Date: 2010

Citation: D'Alfonso, A. J. (2010). Atomic resolution imaging in two and three dimensions. PhD thesis, School of Physics, The University of Melbourne.

Publication Status: Published

Persistent Link: http://hdl.handle.net/11343/35321

File Description: Atomic resolution imaging in two and three dimensions

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