## Quantitative off-axis Electron Holography and (multi-)ferroic interfaces

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### Abstract

A particularly interesting class of modern materials is ferroic ceramics. Their characteristic order parameter is a result of quantum chemistry taking place on a sub-Å length scale and long-range couplings, e.g. mediated by electrostatic or stress fields. Furthermore, the particular subclass of multiferroics possesses more than one order parameter and exhibits an intriguing coupling between them, which is interesting both from the fundamental physics point of view as well as from a technological vantage point. While on a more fundamental level it is desirable to elucidate the physical details of the coupling mechanism, this knowledge could subsequently lead to new and technologically interesting multiferroic materials, which overcome their current drawback that only one of the multiple order parameters is appreciably large while the others stay small. Due to the short and long range nature of the driving forces, one challenge for thoroughly understanding ferroic ceramics is the characterization of material properties within a large interval of length scales from several tens of  $\mu m$  to sub-Å. To that end, it is useful to exploit that all order parameters can be described as macroscopic fields, e.g. electric polarization or strain, which, in turn, can be either directly or indirectly probed with an electron beam such as used in Transmission Electron Microscopy (TEM). Consequently, TEM is excellently suited for investigating ferroic materials, i.e., state-of-the-art instruments facilitate aberration corrected imaging within a large magnification interval covering the length scales of interest, in particular the atomic regime. A general drawback of conventional TEM techniques is the loss of phase information originally contained in the scattered electron wave introduced by recording only the electron density. Electron Holography is an advanced TEM technique that facilitates the complete evaluation of the complex electron wave, which, in combination with the manifold possibilities of TEM, provides rather straightforward access to static electromagnetic fields within the ceramic. Nevertheless, quantification of order parameters such as the electric polarization or minute details in electromagnetic fields still require to correlate the experimentally gained observations to physical models, which combine the details of the microscopic imaging process, the electron-specimen scattering, and solid state physics of the specimen. The goal of this work is to investigate and advance the limits of Electron Holography as a truly quantitative TEM technique and apply the findings in, e.g., the investigation of ferroic ceramics. In the light of the previously mentioned difficulties, the problem has to be tackled from different directions:

Firstly, the whole holographic imaging process is reviewed and extended, if necessary, in order to provide quantitative measures for systematic and statistical errors inherent to reconstructed waves. In the course of that process, two previously not recognized holography-specific aberrations are identified, firstly, a resolution limiting spatial envelope and secondly, a spatial distortion to the reconstructed wave. Furthermore, several correction strategies have been developed, in order to correct the aforementioned two and other well-known disturbances, e.g. Fresnel fringes from the biprism filament. The previous holographic noise model has been extended to incorporate the important contribution from the detector and consequently to provide realistic statistic error bars of the holographically reconstructed amplitude and phase.

Secondly, an investigation of the electron-specimen scattering process itself is conducted, leading to a density matrix description of the holographic measurement. The general laws of quantum electrodynamics provide the framework of that description. Relativistic phenomena such as retardation of electromagnetic fields exchanged between beam electron and specimen and spin-orbit coupling of the beam electron are quantified, where the latter is found to be negligible within TEM. The decoherence of the electron wave by statistical coupling to the thermally moving crystal lattice of ceramics is treated by a newly developed algorithm facilitating in particular the accurate quantification of elastic scattering on heavy elements. Inelastic excitations in the ceramic, e.g. bulk plasmons or core electrons, are treated in combination with elastic scattering to identify their role in the holographic reconstruction process and to develop methods for an accurate calculation. A new scattering algorithm combining elastic and inelastic scattering is developed and applied to predict peculiar scattering simulations and conventional imaging. To provide a user-friendly and continuing use of the findings, a software package SEMI (Simulation of Electron Microscopy Imaging) has been written, which facilitates the simulation of elastic and inelastic scattering processes and the subsequent imaging within different approximations, incorporating the newly developed algorithms.

Thirdly, Density Function Theory (DFT) solid state calculations have been employed to identify and quantify structural modifications and characteristic electromagnetic fields, such as occurring at domain boundaries,

within typical ferroic ceramics like  $BaTiO_3$  or  $BiFeO_3$ , and concomitantly provide models correlating observables of the (holographic) experiment to characteristics of the materials, e.g. the order parameters. This is particularly important when static electromagnetic fields provide no direct information about the order parameter, e.g. the electric polarization, i.e., it is possible to correlate the measurable atomic positions to the electric polarization within linear response theory. A software package ATA (AuTomated Atomic contrast fitting) has been developed facilitating an automated fitting of atomic positions and a subsequent determination of local polarization.

In a fourth step, electron holographic experiments analyzed with the help of the revised imaging process in combination with the knowledge gained from scattering theory are used as an input to the models established from solid state physics to yield quantitative information about bulk ferroelectric materials such as  $BaTiO_3$  and PbTiO<sub>3</sub> and more complicated configurations such as domain walls in BiFeO<sub>3</sub> and KNbO<sub>3</sub>. It is found that particular atomic shifts characteristic for ferroelectrics provide the most reliable quantitative information about the polarization down to nm length scales, whereas minute wave modification due to characteristic electron distributions within the ceramic are currently insufficiently quantitatively interpretable within Electron Holography. The linear response program, correlating atomic positions to ferroelectric polarization with the help of ab-initio calculated Born effective charges, has been successfully applied to determine finite size effects, screening layer widths and polarization charges in non-ferroelectric/ferroelectric layered systems.

Finally, a special section considers the evaluation of 3D electromagnetic fields by Electron Holographic Tomography, which provides the means to characterize even more complex 3D domain wall configurations. As the capabilities of the technique are still limited by holographic reconstruction errors and particular tomographic issues such as incomplete projection data, the main focus of that section is put on the characterization and improvement of the tomographic reconstruction process. A Singular Value based reconstruction method is developed, which facilitates a quantification and control of the tomographic reconstruction error. Furthermore, vector field reconstruction is extended in order to treat magnetic vector fields leaking out from the reconstruction volume.

## Kurzfassung

Ferroische Keramiken bilden eine besonders interessante Klasse moderner funktionaler Werkstoffe. Ihr charakteristischer Ordnungsparameter ist das Ergebnis quantenchemischer Prozesse innerhalb einer sub-Å Längenskala und spezifischer langreichweitiger Kopplungen, welche beispielsweise durch elektromagnetische oder Spannungsfelder vermittelt werden. Des Weiteren besitzt die besondere Unterklasse der Multiferroika mehr als einen Ordnungsparameter und zeigt eine faszinierende Kopplung zwischen ihnen, was sowohl vom Standpunkt physikalischer Grundlagenforschung als auch aus technologischer Sicht von Interesse ist. Während es vom fundamentalen Standpunkt erstrebenswert ist, die physikalischen Details des Kopplungsmechanismus aufzuklären, könnte in der Folge dieses Wissen zu neuen und technologisch interessanten multiferroischen Materialien führen, welche den derzeit bestehenden Nachteil, dass nur ein Ordnungsparameter genügend groß ist, während die jeweils anderen klein bleiben, hinter sich lassen. Aufgrund der kurz- und langreichweitigen Natur der Antriebskräfte besteht eine Herausforderung für das umfassende Verständnis ferroischer Keramiken aus der Charakterisierung von Materialeigenschaften innerhalb eines breiten Intervalls von Längenskalen, welches von einigen 10  $\mu$ m bis unterhalb eines Å reicht. Um dieses Ziel zu erreichen ist es zweckmäßig auszunutzen, dass alle Ordnungsparameter als makroskopische, beispielsweise elektrostatische oder Verzerrungs-, Felder beschrieben werden können, welche wiederum direkt oder indirekt mit einem Elektronenstrahl, wie er im Transmissionselektronenmikrokop (TEM) zur Anwendung kommt, gemessen werden können. Folglich ist die Transmissionselektronenmikroskopie hervorragend geeignet um ferroische Materialien zu untersuchen, das heißt, modernste Geräte ermöglichen aberrationskorrigierte Aufnahmen innerhalb eines großen Vergrößerungsbereiches, welche die interessanten Längenskalen und insbesondere den atomaren Bereich abdecken. Ein allgemeiner Nachteil der konventionellen TEM Techniken ist der Verlust der Phaseninformationen, welche ursprünglich in der Elektronenwelle vorhanden sind und durch die Aufzeichnung der Elektronenintensität zerstört werden. Elektronenholographie ist eine weiterentwickelte TEM Technik, welche die vollständige Auswertung der komplexen Elektronenwelle ermöglicht, was wiederum in Verbindung mit den vielfältigen Möglichkeiten der TEM einen vergleichsweise direkten Zugang zu elektromagnetischen Feldern in der Keramik ermöglicht. Nichtsdestotrotz erfordert die Quantifizierung von Ordnungsparametern, wie der elektrische Polarisierung, oder von kleinsten Details elektromagnetischer Felder die Korrelation experimenteller Daten mit physikalischen Modellen, welche die Details des mikroskopischen Bildgebungsprozesses mit der Elektronen-Objekt Streuung und der Festkörperphysik des Objektes kombinieren. Das Ziel dieser Arbeit besteht aus der Untersuchung und Erweiterung der Möglichkeiten von Elektronenholographie als quantitative TEM Messmethode und der Anwendung dieser Ergebnisse bei der Untersuchung ferroischer Keramiken. Im Lichte der eben erwähnten Schwierigkeiten muss das Problem von verschiedenen Richtungen bearbeitet werden:

Erstens wird der komplette holographische Bildgebungsprozess mit dem Ziel einer quantitativen Bewertung systematischer und statistischer Fehler der rekonstruierten Welle analysiert und gegebenenfalls erweitert. Im diesem Zuge wurden zwei bisher nicht erkannte holographiespezifische Fehler identifiziert, erstens eine auflösungsbegrenzende räumliche Enveloppe und zweitens eine räumliche Verzerrung der rekonstruierten Welle. Außerdem wurden verschiedene Korrekturmöglichkeiten entwickelt, um die zwei eben genannten und andere wohlbekannte Störungen, wie zum Beispiel die Fresnelstreifen des Biprismafadens, zu korrigieren. Das bisherige holographische Rauschmodel wurde erweitert um den beträchtlichen Einfluss des Detektors zu berücksichtigen und damit realistische Fehlerbalken für die holographisch rekonstruierte Amplitude und Phase zu erhalten.

Zum Zweiten wird der Streuprozess selber untersucht, was zu einer Dichtematrixbeschreibung der holographischen Messung führt. Den Rahmen dieser Untersuchungen liefern die Gesetze der Quantenelektrodynamik. Relativistische Phänomene wie die Retardierung elektromagnetischer Felder, welche zwischen Strahlelektron und Objekt ausgetauscht werden, oder Spin-Bahn Kopplung des Strahlelektrons werden quantifiziert, wobei letzteres als unwichtig für TEM eingestuft werden konnte. Die Dekohärenz der Elektronenwelle durch die statistische Kopplung an das thermisch bewegte Kristallgitter der Keramik wird mit einem neu entwickelten Algorithmus beschrieben, welcher insbesondere die genaue Quantifizierung der elastischen Streuung an schweren Elementen erlaubt. Ein weiterer neuer Streualgorithmus, welcher elastische und inelastische Streuung kombiniert, wird entwickelt und angewendet, um spezifische Streukontraste von Dipolübergängen vorauszusagen und das altbekannte Problem der Kontrastdiskrepanz zwischen simulierten und experimentellen Bildkontrasten zu diskutieren. Um eine anwenderfreundliche und fortdauernde Anwendung der Erkenntnisse zu ermöglichen, wurde das Softwarepaket SEMI geschrieben, welches die Simulation elastischer und inelastischer Streuprozesse und des nachfolgenden Bildgebungsprozesses innerhalb verschiedener Näherungen ermöglicht und die neu entwickelten Algorithmen beinhaltet.

Zum Dritten kommen dichtefunktionalbasierte Festkörperrechenmethoden zur Anwendung um charakteristische elektromagnetische Felder, wie sie beispielsweise an Domänengrenzen entstehen, innerhalb typischer ferroischer Keramiken wie BaTiO<sub>3</sub> oder BiFeO<sub>3</sub> zu identifizieren und zu quantifizieren und gleichzeitig Modelle zu entwickeln, welche Observablen des (holographischen) Experiments mit Charakteristika des Materials, beispielsweise den Ordnungsparamtern, korrelieren. Dies ist besonders wichtig, wenn statische elektromagnetische Felder keinen direkten Zugang zu den Ordnungsparametern, wie zum Beispiel die ferroelektrische Polarisation, liefern; beispielsweise besteht innerhalb linearer Antworttheorie die Möglichkeit, atomare Positionen mit der elektrischen Polarisation zu korrelieren. Ein Softwarepaket wurde entwickelt, welches die automatische Bestimmung der Atompositionen und der daraus resultierenden lokalen Polarisation ermöglicht.

In einem vierten Schritt wurden mit Hilfe des überarbeiteten holographischen Bildgebungsprozesses in Kombination mit den aus der Streutheorie gewonnenen Erkenntnissen holographische Experimente analysiert und als Input für die mit Hilfe der Festkörpertheorie entwickelten Modelle genutzt, um quantitative Informationen über raumferroische Materialien wie BaTiO<sub>3</sub> und PbTiO<sub>3</sub> und kompliziertere Anordnungen wie Domänengrenzen in BiFeO<sub>3</sub> und KNbO<sub>3</sub> zu gewinnen. Es konnte festgestellt werden, dass spezifische atomare Verschiebungen, welche charakteristisch für Ferroelektrika sind, die zuverlässigste quantitative Information über die Polarisation bis in den Längenbereich einiger nm liefern, wogegen kleinste Wellenmodifikationen aufgrund charakteristischer Elektronenverteilungen innerhalb der Keramik mit Hilfe von Elektronenholographie nur unzureichend interpretierbar sind. Das lineare Antwortprogramm, welches die Atompositionen über Bornsche effektive Ladungen mit ferroelektrischer Polarisation korreliert, wurde erfolgreich angewendet, um Größeneffekte und Ausdehnungen von Abschirmschichten und Polarisationladungen in nichtferroelektrisch/ferroelektrischen Schichtsystemen zu bestimmen.

Abschließend widmet sich ein spezieller Abschnitt der Auswertung 3D elektromagnetischer Felder mit Hilfe der elektronenholographischen Tomographie, was die Voraussetzung für die Charakterisierung von noch komplizierteren 3D Domänenwandanordnungen liefert. Da die Möglichkeiten dieser Technik durch den holographischen Rekonstruktionsfehler und spezifisch tomographische Probleme noch beschränkt sind, liegt der Schwerpunkt dieses Abschnitts in der Charakterisierung und Verbesserung des tomographischen Rekonstruktionsprozesses. Es wird eine singulärwertbasierte Rekonstruktionsmethode entwickelt, welche die Quantifizierung und Kontrolle des Rekonstruktionsfehlers ermöglicht. Außerdem wird die Vektorfeldrekonstruktion erweitert, um magnetische Vektorfelder, welche über das Rekonstruktionsvolumen hinausragen, zu behandeln.

# Notation and symbols

unit charge
electron mass
velocity of light
Bohr magneton
Feinstructure constant
reduced Planck constant
electric constant
4-dimensional spatial coordinates
4-dimensional reciprocal coordinates
3-dimensional spatial coordinate
3-dimensional reciprocal coordinates
2-dimensional spatial coordinates
2-dimensional reciprocal lattice coordinates
second rank tensor / 2-dimensional matrix
operator
Fourier transformed function
Radon transformed function
vector scalar product
Transmission Electron Microscopy / Microscope
(off-axis) Electron Holography
High-Resolution/Medium-Resolution
High-Angle-Annular Dark Field
Multislice
Phase Grating Approximation
Mean Inner Potential

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### Chapter 1

### Introduction

"There is plenty of room at the bottom" - R. Feynman

The exploration of the world on a nanometer regime is inextricably connected to much of the technological progress in the past 100 years. Large areas of modern technology are based on structures and mechanisms which are characterized by a length scale in the order of several nm and below. Since the ground breaking investigations of I. Langmuir on monolayers (Nobel Price in Chemistry 1932), the invention of the transistor by J. Bardeen, W. H. Brattain and W. B. Shockley (Nobel Price in Physics 1956) and the mapping of the DNA structure by J. Watson, F. Crick and M. Wilkins (Nobel Price in Medicine 1962) time was not standing still, and we are nowadays used to think in terms of atoms. We investigate the forces between them, which eventually lead to the formation of crystals and molecules. This development would have been impossible without tools giving us the possibility of visualizing the life in the nanoworld. Without the imaging of viruses, the progress in antidotes would be unthinkable (e.g. Kruger et al. (2000)). Without microscopical images of interfaces and defects the shrinking of semiconductor devices would proceed much slower and so on. A list of applications, where microscopic investigations are indispensable, could easily fill the whole thesis. The instruments involved in all these types of investigation are somewhat old fashionably called microscopes (and not nanoscopes) and their working principle is always based on the interaction of the material under investigation with a microscopic probe. It is not surprising that the probe size is then effectively limiting the resolution of the instrument. Lord Rayleigh found the mathematical expression  $\sin \theta \sim \lambda$  (e.g. Born (1999)) for this principle in wave optics, which relates the scattering angle  $\theta$ , a measure for the resolution, to the wave length  $\lambda$ , i.e. the probe size, of the light source. Similar formulations exist for scanning probe microscopes, etc. The ultimate limitation of (angular) resolution by the wave length  $\lambda$  of the illumination triggered the development of microscopes beyond the regime of visible light  $(\lambda \in \mathcal{O}(\mu m))$ , in particular electron microscopes. The -on the microscopic length scales-<sup>1</sup> strongest of all four known fundamental forces, the electromagnetic interaction, provides a mechanism to accelerate electrons to relativistic velocities and consequently pm wave lengths with the help of an accelerator, which is not longer than 50 cm (see Fig. 1.1). The same interaction facilitates a manipulation of the path of the electron by electrostatic or magnetostatic fields as produced by condensators or coils. Last but not least, all sorts of processes are taking place when such fast electrons transverse matter, e.g., a photographic plate changes its "color", when hit by an electron. E. Ruska was the first who ingeniously combined all necessary components to build the first electron microscope (Fig. 1.1). His first microscope had a magnification of 12,000, however, progress was

 $^{1}$ Here, microscopic refers to length scales down to the order of pm. In particular the strong interaction is dominating at smaller length scales.



Figure 1.1: M. Knoll and E. Ruska building the first TEM.



Figure 1.2: D. Geiger operates the FEI Tecnai F20 Cs-corrected TEM at the Triebenberg Laboratory, Technische Universität Dresden.

fast. The first high-resolution images, showing atomic columns, have been acquired in the late 70ies. Due to the recently realized correction of the spherical aberration, state-of-the-instruments are capable of resolving object details smaller than 1 Å. Moreover, not only resolution was improved during the last decades, important progress was also achieved by asking new questions beyond the whereabouts of its flight path to the electron like "How much energy was lost during the way from the accelerator to the detector" or "How long was the optical path length", to name just some more important ones. The first question is addressed by spectroscopic methods, i.e., electrons are analyzed with respect to their "color", exhibiting phenomena very similar to the ones known from light optics. The second question is inseparably connected to the principle of Holography invented by D. Gabor (Gabor (1948)), who was stimulated by the, at his time, insurmountable spherical aberration. Holography is a two-step process: in the first step, the superposition of the object wave and a known reference wave is recorded, which is referred to as hologram. In the second step the hologram is illuminated with the reference wave, thereby reconstructing the object wave. Gabor's first experimental attempts to demonstrate the principle of holography employed light from a mercury lamp (Gabor (1949)). The first electron hologram was recorded and reconstructed in 1952 by M. E. Haine and T. Mulvey, using Gabor's inline holography scheme (Haine and Mulvey (1952)). The invention of the laser in 1960 caused a dramatic break-through in optical holography. The first holograms using laser light and a novel so-called off-axis holography scheme were recorded and reconstructed by E. N. Leith and J. Upatnieks in 1963 (Leith and Upatnieks (1963)).<sup>2</sup> Realization of the same scheme in Electron Holography (EH) required the use of an electron biprism (invented in 1955 by G. Möllenstedt and H. Düker (Düker and Möllenstedt (1955))), which superimposes two spatially separated parts of the electron beam. The first off-axis electron hologram of an object (a filament) was recorded and optically reconstructed by G. Möllenstedt and H. Wahl (Möllenstedt and Wahl (1968)). The major hurdle for electron holography, which delayed its application as a common scientific tool, was the lack of a bright source of coherent electrons. In 1968 A. V. Crewe designed such an electron gun using a field emission source (Crewe et al. (1968)), thereby opening the way for numerous successful applications of electron holography (e. g. (Lichte (2002); Lichte and Lehmann (2008))). With the invention of extremely sharp tips as field emission sources, acquiring inline holograms with coherent low-energy electrons became possible (Fink (1988); Fink and Schmidt (1990)). Due to the very low radiation damage in the low-energy regime, holographic imaging with low-energy electrons opened a new perspective for structural biology.<sup>3</sup>

Electron microscopy has grown to an indispensable tool since the first steps in 1931. Practically all institutions and industries involved in some sort of nanotechnology possess one of the grandchildren of E. Ruska's invention (the FEI Tecnai F20 Cs-corrected microscope installed at the Triebenberg Laboratory at the Technische Universität Dresden is shown in Fig. 1.2). Nevertheless or exactly for this reason, there is still a lot of space at the bottom. The expansion of resolution limits is far from being exhausted, the correction of the chromatic aberration and the development of a new generation of very brilliant electron sources is expected to give access to 0.5 Å details (Dahmen et al. (2009)). Moreover, it is possible to achieve pm precision in the determination of

<sup>&</sup>lt;sup>2</sup>In the following, Electron Holography will be used as a synonym for off-axis Electron Holography to keep the notation short. It is, however, well understood that other holographic schemes exist, which are very successfully applied (see e.g. Cowley (1992)).

structure features, like lattice constants or atomic positions, by fitting to special physical models. The progress in spectroscopic methods achieved by either constructing better detectors or combining different signals will give access to new information, as it has been very successfully demonstrated by the measurement of the Electron Microscopic Magnetic Dichroism (Schattschneider et al. (2006)). It has proved to be particularly fruitful to combine the measurements with extensive computational studies, especially within the field of spectroscopy.

The first intention of this work is to accurately describe and extend the limits of Electron Holography (EH), in particular by taking into account the whole information attached to the transmitted electron, i.e. the probability density in both position and energy space, which is governed by:

- 1. Fundamental principles, namely the laws of electron scattering (Chap. 3). The following questions will be in the center of the investigations: What is the benefit of increasing resolution further and further or how well can we resolve fine details in the electron shell of the atoms? Is there a built-in energy filter in holography, arising from the interference between reference and object wave (Dyck et al. (2000))? How are amplitude and phase of the reconstructed wave connected to physical quantities of the material, like the electrostatic potential?
- 2. The experimental setup, i.e. the Electron Microscope (Chap. 2). Apart from a general review of the whole imaging process, the following topics will be emphasized: What systematic errors are added by the holographic imaging, i.e. are there special aberrations introduced by the Möllenstedt biprism? What are the properties of the reconstruction process in terms of spatial and signal resolution and noise transfer?

Based on the scattering and imaging process discussed in the first part, images and reconstructed waves are quantitatively analyzed in terms of solid state properties in the second part of the thesis. Due to the limited range of directly measurable information about the specimen, one often needs additional models to relate the measured quantities to the desired physical quantities. Consequently, the calculation of solid state properties obtainable by Transmission Electron Microscopy (TEM), and in particular High-Resolution Transmission Electron Microscopy (HRTEM) and Electron Holography (EH), and suitable parametrizations adapted to the experiments are the subject of Chap. 4. By combining the models from scattering theory, imaging and solid state physics, it is finally possible to tackle the so-called inverse problem (e.g. Aster et al. (2005)), i.e. the calculation of certain model parameters (e.g. the electric polarization) from the acquired data in Chap. 5. The following properties will be analyzed:

- 1. The crystal structure, especially in the vicinity of interfaces and planar defects such as domain boundaries (Chap. 4, 5). These investigations are mainly performed by comparing and fitting reconstructed wave details to physical models like, for example, the wave front as produced by a single atom. The correlation between the lattice structure and all types of material properties like electric or magnetic polarization, valence state, etc. provides a very powerful tool to subsequently derive valuable information about the specimen. Due to complex dependencies between the structure and the properties of interest, it is often necessary to combine these measurements with complementary investigations, e.g. ab-initio studies with the help of Density Functional Theory (Hohenberg and Kohn (1964)). The benefit of such theoretical models are manifold, e.g., they facilitate the calculation of the electric polarization due to a measured displacement of a certain atomic species or provide accurate electrostatic scattering potentials of a certain structure (Chap. 4).
- 2. The electrostatic and magnetostatic potentials both on a sub-nm and sur-nm scale (Chap. 4, 5). The sub-nm analysis centers on extracting features in the reconstructed wave, which can be correlated to a redistribution of electrons due to chemical bonding. On the sur-nm scale, the focus will lay on the determination of averaged properties such as the macro- and mesoscopic electromagnetic polarization or functional potentials in pn-junctions and ferroelectric domain boundaries, which will be derived from the mesoscopic, i.e. coarsened, electromagnetic potentials. For instance, the averaged electrostatic potential  $\overline{V}$ , a fingerprint quantity of the total electrostatic potential, is the average of V over a certain volume  $\Omega$  (Bethe (1928)). It can be considered as a measure for the spatial extension of the charge density (e.g. O'Keefe and Spence (1994)) and therefore sensitive to chemical bonding on an atomic length scale, where outer shell electrons are redistributed (Spence (1996)). It is particularly advantageous to combine the holographic measurement with tomographic recording and reconstruction techniques (e.g. Wolf et al. (2009)), yielding 3D information about the electromagnetic fields of the sample. Several types of reconstruction schemes will be considered and compared. A special section is devoted to the peculiarities of magnetic vector field tomography.

The majority of the materials under investigation in this work are ferroic oxides from the perovskite class (Fig. 1.3), namely  $BaTiO_3$ ,  $PbTiO_3$ ,  $BiFeO_3$ ,  $SrTiO_3$ ,  $KNbO_3$ . They attracted a lot of interest over the last decades due to their manifold physical properties, such as ferroic ordering (non-volatile ferroelectric memories, Scott and Paz de Araujo (1989),  $BaTiO_3$ ,  $PbTiO_3$ ,  $BiFeO_3$ ), large coupling between mechanical and electromagnetic

properties (actuators, sensors, Gonzalo and Jiménez (2005), BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, BiFeO<sub>3</sub>), large dielectric constants  $\epsilon$  (high-k dielectrics), interesting conduction phenomena (both ionic Meyer et al. (2006), SrTiO<sub>3</sub>) and electric (Seidel et al. (2009), BiFeO<sub>3</sub>). An overview over the manifold applications can be found in Scott (2007).



Figure 1.3: Basic perovskite unit  $ABO_3$ . The perovskite-like structure, named after the  $CaTiO_3$  perovskite mineral is a ternary compound of formula  $ABO_3$  that A and B cations differ in size. The structure is a network of corner-linked oxygen octahedra, with the smaller cation filling the octahedral holes and the large cation filling the dodecahedral holes. The coordination number of A is 12, while the coordination number of B is 6. Due to variations of ionic size and small displacements of atoms that lead to the distortion of the structure and the reduction of symmetry and have profound effects on physical properties, perovskite structure materials play an important role in dielectric ceramics.

The large class of (multi-)ferroic materials are characterized by one or multiple switchable order parameters, i.e. the ferroelectric polarization  $\vec{P}$ , the ferromagnetic polarization  $\vec{M}$  and the ferroelastic stress  $\varepsilon$ , which can be controlled by applying an external field (Fig. 1.4). The typical hysteresis like dependency of the ordering



Figure 1.4: Ferroic order parameters and possible interdependencies. Multiferroic materials are characterized by multiple order parameters and correlations between them described by piezoelectric, magnetostrictive, etc. coupling parameters.

parameter  $\vec{P}$  ( $\vec{M}$ ) on the applied external electric field  $\vec{D}$  ( $\vec{H}$ ) is illustrated in Fig. 1.5. The deviations from the ideally rectangular hysteresis (as predicted by Landau-Ginzburg-Devonshire theory, e.g. Gonzalo and Jiménez (2005)) can be explained by the deviations of the perfect structure, i.e. the decay into different domains, and the influence of the electrodes on the  $\vec{P} \cdot \vec{D}$  measurement. A detailed knowledge of  $\epsilon$  and  $\vec{P}$  reducing factors is therefore beneficial to further improvements. While detailed structure properties of bulk ferroelectric materials are known through a long history of research in that field, the properties of boundaries of ferroelectrics to other materials or within ferroelectrics are dominating current investigations. The suitability of ferroelectric polarization, but also by factors such as switchability, fatigue and loss, which are in turn controlled by the behavior of the boundaries; furthermore completely new and fascinating physics is generated at the boundaries. The role of High Resolution Transmission Electron Microscopy (HRTEM) and in particular High Resolution Electron Holography (HREH) at the investigation of those boundaries is mainly limited to structural investigations as well as atom



Figure 1.5: Prototype hysteresis of polarization upon reversal of the externally applied electric field  $\vec{D}$ .  $D_c$   $(P_r)$  indicates the coercivity (remanence).

species determination, which will be pointed out in the following. The main obstacle towards a direct observation of electric and magnetic fields is to provide enough signal and spatial resolution. Usually the determination of small potential features requires special imaging conditions (e.g. Formanek and Bugiel (2006),Rosenauer et al. (2005)), restricting the achievable spatial resolution and the inversion of the complicated relationship between wave and potential. A similar approach will be applied to investigate characteristic potential jumps at domain boundaries as calculated in Chap. 5. High resolution characterization will be illustrated with the help of the following experimental results.

- 1. bulk  $BaTiO_3$ : Being one of the best investigated ferroelectric materials, it will serve as a test case for the analysis of structural and electrostatic properties.
- 2. layered systems of  $SrTiO_3/PbTiO_3/SrTiO_3$  and  $SrRuO_3/PbTiO_3/SrRuO_3$ : Through the accumulation of polarization charges, the ferroelectric properties of thin layers depend strongly on the boundary conditions. Large depolarization fields produced by non-complete screening lead to a reduction of the polarization observed as limited size effect in small scale ferroelectrics. As it has been shown by various investigations, conducting electrodes provide better screening than insulating ones and hence reduce the limited size effect. The two layered systems simulate that situation in that  $SrTiO_3$  is an insulator, whereas  $SrRuO_3$  is conducting.
- 3. BiFeO<sub>3</sub> and KNbO<sub>3</sub> domain boundaries: In close relationship to the structural deviations, such domain walls show an intriguing electrostatic behavior which is potentially leading to a changed conduction state as well as other electronic properties (see Chap. 4). Characteristic electrostatic potential changes are predicted to occur on a length scale rather large compared to the inneratomic fields mentioned previously (see 4.2.2). A rather direct measurement is therefore within reach at signal resolution achievable by medium resolution electron holography.

In the tomography section the focus will shift to semiconducting Si, conducting Latex and Au, which is mainly motivated by the larger length scale of the functional potentials (e.g. pn-junction or potential differences between different materials), hence better applicability of the holographic method. Nevertheless, the ultimate resolution goal for the reconstruction of electrostatic and magnetic fields in 3D is that of the microscope, i.e. the Å-regime, which would give access to complicated 3D domain structures and the electromagnetic fields thereof.

### Chapter 2

### Image formation in TEM and EH

Taking an image with a TEM involves a large number of components such as the electron gun, magnetic lenses, the specimen stage, etc., their properties and interplay. The first electron microscope of E. Ruska (see Fig. 1.1) used a thermionic wolfram cathode as electron emitter. The electron beam was subsequently formed by two magnetic coils forming the condenser system. The specimen was inserted directly in front of the objective lens, which consisted of a single magnetic coil at this time. A projective system subsequently magnified the image plane of the objective lens. The image was finally recorded on a photographic plate. This general setup has changed but slightly during the last decades. However, each component was subject to tremendous improvements, e.g., the thermionic wolfram cathode is nowadays usually replaced by Schottky or cold field emission emitters, CCD cameras are used instead of films, etc. One of the most severe drawbacks of TEM, the seemingly insurmountable spherical aberration, was recently remedied by the ingenious combination of non-spherical lenses (Haider et al. (1998)).

To perform off-axis Electron Holography, two additional steps with respect to the conventional setup have to be inserted: The beam splitting introduced by the Möllenstedt biprism, which generates the interference pattern, and the reconstruction process analyzing the interference pattern. The most important parts of the electron holographic image formation and reconstruction are (Fig. 2.1):

- 1. Electron source, beam accelerator
- 2. Condenser system
- 3. Stage
- 4. Objective lens
- 5. Cs-corrector
- 6. Biprism
- 7. Projective system
- 8. Detector
- 9. Holographic reconstruction process

Each of the components has a significant impact on the recorded image, even if the alignment of the instrument is perfect, i.e., the beam is aligned on the optical axis, thermal and mechanical stability is maximal, etc. An accurate quantization of the component's influences through precise mathematical models is therefore indispensable. In spite of differences in the described properties, the models share a common perspective that is the impact of the respective property, e.g. the energy fluctuation in the electron beam, on the only measurable outcome of the experiment, i.e. the recorded image.

The language of these models is provided by quantum mechanical wave optics and detection, if appropriate within the simplified framework of the semiclassical approximation (ray optics). A scalar relativistic approach based on the Klein-Gordon-equation will prove to be sufficient, i.e. Dirac electron dynamics is only used sporadically to estimate the generally small influence of the electron spin in the imaging process. Most thorough and complete treatises of this subject can be found, for instance, in the books of E. Kasper and P.W. Hawkes (Kasper and Hawkes (1995)), L. Reimer (Reimer (1989)) and H. Rose (Rose (2009)).

In the following, only the models and extensions thereof necessary for this work are presented. This chapter is organized in the following way: First, the elements of the holographic imaging process listed above are discussed in the same order. A second section is dedicated to a formulation of the whole imaging process including its statistical properties with particular emphasis on that of the holographic reconstruction.



Figure 2.1: Scheme of an off-axis holographic TEM setup. The specimen is introduced half way into the beam leaving the other half empty. The part of the electron beam passing the empty half plane is not modulated. The numbers correspond to those in the text. The z-axis of the coordinate system points from the source along the optical axis. Vectors in the xy-plane, i.e. parallel to the specimen and detector plane, are denoted by capital letters, e.g.  $\vec{R}$ .

In order to make the discussion of the components short and most thorough, a short anticipation to the detected signal, as the only manifestation of the components influence, is required: In a simple approximation, neglecting effects like the smearing out of the signal by the transfer properties of the detector, e.g. the scintillator (they will be discussed in Sec. 2.8), the recorded signal is the intensity I of the incoming electrons, i.e. the energy (or particle) flux  $\vec{j}$  integrated over the recording time T. The highly accelerated electrons in a TEM are described in the most general fashion by a mixed state  $\hat{\rho}$  of Dirac spinors (Greiner (1981))

$$\Psi_{\rm s} = A \left( \begin{array}{c} \chi\\ \frac{\hbar |\vec{k}_{s0}|\hat{\sigma}}{mc^2 + E_s} \chi \end{array} \right) e^{-i \left(k_{s0z} z + \vec{K}_{s0} \vec{R}_0\right)}$$
(2.1)

$$\boldsymbol{\chi} \quad \epsilon \quad \left(\begin{array}{c} 1\\ 0\end{array}\right), \left(\begin{array}{c} 0\\ 1\end{array}\right)$$

moving with large momentum  $p_{s0z} = \hbar k_{s0z}$  in z-direction. Here, A is the amplitude of the spinor and  $E_s = mc^2 + eU_s$  denotes the energy of the electron with rest mass m and charge e accelerated by the voltage  $U_s$ . The index s indicates that the energy  $E_s$  and the propagation direction  $\vec{K}_{s0}/k_{s0z}$  scatter depending on the properties of the microscope and the specimen. The adjoint spinor  $\Psi_s^{\dagger}$  is defined as the product of the Dirac matrix  $\beta$  with the complex conjugate of  $\Psi_s$ . The energy flux of mixed Dirac wave spinors is obtained by the trace of the product of the density matrix  $\hat{\rho} = \sum_s |\Psi_s\rangle \langle \Psi_s|$  (s denotes different pure states) with the velocity

operator  $\hat{v} = c\vec{\alpha}$  (Dirac matrix  $\vec{\alpha}$ ) (Greiner (1981))

$$\vec{j} = \operatorname{Tr} \hat{\rho} \hat{v}$$

$$= \sum_{s} \Psi_{s}^{\dagger} c \vec{\alpha} \Psi_{s}$$

$$\approx \sum_{s} \Psi_{s}^{\dagger} c \alpha_{z} \Psi_{s}$$

$$\approx \sum_{s} \frac{c \hbar k_{s0z}}{mc^{2} + E_{s}} c \Psi_{s}^{\dagger} \Psi_{s} ,$$
(2.2)

which after integration over the recording time T yields the detected intensity  ${\cal I}$ 

$$I = \int_0^T \vec{j} \cdot \vec{e}_z dt = \frac{c\hbar k_{s0}}{mc^2 + E_s} cT \sum_s \Psi_s^{\dagger} \Psi_s \,. \tag{2.3}$$

The  $\approx$  in the third line of (2.2) reflects the dominant motion into z-direction. According to (2.3), the much more convenient electron density

$$\rho = \Psi^{\dagger} \Psi = \sum_{s} \sum_{n=1}^{4} |\Psi_{s,n}|^2 \tag{2.4}$$

is generally used to equivalently describe the recorded signal in the image plane.<sup>1</sup> The scalar product  $\Psi^{\dagger}\Psi$  couples only similar parts of the spinor, i.e., a scalar product between one spin up and one spin down spinor would vanish. As will be shown in Sec. 3.2, the elastic, i.e. coherent, scattering of high-energetic beam electrons on potentials produced by the specimen or the lenses is only very weakly affected by spin-orbit coupling. The biggest effect is a constant phase factor due to the energy difference of spin-up and spin-down electrons in the strong magnetic field of the objective lens, which, according to (2.4), is lost during recording, though. Consequently, the spinor character of the wave can be dropped and the more convenient scalar relativistic formalism with the electron density  $\rho = \sum_s \Psi_s^* \Psi_s$  will be used in the following. The electrostatic biprism introduced in Sec. 2.6 produces an interference field of the left (right) part of the beam  $(\Psi_l, \Psi_r)$  tilted by an angle  $\gamma$  (- $\gamma$ ). By superimposing the two tilted beams in the image plane a cosinoidal interference pattern ("hologram")<sup>2</sup>

$$\rho = \sum_{s} \left\{ \left| \Psi_{s,l} e^{i\vec{\gamma}k_{0}\vec{R}} + \Psi_{s,r} e^{-i\vec{\gamma}k_{0}\vec{R}} \right|^{2} \right\} \\
= \sum_{s} \left\{ \left| \Psi_{s,l} \right|^{2} + \left| \Psi_{s,r} \right|^{2} + \Psi_{s,l} \Psi_{s,r}^{*} e^{-2i\vec{\gamma}k_{0}\vec{R}} + \Psi_{s,l}^{*} \Psi_{s,r} e^{2i\vec{\gamma}k_{0}\vec{R}} \right\}$$
(2.5)

is generated. The first two terms on the last line correspond to conventional images recorded in a standard TEM setup, the last two terms are the complex interference terms used for reconstructing one part of the electron wave, e.g.  $\sum_{s} \Psi_{s,r}$ . The reconstruction of, e.g., the right part requires a-priori knowledge of the left part, since the complete wave function is not an observable of the experiment. The index *s* denoting the mutually incoherent pure states is essential to incorporate such a wide range of effects like specimen drift, lens aberrations, etc. One can now start to analyze the formation of the electron density  $\rho$  in the detector plane in detail, beginning at the electron source.

#### 2.1 Electron source

The types of sources currently in use can be roughly divided into three groups according to the emission process: thermionic emitters based on W and LaB<sub>6</sub>, Schottky emitters consisting of ZrO covered W and cold Field Emission Guns (FEG), which are consisting of W. Their most characteristic property is the brightness B defined as the particle flux I per area A and solid angle  $\Omega$ 

$$B = \frac{\partial^2 I}{\partial \Omega \partial A} = \frac{\partial j}{\partial \Omega} = \frac{\partial (\rho v)}{\partial \Omega}, \qquad (2.6)$$

which is a crucial value for the attainable signal and spatial resolution of the recorded image and the reconstructed wave (e.g. Reimer (1989), Lichte (2008)). Characteristic brightness values for the three types of sources are shown in Table 2.1.

<sup>&</sup>lt;sup>1</sup>In the following I and  $\rho$  will be therefore, somewhat loosely, used as a synonym.

<sup>&</sup>lt;sup>2</sup>It will be shown in Sec. 2.6 that the scatter of the shear  $\vec{\gamma}k_{s0}$  can be neglected in the arguments of the following exponentials.

	thermionic W	$LaB_6$	$\operatorname{Schottky}$	cold FEG
normalized brightness $B \left[ \text{Am}^{-2} \text{srad}^{-1} \text{V} \right]$	$10^{4}$	$10^{5}$	$10^{7}$	$2 \cdot 10^{7}$
effective source size $\sigma_A \ [\mu m]$	15	5	$15 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$
energy spread $\sigma_E$ [eV]	1.5 - 2.5	1.3 - 2.5	0.35 - 0.71	0.3 - 0.7

Table 2.1: Properties of electron sources according to Carl Zeiss AG. The brightness is normalized with the acceleration voltage to give an acceleration voltage independent measure. The effective source refers to the first cross-over of the beam.

For a complete quantum mechanical characterization, however, the brightness as an essentially classical property is not sufficient. In order to calculate the observables of the experiment, the density operator

$$\hat{\varrho} = \sum_{s} |\Psi_{s}\rangle \langle \Psi_{s}| , \qquad (2.7)$$

i.e. the decomposition of the total density  $\rho$  into multiple pure states denoted by s, is required. Electrons are fermions; hence the theoretically attainable maximum number of electrons  $n_e$  occupying a phase space volume  $\Phi = V_r V_p$  of  $\hbar^3$  is two. One can estimate the phase space density from the brightness B and the lateral momentum spread

$$\sigma_{p_z} \approx \hbar k_0 \frac{\sigma_E}{E} \,, \tag{2.8}$$

according to

$$\frac{n_e}{\Phi} = \frac{\partial^2 n_e}{\partial V_r \partial V_p} = \frac{\partial \rho}{e \partial V_p}$$

$$\approx \frac{1}{\hbar^3 k_0^3} \frac{B}{ev} \frac{E}{\sigma_E}.$$
(2.9)

When inserting the values of the Schottky emitter given in Tab. 2.1 and using an acceleration voltage of  $200 \, kV$ one obtains a phase space density in the range of  $10^{-6} - 10^{-7} \hbar^{-3}$ , i.e., the theoretically achievable phase space density for fermions is far from being exhausted. By comparing the typical extension of an electron state in the conduction band of the tip ( $\mathcal{O}(\text{nm})$ ) with the radius of the emitting area ( $\mathcal{O}(100 \,\text{nm})$ ), one can furthermore assume that the density operator is approximately diagonal in spatial coordinates, i.e., every point on the source is emitting mutually incoherent spherical waves, which translate to mutually incoherent plane waves with wave vector  $\vec{k}_s$  in the specimen plane (see Fig. 2.1). There is a lot of research activity aiming at improving sources, which led for instance to the development of electron emitting single carbon nanotubes with a superior brightness (e.g. de Jonge et al. (2002)) or monoatomic tip emitters (e.g. Fink (1988)). The area of the tip is here reduced below several nm, which implies an increased coherence of the electron current leaving the emitting area. Practical applications in TEM are still hampered by lifetime issues and other technical problems.

Pure states leaving the tip can be described as single electron wave-packets  $\Psi_s(t, \vec{r})$ . Keeping in mind that different directions of the plane wave vector  $\vec{k}_s$  are mutually incoherent, the decomposition of a single electron wave-packet into monoenergetic waves reads

$$\Psi_{s}(t,\vec{r}) = \int \tilde{\Psi}_{s}(t,\vec{k}) e^{i\vec{k}\vec{r}} d^{3}k = \int \tilde{\Psi}_{s}(t=0,\left|\vec{k}_{s}\right|) e^{i\vec{k}_{s}\vec{r}} e^{-i\sqrt{\hbar^{2}\left|\vec{k}_{s}\right|^{2}c^{2}+m^{2}c^{4}}t} dk_{s}.$$
(2.10)

There is little information about the plane wave expansion coefficients  $\tilde{\Psi}_s \left(t = 0, \left|\vec{k}_s\right|\right)$ . They are determined by the nature of the emission process in general and more specifically by the time length  $\Delta t$  of the emission, which is connected to the energy width  $\Delta E$  of the emitted wave-packet through the energy-time uncertainty

$$\Delta E \Delta t \ge \hbar \,. \tag{2.11}$$

Expression (2.10) can be reformulated when performing a Fourier transformation on the time coordinate, yielding

$$\Psi_{s}(E,\vec{r}) = \int \int \tilde{\Psi}_{s}\left(t=0, \left|\vec{k}_{s}\right|\right) e^{i\vec{k}_{s}\vec{r}} e^{i\sqrt{\hbar^{2}\left|\vec{k}_{s}\right|^{2}c^{2}+m^{2}c^{4}t}} e^{-iEt}dk_{s}dt \qquad (2.12)$$
$$= \int \tilde{\Psi}_{s}\left(t=0, \left|\vec{k}_{s}\right|\right) e^{i\vec{k}_{s}\vec{r}}\delta\left(E-\sqrt{\hbar^{2}\left|\vec{k}_{s}\right|^{2}c^{2}+m^{2}c^{4}}\right)dk_{s}.$$

Since the exact shape of  $\tilde{\Psi}_s\left(t=0, \left|\vec{k}_s\right|\right)$  is rather unknown, it is assumed to be Gaussian , i.e.,

$$\tilde{\Psi}_{s}\left(\left|\vec{k}_{s}\right|\right) = \frac{1}{\left(2\pi\right)^{1/4}\sqrt{\sigma_{k}}}e^{-\left(\vec{k}_{s}-\vec{k}_{s}\right)^{2}/\left(4\sigma_{k}^{2}\right)}$$
(2.13)

will be used throughout the following discussion.

It was mentioned above that the electron beam in the specimen plane is a superposition of pure states  $\Psi_s$  (2.7). The corresponding probability densities f of the 2D wave-packet direction  $\vec{\theta_s}$  and the mean energy  $\overline{E}_s = \sqrt{\hbar^2 \left|\vec{k_s}\right|^2 c^2 + m^2 c^4}$ 

$$f\left(\vec{\theta}_{s}\right) = \frac{1}{2\pi\sigma_{x}\sigma_{y}}e^{-\theta_{sx}^{2}/\left(2\sigma_{\theta_{x}}^{2}\right) - \theta_{sy}^{2}/\left(2\sigma_{\theta_{y}}^{2}\right)}$$
(2.14)

 $\operatorname{and}$ 

$$f(E_s) = \frac{1}{\sqrt{2\pi}\sigma_E} e^{-\left(E_s - \overline{E}_s\right)^2 / \left(2\sigma_{E_s}^2\right)}$$
(2.15)

are usually assumed to be Gaussian and independent, i.e. the total probability space of the pure states is described by the probability density  $f(s) = f(E_s) f(\vec{\theta_s})$ . The signal *I* recorded in the detector is proportional to the electron density  $\rho$  in the detector plane  $z_d$  integrated over recording time, hence

$$I = \sum_{s} \int |\Psi_{s}(t, x, y, z = z_{d})|^{2} dt$$

$$= \int_{s} f(s) \int |\Psi_{s}(t, x, y, z = z_{d})|^{2} dt ds$$

$$= \int_{s} \int |\Psi_{s}(E, x, y, z = z_{d})|^{2} dEf(E_{s}) dE_{s} d^{2} \theta_{s}.$$
(2.16)

In the last transformation Parseval's theorem was applied. The double integral over dE and  $dE_s$  of the absolute square  $|\Psi_s|^2$  does not distinguish between coherent (with respect to E) and incoherent (with respect to  $E_s$ ) superposition as long as the recording time is long with respect to the localization of a single wave-packet  $\Psi_s$  in time. Under these restrictions, it does not make sense to distinguish between a coherent and an incoherent distribution of energies and the intensity I can be rewritten as

$$I = \int_{s} |\Psi_{s}(E, x, y, z = z_{d})|^{2} f(E_{s}) dE_{s} d^{2} \theta_{s}, \qquad (2.17)$$

where the energy distribution  $f(E_s)$  has been redefined to incorporate the convolution of the coherent and incoherent energy probability space.

This final form of the electron density operator

$$\hat{\varrho} = \int_{s} f(E_{s}) dE_{s} d^{2} \theta_{s} |\Psi_{s}\rangle \langle\Psi_{s}|$$
(2.18)

can be regarded as the initial object of the whole imaging process. The optical parts of the microscope will almost exclusively modify the shape of the pure states; hence one can restrict the analysis of the optical system to the propagation of a single electron wave by means of wave optics.

#### 2.2 Condenser system

The condenser system consists of an acceleration unit<sup>3</sup> followed by two or three magnetic lenses with intermediate apertures. The latter can be mathematically described as a multiplication of a step function to the wave in the respective plane, whereas the motion of the electrons within the magnetic field of the lenses is highly non-trivial. Due to the small variation of the fields on a length scale of the electron wave length ( $\lambda \in \mathcal{O}$  (pm)), one can describe the dynamics within a semiclassical approach. A further simplification and classification of the electron paths and the optical parameters of the lens according to a strength parameter k can be achieved by approximating the magnetic field close to the optical axis according to W. Glaser (Glaser (1941)).

According to Abbe's imaging theory, a monoenergetic wave is transferred from the front focal plane  $(z = z_f)$  to the back focal plane  $(z = z_b)$  of a magnetic lens via a Fourier transformation, which is reverted again by a subsequent propagation to the detector plane  $z = z_d$  (Fig. 2.2). This ideal and mathematically very convenient situation is unfortunately disturbed by aberrations, modifying the wave in various ways in both Fourier and position space. These modifications are the major obstacle for modern TEMs towards higher resolutions. Technically most easily fabricated round lenses suffer from a large spherical aberration, which cannot be overcome within the standard setup (Scherzer (1936)). Thanks to the work of H. Rose, non-round correction systems have been designed and successfully implemented recently (Haider et al. (1998)). A comprehensive

 $<sup>^{3}</sup>$ The acceleration unit also serves as the first focusing lens in the microscope, hence is here attributed to the condenser. A classification as part of the source is, however, equally possible.



Figure 2.2: Ray diagram of single lens. The object, back focal and image plane are ideally connected by Fourier transformations. The most important isoplanatic aberrations are indicated as an additional phase function.

account of the theory of aberrations is given, for instance, in the books of M. Born and E. Wolf (Born and Wolf (1999)) as well as E. Kasper and P.W. Hawkes (Kasper and Hawkes (1995)). Within the condenser system and the objective lens, the so-called isoplanatic, i.e. position space independent, aberrations dominate. The most important isoplanatic aberrations of the lenses are incorporated into Abbe's imaging theory by multiplying in the back focal plane  $z_b$  a phase function to the object exit wave function  $\Psi_{obj}$ , i.e.  $\tilde{\Psi}_{img}\left(\vec{K}, z = z_b\right) = e^{-i\chi(\vec{K})}\tilde{\Psi}_{obj}\left(\vec{K}, z = z_b\right)$ . The phase distortion function  $\chi$  is an expansion of polynomials in reciprocal space coordinates  $k_x$  and  $k_y$ . Its most important terms are

$$\chi\left(\vec{K}\right) = \frac{2\pi}{\lambda} \left(\frac{1}{4}C_{3}\frac{\left|\vec{K}\right|^{4}}{\left|\vec{k}_{0}\right|^{4}} \qquad \text{spherical aberration} \\ + \frac{1}{2}C_{1}\frac{\left|\vec{K}\right|^{2}}{\left|\vec{k}_{0}\right|^{2}} \qquad \text{defocus} \\ + \frac{1}{2}A_{1}\frac{\left|\vec{K}\right|^{2}}{\left|\vec{k}_{0}\right|^{2}}\cos\left(2\left(\alpha - \alpha_{A1}\right)\right) \qquad \text{two - fold astigmatism} \\ + \frac{1}{3}B_{2}\frac{\left|\vec{K}\right|^{3}}{\left|\vec{k}_{0}\right|^{3}}\cos\left(\alpha - \alpha_{B2}\right) \qquad \text{coma} \\ + \frac{1}{3}A_{2}\frac{\left|\vec{K}\right|^{3}}{\left|\vec{k}_{0}\right|^{3}}\cos\left(3\left(\alpha - \alpha_{A2}\right)\right) \qquad \text{three - fold astigmatism} .$$

The coefficients  $A_n$ ,  $B_n$ ,  $C_n$  determine the strength of the corresponding aberration. It was already mentioned before that the spherical aberration coefficient  $C_3$  (or  $C_s$ ) cannot be reduced to zero in a round lens. Defocus and two-fold astigmatism as well as coma can be corrected on the other hand in a standard TEM, whereas the control over higher order aberrations, like the three-fold astigmatism, requires additional multipole lenses like those used in the Cs-corrector (see Sec. 2.5). It is furthermore possible to minimize the aberrations within a certain region in reciprocal space by compensating different aberrations. For instance, until the advent of hardware  $C_s$ -correctors spherical aberration has been partly corrected by a choosing the so-called Scherzer (de-)focus. Furthermore, the defocus coefficient  $C_1$  depends on the electron energy  $E_s$  according to

$$C_1 = \frac{C_c}{eU_s} E_s \,, \tag{2.20}$$

which is referred to as chromatic aberration (coefficient  $C_c$ ). The mechanism behind the two-fold astigmatism is illustrated in Fig. 2.3 with the help of geometrical optics. Along the two perpendicular directions x and y within the focal plane of the lens, different deflections of the beams are introduced, yielding two separate focal planes for beams along the two directions. This type of beam deformation can be corrected by so-called stigmators, electrostatic or magnetostatic multipole elements removing the asymmetry introduced by the lenses. The standard TEM setup is based on a spherically symmetric illumination, whereas the off-axis holographic setup requires a small angular distribution only in the direction perpendicular to the biprism filament (see 2.6). This is usually achieved by introducing a strong axial demagnification, i.e. astigmatism, by the stigmators of the condenser system.



Figure 2.3: 2-fold astigmatism illustrated by geometrical optics. The x and y axis are focused in different planes allowing a selective demagnification of the beam in a particular direction.

#### 2.3 Stage

The stage cannot be neglected in the imaging process due to the spatial drift of the mechanical shift and rotation mechanism. This problem occurs primarily when recording at long acquisition times, e.g. as required at small but highly coherent beam currents in off-axis EH. A spatial drift of the specimen during image acquisition can be described by a convolution  $\otimes$  of a weighting function  $f(\vec{R}_s)$  of the stage positions  $\vec{R}_s$  with the object wave function  $\Psi_{obj}$  (which is mainly scattered by the electromagnetic potentials of the object), i.e.

$$f\left(\vec{R}\right) \otimes \Psi_{obj}\left(\vec{R}\right) = \int f\left(\vec{R}_s\right) \Psi_{obj}\left(\vec{R} - \vec{R}_s\right) d^2 R_s \,. \tag{2.21}$$

The shift of the specimen directly translates to a shift of the acquired image in conventional imaging and to a shift in the holographically reconstructed wave as can be seen by applying the convolution to the recorded intensity:

$$\rho\left(\vec{R}\right) = f\left(\vec{R}\right) \otimes \left\{1 + |\Psi_{s,r}|^2 + \Psi_{s,r}^* e^{-2i\vec{\gamma}k_0\vec{R}} + \Psi_{s,r} e^{2i\vec{\gamma}k_0\vec{R}}\right\}$$

$$= 1 + f\left(\vec{R}\right) \otimes |\Psi_{s,r}|^2 + f\left(\vec{R}\right) \otimes \Psi_{s,r}^* e^{-2i\vec{\gamma}k_0\vec{R}} + f\left(\vec{R}\right) \otimes \Psi_{s,r} e^{2i\vec{\gamma}k_0\vec{R}}.$$
(2.22)

It is interesting to note that the complex convolution of the interference terms not only modifies reconstructed phases but also the amplitude. The thereby produced resolution reduction stirred intense developments in the field of stable stage mechanisms, eventually leading to stages controlled by piezo-actuators. Another method to reduce the influence of the specimen drift is the acquisition of several images at short acquisition times, which are subsequently aligned and summed up. This method proves highly valuable under STEM imaging conditions and in off-axis electron holography (see Sec. 5.3).

#### 2.4 Objective lens

One can claim without exaggeration that the objective lens is the heart of a TEM. The imaging conditions of that lens are unique in that it is excited much stronger (strength parameter  $k^2 = 3$ ) to exploit a near field imaging mode created by a particularly strong magnetic field gradient (see Fig. 2.4). Due to the increased deflection angles of the electron beam, isoplanatic aberrations are influencing the imaging process stronger than in the condenser system. The influence of the fluctuating energies  $E_s$  and beam directions  $\vec{\theta}_s$  on the very scattering at the object is generally low, provided that they are in the range of the values listed in Table 2.1 (see Chap. 3), hence  $\Psi_{s,obj}\left(E;\vec{\theta}_s\right) = \Psi_{obj}\left(\overline{E};\vec{\theta}\right)$ . The dependency of the objective lens transfer function  $e^{-i\chi(\vec{K})}$  on the electron energy and direction, however, cannot be neglected, and hence

$$\tilde{\Psi}_{s,img}\left(E_s,\vec{K},z=z_d;\vec{\theta}_s\right) = e^{-i\chi\left(E_s,\vec{K};\vec{\theta}_s\right)}\tilde{\Psi}_{obj}\left(\overline{E},\vec{K},z=z_d;\overline{\vec{\theta}}\right).$$
(2.23)

When inserting the expression for  $\tilde{\Psi}_{img}$  into the expression for the image intensity recorded in position space (2.17), one obtains

$$I = \int \int f(E_s) f\left(\vec{\theta}_s\right) \mathcal{F}^{-1} \left\{ e^{-i\chi\left(\vec{K}; E_s, \vec{\theta}_s\right)} \tilde{\Psi}_{obj}\left(\vec{K}, z = z_b\right) \otimes e^{i\chi\left(-\vec{K}; E_s, \vec{\theta}_s\right)} \tilde{\Psi}_{obj}^*\left(-\vec{K}, z = z_b\right) \right\} dE_s d^2\theta_s \,.$$

$$(2.24)$$



Figure 2.4: Ray path of an electron in the magnetic field of the objective lens. The magnetic field is modeled as a Glaser field and the equations of motion are solved as described in Glaser (1941). The focus of the illumination system is placed in the front focal plane of the objective lens and the parallel illumination is produced by the prefield. The object is fully exposed to the magnetic field. Simulation program written by P. Formanek is used.

After changing the integration order,  $\Psi_{obj}$  can be exempted from the energy and incident angle integration, leaving

$$I = \mathcal{F}^{-1} \left\{ \int \tilde{\Psi}_{obj}^* \left( \vec{K}', z = z_b \right) \tilde{\Psi}_{obj} \left( \vec{K} + \vec{K}', z = z_b \right) \operatorname{TCC} \left( \vec{K}', \vec{K} + \vec{K}' \right) d^2 K' \right\}$$
(2.25)

with the Transmission Cross Coefficient TCC defined as

$$\operatorname{TCC}\left(\vec{K}',\vec{K}+\vec{K}'\right) = \int \int f\left(E_s\right) f\left(\vec{\theta}_s\right) e^{i\chi\left(\vec{K}'\right)} e^{-i\chi\left(\vec{K}+\vec{K}'\right)} dE_s d^2\theta_s \,.$$
(2.26)

The energy and spatial distributions  $f(E_s)$  and  $f(\vec{\theta}_s)$  are defined according to (2.15) and (2.14). The aberrations expressed by  $\chi$  are usually sufficiently small to facilitate a first order expansion of  $\chi$  with respect to  $E_s$  and  $\vec{\theta}_s$ 

$$\chi \approx \chi_0 + \frac{\partial \chi_0}{\partial E} E + \vec{\nabla}_\theta \chi_0 \cdot \vec{\theta} , \qquad (2.27)$$

yielding

$$\Gamma CC\left(\vec{K}',\vec{K}+\vec{K}'\right) = e^{i\chi_0\left(\vec{K}'\right)}e^{-i\chi_0\left(\vec{K}+\vec{K}'\right)}E_{sc}\left(\vec{K}',\vec{K}+\vec{K}'\right)E_{tc}\left(\vec{K}',\vec{K}+\vec{K}'\right).$$
(2.28)

The spatial envelope  $E_{sc}$  and the temporal envelope  $E_{tc}$  are defined as

$$E_{sc}\left(\vec{K}',\vec{K}+\vec{K}'\right) = e^{-\frac{\left(\pi\lambda C_{c}\sigma_{E_{s}}\right)^{2}}{2}\left(\left|\vec{K}'\right|^{2} - \left|\vec{K}+\vec{K}'\right|^{2}\right)^{2}}$$
(2.29)

and

$$E_{tc}\left(\vec{K}',\vec{K}+\vec{K}'\right) = e^{-\frac{1}{2}\left(\left(\vec{\nabla}\chi_0\left(\vec{K}'\right)-\vec{\nabla}\chi_0\left(\vec{K}+\vec{K}'\right)\right)\cdot k_0\vec{\sigma}_{\theta_s}\right)^2}.$$
(2.30)

Due to the plane wave character of the reference wave (no modulation by an object), which is always focused in the same sharp point in the back focal plane independent of its energy, the wave  $\tilde{\Psi}$  reconstructed from one of the interference terms of the hologram (2.5) reads

$$\tilde{\Psi}\left(\vec{K}\right) = E_{sc}\left(\vec{K},0\right) E_{tc}\left(\vec{K},0\right) e^{-i\chi_0\left(\vec{K}\right)} \tilde{\Psi}_{obj}\left(\vec{K}\right) \,. \tag{2.31}$$

The linear envelopes  $E_{sc}\left(\vec{K},0\right)$  and  $E_{tc}\left(\vec{K},0\right)$  are strictly positive functions (see (2.29) and (2.30)), which damp large spatial frequencies eventually below the noise level and therefore ultimately restrict the resolution of the reconstructed wave. The linear relationship between the reconstructed wave  $\tilde{\Psi}$  and the object exit wave  $\tilde{\Psi}_{obj}$  has some significant advantages compared to the nonlinear expression for the intensity (2.25). The multiplication of  $\tilde{\Psi}_{obj}$  with the aberration functions of the microscope, i.e.  $\exp\left(-i\chi_0\right)$  and the two envelopes, is generally invertible, if both envelopes are nonzero everywhere. Although this is generally true, the division of  $\tilde{\Psi}\left(\vec{K}\right)$  with  $E_{sc}\left(\vec{K},0\right)$  and  $E_{tc}\left(\vec{K},0\right)$  is in practice restricted to a limited domain in reciprocal space in order to prevent an amplification of large frequency noise. Within that limit, one can correct the aberrations in the reconstructed wave, which was the original motivation for D. Gabor to invent holography.

#### 2.5 Hardware aberration corrector

As pointed out in Sec. 2.4, the lens aberrations of the objective lens introduce an ultimate resolution limit to the microscope. A long and laborious research activity mainly promoted by H. Rose culminated in the successful development of the first Cs-corrected microscopes in the late 90ies (e.g. Krivanek et al. (1999), Haider et al. (1998)). Modern developments aim at the simultaneous correction of higher order geometric aberrations as well as chromatic aberrations, which ultimately leads to resolutions of 0.5 and below (Dahmen et al. (2009)). The core principle of modern hardware correction systems is similar to the previously mentioned Scherzer focus: One tries to compensate the not directly changeable aberration with additional aberrations within a certain domain in reciprocal space. Modern hardware correctors make use of multipole lenses (octupole / hexapole) to produce the compensating aberrations. The proper alignment of the correctors consisting of several conventional (round) and multipole lenses is very complicated and can lead to non-isoplanatic aberrations, e.g. geometric distortions (see Sec. 2.7) in the image. Since the Cs-corrected FEI Tecnai F20 TEM used for high-resolution investigations of ferroelectric layered systems in Sec. 5.3 contained a prototype Cs-corrector, these distortions were particularly strong and had to be corrected by means of image processing.

#### 2.6 Möllenstedt biprism

Off-axis electron holography employs a several hundred nm thin charged filament (filament potential  $V_{bi}$ , radius  $r_{bi}$ ) with the electrostatic potential encircled by a mass potential at some radius  $r_a$ 

$$V = V_{bi} \ln \frac{r}{r_{bi}} \,. \tag{2.32}$$

The biprism is usually inserted close to the back image plane of the objective lens to slightly cant the left and the right part of the beam with respect to the filament around an angle

$$\gamma = -\pi \frac{1 + mc^2}{1 + 2mc^2} \frac{V_{bi}}{2U \ln (r_{bi}/r_a)};$$
(2.33)

i.e.  $\Psi'_l = \Psi_l e^{i\vec{\gamma}k_0\vec{R}}$  and  $\Psi'_r = \Psi_r e^{-i\vec{\gamma}k_0\vec{R}}$ , where the left part of the beam goes through vacuum, i.e.  $\Psi_l \equiv 1$  (see Fig. 2.1). The canting subsequently leads to a superposition of both parts of the beam in the detector plane



Figure 2.5: Ray diagram at the biprism. It is pointed out that the scale is not reflecting the real paraxial situation within the TEMs used within this work, where  $a \gg b$ .

(see Fig. 2.5) with an interference field width w determined by<sup>4</sup>

$$w = 2b\gamma. (2.34)$$

It is pointed out that the last expression is only true within the geometry for high-resolution EH, where the distance from the back focal plane to the biprism a is much larger than b. Several authors (e.g. Missiroli et al. (1981)) discuss possible holographic setups, which employ for instance negative biprism voltages in combination with virtual holograms, to achieve larger hologram widths, etc. Furthermore, it has been proposed to incorporate

<sup>&</sup>lt;sup>4</sup>The shadow of the filament is neglected in that formula. It will be separately discussed in the following.

multiple biprisms into the optical system to decouple the hologram width w from the canting angle  $\gamma$  (Harada et al. (2005)). The interference pattern is ideally described as

$$\rho\left(\vec{R}\right) = \sum_{s} \left\{ \left|\Psi_{s,l}\left(\vec{R}\right)\right|^{2} + \left|\Psi_{s,r}\left(\vec{R}\right)\right|^{2} + \Psi_{s,l}\left(\vec{R}\right)\Psi_{s,r}^{*}\left(\vec{R}\right)e^{-2i\vec{\gamma}k_{0}\vec{R}} + c.c. \right\}$$

$$= \sum_{s} \left\{ 1 + \left|\Psi_{s,r}\left(\vec{R}\right)\right|^{2} + 2\left|\Psi_{s,r}\left(\vec{R}\right)\right|\cos\left(2\vec{\gamma}k_{0}\vec{R} + \phi\right) \right\}$$
(2.35)

in position space and accordingly

$$\mathcal{F}\left\{\rho\left(\vec{R}\right)\right\} = \sum_{s} \left\{\tilde{\Psi}_{s,l}\left(\vec{K}\right) \otimes \tilde{\Psi}_{s,l}^{*}\left(-\vec{K}\right) + \tilde{\Psi}_{s,r}\left(\vec{K}\right) \otimes \tilde{\Psi}_{s,r}^{*}\left(-\vec{K}\right)\right\}$$
(2.36)

+ 
$$\tilde{\Psi}_{s,l}\left(\vec{K}\right) \otimes \tilde{\Psi}_{s,l}^*\left(-\vec{K}\right) \otimes \delta\left(\vec{K}-2\vec{\gamma}k_0\right) + c.c.$$
 (2.37)

in Fourier space. The convolution with the  $\delta$ -function in Fourier space renders a separation of the last two mixed terms from the first two intensity terms possible (see Fig. 2.6). According to the characteristic structure of the Fourier transform the first two terms are referred to as central band, whereas the interference terms are referred to as sidebands. The details of the reconstruction will be discussed in Sec. 2.9. As the mixed terms solely



Figure 2.6: Amplitude image of Fourier transform of a high-resolution hologram of  $BaTiO_3$ . The image was acquired at a FEI Tecnai F20 Cs-corrected microscope.

occur between pure states s, each electron interferes with itself only, the uniformity in terms of propagation direction and energy of the mixed states is mandatory for the recording of an analyzable interference pattern, i.e. the complex sum of fluctuating states s in the interference terms introduces inter alia a damping term  $\mu$  in the interference pattern (a detailed derivation of that term is given further below):

$$\sum_{s} \left\{ 1 + \left| \Psi_{s,r} \left( \vec{R} \right) \right|^{2} + 2 \left| \Psi_{s,r} \left( \vec{R} \right) \right| \cos \left( 2 \vec{\gamma} k_{0} \vec{R} + \phi \right) \right\}$$

$$= 1 + \left| \Psi_{r} \left( \vec{R} \right) \right|^{2} + 2 \left| \Psi_{r} \left( \vec{R} \right) \right| \mu \cos \left( 2 \vec{\gamma} k_{0} \vec{R} + \phi \right) .$$
(2.38)

The fringe visibility (or contrast) V defined as

$$V = \frac{\max \rho - \min \rho}{\max \rho + \min \rho} = \frac{2\mu |\Psi_r|}{1 + |\Psi_r|^2}$$
(2.39)

gives a measure for the quality of the interference pattern<sup>5</sup>. The major contrast reducing factor in modern TEM microscopes can be identified to be the angular spread of the source and the point spread function of the detector. Thus, dedicated experimental setups to minimize that problem are mandatory for off-axis holography. That includes the use of a highly elliptic illumination generated by an astigmatic illumination (see Sec. 2.2) to reduce the angular spread in the direction perpendicular to the biprism.

Because of the canting property of the filament the terminus biprism was adopted from light optics. Similar to its optical counterpart, a proper description of the electron path in the field of the biprism has to consider

<sup>&</sup>lt;sup>5</sup>There will be only one other occurrence of the fringe visibility, otherwise V will denote the electrostatic potential as usual.

the following effects:

1. Electrons possessing different energies are deflected at different angles. An energy difference of 0.5 eV at 200 kV acceleration voltage translates into an angle difference in the order of nrad. This is much smaller than the angular spread in the beam hence can be safely neglected in the following.

2. The modification of the optical path length of the tilted beams can be incorporated by the following procedure. First, the wave is defocused over the distance b from the intermediate image plane to the biprism plane, then the left and the right part of the wave are tilted in different directions, which is described by a convolution operation  $\otimes$  in Fourier space. Finally, the wave is focused back to the image plane:

$$\Psi_{l,r}'\left(\vec{K}\right) = \Psi_{l,r}\left(\vec{K}\right)e^{-i\frac{b}{2k_0}|\vec{K}|^2} \otimes \delta\left(\vec{K} \mp k_0\vec{\gamma}\right)e^{i\frac{b}{2k_0}|\vec{K}|^2}$$

$$= \Psi_{l,r}\left(\vec{K} \mp k_0\vec{\gamma}\right)e^{-i\frac{b}{2k_0}\left(\vec{\gamma}^2k_0^2\mp 2k_0\vec{\gamma}\cdot\vec{K}\right)}$$

$$= \left(\Psi_{l,r}\left(\vec{K}\right)\otimes\delta\left(\vec{K} \mp k_0\vec{\gamma}\right)\right)e^{\pm ib\vec{\gamma}\cdot\vec{K}}.$$
(2.40)

If the constant phase term  $b\vec{\gamma}^2 k_0/2$  in the second line of (2.40) is dropped, the effect of the biprism is readily visible in the third line as a beam tilt combined with an image shift of the left and right part of the wave in position space. The different terms can be equivalently derived by analyzing the Gaussian beams of the biprism assuming that b is much shorter than the distance of the biprism plane to the back focal plane of the objective lens. Assuming a typical off-axis holographical setup with a small incident angle  $\vec{K}_0 \ll k_{0z}$  and assuming parallel and monochromatic illumination, the left part of the beam  $\Psi_l$  passes the specimen plane unmodulated, i.e.<sup>6</sup>

$$\Psi_l'\left(\vec{K}\right) = \delta\left(\vec{K} - \vec{K}_0 - k_0\vec{\gamma}\right)e^{i\frac{b}{M}\vec{\gamma}\cdot\vec{K}}.$$
(2.41)

The magnification M between object and the biprism plane was inserted to accommodate the combination of the phase function of the biprism into the phase function of the objective lens within the same coordinate system  $\vec{K}$ . The right part is modulated by the specimen and the objective lens aberrations, i.e.

$$\Psi_r'\left(\vec{K}\right) = \Psi_r\left(\vec{K} - \vec{K}_0 + k_0\vec{\gamma}\right)e^{-i\chi\left(\vec{K} + k_0\vec{\gamma}\right)}e^{-i\frac{b}{M}\vec{\gamma}\cdot\vec{K}}.$$
(2.42)

The superposition in the image plane then reads

$$\begin{aligned} \left|\Psi_{l}'\left(\vec{R}\right) + \Psi_{r}'\left(\vec{R}\right)\right|^{2} &= \left|e^{i\left(\vec{\gamma}k_{0} + \vec{K}_{0}\right)\left(\vec{R} - \frac{b}{M}\vec{\gamma}\right)} + e^{-i\left(\vec{\gamma}k_{0} - \vec{K}_{0}\right)\left(\vec{R} + \frac{b}{M}\vec{\gamma}\right)} \int \Psi_{r}\left(\vec{K}\right) e^{-i\chi\left(\vec{K} + \vec{K}_{0}\right)} e^{i\vec{K}\left(\vec{R} + \frac{b}{M}\vec{\gamma}\right)} d^{2}K\right|^{2} \\ &= \left|e^{ik_{0}\vec{\gamma}\cdot\vec{R}} + e^{-ik_{0}\vec{\gamma}\cdot\vec{R}} \int \Psi_{r}\left(\vec{K}\right) e^{-i\chi'\left(\vec{K} + \vec{K}_{0}\right)} e^{i\vec{K}\left(\vec{R} + \frac{b}{M}\vec{\gamma}\right)} d^{2}K\right|^{2}. \end{aligned}$$
(2.43)

Here, the phase term occurring due to the biprism (see (2.40)) is incorporated into the objective lens aberration function  $\chi$ , which is now redefined as

$$\chi'\left(\vec{K}\right) \equiv \chi\left(\vec{K}\right) + \frac{2b}{M}\vec{\gamma}\cdot\vec{K}_0.$$
(2.44)

The aberration of the biprism has no influence on the conventional image because the constant phase factor is canceled there. Using the modified phase function  $\chi'$  from (2.44) for the integration over the incoherent plane wave components of the incoherent effective source, one gets - after the usual Taylor series expansion of  $\chi'\left(\vec{K}\right)$  in  $\vec{K}$  (e.g. Kirkland (1998)) - the following result for the reconstructed wave<sup>7</sup>

$$\tilde{\Psi}\left(\vec{K}\right) = \tilde{\Psi}_{obj}\left(\vec{K}\right) \int f\left(\tilde{\theta}_{s}\right) e^{i\chi'\left(\vec{K}+k_{0}\tilde{\theta}_{s}\right)} d^{2}\theta_{s} \qquad (2.45)$$

$$\approx \tilde{\Psi}_{obj}\left(\vec{K}\right) e^{i\chi\left(\vec{K}\right)} e^{-\frac{1}{2}\left(\left(\vec{\nabla}\chi\left(\vec{K}\right)+\frac{2b\tilde{\gamma}}{M}\right)\cdot k_{0}\vec{\sigma}_{\theta_{s}}\right)^{2}}.$$

The exponential damping term is the modified form of the spatial envelope function  $E_{sc}$  (2.29), which now incorporates the biprism aberration. The modification only affects the direction perpendicular to the biprism by introducing an additional uniform damping, if  $\vec{\nabla}\chi\left(\vec{K}\right)$  is small (medium-resolution holography /  $C_s$ -corrected holography) and additionally a slight asymmetry of the order of several percent within the attainable resolution, if  $\vec{\nabla}\chi\left(\vec{K}\right)$  is large like in high-resolution holography (medium-resolution at Lorentz lens with particular large

 $<sup>{}^{6}\</sup>vec{K}_{0} \ll k_{0z}, \ k_{0} \approx k_{0z}.$ 

<sup>&</sup>lt;sup>7</sup> The energy fluctuations have been neglected here, but can be easily introduced by multiplying with the linear temporal envelope  $E_{tc}$ .

 $C_s$ ) in the pre- $C_s$ -corrected era or possibly in the post- $C_c$ -corrected era at particularly high resolutions. In Fig. 2.7 results for a FEI Tecnai F20 equipped with a  $C_s$ -corrector and a Phillips CM30 special Tübingen, both with typical high-resolution holography settings, are shown. The settings neglect residual aberrations in the  $C_s$ -corrected microscope and use the optimum (Scherzer) focus  $D_z$  in the Phillips CM30 combined with typical values for the ratio  $\epsilon$  between the large and the small axis of the elliptic illumination as generated by the condenser system. The influence of the elliptic illumination is visible as a stretching of the spatial envelope. The spatial envelope can change significantly upon parameter changes due to the quadratic dependency in the



Figure 2.7: Spatial envelope for (a) a FEI Tecnai F20 ( $U_a = 200$ kV, M = 60,  $\theta_s = 0.3$ mrad,  $\epsilon = 30$ , b = 2mm,  $U_b = 300$ V,  $D_z = 0$ nm,  $C_s = 0\mu$ m) and (b) a Phillips CM30 special Tübingen ( $U_a = 300$ kV, M = 50,  $\theta_s = 0.3$ mrad,  $\epsilon = 30$ , b = 2mm,  $U_b = 600$ V,  $D_z = -80$ nm,  $C_s = 623\mu$ m).

exponent of the spatial envelope (see (2.29)). The prominent part of the asymmetry in Figure 2.7a is dampened by the temporal envelope function of the Philips CM30 special Tübingen, whereas a small contribution in the range of several percent between  $-10 \text{ nm}^{-1}$  and  $10 \text{ nm}^{-1}$  spatial frequency remains. This complicated behavior of the spatial envelope function reduces to a constant in a  $C_s$ -corrected microscope and at medium resolution settings (see Figure 2.7b).

3. Behind the filament with radius  $r_{bi}$  a shadow and Fresnel scattering according to

$$\Psi_{l,r}'\left(\vec{R}\right) = -\frac{ik}{2\pi z} \int_{-\infty,r_{bi}}^{-r_{bi},\infty} \Psi_{l,r}\left(\vec{R}'\right) e^{i\frac{k_0}{2b}\left|\vec{R}-\vec{R}'\right|^2} dx' dy'$$

$$= \frac{ik}{2\pi z} \int_{x+r_{bi},-\infty}^{\infty,x-r_{bi}} \Psi_{l,r}\left(\vec{R}-\vec{R}'\right) e^{i\frac{k_0}{2b}\left|\vec{R}'\right|^2} dx' dy'$$
(2.46)

is generated. The Fresnel fringes produce a signature in the recorded holograms, hampering the reconstruction process (Fig. 2.8). Thus, the hologram is usually taken in the center region of the interference field, sufficiently



Figure 2.8: Left: Fresnel fringes in an empty hologram. Right: Empty hologram after analytic Fresnel fringes removal. The magnified subimages show the hologram fringes.

far away from the modulated edges. If that is not possible, e.g., when the interference field is small due to

a large fringe spacing, the Fresnel fringes can be removed by analytical propagation of the part of the wave blocked by the biprism, provided that the missing part of the wave in the biprism plane is known. To identify the removed signal in the detector plane, the cut-off introduced in (2.46) is removed:

$$\Psi_{l,r}\left(\vec{R}\right) = \frac{ik}{2\pi b} \left(\int \int_{x+r_{bi},-\infty}^{\infty,x-r_{bi}} \Psi_{l,r}'\left(\vec{R}-\vec{R}'\right) e^{i\frac{k_0}{2b}\left|\vec{R}'\right|^2} dx' dy' + \int \int_{-\infty,x-r_{bi}}^{x+r_{bi},\infty} e^{i\frac{k_0}{2b}\left|\vec{R}'\right|^2} dx' dy'\right) \quad (2.47)$$
$$= \Psi_{l,r}'\left(\vec{R}\right) + S_{l,r}\left(\vec{R}\right) \,.$$

Here, the unknown part

$$S_{l,r} = \begin{cases} Fc \left( -\sqrt{\frac{k_0}{2b}} \left( x + r_{bi} \right) \right) \\ Fc \left( \sqrt{\frac{k_0}{2b}} \left( x - r_{bi} \right) \right) \end{cases}$$
(2.48)

of the wave given by complementary complex Fresnel integrals (see A.1), if the cut-out wave is a plain wave as in the standard off-axis holographical setup. Using the same argument, the superposition assumes the following form:

$$\left|1 + \Psi_r\left(\vec{R}\right)\right|^2 = \left|\Psi_l'\right|^2 + \left|\Psi_r'\right|^2 + \Psi_l'\Psi_r'^* + \Psi_r'\Psi_l'^*$$

$$+ S_l S_r^* + \Psi_l' S_r^* + \Psi_r'^* S_l$$

$$+ S_r S_l^* + \Psi_r' S_l^* + \Psi_l'^* S_r$$

$$+ \left|S_l\right|^2 + \left|S_r\right|^2 + \Psi_l' S_l^* + \Psi_r' S_r^* + \Psi_l'^* S_l + \Psi_r'^* S_r$$

$$(2.49)$$

with

$$\Psi_l' = Fc\left(\sqrt{\frac{k_0}{2b}} \left(x + r_{bi}\right)\right).$$
(2.50)

The first line of (2.49) represents the raw hologram data, whereas the missing parts due to Fresnel diffraction show up in the following lines. The second line represents the Fresnel fringes in the left sideband, the third line the according fringes in the right sideband. The last line contains all terms in the center band. All missing parts can be calculated analytically with the help of Fresnel integrals and thus, can be added to the original hologram. However, the subtlety is that the wave  $\Psi'_l\left(\vec{R}\right)$  is not identical to the reconstructed wave, if  $\Psi'_l\left(\vec{R}\right)$  contains Fourier components larger than the masked side band (see Fig. 2.8). Then, all terms containing  $\Psi'_l\left(\vec{R}\right)$  cannot be calculated accurately, even if the free parameters *b* and  $r_{bi}$  have been determined accurately. The latter can be achieved by fitting the Fresnel contrast in the raw hologram (see Fig. 2.8) to the first line in (2.49). In the simplest case of an empty hologram, the procedure works well (see Fig. 2.8). A further improvement of the method will remain a task for the future.

4. The electric potential of the biprism is ideally described as that of a cylindrical condenser

$$V = -V_{bi} \ln \frac{r}{r_{bi}} \,. \tag{2.51}$$

However, the design of the biprism holder and the fabrication of the filament distort that potential, with the major contribution stemming from the unevenly charged and unevenly thick filament. The distorted potential leads to distorted interference fringes, i.e. an effect identical to the geometric distortions produced by the projective system (see Sec. 2.7) and the hardware corrector (see Sec. 2.5). The measurement and removal of geometric distortions is discussed below (see Sec. 2.7).

5. During image acquisition the biprism oscillates slightly. The oscillation amplitude rises with growing distance from the suspension of the filament at the biprism holder. The oscillations introduce a shift of the filament resulting in a contrast damping of the interference fringes. One therefore has to find a compromise between a close position to the holder with a still sufficiently undistorted potential.

It is pointed out here that the biprism makes a superposition of very well defined waves feasible, and hence the reconstruction process is straight forward. Other holographic techniques, like inline holography, rely on a more difficult mixture of phase and amplitude information in the recorded signal, requiring a more elaborate reconstruction process. Furthermore, as will be shown in Sec. 2.10, the statistical properties of the wave reconstructed by means of electron holography are significantly easier to describe than that resulting from other reconstruction processes. Where there is light there is always shadow, i.e., the biprism introduces also several drawbacks. Off-axis holography requires a vacuum region close to the investigated part of the sample to provide an undisturbed reference wave. The vibrations of the biprism and the superposition of waves with different  $\vec{k}_0$  produce a significant damping of the reconstructed wave. The minimization of those drawbacks requires dedicated microscopes (small energy width, high stability) and skilled operators (good alignment, elliptic illumination).

#### 2.7 Projective system

The purpose of the projective system is to sufficiently magnify the intermediate image of the specimen generated by the objective lens in order to finally record it on the detector. This is achieved by two or three normally excited lenses (strength parameter  $k^2 = 1$ .). In contrast to the lens in the condenser system and the objective lens, non-isoplanatic distortive, i.e. position space dependent and Fourier space independent, aberrations dominate. They can be described by an affine transformation of the position space coordinates x and y

$$\begin{pmatrix} x'\\ y' \end{pmatrix} = \mathbf{D}(x,y) \begin{pmatrix} x\\ y \end{pmatrix} + \begin{pmatrix} x_0\\ y_0 \end{pmatrix}.$$
(2.52)

Thus, the image is distorted, whilst the original resolution is maintained. The transformation matrix **D** may be assumed to have a determinant equal to 1, i.e. no additional isotropic magnification (which could be easily measured) is present. The constant image shift  $x_0$ ,  $y_0$  can be easily corrected at the microscope as well. The most important distortive aberrations can be classified according to the diagonal entries  $d_{1,2}$  in the transformation matrix, which has been diagonalized with respect to the coordinate system (this is achieved by rotating the original matrix by applying a rotation matrix **R**):

$$\mathbf{D} = \begin{pmatrix} D_{1,1} & D_{1,2} \\ D_{2,1} & D_{2,2} \end{pmatrix}$$

$$= \mathbf{R} \begin{pmatrix} d_1 & 0 \\ 0 & d_2 \end{pmatrix} \mathbf{R}^{-1} :$$
(2.53)

$$\{d_1, d_2\} = \text{ const.} \qquad \text{non-isotropic magnification} \\ \{1 + d_1 \left(x^2 + y^2\right), 1 + d_2 \left(x^2 + y^2\right)\} \quad \text{barrel distortion} \\ \{1 - d_1 \left(x^2 + y^2\right), 1 - d_2 \left(x^2 + y^2\right)\} \quad \text{pincussion distortion}.$$
 (2.54)

There are several ways to measure and finally remove the geometric distortions. Usually one prepares a welldefined pattern in the electron wave, e.g. by scattering at a perfectly periodic crystal lattice. The deviations from that pattern are then directly proportional to the geometric distortions. The generation of a well-defined pattern is, however, complicated particularly at small length scales, due to e.g. imperfect crystal lattices. Another way, proposed for holograms recorded by off-axis Electron Holography, makes use of the superposition of two empty plane waves and the determination of deviations in the interference pattern<sup>8</sup>

$$\left|e^{-i\vec{\gamma}k_0\vec{R}'} + e^{i\vec{\gamma}k_0\vec{R}'}\right|^2 = 2 + 2\cos\left(2\gamma_x k_0\left(\vec{R} + D_{1,1}x + D_{1,2}y\right)\right)$$
(2.55)

or equivalently from the phase of the reconstructed wave

$$\Psi_d = e^{i2\gamma_x k_0(D_{1,1}x + D_{1,2}y)} \,. \tag{2.56}$$

Here, the biprism was oriented along y-direction ( $\vec{\gamma} = (\gamma_x, 0)$ , and hence any distortions in y-direction ( $D_{2,1}, D_{2,2}$ ) would not affect the interference pattern. An uni-axial distortion pattern obtained from a series of 100 holograms recorded at a magnification of  $1.5 \cdot 10^6$  at a Cs-corrected FEI Tecnai F20 is depicted in Fig. 2.9.

<sup>&</sup>lt;sup>8</sup>The mixed state can be dropped here to simplify the expressions.



Figure 2.9: Uni-axial distortion map measured at the  $C_s$ -corrected FEI Tecnai F20 equipped with a 1024k Gatan Multiscan camera (model 794) determined from a hologram series recorded by D. Geiger (TU Dresden). The line pattern stems from the fiber optic of the camera (see next section), whereas the large distortion over the whole field of view stems from the projective system. The small subimage in the lower left corner indicates the direction of the hologram fringes.

A second measurement with the biprism oriented along x has to be conducted to determine all coefficients in the transformation matrix **D** independently. However, one must distinguish between geometric distortions occurring in front or behind the biprism plane. Distortions in front of the biprism plane, e.g. stemming from the hardware  $C_s$ -corrector, are not measured by this method because not tilted plane waves cannot be distorted, whereas distortions behind the biprism plane, e.g. generated by the projective lenses, are accurately determined.

To remove geometric distortions from the recorded electron density, one has to interpolate the latter on the not distorted grid x, y. The interpolation itself is introducing artifacts, depending on the type of interpolation method used. The within this work applied standard method of removing geometric distortions by dividing the reconstructed wave with the empty wave from (2.56) seems to be very elegant, however, there are several drawbacks of that method which cannot be neglected:

- 1. Distortions parallel to the hologram fringes are not removed.
- 2. There is a difference between distortion phases (2.56)  $\phi_d$  from empty holograms and distorted phases from object holograms, i.e.

$$\begin{aligned} \left| e^{-i\vec{\gamma}k_{0}\vec{R}'} + \Psi\left(\vec{R}'\right)e^{i\vec{\gamma}k_{0}\vec{R}'} \right|^{2} &= 1 + \left| \Psi\left(\vec{R}'\right) \right|^{2} + A\left(\vec{R}'\right)\cos\left(2\vec{\gamma}k_{0}\left(\vec{R} + D_{1,1}x + D_{1,2}y\right) + \phi\left(\vec{R}'\right)\right) \\ &= 1 + \left| \Psi\left(\mathbf{D}\vec{R}\right) \right|^{2} + A\left(\mathbf{D}\vec{R}\right)\cos\left(2\vec{\gamma}k_{0}\vec{R} + \phi_{d} + \phi\left(\mathbf{D}\vec{R}\right)\right) \tag{2.57} \\ &\neq 1 + \left| \Psi\left(\vec{R}\right) \right|^{2} + A\left(\vec{R}\right)\cos\left(2\vec{\gamma}k_{0}\vec{R} + \phi_{d} + \phi\left(\vec{R}\right)\right). \end{aligned}$$

Consequently, amplitude and phase of the reconstructed wave itself remain distorted, if only dividing with the empty wave.

3. The division with the empty wave additionally increases the noise level in reconstructed waves.

It remains a task for the future to replace the division with the empty wave by a more accurate correction of distortions by interpolation of the original hologram on an undistorted grid.

#### 2.8 Detector

Parallel to the advances of electron sources and electron optical components, detectors have been improved tremendously. Photographic films have been replaced by dedicated electron recording devices such as scintillator coupled CCD cameras or imaging plates. An electron detector suited for TEM has to linearly record high-energetic electrons at a high spatial resolution within a large dynamic range. Due to the sufficiently large dynamic range, the fast readout and computational convenience, the most common detectors are CCD cameras. Although direct recording devices have been adopted to Transmission Electron Microscopes recently (e.g. Denes et al. (2007); Deptuch et al. (2007)), the standard design consists of a scintillator layer, where the high energetic beam electrons produce photons and a fiber optic, where the photons are transmitted to the CCD detector (see



Figure 2.10: Scheme of a fiber optic coupled CCD detector.

Fig. 2.10). All three components have a significant impact on the recorded image:

1. The scintillator blurs the impact point of the detected electron described by a convolution of the density with the point spread function psf

$$\rho'\left(\vec{R}\right) = \rho\left(\vec{R}\right) \otimes psf\left(\vec{R}\right) \,. \tag{2.58}$$

Two mechanisms can be distinguished to cause the spreading: First, the relatively small scattering volume excited by the impinging electron and secondly, the wide spread part due to backscattered electrons stemming from the scintillator fiber optic interface (see Fig. 2.10).

2. The fiber optic adds a geometric distortion, which is particularly large in the vicinity of the boundaries of the building blocks, usually hexagonal bundles, of the fiber optic.

3. The detectors finite efficiency damps the signal inhomogeneously over the detector area according to a 2D damping function  $d_f$ :

$$\rho'\left(\vec{R}\right) = \rho\left(\vec{R}\right) d_{\rm f}\left(\vec{R}\right) \,. \tag{2.59}$$

Furthermore, the signal is collected within pixels, which can be described by a convolution with a 2D rectangular top hat function  $h_p$  of the length of a pixel p centered at the sampling points  $\vec{R}_{m,n}$ , i.e.

$$\rho_{m,n} = \int h_p \left( \vec{R}_{m,n} - \vec{R} \right) \rho \left( \vec{R} \right) d^2 R \tag{2.60}$$

Both the psf as well as the  $d_f$  cannot be considered as stable during acquisition time, i.e. they add noise to the imaging process. The dominant part of that noise has a multiplicative character as indicated by 2.81 and 2.59. A small part stemming from the read-out noise of the CCD chip is additive. Comprehensive accounts on the detection process in CCD cameras can be found in the literature (e.g. Ruijter W. J. de (1992), Ishizuka (1993), Meyer and Kirkland (1998)). The details of the implications of the detector noise on the imaging and reconstruction process will be discussed in Sec. 2.10.

#### 2.9 Reconstruction process

Historically, the reconstruction process had to be performed experimentally, i.e., the recorded interference pattern was coherently illuminated on an optical bench with coherent laser light possessing the same lateral frequency  $\vec{K}_0 = 2k_0\vec{\gamma}$  like the recorded sampled interference pattern  $\rho_{m,n}$ . The laborious optical reconstruction could be simplified significantly by digital image processing and is nowadays completely performed with the help of the computer. This has the additional advantage of removing or incorporating the previously mentioned influences (like lens aberrations) and modifying the reconstruction process itself. By denoting the sampled reconstructed wave, incorporating all previously discussed influences from the instrument, with  $\Psi_{m,n}$  and in the same manner the conventional parts of the signal with  $\rho_{m,n}^c$ , the reconstruction process reads

$$e^{ik_0\vec{\gamma}\vec{R}_{m,n}}\rho_{m,n} = e^{ik_0\vec{\gamma}\vec{R}_{m,n}}\rho_{m,n}^c + e^{i2k_0\vec{\gamma}\vec{R}_{m,n}}\Psi_{m,n}^* + \Psi_{m,n}$$
(2.61)

The thereby generated three different diffraction angles 0,  $k_0\vec{\gamma}$ ,  $2k_0\vec{\gamma}$  could be spatially separated and independently reconstructed by applying an aperture  $h_{a/2}$  in diffraction space, the width a of which being smaller than  $k_0\vec{\gamma}$ 

$$\Psi_{m,n} = \mathcal{F}^{-1} \left\{ \mathbf{h}_{a/2} \mathcal{F} \left\{ e^{i\vec{K}_0\vec{R}_{m,n}} \rho_{m,n} \right\} \right\} \,. \tag{2.62}$$

#### 2.9. RECONSTRUCTION PROCESS

This type of reconstruction will be referred to as Fourier method in the following. In fact, the separation between the three different diffraction angles can only be achieved approximately either due to large diffraction angles in the object wave function itself (scattering with large momentum transfer as discussed in Chap. 3) and due to the statistical properties of the detection process (see Sec. 3.2.7). In particular, the noise of the detection process contains large spatial frequencies always leaking from central band into the sidebands. The truncation of an infinite spectrum with a sharp mask (aperture) is always producing aliasing effects, which could obscure the information in the image (see Fig. 2.11). A very promising approach to remove this reconstruction



Figure 2.11: Phase image  $(3.14-6.28 \pi)$  from a Latex sphere reconstructed with the sinc mask (left) and a sharp mask (right). The overshoots at the edges as well as the speckle noise vanish when using the sinc filter. The original hologram was recorded by P. Formanek (TU Dresden).

artifact and to facilitate a quantification of the noise properties of the reconstructions is the so-called real space reconstruction based on a least square fit

$$\sum_{m,n=1}^{Z_m,Z_n} \left| \rho_{m,n} - I - A \cos\left(\vec{K}_0 \vec{R}_{m,n} + \phi\right) \right|^2 \to \min$$
(2.63)

within a subarea or patch of the recorded image with the dimension  $Z_m \times Z_n$ . This method was originally proposed by F. Lenz (Lenz (1988)) and implemented by M. Lehmann (Lehmann et al. (1994)). In this method, the experimentally obtained image  $\rho_{m,n}$  is locally fitted to an interference patch  $I + A \cos\left(\vec{K}_0 \vec{R}_{m,n} - \phi\right)$  with three free parameters I (the central band), A (sideband amplitude) and  $\phi$  (sideband phase). The fit is linearized by a reparametrization to I (the central band),  $\Re = A \cos\left(0.5\vec{Z}\vec{K}_0 - \phi\right)$  and  $\Im = A \sin\left(0.5\vec{Z}\vec{K}_0 - \phi\right)$  connected to the original parameters through

$$A = \sqrt{\Re^2 + \Im^2}$$

$$\phi = -\arctan\frac{\Im}{\Re} + \frac{1}{2}\vec{Z}\vec{K_0}.$$
(2.64)

The minimization yields the following normal equation

$$\begin{pmatrix} N \\ \Re \\ \Im \end{pmatrix} = \mathbf{M}_{R} \begin{pmatrix} P \\ C \\ S \end{pmatrix}$$

$$= \frac{1}{Z_{m}Z_{n}} \begin{pmatrix} \frac{1+C_{2}}{1+C_{2}-2C_{1}^{2}} & \frac{-C_{1}}{1+C_{2}-2C_{1}^{2}} & 0 \\ \frac{-2C_{1}}{1+C_{2}-2C_{1}^{2}} & \frac{1}{1+C_{2}-2C_{1}^{2}} & 0 \\ 0 & 0 & \frac{1}{1-C_{2}} \end{pmatrix} \begin{pmatrix} P \\ C \\ S \end{pmatrix}$$
(2.65)

relating the fit parameters N,  $\Re$  and  $\Im$  to the experimentally obtained image data

$$\begin{pmatrix} P \\ C \\ S \end{pmatrix} = \begin{pmatrix} \sum_{m,n=1}^{Z_m,Z_n} \rho_{m,n} \\ 2\sum_{m,n=1}^{Z_m,Z_n} \rho_{m,n} \cos\left(\frac{1}{2}\left(\vec{Z} - \begin{pmatrix} 2m+1\\2n+1\\\end{pmatrix}\right)\vec{K}_0\right) \\ 2\sum_{m,n=1}^{Z_m,Z_n} \rho_{m,n} \sin\left(\frac{1}{2}\left(\vec{Z} - \begin{pmatrix} 2m+1\\2n+1\\\end{pmatrix}\right)\vec{K}_0\right) \end{pmatrix}.$$
 (2.66)

The constants occurring in (2.65) are

$$C_1 = \frac{1}{Z_m Z_n} \frac{\sin\frac{1}{2} Z_m K_{0,x}}{\sin\frac{1}{2} K_{0,x}} \frac{\sin\frac{1}{2} Z_n K_{0,y}}{\sin\frac{1}{2} K_{0,y}}$$
(2.67)

and

$$C_2 = \frac{1}{Z_m Z_n} \frac{\sin Z_m K_{0,x}}{\sin K_{0,x}} \frac{\sin Z_n K_{0,y}}{\sin K_{0,y}} \,. \tag{2.68}$$

The normal equation (2.65) is significantly simplified, if the fitting patch is chosen commensurate to the spatial frequency of the hologram fringes, i.e.  $\vec{Z}\vec{K}_0 \epsilon 2\pi \mathbb{Z}$ . In this case  $C_1$  and  $C_2$  vanish and the reconstruction matrix  $\mathbf{M}_R$  (2.65) becomes the identity matrix divided by the number of pixels  $Z_m Z_n$  in the fitting patch. Under this prerequisite, this method is equivalent to the Fourier method, if a sinc-filter (Fourier transform of top hat function) instead of a sharp mask is used to cut out the sideband, i.e.

$$\Psi_{m,n} = \mathcal{F}^{-1} \left\{ \frac{\sin K_{0x} R_m}{K_{0x} R_m} \frac{\sin K_{0y} R_n}{K_{0y} R_n} \mathcal{F} \left\{ e^{i \vec{K}_0 \vec{R}_{m,n}} \rho_{m,n} \right\} \right\} \,. \tag{2.69}$$

The sinc filter avoids the delocalized reconstruction artifacts introduced by the convolution with the Fourier transform of a sharp mask in an optimized way (see Fig. 2.11). A drawback of the method is that spatial frequencies apart from the origin of the center band are reconstructed as wave components, making the use of additional, preferably soft masks around the centerband necessary.<sup>9</sup> A possible remedy of this effect within the least square fit is investigated by R. Meyer (Meyer (1996)), leading to additional weighting factors in the fitting procedure. Additionally, it is conceivable to apply maximum likelihood or maximum entropy methods instead of least square fits. Within this work, the Fourier method in combination with a sinc (or modified sinc) filter is applied for reconstructing holograms. The equivalence to the least square fit will prove to be very helpful when determining the noise properties of the reconstructed wave in the next section.

# 2.10 The total imaging and reconstruction process and its statistical properties

An image acquired in an electron microscope is always more or less noisy with respect to the ideal, or more precisely the average signal described in the previous section. Generally, a large signal to noise ratio defined as the ratio of the squared mean value  $\mu$  and the variance  $\sigma^2$ 

$$SNR = \mu^2 / \sigma^2 \tag{2.70}$$

is desirable, which, in the case of the above mentioned noise sources, can be achieved by increasing the number of electrons in the image. However, the possibilities of doing so are restricted to a prolongation of recording time and / or an increase of the electron flux in the beam. A larger recording time will eventually lead to a significant blurring by drift of the specimen due to thermal or mechanical instabilities and is therefore limited when aiming at a certain resolution. A higher flux, on the other hand, can damage the specimen and will increase the incoherent aberrations because of the Boersch effect (e.g. Reimer (1989)). Consequently, the number of electrons in an image is restricted by the possibilities of the microscope and the desired resolution. Under these circumstances, an accurate description of the noise during detection and further on the holographic reconstruction process is mandatory to provide measures for the signal to noise ratio and therefore for interpretable information in the image or the reconstructed wave (e.g. Lenz (1988); Ruijter (1993); Harscher and Lichte (1996)). In the following, averages or expectation values are denoted with a bar, i.e.  $\mu(\rho) = \overline{\rho}$ , to distinguish them from the measured quantity. The most important noise sources together with their characteristics are:

1. Additive fluctuations of energy and angle in the beam, as generated by the emission process and fluctuation in the acceleration voltage as well as the lens currents. These can be considered to be independent from the following two sources. It is furthermore assumed that under normal imaging conditions, i.e. at doses of several thousand electrons per pixel corresponding to a total number N of electrons in the order of  $10^9$ , enough samples in the probability space of energy and angles have been drawn to yield a precise average with a standard deviation of the mean proportional to  $\sqrt{N}/N$  within the probability space of energies and angles. The variance of that noise will therefore be neglected. Depending on the illuminated specimen and the overall imaging conditions, there are additional X- or  $\Gamma$ -rays hitting the detector. Those events are rare (<10 per image), hence cannot be treated in a statistical manner. They can be identified due to the bright contrast and are removed with the help of a point blemish function (Wolf (2004)).

<sup>&</sup>lt;sup>9</sup>The problem occurs because the least square fit assumes a constant intensity I within the fitting patch, which is not fulfilled when the central band contains large spatial frequencies.
2. Shot or quantum noise, inevitably due to the statistical meaning of quantum mechanical wave functions. The position dependent probability space  $Q\left(\vec{R}\right)$  in this case is spanned by all possible position dependent,  $\delta$ -like, electron signals  $\delta_{\varrho}\left(\vec{R}\right) = \varrho\delta\left(\vec{R}\right)$ . The mean value  $\overline{\rho}_{in}\left(\vec{R}\right)$  is the quantum mechanical probability considered in the previous sections. The originally discrete Poisson statistics with the according probability density at a certain point on the detector  $\vec{R}$  can be approximated to a Gaussian form, if the average electron density  $\overline{\rho}_{in}$  is larger than 500 (normal imaging conditions):

$$f_{\overline{\rho}_{in}}\left(\varrho,\vec{R}\right) = \frac{1}{\sqrt{2\pi}\overline{\rho}_{in}\left(\vec{R}\right)}e^{-\frac{\left(\varrho(\vec{R})-\overline{\rho}_{in}(\vec{R})\right)^{2}}{2\left(\overline{\rho}_{in}(\vec{R})\right)^{2}}}.$$
(2.71)

The probability measure  $f_{\rho_{in}}\left(\varrho,\vec{R}\right)d\varrho\left(\vec{R}\right)$  will be abbreviated with  $dQ\left(\vec{R}\right)$  in the following. It is important to note that the spatial covariance of the shot noise

$$Cov_{in}\left(\vec{R},\vec{R}'\right) = \int \int \delta_{\varrho}\left(\vec{R}-\vec{R}'''\right)\delta_{\varrho}\left(\vec{R}'-\vec{R}'''\right)dQ\left(\vec{R}'''\right)dR'''-\bar{\rho}_{in}\left(\vec{R}\right)\bar{\rho}_{in}\left(\vec{R}\right)$$
(2.72)  
+ 
$$\int \int \delta_{\varrho}\left(\vec{R}-\vec{R}'''\right)\delta_{\varrho}\left(\vec{R}'-\vec{R}'''\right)dQ\left(\vec{R}'''\right)dQ\left(\vec{R}''''\right)dR'''dR''''-\bar{\rho}_{in}\left(\vec{R}\right)\bar{\rho}_{in}\left(\vec{R}'\right)$$
  
= 
$$\delta\left(\vec{R}-\vec{R}'\right)\bar{\sigma}_{in}^{2}\left(\vec{R}\right)$$
  
= 
$$\delta\left(\vec{R}-\vec{R}'\right)\bar{\rho}_{in}\left(\vec{R}\right)$$

vanishes for  $\vec{R} \neq \vec{R'}$  per definition (shot noise is spatially uncorrelated). In case of an off-axis hologram, the following variance is obtained:

$$Cov_{in}\left(\vec{R},\vec{R}\right) = \sigma_{in}^{2}\left(\vec{R}\right) = I\left(\vec{R}\right) + A\left(\vec{R}\right)\cos\left(\vec{K}_{0}\vec{R} + \phi\left(\vec{R}\right)\right) \,. \tag{2.73}$$

3. The noise contribution from the detector. It can be distinguished with respect to the different components (see Sec. 2.8). The most important noise stems from the generation of photons along a random trajectory of the electron through the scintillator. There are other noise sources in the CCD camera beside the scintillator, e.g. the additive read-out noise or the dark current noise. They, however, play a minor role under the normal imaging conditions used in this work and will be neglected in the following. Following the work of R. Meyer (Meyer (2002)), the noise in the scintillator of a CCD camera as described in Sec. 2.8 is generated by the random paths of both the electron and the thereby produced photons. The probability space of the possible signals  $pf_s(\vec{R}; \vec{0})$  generated by a  $\delta$ -like single electron density at the origin  $\vec{0}$  will be denoted by  $S_1$ , i.e. each spread  $pf_s$  belonging to a single electron is one element  $s \in S_1$  with a probability measure  $dS_1 = p_1(s) ds$  (see Fig. 2.12). The mean value of all single electron spreads centered on the origin is

$$psf_1\left(\vec{R};\vec{0}\right) = \int pf_s\left(\vec{R};\vec{0}\right) dS_1 \tag{2.74}$$

and the covariance between different positions  $\vec{R}$  and  $\vec{R'}$  is defined accordingly

$$Cov_{sz1}\left(\vec{R}, \vec{R}'; \vec{0}\right) = \int pf_s\left(\vec{R}; \vec{0}\right) pf_s\left(\vec{R}'; \vec{0}\right) dS_1 - psf_1\left(\vec{R}; \vec{0}\right) psf_1\left(\vec{R}'; \vec{0}\right) .$$
(2.75)

It is assumed in the following that the scintillator is homogeneous, i.e. both point spread functions  $(pf_s, psf)$  and covariances (Cov) do only depend on the difference of the spatial coordinates from the impinging coordinate  $\vec{R}''$  of the electron, i.e.

$$psf_{1}\left(\vec{R};\vec{R}''\right) = psf_{1}\left(\vec{R}-\vec{R}''\right)$$

$$Cov_{sz1}\left(\vec{R},\vec{R}';\vec{R}''\right) = Cov_{sz1}\left(\vec{R}-\vec{R}'',\vec{R}'-\vec{R}''\right).$$
(2.76)

The usage of the coordinates  $\vec{R}$ ,  $\vec{R'}$  and  $\vec{R''}$  is additionally illustrated in Fig. 2.12. It is now useful to generalize the single electron spread probability space  $S_1$  to the space  $S_{\varrho}$  of possible spreads for an arbitrary number of electrons  $\varrho$  impinging at the origin. The elements *s* of both spaces are the same (*s* denotes all possible spreads), however, the probability measure  $p_{\varrho}(s) ds$  changes according to the laws describing the average of independent



Figure 2.12: Exemplary trajectory plots for three 200 keV-electrons in a glass supported 50 mm YAG with anti-reflection coating according to R. Meyer and A. Kirkland (Meyer and Kirkland (1998)). In the upper panel (a) the vertical motion is indicated. In plot (b), the horizontal positions, where electron-hole pairs are generated in the CCD chip ( $\vec{R}$ -plane), are shown. The average area illuminated by a single electron indicated by the red box is substantially smaller than the area illuminated by many electrons hitting the same spot (blue box). Within the illumination patch of one electron hitting the detector at the position  $\vec{R}'' = 0$  non-zero covariances  $Cov_{sz1} (\vec{R}.\vec{R'})$  between two spatial points  $\vec{R}$  and  $\vec{R'}$  are generated. Electron 3 creates a sharp spot of illumination far from the incident point, since after being back-scattered it re-enters the scintillator.

identical probability variables: The mean of an average of independent probability variables equals the average of the mean of those variables, i.e.

$$psf = \int pf_s dS_{\varrho}$$
(2.77)  
=  $psf_1$ .

The (co-)variance of the joint process is obtained by dividing the covariance of the single process by the number of independent processes  $\rho\left(\vec{R}''\right)$ , i.e.

$$Cov_{sz\varrho}\left(\vec{R} - \vec{R}'', \vec{R}' - \vec{R}''\right) = \frac{1}{\varrho\left(\vec{R}''\right)} Cov_{sz1}\left(\vec{R} - \vec{R}'', \vec{R}' - \vec{R}''\right).$$
(2.78)

It is furthermore useful to slightly generalize the covariance of the joint process in the following way

$$Cov_{sz\varrho} \left( \vec{R} - \vec{R}'', \vec{R}' - \vec{R}''' \right) = Cov_{sz\varrho} \left( \vec{R} - \vec{R}'', \vec{R}' - \vec{R}'' \right) \delta \left( \vec{R}'' - \vec{R}''' \right)$$
(2.79)

$$= \int pf_s \left(\vec{R} - \vec{R}^{\prime\prime}\right) pf_s \left(\vec{R}^{\prime} - \vec{R}^{\prime\prime}\right) dS_{\varrho} + \int pf_s \left(\vec{R} - \vec{R}^{\prime\prime}\right) pf_{s^{\prime}} \left(\vec{R}^{\prime} - \vec{R}^{\prime\prime\prime}\right) dS_{\varrho} dS_{\varrho}^{\prime}$$
  
$$- psf \left(\vec{R} - \vec{R}^{\prime\prime}\right) psf \left(\vec{R}^{\prime} - \vec{R}^{\prime\prime\prime}\right)$$

in order to express that spreads originating from different points  $\vec{R}''$  and  $\vec{R}'''$  (and there from different electrons) are not correlated. A single initial intensity distribution  $\delta_{\varrho}\left(\vec{R}'\right)$  combined with a particular spread  $pf_s$  gives the following contribution to the final signal:

$$\int \delta_{\varrho} \left( \vec{R}' \right) p f_s \left( \vec{R} - \vec{R}' \right) dS_{\varrho} dQ \left( \vec{R}' \right) dR' \,. \tag{2.80}$$

The mean electron density  $\overline{\rho}$  is obtained by integrating over the probability spaces  $S_{\varrho}$ ,  $Q\left(\vec{R}\right)$  and the whole detector area:

$$\overline{\rho}\left(\vec{R}\right) = \int \delta_{\varrho}\left(\vec{R}' - \vec{R}''\right) p f_{s}\left(\vec{R} - \vec{R}'\right) dS_{\varrho} dQ\left(\vec{R}''\right) dR' dR''$$

$$= \int \delta_{\varrho}\left(\vec{R}' - \vec{R}''\right) p sf\left(\vec{R} - \vec{R}'\right) dQ\left(\vec{R}''\right) dR' dR''$$

$$= \int \overline{\rho}_{in}\left(\vec{R}'\right) p sf\left(\vec{R} - \vec{R}'\right) dR'$$
(2.81)

The convolution with the point spread function psf in position space can be carried out as multiplication in reciprocal space, effectively limiting the transferred spatial frequency hence resolution. The psf resolution limit is currently one of the dominating contrast dampening factors in high-resolution holography.

Similarly to the mean intensity, the spatial covariance  $Cov(\vec{R}, \vec{R'})$  of the signal is calculated according to

$$Cov\left(\vec{R},\vec{R}'\right) = \int \left(\int \delta_{\varrho''''}\left(\vec{R}''-\vec{R}''''\right)pf_s\left(\vec{R}-\vec{R}''\right)dR''\right) dR'''\right) \\ \cdot \left(\int \delta_{\varrho''''}\left(\vec{R}''-\vec{R}''''\right)pf_s\left(\vec{R}'-\vec{R}''\right)dR''\right)dS_{\varrho}dQ\left(\vec{R}''''\right)dR'''\right) dR''''$$

$$(2.82)$$

$$- \overline{\rho}\left(\vec{R}\right)\overline{\rho}\left(\vec{R}'\right),$$

$$(2.83)$$

which assumes the following form after several calculation steps shown in detail in appendix A.2

$$Cov\left(\vec{R},\vec{R}'\right) = \int \overline{\rho}_{in}\left(\vec{R}''\right)Cov_{sz1}\left(\vec{R}-\vec{R}'',\vec{R}'-\vec{R}''\right)dR'' + \int \sigma_{in}^{2}\left(\vec{R}''\right)psf\left(\vec{R}-\vec{R}''\right)psf\left(\vec{R}'-\vec{R}''\right)dR'' .$$

$$(2.84)$$

Accordingly, two different terms can be distinguished. The term on the last line describes the spreading of the noise due to a deterministic spreading of the signal, i.e., due to the spread function adjacent coordinates in the detector become correlated. The product on the first line has a similar meaning, this time a deterministic initial density is statistically spread into a covariance matrix. In contrast to the case of the product of two independent probability variables, there are no mixed terms between standard deviations, because the scintillator noise is not independent from the shot noise, as the original signal  $\delta_{\varrho}$  determines the spread probability space  $S_{\varrho}$ . The expression for the covariance matrix further simplifies, when inserting the variance of the shot noise  $\sigma_{in}^2 = \overline{\rho}_{in}$  into (2.84)

$$Cov\left(\vec{R}, \vec{R}'\right) = \int \overline{\rho}_{in}\left(\vec{R}''\right) \left(Cov_{sz1}\left(\vec{R} - \vec{R}'', \vec{R}' - \vec{R}''\right) dR'' + psf\left(\vec{R} - \vec{R}''\right) psf\left(\vec{R}' - \vec{R}''\right)\right) dR''(2.85)$$
  
$$= \int \overline{\rho}_{in}\left(\vec{R}''\right) nsf_1\left(\vec{R} - \vec{R}'', \vec{R}' - \vec{R}''\right) dR'',$$

where the noise spread function nsf<sub>1</sub> has been defined. The most important consequence of this result is that the covariance  $Cov\left(\vec{R}, \vec{R'}\right)$  depends on the average signal  $\overline{\rho}_{in}\left(\vec{R''}\right)$  through a convolution law in two variables, which can be calculated for arbitrary signals if the covariance of a single spread  $Cov_{sz1}$  and the point spread function psf of the camera are known. Measurement strategies to determine both functions are discussed below. The calculation of the convolution in (2.85) is most simple, if  $\overline{\rho}_{in}\left(\vec{R''}\right)$  is a  $\delta$ -spot or a constant, corresponding to a perfectly focused electron beam or plain illumination. To further illustrate the influence of the scintillator noise, some special cases can be considered:

(a) In the case of a perfect noise free camera,  $pf_s = psf = \delta\left(\vec{R}\right)$  and

$$\sigma^2\left(\vec{R}\right) = \sigma_{in}^2\left(\vec{R}\right)\,,\tag{2.86}$$

i.e., the quantum noise is not affected by the scintillator. If, however,  $pf_s = psf \neq \delta$ , the same analysis yields

$$\sigma^2\left(\vec{R}\right) = \int \sigma_{in}^2\left(\vec{R}'\right) \int \left(\operatorname{psf}\left(\vec{R} - \vec{R}'\right)\right)^2 dR' \tag{2.87}$$

i.e., shot noise is dampened, which can be seen by the Minkowski inequality

$$\int \operatorname{psf}\left(\vec{R}\right) \operatorname{psf}\left(\vec{R}\right) dR \le \left(\int \operatorname{psf}\left(\vec{R}\right) dR\right)^2 = 1.$$
(2.88)

The cost for the reduction in the diagonal elements of the covariance matrix  $(\sigma^2\left(\vec{R}\right) = Cov\left(\vec{R}, \vec{R}' = \vec{R}\right))$ consists, however, of non-zero off-diagonal elements  $(Cov\left(\vec{R}, \vec{R}' \neq \vec{R}\right))$ , i.e. correlation in the spatial domain. (b) A noisy detector with a perfectly spread signal is characterized by  $pf_s = s\delta\left(\vec{R}\right)$ , i.e.  $psf = \delta\left(\vec{R}\right)$ . The variance behind the scintillator (Ishizuka (1993))

$$\sigma^{2} = \overline{\rho}_{in} \left( \vec{R} \right) \sigma_{sz1}^{2} + \sigma_{in}^{2}$$

$$= \overline{\rho}_{in} \left( \vec{R} \right) \left( \sigma_{sz1}^{2} + 1 \right)$$
(2.89)

is then still proportional to the mean signal similar to the shot noise, the amplification factor is, however, not 1 but  $(\sigma_{sz1}^2 + 1)$ .

(c) The worst case infinite spread white noise camera, as characterized by  $pf_s = s\delta\left(\vec{R} - \vec{R}_s\right)$ , yields

$$psf = const.$$
 (2.90)

 $\operatorname{and}$ 

$$\sigma^2 = \int \overline{\rho}_{in} \left( \vec{R}^{\prime\prime} \right) dR^{\prime\prime} \sigma_{sz1}^2 \,, \tag{2.91}$$

which demonstrates that in this case the camera alone determines the noise since the incident noise is infinitely spread and averaged out. If the original intensity is normalized to one, the noise behind the detector is just the scintillator noise.

Both psf and nsf can be determined from Monte-Carlo simulations (Meyer (2002)) and also experimentally: A  $\delta$ -like signal would yield the most direct way to both functions. Generating a focused beam illuminating one pixel on the CCD chip is, however, hampered by large aberrations in the required low magnification modes. Alternatively, the psf can be estimated from a series of images containing an object with a known large spectrum (e.g. sharp edge) according to

$$\frac{\tilde{\rho}\left(\vec{K}\right)}{\tilde{\rho}_{in}\left(\vec{K}\right)} = \mathcal{F}\left\{ psf\left(\vec{R}\right) \right\} \,. \tag{2.92}$$

Unfortunately, it is much more complicated to determine the covariance of a single spread  $Cov_{sz1}$ , e.g., it is not possible to evaluate  $Cov\left(\vec{R},\vec{R'}\right)$  from a series of empty images (i.e. images with plain illumination and no object):

$$Cov\left(\vec{R},\vec{R}'\right) = \bar{\rho}_{in} \int \operatorname{nsf}_1\left(\vec{R}-\vec{R}'',\vec{R}'-\vec{R}''\right) dR'' \,. \tag{2.93}$$

Due to the integration over the scintillator coordinate  $\vec{R}''$  not the single spread itself but an integral measure is determined by this type of measurement. It is useful to rewrite the last result with the help of Fourier transformations

$$Cov\left(\vec{R},\vec{R}'\right) = \frac{1}{2\pi} \quad \overline{\rho}_{in} \int \int \int \tilde{\mathrm{nsf}}_{1}\left(\vec{K},\vec{K}'\right) e^{i\vec{K}\left(\vec{R}-\vec{R}''\right)} e^{i\vec{K}'\left(\vec{R}'-\vec{R}''\right)} dK dK' dR''$$

$$= \quad \overline{\rho}_{in} \int \int \delta\left(\vec{K}+\vec{K}'\right) \tilde{\mathrm{nsf}}_{1}\left(\vec{K},\vec{K}'\right) e^{i\vec{K}\vec{R}} e^{i\vec{K}'\vec{R}'} dK dK' \qquad (2.94)$$

$$Cov\left(\vec{R}-\vec{R}'\right) = \quad \overline{\rho}_{in} \int \int \tilde{\mathrm{nsf}}_{1}\left(\vec{K},-\vec{K}\right) e^{i\vec{K}\left(\vec{R}-\vec{R}'\right)} dK,$$

which illustrates that only the main diagonal  $\vec{K'} = -\vec{K}$  of the Fourier transformed nsf is obtained by using plain illumination and that the covariance depends only on the difference between  $\vec{R}$  and  $\vec{R'}$ . This result is alternatively obtained by applying the Wiener-Khintchin theorem, which relates the power spectrum to the

autocorrelation function via a Fourier transformation (see appendix A.3). Similarly, one can show that by using holograms with a certain fringe spacing, one can obtain certain off-diagonal elements of the  $nsf_1$ . By combining measurements with different fringe spacings it is thus possible to obtain all off-diagonal elements, which offers an alternative route to the  $nsf_1$  if illuminating single pixels is experimentally not feasible.<sup>10</sup>

Finally, the corresponding pixelwise expression for the psf and Cov obtained through an additional convolution with the top-hat function function  $h_p$  in position space are given

$$psfs_{m,n} = \int psf\left(\vec{R}'\right) h_p\left(\vec{R}_{mn} - \vec{R}'\right) dR'$$
(2.95)

$$Covs_{m,n,m',n'} = \int Cov\left(\vec{R}'',\vec{R}'''\right) h_p\left(\vec{R}_{mn}-\vec{R}''\right) h_p\left(\vec{R}'_{mn}-\vec{R}'''\right) dR'' dR''' \,.$$
(2.96)

The integrated pixelwise covariance as determined from a 1024k Gatan Multiscan Camera (model 794) is shown in Fig. 2.13. It can be seen that the spatial extension of the covariance is somewhat smaller than the extension



Figure 2.13: Sampled integrated covariance matrix  $\int Cov_{sz1} \left( \left| \vec{R}_{m,n} \right| - \vec{R}'', 0 - \vec{R}'' \right) dR''$  of a 1024k Gatan Multiscan Camera (model 794).

of the psf, which can be related to the ratio of the area of the spread of one electron to the spread of all electrons (Fig. 2.12).

The next step is to derive expressions for the mean and variance of amplitude and phase of the reconstructed wave. A general lower bound for the variance of the reconstructed quantities is given the Cramer-Rao inequality (e.g. Krengel (2005)). Several authors derive lower bounds based on maximum-likelihood estimators (Ruijter (1993); Lenz (1988)). The standard reconstruction process, however, is that described in Sec. 2.9 and reads

$$\Psi_{m,n} = \mathcal{F}^{-1} \left\{ \frac{\sin K_{0x} R_m}{K_{0x} R_m} \frac{\sin K_{0y} R_n}{K_{0y} R_n} \mathcal{F} \left\{ e^{i \vec{K}_0 \vec{R}_{m,n}} \rho_{m,n} \right\} \right\},$$
(2.97)

which incorporates a sinc-mask in Fourier space corresponding to a least-square fit of a local interference patch. Thus, the normal equation derived from the fit (2.65) gives the following uncertainty propagation (e.g. Krengel (2005))

$$Cov \begin{pmatrix} N \\ \Re \\ \Im \end{pmatrix} = \mathbf{M}_R^T Cov \begin{pmatrix} P \\ C \\ S \end{pmatrix} \mathbf{M}_R, \qquad (2.98)$$

relating the covariance of the image values P, C, S to the covariance in the reconstructed values  $N, \Re, \Im$  and subsequently to the noise properties of amplitude and phase. For the sinc filter or commensurate size of the fit patch (see 2.65) the reconstruction matrix  $\mathbf{M}_R = I/(Z_m Z_n)$  diagonalizes and consequently

$$Cov \begin{pmatrix} N\\ \Re\\ \Im \end{pmatrix} = \frac{1}{(Z_m Z_n)^2} Cov \begin{pmatrix} P\\ C\\ S \end{pmatrix}.$$
(2.99)

 $<sup>^{10}</sup>$ Illuminating single pixels is experimentally hampered by several problems such as an insufficient reduction of intensity and magnification or artifacts of the beam blanker.

To calculate  $Cov \begin{pmatrix} P \\ C \\ S \end{pmatrix}$  the laws of error propagation yield

$$Cov \begin{pmatrix} P \\ C \\ S \end{pmatrix} = \mathbf{A}^T Cov_{m,n,m',n'} \mathbf{A}, \qquad (2.100)$$

where the entries of the matrix  $\mathbf{A}$  are given by the partial derivatives of P, C, S on the pixel value at m, n. With the covariance of the pixels given by the expressions (2.84,2.96), the following covariances of the reconstructed values are obtained:

$$Cov(P,P) = \sum_{\substack{m,n\\m',n'}} Covs_{mn,m'n'}$$
(2.101)

$$Cov(P,C) = 2 \sum_{\substack{m,n \\ m',n'}} Covs_{mn,m'n'} \cos\left(\frac{1}{2} \begin{pmatrix} 2m+1 \\ 2n+1 \end{pmatrix} \vec{K}_0\right)$$
(2.102)

$$Cov(P,S) = 2 \sum_{\substack{m,n \\ m',n'}} Covs_{mn,m'n'} \sin\left(\frac{1}{2} \begin{pmatrix} 2m+1 \\ 2n+1 \end{pmatrix} \vec{K}_0\right)$$
(2.103)

$$Cov(C,C) = 4 \sum_{\substack{m,n \\ m',n'}} Covs_{mn,m'n'} \cos\left(\frac{1}{2} \begin{pmatrix} 2m+1 \\ 2n+1 \end{pmatrix} \vec{K_0}\right) \cos\left(\frac{1}{2} \begin{pmatrix} 2m'+1 \\ 2n'+1 \end{pmatrix} \vec{K_0}\right)$$
(2.104)  
$$= 2 \sum_{\substack{m,n \\ m',n'}} Covs_{mn,m'n'} \left(\cos\left(\begin{pmatrix} m-m' \\ n-n' \end{pmatrix} \vec{K_0}\right) + \cos\left(\begin{pmatrix} m+m'+1 \\ n+n'+1 \end{pmatrix} \vec{K_0}\right)\right)$$

$$Cov(C,S) = 4 \sum_{\substack{m,n \\ m',n'}} Covs_{mn,m'n'} \cos\left(\frac{1}{2} \left(\begin{array}{c} 2m+1 \\ 2n+1 \end{array}\right) \vec{K_0}\right) \sin\left(\frac{1}{2} \left(\begin{array}{c} 2m'+1 \\ 2n'+1 \end{array}\right) \vec{K_0}\right)$$
(2.105)  
$$= 2 \sum_{\substack{m,n \\ m',n'}} Covs_{mn,m'n'} \left(\sin\left(\left(\begin{array}{c} m-m' \\ n-n' \end{array}\right) \vec{K_0}\right) + \sin\left(\left(\begin{array}{c} m+m'+1 \\ n+n'+1 \end{array}\right) \vec{K_0}\right)\right)$$

$$Cov(S,S) = 4 \sum_{\substack{m,n \\ m',n'}} Covs_{mn,m'n'} \sin\left(\frac{1}{2} \begin{pmatrix} 2m+1 \\ 2n+1 \end{pmatrix} \vec{K}_0\right) \sin\left(\frac{1}{2} \begin{pmatrix} 2m'+1 \\ 2n'+1 \end{pmatrix} \vec{K}_0\right)$$
(2.106)  
$$= 2 \sum_{\substack{m,n \\ m',n'}} Covs_{mn,m'n'} \left(\cos\left(\begin{pmatrix} m-m' \\ n-n' \end{pmatrix} \vec{K}_0\right) - \cos\left(\begin{pmatrix} m+m'+1 \\ n+n'+1 \end{pmatrix} \vec{K}_0\right)\right).$$

The expression for the covariances simplifies drastically if the pixels are uncorrelated  $(Covs_{mn,m'n'} = \sigma^2 (mn) \delta_{mn,m'n'})$ , i.e. Cov(C,S) = 0, Cov(P,S) = 0, Cov(P,C) = 0 and

$$\sigma^2(P) = \sum_{mn} \sigma^2(mn) \tag{2.107}$$

$$\sigma^{2}(C) = 4 \sum_{mn} \sigma^{2}(mn) \cos\left(\frac{1}{2} \left(\begin{array}{c} 2m+1\\ 2n+1 \end{array}\right) \vec{K}_{0}\right)^{2}$$
(2.108)

$$\sigma^{2}(S) = 4\sum_{mn} \sigma^{2}(mn) \sin\left(\frac{1}{2} \left(\begin{array}{c} 2m+1\\2n+1\end{array}\right) \vec{K}_{0}\right)^{2}.$$
(2.109)

The influence of correlations can be discussed qualitatively with the help of a hat shaped covariance function characterized by a positive constant  $\sigma^2$  within the correlation length  $l_{cor}$  and zero outside:

$$Cov (P, P) = \sum_{\substack{m,n \\ m',n'}} Covs_{mn,m'n'} = Z^{2}\sigma^{2}$$

$$(2.110)$$

$$Cov (C, C) = 2 \sum_{\substack{m,n \\ m',n'}} Covs_{mn,m'n'} \left( \cos\left(\left(\begin{array}{c}m-m' \\ n-n'\end{array}\right)\vec{K}_{0}\right) + \cos\left(\left(\begin{array}{c}m+m'+1 \\ n+n'+1\end{array}\right)\vec{K}_{0}\right)\right)$$

$$(2.111)$$

$$= 2\sigma^{2} \sum_{\substack{m-m',n-n' \\ m+m',n+n'}} \sum_{\substack{m-m' \\ n-n'}} \left( \cos\left(\left(\begin{array}{c}m-m' \\ n-n'\end{array}\right)\vec{K}_{0}\right) + \cos\left(\left(\begin{array}{c}m+m'+1 \\ n+n'+1\end{array}\right)\vec{K}_{0}\right)\right)$$

$$\approx 8\sigma^{2}Z^{2} \sum_{\substack{m-m',n-n' \\ m-m'}} \cos\left(\left(\begin{array}{c}m-m' \\ n-n'\end{array}\right)\vec{K}_{0}\right) = 8\sigma^{2}Z^{2} \sin\left(l_{cor}\vec{K}_{0}\right)$$

$$Cov (S,S) = 2 \sum_{\substack{m,n \\ m',n'}} Covs_{mn,m'n'} \left( \cos\left(\left(\begin{array}{c}m-m' \\ n-n'\end{array}\right)\vec{K}_{0}\right) - \cos\left(\left(\begin{array}{c}m+m'+1 \\ n+n'+1\end{array}\right)\vec{K}_{0}\right)\right)$$

$$(2.112)$$

$$= 8\sigma^{2}Z^{2} \sin\left(l_{cor}\vec{K}_{0}\right) .$$

Accordingly, the variance of the central band is increased by covariances between the pixel. This effect has been thoroughly analyzed by J. Verbeeck for EELS measurements (Verbeeck and Berton (2008)). The influence of the correlation on the real and imaginary part of the sideband depends on the ratio of the correlation length  $l_{cor}$  to the fringe spacing. E.g., if the correlation length is an even multiple of the half of a fringe spacing, the variances are maximally reduced (zero in the case of the artificial case of the hat shaped pixel covariance). If, however, it is an odd multiple, the variances are increased with respect to the uncorrelated case.

Since amplitude and phase are non-linearly related to the real and the imaginary parts  $\Re$  and  $\Im$ , the covariance is generally not sufficient to describe the noise properties in amplitude and phase. The experimental noise levels are, however, sufficiently small to allow for a linearization of  $\phi = -\arctan\frac{\Im}{\Re} + \pi \vec{Z}\vec{K_0}$  and  $A = \sqrt{\Re^2 + \Im^2}$ , i.e.

$$Cov (A, A) \approx \left(\frac{\overline{\Re}}{\overline{A}}\right)^2 Cov \left(\overline{\Re}, \overline{\Re}\right) + \left(\frac{\overline{\Im}}{\overline{A}}\right)^2 Cov \left(\overline{\Im}, \overline{\Im}\right) + \left(\frac{2\overline{\Re\Im}}{\overline{A}^2}\right) Cov \left(\overline{\Re}, \overline{\Im}\right)$$
(2.113)  
$$Cov (\phi, \phi) \approx \left(\frac{\overline{\Im}}{\overline{A}^2}\right)^2 Cov \left(\overline{\Re}, \overline{\Re}\right) + \left(\frac{\overline{\Re}}{\overline{A}^2}\right)^2 Cov \left(\overline{\Im}, \overline{\Im}\right) - 2\frac{\overline{\Re\Im}}{\overline{A}^4} Cov \left(\overline{\Re}, \overline{\Im}\right) .$$

Through incorporating the non-negligible scintillator influence, it is now possible to derive realistic noise figures, i.e. phase and amplitude detection limits, which take into account the effects of correlated pixels, etc. Due to the complicated structure of the general problem, it is again useful to consider some special examples of empty holograms recorded with different cameras :

(a) The perfect deterministic camera without noise is characterized by  $psfs_{m,n} = \delta_{m,n}$ . The variance of the amplitude and phase becomes equivalent to the term derived by F. Lenz (Lenz (1988))<sup>11</sup>, as can be seen by deliberately tilting the complex plane to set  $\overline{\phi} = 0$  ( $\overline{\Im} = 0$ )

$$\sigma_A^2 = \left(\frac{\overline{\Re}}{\overline{A}}\right)^2 Cov\left(\overline{\Re}, \overline{\Re}\right)$$
(2.114)  
$$= 2\overline{I}$$

$$= 2I$$

$$\sigma_{\phi}^{2} = \left(\frac{\overline{\Re}}{\overline{A}^{2}}\right)^{2} Cov\left(\overline{\Im},\overline{\Im}\right)$$

$$= \frac{2\overline{I}}{\overline{A}^{2}}.$$
(2.115)

(b) If the camera is still deterministic but has a certain spread psfs  $\neq \delta_{m,n}$ , the pixels become correlated, yielding the possibility of tuning the phase and amplitude noise by choosing the proper fringe spacing with respect to the correlation length.

<sup>&</sup>lt;sup>11</sup>They used a slight different notation, that is instead of the amplitude A, the fringe visibility V = A/I (see expression (2.39)) was used. This leads to modifications in the following expressions.

(c) If the scintillator introduces additional noise, the argumentation of (b) is still valid. However, the total noise levels itself have been raised.

In Chap. 5 an experimental comparison between the corrected signal variance (2.113) and the simplified formulas (2.114) will be shown, proving that the corrected amplitude and phase variances are more accurate. Consequently, one can calculate accurate signal resolution numbers from one acquired image, providing error bars for the reconstructed waves. Due to the complexity of deriving accurate noise levels from input data, it is furthermore always advisable to measure the standard deviations directly from the image, which would ideally require the acquisition of a series of identical holograms. Since this procedure introduces additional artifacts due to a drift in the specimen position or the illumination, one can also use the spatial noise in the vacuum region as a measure for the noise in the reconstructed wave. As the amplitude usually assumes rather large values in the vacuum (no damping, scattering, etc.), this value can serve as a lower bound for the noise. It is furthermore emphasized that the statistics used for determining the vacuum noise should include only mutually non-correlated pixels, i.e. pixels lying outside the correlation distance depicted in Fig. 2.13.

Last but not least, various strategies to decrease the noise levels in the reconstructed waves beside the above mentioned tuning of the fringe spacing are discussed. The phase resolution as given by (2.113) can be enhanced by increasing the contrast and/or the dose in the image. Both can be improved by various methods. The most natural choice is to increase the dose in the image by either raising the current or the acquisition time. Both approaches are limited by coherence and stability issues as described in this chapter and the saturation level of the camera. Both specimen drift and camera saturation can be overcome by acquiring several images and correcting the drift by cross-correlating subsequent images. The combination of that technique with standard electron holography requires the intermediate recording of empty holograms. The thereby introduced additional stage motion poses an additional obstacle to an accurate alignment of the images in high resolution imaging. Another drawback is the resolution loss generated by the interpolation to the drift corrected image position. This effect can be reduced by replacing the distortion correction through empty holograms by an interpolative distortion correction discussed in Sec. 2.7.

# 2.11 Summary

The whole off-axis holographic imaging and reconstruction process can be split into two parts, the image acquisition and the reconstruction process. In spite of the in large parts similar optical setup of the microscope the properties of the interference terms produced by the biprism differ fundamentally from the conventional image:

- The statistical superposition (or trace of the density operator) leads to reconstructed wave averages instead of intensity averages, hence amplitude (or contrast) damping due to destructive decoherence. Consequently, the averaging over lens aberrations produces chromatic and spatial envelope functions; a directional damping function is introduced by specimen drift.
- The Möllenstedt biprism introduces two additional optical effects, which have to be considered when reconstructing holograms. Firstly, diffraction at the sharp edge of the filament leads to Fresnel fringes in the image plane. It was shown in this work that the effects can be removed by calculating the missing terms analytically and adding them to the interference pattern. Secondly, the beam angle dependent modulation of path lengths in the tilted beams behind the biprism produces a shift of the interference pattern, which yields a contrast damping, when summed over the convergence angle of the illumination. It was shown in this work that the aberrations of the objective lens have to be incorporated in that summation, yielding a modified form of the previously considered spherical envelope.
- The interference terms can be analyzed with respect to the spatial distortions introduced mainly by the hardware  $C_s$ -corrector, the biprism, the projective system and the fiber optic of the camera. Based on accurate distortion measurements a digital distortion removal as part of the standard reconstruction process has been proposed, which removes the drawbacks of the usual division with a parallely reconstructed noisy empty wave.

A review of the reconstruction process leads to the following results:

- It was shown that the numerical filtering of the sideband with a sinc mask corresponds to a local fit, i.e. a least-square fit of a rectangular patch of the hologram to a cosinoidal interference pattern. This mask is therefore optimal with respect to minimizing delocalization effects due to the reconstruction, i.e. the resolution is maximally preserved.
- The noise figures of reconstructed amplitude and phase are mainly determined by shot noise smeared and amplified by the scintillator. Accurate amplitude and phase detection limits have been derived, which

# 2.11. SUMMARY

consider both shot noise and scintillator noise and differ substantially from the previously used amplitude and phase detection limits based on shot noise only.

# Chapter 3

# Scattering theory

After considering the imaging process in the previous chapter, the ultimate purpose of transmission electron microscopy, i.e. the investigation of electron-specimen interactions, will be discussed. Most emphasis is put on electron specimen interactions explored by off-axis Electron Holography, i.e., elastic interactions will be analyzed in detail, whereas inelastic interactions are mainly treated as perturbations to the elastic signal. The main goal of the analysis of inelastically scattered electrons will be discussed. As a side product, double differential cross sections for various inelastic processes are analyzed, and a fast and accurate algorithm to calculate combined elastic and inelastic scattering is presented.

The geometry of the scattering experiment is sketched in Fig. 3.1. Three different domains can be distinguished: two vacuum regions and one region with a non-vanishing electromagnetic potential stemming from the specimen. The incident electron moves in z-direction and eventually impinges on the specimen, where it is



Figure 3.1: Scheme of electron-specimen scattering including the coordinate system. The Feynman diagram-like scheme on the right-hand side outlines the major interactions between electron beam and specimen, i.e. elastic scattering, inelastic scattering mediated by virtual photon, generation of photons (Bremsstrahlung, Cerenkov radiation), change of the inner state of the specimen through various interactions (phonon, plasmon generation, etc.).

scattered into all directions.

The specimen-electron interaction can be described within the theoretic framework of Quantum Electrodynamics (QED). The theory describes the dynamics and interaction of charged quantum particles under the influence of electromagnetic fields, where the coupling strength between both is governed by the fine structure constant  $\alpha = e^2/4\pi\hbar c \approx 1/137$ . As the probability amplitude of the dominating processes depends strongly on the energy of the particles involved, the acceleration voltage in the microscope determines the specificity of the QED. In the range of  $80 - 300 \,\text{kV}$  acceleration voltage scattering processes involving creation or annihilation of massive particles, in particular electrons and positrons, can be neglected<sup>1</sup>. Moreover, the atom core can be described as a single particle, i.e., core form factors can be safely neglected (Greiner and Reinhardt (1984)). The beam electron energy is, on the other hand, large enough to apply the perturbation expansion known as Feynman diagrams. Sufficiently accurate results are obtained within second order perturbation.<sup>2</sup> The idealized energy electron loss spectrum shown in Fig. 3.2 illustrates the classification of scattering processes with respect to energy loss: The total inelastic cross-section can easily surmount the elastic one at thicknesses beyond the

 $<sup>^{1}</sup>$ The energy for creating an electron-positron pair is  $1022 \, \mathrm{keV}$ .

 $<sup>^{2}</sup>$  There are two conventions for counting the perturbation order. It is either derived from the power of the fine structure constant (number of virtual photons) in the scattering cross-section or the number of vertices in the Feynman diagram. Here, the number of vertices is twice as large as the number of virtual photons.

so-called inelastic mean free path length  $\lambda_{in}$ , which is the average distance an electron must travel in order to undergo one inelastic scattering process. Typical inelastic mean free path lengths reported in literature are in the order of several tens of nm (see Tab. 3.3). They, however, do not consider inelastic processes with an energy transfer below the spectral resolution of the microscope, which is typically larger than 0.1 eV. Typical low-loss excitations occurring within that energy range are phonon excitations, electron-ion scattering or the Cerenkov radiation.<sup>3</sup> Therefore, the elastic scattering theory, which will be considered in Sec. 3.2, yields useful results only if the thickness t is small. This condition is fulfilled for specimens prepared for high-resolution imaging  $(t \in \mathcal{O} (10 \text{ nm}).$ 



Figure 3.2: Idealized electron-energy loss spectrum. The low-loss regime ( $\Delta E < 50 \,\text{eV}$ , main plot) contains amongst others Phonon and Plasmon resonances, excitation of Cerenkov radiation and Bremsstrahlung. The characteristic excitation of inner shell electrons occurring at energies beyond 50 eV has a comparatively low probability.

As the fundamental quantity, determining the outcome of both elastic and inelastic scattering experiments, is the scattering matrix  $\mathbf{S}_{fi}$  (see App. A.11), a large portion of this chapter aims at calculating  $\mathbf{S}_{fi}$  for electron scattering within TEM. When considering scattering experiments, i.e. the transition from an initial to a final state, it is sometimes convenient to separate unity from the scattering matrix  $\mathbf{S}_{fi}$  as reflected in the defining expression  $\mathbf{S}_{fi} = 1 + i\mathbf{T}_{fi}$  for the  $\mathbf{T}_{fi}$  matrix. The conservation of the total transition probability is expressed by the unitary property of the scattering matrix  $\mathbf{S}_{fi}\mathbf{S}_{if}^* = \mathbf{I}$ , which translates to the following equality referred to as optical theorem:

$$2\Im\left\{\mathbf{T}_{nn}\right\} = \sum_{m} \left|\mathbf{T}_{mn}\right|^{2} \,. \tag{3.1}$$

In other words, the elastic part of the scattering (quantum number n is zero) contains information on all inelastic transitions in the system. The implication of this result on Electron Holography will be discussed in Sec. 3.2. The remaining part of this chapter concentrates on the calculation of scattering matrices  $\mathbf{S}_{fi}$  or  $\mathbf{T}_{fi}$ .

Throughout the chapter the following conventions will be frequently employed:  $\hbar = c = 1$  and Gaussian units will be used for electromagnetic quantities. Greek subscripts will denote 4-vector entries with the metric tensor being

$$g_{\mu\nu} = g^{\mu\nu} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} .$$
(3.2)

A 4-product  $x_{\mu}x^{\mu}$  will sometimes be separated into the spatial and time component employing the following notation  $x_{\mu}x^{\mu} = x_0x^0 - \vec{x}\cdot\vec{x}$ . Furthermore, the following definition of the delta-function will be frequently used

$$\int e^{ikx} \mathrm{d}x = 2\pi\delta\left(k\right) \,. \tag{3.3}$$

Free relativistic spinor states will be normalized to  $\delta$ -functions in a covariant manner, i.e., Dirac plane wave spinors read

$$\Psi = \left(\frac{1}{2\pi}\right)^{3/2} \sqrt{\frac{m}{E}} \mathbf{u}_s e^{-ip_\mu x^\mu}$$
(3.4)

and

$$\mathbf{u}_s = \sqrt{\frac{m+E}{2m}} \left(\begin{array}{c} \chi_s \\ \frac{p\sigma}{m+E} \chi_s \end{array}\right)$$

 $<sup>^{3}</sup>$ Currently, the best energy resolution is around 0.1 eV achieved at the Zeiss SESAM TEM at the Max-Planck-Institute for Metals Research in Stuttgart, Germany.

with  $\chi_{1,2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ . Accordingly, the spinor scalar product  $\langle \Psi^{\dagger} | \Psi \rangle = \int d^3 r \Psi^{\dagger}(\vec{r}) \Psi(\vec{r}) = \delta_{ss'} \delta(p-p')$  is independent from the reference frame normalized to  $\delta$ -distributions. In a non-relativistic regime the prefactors can be dropped since the integration volume  $\int d^3 r$  itself becomes invariant, hence non-relativistic wave functions are defined as

$$\Psi = \left(\frac{1}{2\pi}\right)^{3/2} e^{-i(Et - \vec{p}\vec{r})}.$$
(3.5)

# 3.1 General scattering formalism

There are several standard approaches to formulate the QED scattering theory. One approach is based on the second quantization and leads to the calculation of vacuum expectation values of time ordered products of creation and annihilation operators. A second method is based on the evaluation of propagators or Green's functions. Yet another approach uses the path integral formalism. Well known results from these techniques will be used in Sec. 3.3 to calculate certain inelastic scattering events like Bremsstrahlung. In order to keep the amount of equations small and to facilitate a computationally effective way to describe the electron specimen scattering, yet another alternative based on a direct evaluation of coupled differential equations is considered in the following. This approach is less general compared to the previously mentioned one due to the restriction to electron specimen interactions without particle (e.g. photon) generation or annihilation. However, as discussed in the beginning of this chapter, pair generation does not play a role, so that the missing photon generation remains the most severe drawback. Phonon generation will therefore be discussed separately in Sec. 3.3.2.

The starting point of the following considerations is the many body time-dependent Dirac equation

$$\left(\hat{\mathbf{H}}_{e} + \hat{\mathbf{H}}_{s} + \hat{\mathbf{H}}_{es}\right) |\mathbf{\Xi}\rangle = \hat{E} |\mathbf{\Xi}\rangle .$$
(3.6)

Here,  $\Xi$  is a many-particle wave function describing all contributing particles, i.e. the beam electron, the specimen electrons and the specimen ions. The total Hamiltonian has been separated into three different parts:  $\hat{H}_s$  acts solely on specimen degrees of freedom,  $\hat{H}_e$  is the single particle Dirac operator

$$\hat{\mathbf{H}}_e = -i\boldsymbol{\gamma}^\mu \hat{\mathbf{p}}_\mu + m \tag{3.7}$$

acting solely on the beam electron and  $\hat{H}_{es}$  describes the interaction between both the beam electron and the specimen.  $\hat{H}_{es}$  is a two-particle operator and is determined by the electromagnetic fields generated by both the specimen constituents and the beam electron acting on each other, i.e., so-called virtual photons as described by the photon (or Stückelberg-Feynman) propagator in q-space

$$D_F = \int \frac{d^4q}{(2\pi)^4} \frac{-4\pi e^{-iq_\mu \left(r^\mu - r'^\mu\right)}}{q^2 + i0}$$
(3.8)

are exchanged between the specimen wave function living on the spatial coordinate r' and the beam electron living on r:<sup>4</sup>

$$\hat{\mathbf{H}}_{es} = e^2 \boldsymbol{\gamma}_{\mu} \int \frac{\mathrm{d}^4 q}{(2\pi)^4} \frac{-4\pi e^{-iq_{\nu} \left(r^{\nu} - r'^{\nu}\right)}}{q^2 + i0} \boldsymbol{\gamma}^{\mu} \,. \tag{3.9}$$

The small imaginary term *i*0 in the denominator guaranties the proper causality of the virtual photon after performing the integration over q with the help of the residue theorem. The Dirac matrices  $\gamma_{\mu}$  act solely on the specimen part of the total wave function, whereas  $\gamma^{\mu}$  are multiplied on the beam electron subspinors. This prescription ensures the correct coupling of the vector fields, e.g., the Coulomb coupling is generated by the zero components  $\gamma_0$  and  $\gamma^0$ . There are other possibilities for gauging the photon propagator, e.g. the Coulomb gauge (e.g. Schattschneider et al. (2005)), leading to different formulas with identical results. By carrying out the spatial q integration,  $\hat{H}_{es}$  can be equivalently written as a retarded 4-potential

$$\hat{\mathbf{H}}_{es} = \frac{e^2}{2\pi} \gamma_{\mu} \int \mathrm{d}q_0 \frac{e^{iq_0} |\vec{r} - \vec{r'}|}{|\vec{r} - \vec{r'}|} e^{-iq_0 (r^0 - r'^0)} \gamma^{\mu} \,.$$
(3.10)

In contrast to the non-relativistic Coulomb coupling, the relativistic photon propagator contains the retardation as well as the full 4-dimensional coupling, i.e., magnetic interactions are incorporated. A key property of the electromagnetic interaction is the long-range behavior, i.e., a beam electron at the coordinate  $\vec{r}$  can exchange a

 $<sup>^{4}</sup>$  The specific interaction Hamiltonian used here implies that all but one internal degree of freedom of the specimen wave function have been neglected, i.e. no parallel virtual photon exchanges of the beam electron with multiple specimen degrees of freedom, e.g. one ion and one electron, are considered. The approximation holds, if the cross-sections of single excitation processes are small.

virtual photon with a specimen constituent at coordinate  $\vec{r}'$  far away from  $\vec{r}$ , which has important consequences on the interpretation of waves reconstructed by means of Electron Holography (see Sec. 3.3). The stationary equation for the specimen eigenfunctions

$$\hat{\mathbf{H}}_{s}\left|\phi_{n}\right\rangle = E_{n}\left|\phi_{n}\right\rangle \tag{3.11}$$

can be solved separately, yielding a complete orthonormal set of eigenfunctions  $\phi_n$  with respect to a set of quantum numbers n (containing for instance the energy and spin), which can be used in a time dependent expansion of  $\Xi$  (e.g. Dürr (2001))

$$\Xi(r,r') = \sum_{n} \Psi_n(r) \phi_n(\vec{r'}) e^{iE_n r'^0} \,.$$
(3.12)

In this equation, a possibly occurring exchange term between specimen constituents and beam electrons can be safely neglected due to the large energy difference between both (Greiner and Reinhardt (1984)).<sup>5</sup> Inserting (3.11) and (3.12) into (3.6) and multiplying with the time dependent basis  $\sum_{n} |\phi_n\rangle \langle \phi_n| = 1$ , one gets the following system of coupled equations:

$$\left(\hat{\mathbf{H}}_{e} - E_{e}\right) \left| \boldsymbol{\Psi}_{m} \right\rangle = -\sum_{n} \left\langle \phi_{m} \right| \hat{\mathbf{H}}_{es} \left| \phi_{n} \right\rangle \left| \boldsymbol{\Psi}_{n} \right\rangle .$$
(3.13)

The matrix elements of the interaction Hamiltonian on the right hand side of (3.13) read

$$\begin{aligned}
\mathbf{H}_{mn} & (3.14) \\
&= & \langle \phi_m | \, \hat{\mathbf{H}}_{es} | \phi_n \rangle \\
&= & \frac{e^2}{2\pi} e^{i(E_n - E_m)r'^0} \int \mathrm{d}^3 r' \left[ \phi_m^{\dagger}(\vec{r}') \boldsymbol{\gamma}_{\mu} \phi_n(\vec{r}') \right] \int \mathrm{d}q_0 \frac{e^{iq_0} |\vec{r} - \vec{r}'|}{|\vec{r} - \vec{r}'|} e^{-iq_0 \left( r^0 - r'^0 \right)} \boldsymbol{\gamma}^{\mu} \,.
\end{aligned}$$

An additional integration of (3.13) over  $r'^0$  does only modify the matrix elements  $H_{mn}$  (the other terms do not depend on  $r'^0$ ), i.e.

$$\mathbf{H}_{mn} = e^2 \int d^3 r' \left[ \phi_m^{\dagger}(\vec{r}') \boldsymbol{\gamma}_{\mu} \phi_n(\vec{r}') \right] \frac{e^{i(E_n - E_m) \left| \vec{r} - \vec{r}' \right|}}{\left| \vec{r} - \vec{r}' \right|} e^{-i(E_n - E_m) r^0} \boldsymbol{\gamma}^{\mu} \,. \tag{3.15}$$

Equation (3.13) is a coupled system of time-dependent Dirac equations. The equation exactly describes a coupled quantum system under the restrictions mentioned above (no particle generation), where the form of the specimen eigenstates  $\phi_n$  can be arbitrarily chosen with respect to the corresponding excitation process (e.g. core-loss, phonon). The different beam electron wave functions  $\Psi_m$  entangled with a specimen eigenstate  $\phi_m$  are sometimes referred to as channels (e.g. Friedrich (1994)), in particular the channel belonging to the ground state specimen wave function  $\phi_0$  will be denoted as elastic channel in the following. The interaction matrix elements  $\mathbf{H}_{mn}$  are hermitian, i.e.  $\mathbf{H}_{mn} = \mathbf{H}_{nm}^{\dagger}$ . Time-dependent perturbation theory can be applied to decouple and solve the system. For instance, when considering a single free electron as specimen wave function  $\boldsymbol{\Phi}(r')$ , the transition matrix element  $\mathbf{T}_{fi}$  from a free initial state  $\Psi_i \boldsymbol{\Phi}_i$  to a free final state  $\Psi_f \Phi_f$  is obtained within second order perturbation by calculating the scalar product  $\mathbf{T}_{fi} = \lim_{t_f \to \infty} \langle \Psi_f(t_f) \, \Phi_f(t_f) \, | \Psi_i(t_f) \, \Phi_i(t_f) \rangle$  between the

ith summand from the right hand side of (3.13) with the particular free electron wave function  $\Psi_f$  yielding

$$\mathbf{T}_{fi} = \delta\left(E_n - E_m - \Delta E\right)$$

$$ie^2 \int \mathrm{d}^3 r \mathrm{d}^3 r' \left[\mathbf{\Phi}_f^{\dagger}\left(\vec{r'}\right)\left(-i\boldsymbol{\gamma}^{\mu}\right)\mathbf{\Phi}_i\left(\vec{r'}\right)\right] \frac{e^{i(E_m - E_n)\left|\vec{r} - \vec{r'}\right|}}{\left|\vec{r} - \vec{r'}\right|} \left[\mathbf{\Psi}_f^{\dagger}\left(\vec{r}\right)\left(-i\boldsymbol{\gamma}_{\mu}\right)\mathbf{\Psi}_i\left(\vec{r}\right)\right]$$
(3.16)

which is equivalent to the textbook result (3.117) presented in Sec. 3.3 on inelastic scattering between two charged particles. Like in expression (3.117) the time integral over  $r^0$  is the  $\delta$ -function  $\delta (E_i - E_f - \Delta E)$ , which can be interpreted as energy conservation.

Without explicitly performing the complicated integration over r and r', the expression (3.16) for the scattering matrix  $\mathbf{T}_{fi}$  already gives some useful estimates on the implications of the electron spin on the scattering process. The idea is to analyze the integration kernel in (3.16) for different spin-flip processes at arbitrary points r, r' in space-time, which breaks down to evaluate the vector scalar products

$$\left[ \mathbf{\Phi}_{f}^{\dagger}\left(\vec{r}'\right)\left(-i\gamma^{\mu}\right)\mathbf{\Phi}_{i}\left(\vec{r}'\right) \right]$$
(3.17)

 $<sup>{}^{5}</sup>$ It is again important to note that (3.11) determines specimen eigenstates with respect to a single degree of freedom within the specimen. Which degree of freedom is considered, however, remains open. It can be a single core electron or a quasiparticle like a phonon.

and

$$\left[\boldsymbol{\Psi}_{f}^{\dagger}\left(\vec{r}\right)\left(-i\gamma_{\mu}\right)\boldsymbol{\Psi}_{i}\left(\vec{r}\right)\right]$$
(3.18)

since the remaining terms of the kernel do not depend on the spin. For the following example calculation, the initial state of the specimen wave function is deliberately chosen to be relativistic, i.e., the small part of the wave function amounts up to 15 % of the large part, which corresponds to inner shell states of heavy atoms. Furthermore, the final specimen state is non-relativistic, which corresponds to a free state slightly above the Fermi level. The momentum and energy change in the beam electron is assumed to be negligible, which corresponds to the small angle scattering setup usually used in TEM imaging, hence the small part of both the initial and final beam wave function reaches 5 % of the large part at 300 kV acceleration voltage. By inserting these values into the expressions (3.17) and (3.18), one obtains relative probability amplitudes for different spin configurations at single points in space time (see Table 3.1). The results indicate, that the two scattering

${oldsymbol{\Psi}}_i {oldsymbol{\Psi}}_f {oldsymbol{\Phi}}_i {oldsymbol{\Phi}}_f$		$\uparrow \uparrow \downarrow \downarrow$	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow\downarrow\uparrow$
amplitude / influence of small component	$\mathcal{O}\left(1 ight)/5\%$	$\mathcal{O}\left(1 ight)/15\%$	$\mathcal{O}\left(10^{-4} ight)/100\%$	$\mathcal{O}\left(10^{-5} ight)/100\%$

Table 3.1: Relative scattering amplitudes of a 300 kV beam electron scattered plane wave state for a single space time point. The events in the first two columns, in contrast to the last two columns, do not incorporate spin flips. Scattering processes involving spin flips on only one side are not allowed within second order perturbation.

events involving spin flips possess 50 % different probabilities in this example, i.e., in principle it is possible to distinguish between spins in the specimen flipping from up to down or vice versa, if the beam electrons are in the spin eigenstate up. However, the relative cross-section of those events stays well below 0.1% of processes involving no spin flip. Other spin-dependent signals, which are used to investigate magnetic materials, such as the Electron Microscopic Chiral Dichroism (EMCD), are much stronger (Schattschneider et al. (2006)). Thus, the distinct measurement of the third and the fourth channel in order to investigate magnetic materials by using a spin-polarized beam in connection with a spin sensitive detector is a less promising endeavor. Other implications of the fully relativistic treatment, namely the vector potential interaction additionally introduced by the small component have a significant influence, hence cannot be neglected in an accurate treatment of inelastic excitations of core electrons (see for instance the solved "mystery" of the magic angle (Jouffrey et al. (2004))). The incorporation of realistic fully relativistic core states into explicit core excitation calculations will not be pursued in this work<sup>6</sup> due to the small impact on electron holographic measurements, which are mainly affected by low-loss, hence scalar relativistic inelastic scattering.

By expanding the beam electron wave function  $\Psi_m$  into not normalized eigenfunctions, i.e.

$$\Psi_{m}(r) = \sum_{\mu} \psi_{m_{\mu}}(\vec{r}) e^{-iE_{e,m_{\mu}}r^{0}},$$

and integrating over  $r^0$ , equation (3.15) can be stationarized to

$$\sum_{\mu} \left( \hat{\mathbf{H}}_{e} - E_{e,\mu} \right) \left| \psi_{m_{\mu}} \right\rangle = -\sum_{n\mu} \mathbf{H}_{mn} \left| \psi_{n_{\mu}} \right\rangle \tag{3.19}$$

with the sum extending over those  $\mu$ , which fulfill

$$E_{e,m_{\mu}} - E_{e,n_{\mu}} = E_n - E_m \tag{3.20}$$

and

$$\mathbf{H}_{mn} = e^2 \int d^3 r' \left[ \phi_f^{\dagger}(\vec{r}') \gamma_{\mu} \phi_n(\vec{r}') \right] \frac{e^{i(E_n - E_m)|\vec{r} - \vec{r}'|}}{|\vec{r} - \vec{r}'|} \gamma^{\mu} \,.$$
(3.21)

Equation (3.19) is fulfilled, if

$$\left(\hat{\mathbf{H}}_{e} - E_{e,\mu}\right) \left|\psi_{m_{\mu}}\right\rangle = -\sum_{n} \mathbf{H}_{mn} \left|\psi_{n_{\mu}}\right\rangle \tag{3.22}$$

holds independently of  $\mu$ . The determination of the stationary transition matrix elements  $\mathbf{H}_{mn}$  usually requires numerical methods (e.g. based on Density Functional Theory (DFT), Hartree-Fock Approximation, etc.) in order to provide accurate specimen states  $\phi_m$ . A large class of scattering processes, however, can be at least qualitatively explained with the help of approximations. Especially useful is the dipole approximation, if the specimen states are spatially localized in  $\vec{r}'$  such, that the Fourier expansion factor in the original form of the interaction Hamiltonian can be expanded according to  $e^{i\vec{q}\vec{r}'} \approx 1 + i\vec{q}\vec{r}'$ , which facilitates a particularly

<sup>&</sup>lt;sup>6</sup>Nevertheless, the inelastic scattering equations derived below can, with small changes, be adopted to the full relativistic formalism. The results thereby obtained will be published elsewhere.

convenient evaluation of the stationary transition matrix elements (3.21) on spherical coordinates (see Sec. 3.3). A particularly simple form of  $\mathbf{H}_{mn}$  is furthermore obtained, if the specimen eigenfunctions are plane waves<sup>7</sup>

$$\phi_n = \left(\frac{1}{2\pi}\right)^{3/2} \sqrt{\frac{m}{E_n}} \mathbf{u}_n e^{i\vec{k}_n \vec{r}'} \,. \tag{3.23}$$

Inserting this plane wave into the transition matrix element (3.21) yields

$$\mathbf{H}_{mn} = e^{2} \left(\frac{1}{2\pi}\right)^{3} \sqrt{\frac{m}{E_{n}}} \sqrt{\frac{m}{E_{m}}} \left[\mathbf{u}_{m}^{\dagger} \boldsymbol{\gamma}_{\mu} \mathbf{u}_{n}\right] \int \int \mathrm{d}^{3} r' \frac{\mathrm{d}^{3} q}{(2\pi)^{3}} \frac{-4\pi e^{i\vec{q}\left(\vec{r}-\vec{r}'\right)}}{\Delta E^{2} - \left|\vec{q}\right|^{2}} e^{-i\vec{k}_{m}\vec{r}'} e^{i\vec{k}_{n}\vec{r}'} \boldsymbol{\gamma}^{\mu} \qquad (3.24)$$

$$= e^{2} \left(\frac{1}{2\pi}\right)^{3} \sqrt{\frac{m}{E_{n}}} \sqrt{\frac{m}{E_{m}}} \left[\mathbf{u}_{m}^{\dagger} \boldsymbol{\gamma}_{\mu} \mathbf{u}_{n}\right] \frac{-4\pi e^{i\left(\vec{k}_{n}-\vec{k}_{m}\right)\vec{r}}}{\Delta E^{2} - \left|\vec{k}_{n}-\vec{k}_{m}\right|^{2}} \boldsymbol{\gamma}^{\mu},$$

which is again a plane wave. It will be shown below that this transition matrix element leads to a global tilt by  $\vec{k}_n - \vec{k}_m$  of the inelastically scattered wave.

The non-relativistic form of the equation system (3.19) is commonly considered in many-particle systems (see e.g. Friedrich (1994)), in electron microscopy, however, it is named after H. Yoshioka (Yoshioka (1957)). The scalar relativistic form of the Yoshioka equations is obtained by replacing spinor fields in (3.19) with scalar fields and omitting the  $\gamma$  matrices.<sup>8</sup> The coupled system of equations can be solved approximately, if restricting the number of channels and assuming particular boundary conditions like a fast incoming beam electron. Furthermore, perturbation methods can be applied, if the matrix elements (3.14) coupling the channels are small. In the following, two cases, which, however, cover a large class of experimental scenarios, will be analyzed assuming a fast incoming beam electron described by a single plane wave, i.e.:

1. In Sec. 3.2 the elastic channel is calculated under the prerequisite that the channels are very weakly coupled, i.e.  $\mathbf{H}_{m,n\neq m} \ll 1$ , and the channels can be decoupled pertubatively. In off-axis Electron Holography, an empty, i.e. not on the specimen scattered, wave  $\psi_{0,ref}\phi_0$  is superimposed on a mixed state  $\sum_n \psi_{n,obj}\phi_n$  modified by the object. As the detected intensity is defined as the absolute square of the total wave function

$$\begin{aligned} |\Xi_{ref} + \Xi_{obj}|^2 &= \left| \psi_{0,ref} \phi_0 + \sum_n \psi_{n,obj} \phi_n \right|^2 \\ &= \left| \psi_{0,ref} \right|^2 + \sum_n \left| \psi_n \right|^2 + \psi_{0,ref} \psi_{0,obj}^* + \psi_{0,ref}^* \psi_{0,obj} \,. \end{aligned}$$
(3.25)

inelastic channels  $m \neq 0$  do not contribute to the interference pattern. This is equivalent to describing off-axis holography as a which-way type of experiment, i.e. an inelastic interaction gives information about the path by changing the object state, hence destroying the interference pattern. There is a subtlety in this argument, introduced by the long range character of the electromagnetic interaction. In a typical high-resolution holographic setup, the reference wave is separated only several tens of nm from the object wave. Therefore, depending on the particular type of the inelastic excitation, a non-vanishing probability of changing the specimen state with the empty wave and consequently destroying the which-way information exists. The magnitude of this probability is usually low and will be discussed in the Sec. 3.3 on inelastic interactions. Keeping that in mind, Electron Holography can be but approximately regarded as a perfect energy filter.

The scattering in the elastic channel mainly depends on the electrostatic potential of the specimen, which in turn is dominated by the atomic potentials. Consequently, the focus of the elastic scattering section is placed on considering scattering on multiple atoms, i.e. deriving different approximations suited for different boundary conditions, investigating the influence of relativistic effects therein, calculating crosssection, etc. Particular emphasis is put on the effect of the thermal motion of the atoms as it influences the holographic reconstruction in a fundamentally different way than other imaging techniques. The scattering on magnetostatic potentials will be incorporated in the scattering equations as well, however, explicit results will only be discussed in connection with spin-orbit coupling of the scattering and the tomographic reconstruction in Chap. 5.

2. The most simple extension to the elastic scattering, i.e. the single channel case, is the two channel case, which covers a wide variety of phenomenons like a core-loss excitation, electron-ion scattering, electron-plasmon scattering, etc. This situation is explored in Sec. 3.3 on inelastic scattering. The main goal will

<sup>&</sup>lt;sup>7</sup>Collective specimen modes such as plasmons or phonons can be described by plane waves.

<sup>&</sup>lt;sup>8</sup>This formulation leads to a restriction of the electromagnetic interaction to Coulomb coupling, which is generally not necessary and sometimes even erroneous (see magic angle).

be the description of the low-loss regime and its influence on the off-axis holographic imaging process. This includes a discussion of holographic superposition of inelastically scattered electrons and the Stobbs factor, a contrast mismatch between scattering simulations and conventional imaging reported in literature (e.g. Hytch and Stobbs (1994), Boothroyd (1997), Howie (2004)). As a side effect, an efficient algorithm for calculating spatially localized inelastic excitations, such as core-loss excitations, will be derived and used for a discussion of relativistic effects such as retardation of the virtual photon or the influence of elastic scattering on inelastic cross-sections.

All theoretic considerations will be supplemented with explicit numerical experiments, which illustrate the most important findings for the interpretation of the experimental results. That includes the influence of typical scattering geometries used in the high-resolution regime (low-index zone-axis orientation, small thickness, etc.) and the medium resolution regime (out-of-zone axis, large thicknesses).

# 3.2 Elastic scattering theory

The elastic scattering theory presented in this section aims at calculating  $\psi_0$  if  $\mathbf{H}_{m,n\neq m} \ll 1$ . In this case all  $m \neq n$  Yoshioka equations can be decoupled, i.e.

$$\left(\hat{\mathbf{H}}_{e} - E_{e,0}\right) |\psi_{0}\rangle = -\mathbf{H}_{00} |\psi_{0}\rangle . \qquad (3.26)$$

Corrections to the elastic channel occur when considering coupling up to the second order, i.e. double virtual photon exchange (Fig. 3.3). This process can be regarded as a two step inelastic scattering process exciting the specimen by transferring energy in a first step and subsequently relaxing the specimen by backtransferring exactly the same amount of energy back to the beam electron. As a consequence, the initial and final specimen states are equal and the beam electron is elastically scattered. This effect is illustrated at a coupled two-level system

$$\begin{pmatrix} \hat{\mathbf{H}}_{e} - E_{e,0} + \mathbf{H}_{00} \end{pmatrix} |a_{0}\psi_{0}\rangle = -\mathbf{H}_{0m} |\psi_{n}\rangle$$

$$\begin{pmatrix} \hat{\mathbf{H}}_{e} - E_{e,0} + \mathbf{H}_{mm} \end{pmatrix} |\psi_{m}\rangle = -\mathbf{H}_{m0} |a_{0}\psi_{0}\rangle .$$

$$(3.27)$$

The excitation coefficient  $a_0$  is inserted to distinguish the elastic channel modified by the double exchange from the undisturbed and normalized channel  $\psi_0$ . The second equation can be equivalently written as an integral equation by using the Green's operator  $\hat{\mathbf{G}}_m = \left(\hat{\mathbf{H}}_e - E_{e,m}\right)^{-1}$ 

$$|\psi_m\rangle = |\psi_{m,hom}\rangle + \hat{\mathbf{G}}_m \mathbf{H}_{m0} |a_0\psi_0\rangle . \qquad (3.28)$$

That result can again be inserted into the m = 0 equation of the elastic channel to yield

$$\left(\hat{\mathbf{H}}_{e} - E_{e,0} + \mathbf{H}_{00}\right) |a_{0}\psi_{0}\rangle = \mathbf{H}_{0m} |\psi_{m,hom}\rangle + \mathbf{H}_{0m} \hat{\mathbf{G}}_{m} \mathbf{H}_{m0} |a_{0}\psi_{0}\rangle .$$

$$(3.29)$$

By multiplying the normalized eigenfunction  $\langle \psi_0 |$  from the left, one obtains the excitation coefficient

$$a_{0} = \frac{\langle \psi_{0} | \mathbf{H}_{0m} | \psi_{m,hom} \rangle}{E - E_{e,0} - \langle \psi_{0} | \mathbf{H}_{0m} \hat{\mathbf{G}}_{m} \mathbf{H}_{m0} | \psi_{0} \rangle}.$$
(3.30)

Each double exchange scattering process is therefore modifying the elastically scattered wave function ( $\psi_0 \rightarrow \psi_0$ )



Figure 3.3: Fourth order scattering graph, describing a double exchange of energy between two particles. The double virtual photon exchange (wavy line) facilitates a vanishing total energy exchange.

 $a_0\psi_0$ ), i.e., the total influence of double scattering is obtained by summing over all inelastic channels m

$$a_{0} = \frac{\psi_{0} \sum_{m} \mathbf{H}_{0m} |\psi_{m,hom}\rangle}{E - E_{e,0} - \psi_{0} \sum_{m} \mathbf{H}_{0m} \hat{\mathbf{G}}_{m} \mathbf{H}_{m0} |\psi_{0}\rangle} .$$
(3.31)

The factor  $a_0$  is generally complex, hence introduces phases bearing information on inelastic scattering events. The complete equation (3.29) is very difficult to solve, not only due to the integro-differential structure but also due to the problems with calculating the Green's functions  $\hat{\mathbf{G}}_m$  and the transition matrices  $\mathbf{H}_{m0}$ . The magnitude of the effect is determined by dominating inelastic excitations in the low-loss regime. The calculation of absolute values remains an open task for the future. Furthermore, an experimental proof of additional phase shifts not stemming from the electrostatic potential is also not reported until now.<sup>9</sup>

An additional consequence of inelastic scattering on the elastic channel, besides the double scattering considered above, is derived from the conservation of the total particles in all channels. That means that the intensity of the incoming wave must be equal to the intensity of all outgoing channels. The mathematical formulation of that argument is referred to as optical theorem (e.g. Schiff (1968)) and leads to an imaginary absorption potential in the equation for the elastic channel (e.g. Wang (1995), Croitoru et al. (2006), Dinges et al. (1995)), which correlates to the total strength of the inelastic scattering characterized by the inelastic mean free path  $\lambda_{in}$ . The dispersive character of coupled channels stemming from double inelastic scattering is, however, not properly considered by the imaginary potential.

In the following, both the imaginary part of the potential as well as the real part stemming from the electrostatic potential and the double inelastic scattering will be denoted by V, where it is understood that the electrostatic part usually dominates. If neglecting chemical bonding between the atoms the electrostatic potential of a solid consists of the screened atomic Coulomb potentials, which are (periodically) arranged on the lattice positions of the solid and can be approximately described as

$$V = \frac{Ze}{r}e^{-br} \tag{3.32}$$

according to G. Wentzel (Wentzel (1926)). Here, Z is the core charge and b the screening length due to the electronic shell. More accurate parametrizations are obtained by combining several Wentzel potentials and Gauss functions (e.g. Kirkland (1998), Weickenmeier and Kohl (1991)). Throughout this work, the parametrization of Weickenmeier and Kohl (1991) will be used exclusively, if elastic scattering potentials are generated by placing free atoms on particular lattice positions. Additionally, one can consider the modification of the potentials due to chemical bonding by using electron densities obtained e.g. from ab-initio calculations (see Chap. 4). Several free atom potentials are depicted in Fig. 3.4. It is clear that the Coulomb part close to the atom core is dominant and exceeds the potential on the outer regions, which correlates to the shape of the electron shell, by several orders of magnitude. It is this particular topology of the potential, which is giving rise to the properties of electron scattering, i.e. the strong dependence on atomic positions and the comparatively small sensitivity on the shape of the electron shell. Before actually solving the single particle Dirac equation (3.26),



Figure 3.4: Free atom potentials according to Weickenmeier and Kohl (1991). The region in the vicinity of the core is dominated by the Coulomb part, whereas the mean radius correlates to the size of the atoms. The Ba atom has loosely bound  $6s^2$  electrons, leading to an extension similar to the heavier Pb atom.

some well-known results for fully relativistic scattering like elastic scattering cross-sections are recapitulated to give an outlook to additional effects occurring within a fully relativistic description in comparison to scalar

<sup>&</sup>lt;sup>9</sup>An experimental setup would aim at changing the coefficient  $a_0$  without altering the electrostatic potential and other parameters of the experiment, which could for instance be accomplished by changing the acceleration voltage.

relativistic ones.<sup>10</sup> Writing out  $H_{00}$ , the single particle Dirac equation reads

$$E\psi(\vec{r}) = \left[c\vec{\alpha}\cdot\hat{\vec{p}} + mc^2\beta + V(\vec{r})\right]\psi(\vec{r}), \qquad (3.33)$$

 $\vec{\alpha}$  and  $\beta$  denote the Dirac matrices,  $\hat{\vec{p}}$  the momentum operator and  $\vec{r}$  the three-dimensional space coordinate.

The differential scattering cross sections  $d\sigma/d\alpha$  derived from (3.33) for scattering of a randomly spin-polarized electron beam on an atom core with charge Z (no momentum transfer to the core) is described by the famous Mott formula (e.g. Greiner and Reinhardt (1984))

$$\frac{d\sigma}{d\Omega}\left(\theta\right) = \frac{Z^2 \alpha^2 \left(1 - \beta_r^2 \sin^2 \frac{\theta}{2}\right)}{4\beta_r^2 \left|\vec{p}\right|^2 \sin^4 \frac{\theta}{2}}.$$
(3.34)

Here,  $\beta_r$  denotes the quotient of the projectile particle velocity with the speed of light. In the limit of small velocities  $v/c = \beta_r \ll 1$  or small scattering angles  $\theta$ , (3.34) becomes

$$\frac{d\sigma}{d\Omega}\left(\theta\right) = \frac{Z^2 \alpha_s^2}{4\beta_r^2 \left|\vec{p}\right|^2 \sin^4 \frac{\theta}{2}},\tag{3.35}$$

which is the Rutherford cross-section (e.g. Greiner and Reinhardt (1984)), derived from the Klein-Gordon equation. The additional term in (3.34) only affects large angle scattering, e.g., scattering angles of 200 mrad differ about 1.15 % at 200 kV. The differential cross-section at large scattering angles, however, is very small and can only be explored by integrating large solid angles like in high angle diffraction techniques such as High-Angle Annular Dark Field (HAADF) TEM. The off-axis holographic imaging considered within this work is restricted to scattering angles well below 50 mrad. Consequently, only very small effects are expected due to a fully relativistic description in the case of scattering on electrostatic potentials. The scattering on magnetostatic potentials can be discussed on the basis of an alternative form of the Dirac equation (Strange (1998); Kasper and Hawkes (1995))

$$\left[ (E-V)^2 - c^2 \hat{\vec{p}}^2 - m^2 c^4 - ie\hbar c \vec{E} \cdot \tilde{\alpha} - e\hbar c^2 \vec{B} \cdot \tilde{\sigma} \right] \psi = 0, \qquad (3.36)$$

which shows the relationship of the Dirac equation to the scalar relativistic Klein-Gordon equation. Here  $\vec{\sigma}$  are the 4-dimensional spin matrices. By neglecting the last two terms in the brackets one ends up with four decoupled Klein-Gordon equations

$$\left[ \left( E - V \right)^2 - c^2 \hat{\vec{p}}^2 - m^2 c^4 \right] \psi = 0.$$
(3.37)

The validity of this step depends on the relative strength of the two electromagnetic field terms containing  $\vec{E}$  and  $\vec{B}$ . The electric field  $\vec{E}$  in the vicinity of an atom core diverges strongly with  $1/r^2$  (see Wentzel potential (3.32)), making the fourth term in (3.36) eventually larger than the other ones. Since this region close to the atom core is very small, the neglecting of the electric field term in (3.36) is indeed possible though, in particular when considering small angle scattering only. This is verified by the small difference between the Mott and Rutherford cross-sections given above and explicit numerical calculations below. Strong magnetic fields, however, can possibly couple more significantly the different parts of the spinor, due to an additional factor of c in the coupling term containing the magnetic field  $\vec{B}$ . The magnitude of the coupling can be estimated by inserting a typical value for atomic scale magnetic fields present in ferromagnetic solids of 100 T in (3.36)

$$\left|e\hbar c^2 \vec{B} \cdot \tilde{\sigma}\right| \approx 5600 \ (eV)^2 \ , \tag{3.38}$$

which is of the same order of magnitude like the kinetic terms perpendicular to the beam direction. These strong magnetic fields, produced by the localized spin current density of partly filled shells, are divergence free and strongly rotating, thus changing direction in each unit cell. Consequently, the average magnetic field in ferromagnetic solids is much lower, reaching several Tesla at maximum. In section 3.2.3 it will be shown by explicit numerical calculations at the deliberately chosen ferromagnet  $\alpha$ -Fe that the influence of magnetic fields is negligible, when considering scattering at atomic resolution. It is interesting to note that the evaluation of (3.38) for magnetic field strengths of 5T, as produced by the objective lens, leads to an energy term in the order of 280  $(eV)^2$  between spin up and spin down electrons. The relative strength of this term in comparison to the squared kinetic energy of the electrons  $(4e10 \ (eV)^2$  at 200 kV acceleration voltage) is of the order of 1e - 7, which is sufficient to introduce several rotations of the spin on a length scale of several mm in the magnetic field of the objective lens. It is, however, not enough to introduce any appreciable spin orbit coupling, hence spin dependent defocus. Consequently, electron spin can be totally neglected in elastic electron scattering simulations, i.e. the Klein-Gordon-equation (3.37) incorporates all physical effects important for TEM imaging.

 $<sup>^{10}</sup>$  The following considerations are actually analytical expressions for the results obtained by integrating over singular space time points used to discuss the spinor influence on inelastic scattering in the previous section.

# 3.2.1 The approximated Klein-Gordon equation

At an early stage in electron scattering investigations it has been demonstrated, that relativistic effects occurring due to the relativistic velocities can be considered by applying a so-called relativistic correction to the Schrödinger equation (e.g. Reimer (1989)). A short derivation will follow, which will shed some light on this approximation. The starting point is again the stationary Dirac equation. In a first step, spin contributions (see 3.36) are neglected, ending up with a Klein-Gordon equation:

$$\left[ (E - V)^2 - c^2 \hat{\mathbf{p}}^2 - m^2 c^4 \right] \psi = 0.$$
(3.39)

Now it is assumed, that the electrostatic potential V is small compared to the total energy E, i.e.  $V \ll 2E$ . That means  $V^2$  can be omitted, yielding

$$\left[E^2 - m^2 c^4\right]\psi = \left[2EV + c^2 \widehat{\vec{\mathbf{p}}}^2\right]\psi.$$
(3.40)

Inserting  $E = \gamma mc^2$  with  $\gamma = (1 - v^2/c^2)^{-1}$  into the approximated Klein-Gordon equation (3.40) and performing some rearrangements, one gets

$$\left[\frac{E^2 - m^2 c^4}{2\gamma m c^2}\right]\psi = \left[\frac{\widehat{\mathbf{p}}^2}{2\gamma m} + V\right]\psi = \left[-\frac{\hbar^2 \Delta}{2\gamma m} + V\right]\psi.$$
(3.41)

This is the so-called relativistically corrected Schrödinger equation, where both the rest mass m of the electron and the wave length are modified. In this work, the equation will be referred to as approximated Klein-Gordon equation, since the approximation applied was to neglect the squared part of the electrostatic potential and no 1/c expansion, usually termed as relativistic correction (e.g. Greiner (1981)). The assumption  $V \ll 2E$ is usually valid in the case of electrostatic potentials, produced by the deflectors of the microscope. The electrostatic potential of a single atom within the specimen, however, shows a Z/r asymptote close to the atom core. Hence, the assumption eventually fails in the vicinity of atom cores, especially when the atomic number Z is large. It is difficult to assess the error introduced by this approximation analytically. Thus, the error will be examined by comparing the standard approach to the Dirac (3.51) and Klein-Gordon (3.52) equation by explicit numerical calculations developed below.

#### 3.2.2 Bloch-wave-solution

A general solution of the approximated Klein-Gordon equation (3.40) on the domain depicted in Fig. 3.1 can be found by providing a basis set consisting of eigenfunctions of the Hamiltonian for each of the domains, performing a series expansion of the wave function with respect to these basis sets and determine the coefficients of that expansion by applying boundary conditions, i.e. continuity of the wave function and the first derivative at the boundary between the domains. The mathematical notation for the three steps reads:

1. The appropriate expansion for the vacuum regions consists of plane waves with expansion coefficients a:

$$\psi = \oint_{E=E(\vec{k})} a\left(\vec{k}\right) e^{i\vec{k}\vec{r}} \mathrm{d}^{3}k \,. \tag{3.42}$$

In order to fulfill (3.40) the wave vector  $\vec{k}$  must obey the relativistic dispersion relation

$$E = \sqrt{c^2 \hbar^2 \left| \vec{k} \right|^2 + m^2 c^4} \,. \tag{3.43}$$

2. The specimen region can be expanded (coefficients  $\alpha$ ) into generalized Bloch waves, i.e. Bloch waves with a complex Bloch vector  $\vec{q}$ , if the specimen potential is periodic:<sup>11</sup>

The integral extends over the plane in the Brillouin zone B, where the energy of the Bloch wave matches E. The imaginary part of the generalized Bloch vector corresponds to evanescent waves and occurs only in z-direction due to the finite extension of the crystal. The in-plane component of the Bloch vector

 $<sup>^{11}</sup>$ Contrary to the plane waves in the vacuum region, the generalized Bloch waves are not orthogonal. However, they are linearly independent, which is sufficient for a unique series expansion.

 $\vec{Q} = \vec{K}_0$  is fixed by the boundary conditions at the entrance plane of the crystal, i.e. continuity to the component of the incoming plane wave  $e^{i\vec{K}_0\vec{R}}$  lying in the *xy*-plane. The *z*-component has to be calculated independently by solving the quadratic eigenvalue problem

$$\left(q_z^2 - 2q_z g_z + g_z^2 + \left(\vec{K}_0 - \vec{G}\right)^2 - k_0^2\right) c_{\vec{q}-\vec{g}} = -\frac{2\gamma m}{\hbar^2} \sum_{\vec{g}'} \tilde{V}_{\vec{g}'-\vec{g}} c_{\vec{q}-\vec{g}'}$$
(3.45)

obtained from a plane wave expansion of the approximated Klein-Gordon equation (3.40). The quadratic form of this problem reflects the usually complex nature of the Bloch vectors in z-direction. The exact solution of this eigenvalue problem is computationally very demanding (e.g. Rother (2005)) and not suited for practical application. Therefore, one usually reduces the number of reciprocal lattice points by keeping only points close to the Ewald sphere  $\left(\vec{k}_0 + \vec{g}\right)^2 = k_0^2$ , i.e. points, where the plane wave coefficients  $c_{\vec{q}-\vec{g}}$  are supposed to be large. For the same reason one usually sets  $q_z^2 \approx k_{0z}^2$ , leaving

$$\left(-2q_zg_z + g_z^2 - 2\vec{K}_0\vec{G} + \vec{G}^2\right)c_{\vec{q}-\vec{g}} = -\frac{2\gamma m}{\hbar^2}\sum_{\vec{g}'}\tilde{V}_{\vec{g}'-\vec{g}}c_{\vec{q}-\vec{g}'},\qquad(3.46)$$

which is referred to as the high-energy approximation of the Bloch wave formalism. Due to removing the quadratic character in  $q_z$ , the high-energy approximation becomes hermitian, i.e. has real eigenvalues  $q_z$ , i.e. evanescent waves are neglected.

3. In the third step, the excitation coefficients a and  $\alpha$  are calculated by requiring the wave function  $\psi$  and its first derivative to be continuous.

The procedure outlined above has first been conducted by E. Lamla (Lamla (1938)), the corresponding analysis for the Dirac equation is still missing. Although leading to an exact solution, several practical problems arise with respect to the Bloch wave formalism. The periodicity of the potential V after one unit cell in the xy-plane is often broken, due to non-periodicities in the specimen such as defects in the crystal structure or interfaces, etc., or more generally due to the thermal motion of the atoms. An accurate incorporation of those effects would require large supercells, which are computationally very demanding. The structure of the general solution furthermore suggests to neglect back-scattered electrons and electrons scattered into directions between the Laue zones, which can not be incorporated into the method straight forward: Which eigensolutions occur in the expansion of the transmitted and backscattered wave is determined by the continuity requirement at the interfaces. The most difficult part of the problem is, however, the polynomial eigenvalue problem in the crystal yielding the Bloch eigensolutions. It is important to note that the eigenvalue problem is independent of the boundary conditions in z-direction. In practice, however, the polynomial eigenvalue problem itself is truncated to get rid of those Bloch vectors, which are pointing into the backward direction and are far away from the Ewald sphere. This truncation, however, influences the forward scattered solutions as well, e.g. it removes evanescent waves, and it is difficult to estimate the error introduced thereby by perturbation theory.

In spite of the issues mentioned above, the Bloch wave method remains one of the most frequently used schemes to calculate the elastic channel of the scattering. This is mainly due to a particular fast numerical and even analytical treatment of the eigenvalue problem, if the number of scattered beams is kept low. Furthermore, a close relationship to other reciprocal space solutions, like the first order Born approximation, can be established. In the following, another approach will be exploited removing some of the drawbacks mentioned above.

#### 3.2.3 Elastic scattering in the forward scattering approximation

If back-scattered electrons can be neglected, the boundary conditions at the entrance face of the specimen are determined by the incoming electron wave. Thus, one can alternatively circumvent the problematic eigenvalue problem by directly integrating the differential equation till the exit face is reached. The pin-pointing of the boundary conditions at the entrance face to the incoming wave is referred to as the forward scattering approximation (Reimer (1989)), since no back-scattered electrons occur within this approach. It is phenomenologically verified by the large incident velocity of the electrons and the small thickness of the specimen, giving rise to scattering angles predominantly in forward direction. A strict mathematical verification, however, would require an analysis conducted in the previous section with back scattered electrons allowed. Nevertheless, the forward scattering approximation renders an integration of the Dirac equation as a coupled set of ordinary differential equations possible, which can be solved numerically by standard algorithms (e.g. Runge-Kutta (Press et al. (2002))). First one writes both, the electromagnetic potentials and the spinor, as a Fourier series in the xy- or  $\vec{R}$ -plane with the 2D reciprocal space denoted by  $\vec{G}$ . This requires the periodicity of both the electrostatic and the vector potential in the  $\vec{R}$ -plane.<sup>12</sup> The expansion of the wave function is possible due to the Bloch theorem

 $<sup>^{12}</sup>$  This condition is fulfilled in practice by generating sufficiently large supercells, which is less problematic here than in the Bloch wave method discussed previously.

applied to the Dirac equation (Greiner (1981)):

$$V(\vec{r}) = \sum_{\vec{G}} \tilde{V}(\vec{G}, z) e^{i\vec{G}\vec{R}}$$
(3.47)

$$\vec{A}(\vec{r}) = \sum_{\vec{G}} \vec{A}\left(\vec{G}, z\right) e^{i\vec{G}\vec{R}}$$
(3.48)

$$\psi\left(\vec{r}\right) = \sum_{\vec{G}} \tilde{\psi}\left(\vec{G} - \vec{K}_{0}, z\right) e^{i\left(\vec{G} - \vec{K}_{0}\right)\vec{R}}.$$
(3.49)

In the next step, for the sake of simplicity, we set the incident beam direction  $\vec{K}_0$  to zero, use the Lorentz gauge for the electromagnetic potentials and insert the expressions (3.47), (3.48) and (3.49) in equation (3.33) to get

$$E\tilde{\psi}(\vec{G},z) = \left[\hbar c\vec{\alpha}_{\vec{R}} \cdot \vec{G} - c\vec{\alpha} \cdot \vec{A}\left(\vec{G},z\right) \otimes -i\hbar c\alpha_{z}\frac{\partial}{\partial z} + mc^{2}\beta + \tilde{V}\left(\vec{G},z\right) \otimes\right]\tilde{\psi}(\vec{G},z), \qquad (3.50)$$

since the coefficients of every plane wave must be equal on each side of (3.50).  $\otimes$  denotes a convolution with the wave function outside of the brackets. Multiplying with  $i\alpha_z/(\hbar c)$  and using  $\alpha_z^2 = -1$ , equation (3.50) can now be transformed to

$$\frac{\partial \tilde{\psi}(\vec{G},z)}{\partial z} = i\boldsymbol{\alpha}_z \left( \tilde{\boldsymbol{\alpha}}_{\vec{R}} \cdot \left( \vec{G} - \frac{1}{\hbar} \vec{\tilde{A}}_{\vec{R}} \left( \vec{G}, z \right) \otimes \right) - \frac{1}{\hbar} \boldsymbol{\alpha}_z \cdot \tilde{A}_z \left( \vec{G}, z \right) \otimes + \frac{mc\boldsymbol{\beta}}{\hbar} - \frac{E}{c\hbar} + \frac{1}{c\hbar} \tilde{V} \left( \vec{G}, z \right) \otimes \right) \tilde{\psi}(\vec{G},z) \,. \tag{3.51}$$

These are four coupled ordinary differential equations of the first order, which can be solved numerically, providing the boundary conditions, i.e. the possibly spin-polarized plane wave at the entrance face of the crystal. The approach outlined above for casting the Dirac equation into a set of coupled ordinary differential equations can be used in the same manner for the Klein-Gordon case. Again, one makes use of the expansions (3.47), (3.48) and (3.49), being aware that the wave function  $\Psi(\vec{r})$  is now a scalar one, and inserts them into the Klein-Gordon equation (3.37). Performing the same steps like in the Dirac case, one gets

$$\begin{bmatrix} -c^{2}\hbar^{2}\frac{\partial^{2}}{\partial z^{2}} - 2ic^{2}\hbar A_{z}\left(\vec{G},z\right)\otimes\frac{\partial}{\partial z}\end{bmatrix}\tilde{\psi}(\vec{G},z) = \begin{bmatrix} E^{2} - 2E\tilde{V}\left(\vec{G},z\right)\otimes+\tilde{V}^{2}\left(\vec{G},z\right)\otimes-c^{2}\tilde{A}_{z}^{2}\left(\vec{G},z\right)\otimes\\ & - c^{2}\hbar^{2}\left(\vec{G}-\frac{1}{\hbar}\vec{A}_{\vec{R}}\left(\vec{G},z\right)\right)^{2}\otimes-m^{2}c^{4}\end{bmatrix}\tilde{\psi}(\vec{G},z), \quad (3.52)$$

which is again a set of ordinary coupled hyperbolic differential equations, this time of the second order. One can, however, reduce the order to the first by doubling the number of equations. These equations can be solved by providing the boundary conditions at the entrance face, using standard numerical algorithms (e.g. Runge-Kutta). The two relativistic formulations (3.51) and (3.52) solely rely on the forward scattering approximation, thus providing a reference solution for more stringent approximations, developed in the next section.

To illustrate the properties of the forward scattering solution and the ideas standing behind further approximations, it is useful to illustrate the scattering of a 200 kV electron scattered on a single gold atom (Fig. 3.5).



Figure 3.5: Amplitude (a) and phase (b) of a 200 kV electron wave scattered on a single gold atom at z = 0.5 nm (indicated by white dot) calculated with the forward scattering algorithm. The phase shows a sharp increase at the atom position and is subsequently smeared out, the increase in the amplitude is not as abrupt and delayed with respect to the phase. A linescan of amplitude and phase at y = 0.25 nm is shown in (c).

It can be observed that the scattering cone of the wave behind the atom has an opening angle of approximately

#### 3.2. ELASTIC SCATTERING THEORY

60 mrad. Furthermore, amplitude and phase show a different behavior close to the atomic potential: The phase is sharply increased in the region of the atomic scattering potential, whereas the amplitude is delayed reaching its maximum several Ångström behind the atom position. Both observations will be used in the next section to simplify the relativistic differential equations (3.51) and (3.52) in order to facilitate a more convenient and fast solution. The sharp increase of the phase at the atom potential also illustrates another drawback of the Bloch wave solution discussed in the previous section: The large number of Fourier components, i.e. Bloch waves, required to sample this step, usually cannot be calculated in order to keep the eigenvalue problem sufficiently small. This drawback is not important, when considering planes well behind the atom, e.g. an object exit plane. However, when considering inelastic core-loss processes, where the exact shape of the elastic wave function at the atom position is important, it might be necessary to discard the Bloch wave method in favor of other methods correctly describing the abrupt change of the wave function.

In a second example, the scattering of spin-down  $\Psi_{\downarrow}$  and spin-up  $\Psi_{\uparrow}$  electrons on strong magnetic fields present in a deliberately chosen ferromagnetic material  $\alpha$ -Fe (Im3m, a = 2.87Å) is calculated to analyze the role of the spin in the scattering of fast electrons at strong local magnetic fields  $\vec{B}$ . The major part of the magnetic field within  $\alpha$ -Fe is produced by the spin current density  $\vec{j}_s$  of the partially filled d-shells. The splitting of the total current density  $\vec{j}$  into a convectional and a spin part generally holds due to the Gordon transformation applied to the Dirac equation (Greiner (1981)). In the non-relativistic regime valid for the iron *d*-shell states, the spin part dominates and reads

$$\vec{j}_{s} = \frac{e\hbar}{2m} \vec{\nabla} \times \Psi^{\dagger} \vec{\sigma} \Psi \qquad (3.53)$$

$$= \frac{e\hbar}{2m} \vec{\nabla} \times \Psi^{\dagger}_{\uparrow} \Psi_{\uparrow} - \Psi^{\dagger}_{\downarrow} \Psi_{\downarrow}$$

$$= \frac{e\hbar}{2m} \begin{pmatrix} \frac{\partial}{\partial y} \left(\rho_{\uparrow} - \rho_{\downarrow}\right) \\ -\frac{\partial}{\partial x} \left(\rho_{\uparrow} - \rho_{\downarrow}\right) \\ 0 \end{pmatrix}.$$

The transformations assume that the electrons are polarized along a certain axis, i.e. along the optical axis in the microscope, rendering the calculation of the current density from the difference in the spin densities feasible. The spin densities of  $\alpha$ -Fe are calculated with FPLO, an all-electron full-potential local-orbital implementation of Density Functional Theory (Koepernik and Eschrig (1999); Eschrig et al. (2004), also see Chap. 4). The laws of magnetostatics give the connection of the current density and the vector potential or the magnetic field.

$$\begin{aligned} \Delta \vec{A} &= \vec{j}_s \\ \vec{B} &= \operatorname{rot} \vec{A} \end{aligned} \tag{3.54}$$

The solution of the expression (3.54) separates into the homogeneous part determined by the boundary conditions and the particular solution. The homogeneous solution is a wedge representing the macroscopic magnetic polarization of the sample. The macroscopic polarization of  $\alpha$ -Fe saturates at 1.7 T (Kittel (1999)), thus can be safely neglected in comparison to the magnetic fields within the unit cell stemming from the particular solution (Fig. 3.6). When imaging large areas of the sample using medium resolution electron microscopy, the



Figure 3.6: Magnetic field B in z-direction at iron position. The local magnetic field can reach several hundred Tesla.

enclosed magnetic flux produced by the macroscopic fields grows large enough to produce a significant signal, though. The vector potential  $\vec{A}$  calculated from (3.54) is now inserted into (3.51). Two spin polarized beams were separately calculated by preparing the starting spinors accordingly. Fig. 3.7 shows the differences between

the two differently polarized object exit waves. The relative difference is not visible with the bare eye and stays below 0.1 %, indicating that the magnetic field does not couple to the spin of the wave on a microscopic length scale. This result indicates again, that the electron spin can be neglected, when considering small-angle elastic



Figure 3.7: [00] beam (a) and [0,14] beam (b) of electron waves scattered on iron. Acceleration voltage 300 kV, sampling rate 128x128x128. The differences between spin up and spin down are negligible.

scattering, which is in agreement with the behavior of inelastic scattering discussed in the introduction of this chapter.

# 3.2.4 Relativistic multislice

Although being solvable, the equations (3.51), (3.52) and (3.52) without  $V^2$  are of limited applicability, since they need large computer power for the solution of a typical problem in high-resolution image simulation. One therefore applies further approximations to the solution of the relativistic equations within the forward scattering approximation, finally ending at an algorithm very similar to the multislice (MS) algorithm presently used in scattering simulations (e.g. Kirkland (1998)). We start with the Dirac equation (3.36) and rewrite it by separating the incident plane wave  $\mathbf{u}e^{ik_0z}$  in the following ansatz  $\psi(\vec{r}) = \varphi(\vec{r}) \mathbf{u}e^{ik_0z}$ 

$$0 = \left[2EV - V^2 + c^2\hbar^2\Delta_{\vec{R}} - 2ic^2\hbar\vec{A}_{\vec{R}} \cdot \vec{\nabla R} - c^2\vec{A}^2 + c^2\hbar^2\frac{\partial^2}{\partial z^2} + 2ic^2\hbar^2k_0\frac{\partial}{\partial z} + 2ic^2\hbar A_z\frac{\partial}{\partial z} - c^2\hbar k_0A_z - ie\hbar c\vec{E}\cdot\tilde{\alpha} - e\hbar c^2\vec{B}\cdot\tilde{\sigma}\right]\varphi(\vec{R},z)\mathbf{u}.$$
(3.55)

Given a large acceleration voltage,  $k_0$  becomes large and one can make the assumptions that  $\partial^2 \varphi / \partial z^2 \ll k_{0z} \partial \varphi / \partial z$  and  $A_z \frac{\partial}{\partial z} \ll k_0 A_z$ . Consequently, the two small terms can be omitted. This is equivalent to assuming that the incident wave is mainly scattered into a small angle around the incident direction and hence, the approximation is called small angle approximation (e.g. Reimer (1989)). Again, one can not prove the correctness of this assumption at this stage, since this proof would require the knowledge of the exact  $\psi(\vec{r})$  as a solution of (3.55). Therefore, scattering simulations based on the exact expressions (3.51), (3.52) and (3.52) without  $V^2$  are performed and compared to simulations based on the solution of (3.55) in the forward scattering approximation. If they agree, the small angle scattering approximation holds. Neglecting  $\partial^2 / \partial z^2$  and  $A_z \frac{\partial}{\partial z}$ , after some rearrangements

$$\frac{\partial}{\partial z}\varphi(\vec{R},z)\mathbf{u} = \frac{i\left[2EV - V^2 - c^2\vec{A}^2 + c^2\hbar^2\Delta_{\vec{R}} - 2ic^2\hbar\vec{A}_{\vec{R}}\cdot\vec{\bigtriangledown}_{\vec{R}} - 2c^2\hbar k_0A_z - ie\hbar c\vec{E}\cdot\vec{\alpha} - e\hbar c^2\vec{B}\cdot\vec{\sigma}\right]}{2c^2\hbar^2k_{0z}}\varphi(\vec{R},z)\mathbf{u}$$
(3.56)

is obtained. It is interesting to note that this differential equation is a similar structure like a time-dependent Schrödinger equation in 2 spatial dimensions (x, y) with the z-coordinate assuming the role of the time coordinate. <sup>13</sup> The solution of the now parabolic differential equation (3.56) can be formally written as

$$\varphi(\vec{R}, z + \Delta z)$$

$$= \hat{T}_{z} e^{\frac{i\int_{z}^{z+\Delta z} \left[2EV - V^{2} - c^{2}\vec{A}^{2} + c^{2}\hbar^{2}\Delta_{\vec{R}} - 2ic^{2}\hbar\vec{A}_{\vec{R}} \cdot \vec{\nabla}_{\vec{R}} - 2c^{2}\hbar k_{0}A_{z} - ie\hbar c\vec{E} \cdot \vec{\alpha} - e\hbar c^{2}\vec{B} \cdot \vec{\sigma}\right] dz'}}{2c^{2}\hbar^{2}k_{0z}} \varphi(\vec{R}, z) ,$$
(3.57)

by using the z-ordering operator  $\hat{T}_z$ . If the exponent in (3.57) is sufficiently small, the different operators in the exponent can be separated according to the Baker-Campbell-Hausdorff formula  $e^{\epsilon(\hat{A}+\hat{B})} = e^{\epsilon \hat{A}} e^{\epsilon \hat{B}} e^{\mathcal{O}(\epsilon^2)} (\hat{A})$ 

 $<sup>^{13}</sup>$ An analytical solution by a product ansatz is, however, prevented by the z-dependence of the scattering potentials.

and  $\hat{B}$  denote arbitrary operators) (Kirkland (1998)). To assure the smallness of the exponent, the intervals  $\Delta z$  have to be determined accordingly. Furthermore, the smallness of  $\Delta z$  makes the differential operators in the exponent approximately independent from the z-coordinate, hence the z-ordering operator  $\hat{T}_z$  can be dropped. Finally, if we make use of Bloch's theorem again and assume that  $\vec{A}_{\vec{R}}$  is constant over the region  $\vec{R}$ , the Laplace and the Nabla operator can be evaluated in Fourier space. We end up with the following expression for (3.57):

$$\varphi(\vec{R}, z + \Delta z) \approx \mathcal{F}^{-1}$$

$$\begin{cases} e^{\frac{i\Delta z \left(\hbar^2 \vec{G}^2 + 2\hbar \vec{A}_{\vec{R}} \cdot \vec{G}\right)}{2\hbar^2 k_0}} \\ \mathcal{F}\left\{e^{\frac{i\int_z^{z + \Delta z} 2EV - V^2 - c^2 \vec{A}^2 - 2c^2 \hbar k_0 A_z dz'}{2c^2 \hbar^2 k_0}} e^{\frac{i\int_z^{z + \Delta z} e\hbar c \vec{\alpha} \cdot \vec{E} + e\hbar c^2 \vec{\sigma} \vec{B} dz'}{2c^2 \hbar^2 k_0}} \varphi(R, z)\right\} \right\}.$$

$$(3.58)$$

One can interpret it as a numerical integration of the small angle approximation (3.56) of the Dirac equation with a predefined step size: A short first step contains only the influence of the scattering potentials on the initial wave function  $\varphi^{14}$ , whereas the second, larger, step  $\Delta z$  is a Fresnel propagator describing the propagation. In other words, in a small slice containing the atomic potential, both the Laplace and the Nabla operators are small compared to the potential terms, hence can be neglected, whereas in the space between the atoms, the potential term can be safely neglected. The second exponential term applied to the wave function  $\varphi$  is therefore, according to the normal convention, called transmission function tf. For the same reasons, the third exponential term is called propagator function pf. The first term applied to the wave function has no counterpart in the standard scalar relativistic formalism, it solely arises from the spinor nature of the wave function. It couples the different spinor components under the influence of electromagnetic fields. If electromagnetic fields occurring inside the specimen are sufficiently small, equation (3.58) can be approximated as

$$\varphi(R, z + \Delta z)$$

$$= \mathcal{F}^{-1} \left\{ e^{\frac{i\Delta z \left( \hbar^2 \vec{G}^2 + 2\hbar \vec{A}_{\vec{R}} \cdot \vec{G} \right)}{2c^2 \hbar^2 k_0}} \mathcal{F} \left\{ e^{\frac{i\int 2EV - V^2 - c^2 \vec{A}^2 - 2c^2 \hbar k_0 A_z dz'}{2c^2 \hbar^2 k_0}} \varphi(R, z) \right\} \right\},$$
(3.59)

which would have occurred in the same way, if we had originally started with the Klein-Gordon equation and made the same derivations leading to (3.58). By neglecting  $V^2$  and  $\vec{A}^2$ , the standard MS algorithm would be obtained, which is abbreviated by defining the so-called interaction constant

$$\sigma = \frac{E}{c^2 \hbar^2 k_0} \tag{3.60}$$

and consequently

$$tf = \exp\left(i\sigma \int V dz\right) = \exp\left(i\sigma V_{proj}\right) \exp\left(i/\hbar A_{z,proj}\right) , \qquad (3.61)$$

where  $V_{proj}$  and  $A_{z,proj}$  have been introduced for the potentials projected along z. If the thickness of the specimen is sufficiently thin, the propagation function can be approximated by  $\delta\left(\vec{R}\right)$ , hence the convolution operation with the propagator can be neglected. This approximation is referred to as Phase Grating Approximation (PGA). The successive application of the previous single numerical integration steps, i.e.

$$\varphi\left(\vec{R}, z_f\right) = \left\{\prod_n \mathrm{pf}_n\left(\vec{R}\right) \otimes \mathrm{tf}_n\left(\vec{R}\right)\right\} \varphi\left(\vec{R}, z_i\right) , \qquad (3.62)$$

is referred to as Multislice (MS) algorithm, illustrated in Fig. 3.8. The algorithm works particularly fast by performing the convolution with the help of the Fast Fourier Transformation.

The scattering of a plane wave at a single gold atom as calculated by the MS algorithm is depicted in Fig. 3.9. In contrast to the Bloch wave solution with a limited number of Bloch waves and in good agreement with the more accurate forward scattering solution, the sharp increase of the phase in the vicinity of the atom core is obtained. After a short propagation distance, the amplitude increases as well, however, in contrast to the forward scattering solution, there is no wavy structure of both amplitude and phase in z-direction visible and the scattering into large angles comes out different due to the small angle scattering approximation.

<sup>&</sup>lt;sup>14</sup>The accuracy of the numerical integration does actually not depend significantly on the integral boundaries since the atomic potentials are confined to a small region. The originally short first step can be therefore extended to the whole slice  $\Delta z$ .



Figure 3.8: Scheme of the Multislice algorithm.



Figure 3.9: Amplitude (a) and phase (b) of a 200 kV electron wave scattered on a single gold atom calculated with the multislice algorithm (sampling rate: 128x128x128). The phase depicted shows a sharp increase at the atom position and is subsequently smeared out; the increase in the amplitude is not as abrupt and delayed with respect to the phase. The line scans depicted in (c) show amplitude and phase calculated with both the forward scattering formalism (see Fig. 3.5) and the multislice algorithm at y = 0.25 nm.

For all the algorithms derived above, numerical scattering simulations on different crystal lattices have been performed, namely Au (Fm3m, a = 4.038 Å) and GaAs ( $F\overline{4}3m$ , a = 5.65 Å). To show the explicit influence of the different expressions, no other contributions, e.g. those of the microscope or thermal movement of the atoms, have been incorporated. It should be noted, however, that if in particular the thermal motion of the atoms is incorporated, the results change significantly (see Sec. 3.2.7). In all simulations, scattering potentials in the parametrization according to Weickenmeier and Kohl (1991),  $300 \,\mathrm{kV}$  acceleration voltage and a  $128 \times 128 \times 128$ sampling of the respective unit cell have been used. To investigate the differences between fully relativistic and scalar relativistic scattering, a comparison between the Dirac, Klein-Gordon and approximated Klein-Gordon equation in the forward scattering formalism as developed in Sec. 3.2.3 is conducted. In Fig 3.10 the modulus of an object exit wave of Au is depicted. The difference between object exit waves calculated by different relativistic formalisms can hardly be inspected visually from the real space images. It is, however, conveniently illustrated in the Fourier-transforms of the object exit waves by measuring the amplitude of certain plane wave components, referred to as beams. In Fig 3.11 two different beams are depicted, the first one being the zero beam and the second one being a large angle scattering component taken from the first order Laue zone. There is no difference within the numerical accuracy between the Dirac and the Klein-Gordon simulations, which demonstrates that spin effects are negligible. The neglecting of  $V^2$  shows a very small influence below 0.1 % in the high order reflexion. The difference is larger in the case of Au than in the GaAs, due to the stronger scattering potential of Au, however, it is still small compared to other approximations previously mentioned, like the neglecting of inelastic scattering.

Now, the difference between the MS algorithm and the numerical forward scattering is analyzed. The difference is again illustrated by comparing the two previously used beams in Fourier-space. From Fig. 3.11



Figure 3.10: Modulus of object exit wave of Au after propagation through 25 unit cells calculated by means of the MS algorithm. Acceleration voltage 300 kV, sampling rate 128x128x128.



Figure 3.11: Comparison of [00] beam (a,c), [0,28] beam (b) and [5,21] beam (d) of electron waves scattered on Au (a,b) and GaAs (c,d) calculated from Dirac-, Klein-Gordon-, and approximated Klein-Gordon equation. Acceleration voltage 300 kV, sampling rate 128x128x128.

one can see that the difference in the small angle scattering (zero beam) remains small contrary to large angle scattering in the first order Laue zone. Again, the effect is larger in the case of the Au specimen, since more electrons are scattered into large angles. This difference follows from the small angle approximation needed to derive the MS formalism, which is not valid for the scattering angles in the first order Laue zone.

The results derived up to this stage are calculated for small specimen thicknesses as used for high-resolution imaging and holography. A large number of interesting and important results within Electron Holography are, however, obtained at medium resolution employing specimen thickness from several ten to several hundred nanometers. The main focus of these investigations is the determination of averaged electromagnetic potentials as discussed in the introduction of this thesis. A direct interpretation of the scattered waves is typically hampered by the complicated nature of multiple scattering illustrated in Fig. 3.12. The situation simplifies at dedicated imaging conditions, i.e. imaging of light and / or thin materials tilted away from a low-index zone axis (Formanek and Bugiel (2006)). The next section is dedicated to the calculation of elastic scattering as observed in medium resolution off-axis holography.



Figure 3.12: Diagram illustrating dynamical scattering. The arrows denote different scattering angles occurring at the scattering centers (atoms). Scattering at subsequent atoms leads to zero beam contributions incorporating an elongation of the optical path due to non-zero intermediate scattering angles (red arrows). The black arrows denote non-zero final scattering angles. The coordinate system with the z-axis pointing along the beam direction will be used throughout the paper.

## 3.2.5 Medium resolution off-axis holography

Numerous investigations using various methods have been conducted in the past to accurately determine the average electrostatic potential (AEP) or mean inner potential (MIP)

$$\overline{V} = 1/\Omega \int_{\Omega} V\left(\vec{r}\right) \mathrm{d}^{3}r \,, \tag{3.63}$$

or the corresponding magnetic counterpart

$$\overline{A}_{z} = 1/\Omega \int_{\Omega} A_{z}\left(\vec{r}\right) \mathrm{d}^{3}r \tag{3.64}$$

of a certain volume  $\Omega$  spanned by an area S and a thickness t ( $\Omega = S \times t$ ) in different materials (e.g. Kruse et al. (2003), Gajdardziska-Josifovska et al. (1993), Möllenstedt and Keller (1957), Kasama et al. (2006), Bromwich et al. (2005)).<sup>15</sup> It has been shown in Sec. 3.2.3 that scattering on magnetic fields in solids is usually several orders of magnitudes weaker than the deflections produced by electrostatic fields. Furthermore, variations of magnetic fields on the nanoscale are not visible by the scattered electron. Therefore, the magnetic field will be treated as a perturbation of the electrostatic field in this section. Medium resolution off-axis Electron Holography proved to be particularly useful, if the following rather simple relationship between the reconstructed wave  $\psi$ , which is approximately equivalent to the zero component in Fourier space  $\vec{K}$ , and  $\overline{V}$  is fulfilled:

$$1/S \int_{S} \psi\left(\vec{R}\right) d^{2}R \approx \psi\left(\vec{K}=0\right)$$

$$= |\psi_{0}| e^{i\sigma \overline{V}t}.$$
(3.65)

The normalization factor 1/S results from the convention used for the 2D Fourier transformation within a finite area S and t denotes the thickness of the sample. The size of the averaging area S in (3.65) determines the coarsening, i.e. experimentally the resolution, of the wave function. The approximation introduced in (3.65) becomes exact, if perfect crystals are considered and S equals one face of the unit cell. In the case of inhomogeneous materials, one would get coarsened waves, which depend on the position of S (similar to the AEP). The restriction to perfect crystals is therefore equivalent to concentrating on one spatially resolved element in the reconstructed medium resolution wave. A derivation of (3.65) from the basic equations governing the elastic electron scattering, however, is restricted to approximations, e.g. the semiclassic approximation (Kasper and Hawkes (1995)) or the Phase Grating Approximation (PGA, see Sec. 3.2.4), which are often violated to some extent (see previous sections). Accurate MIP measurements therefore incorporated dynamical scattering simulations to take those effects into account (e.g. Kruse et al. (2003); Gajdardziska-Josifovska et al. (1993)).

The deviations of (3.65) from the measured phase can be roughly divided into two categories depending on the sample properties:

1. If the sample is sufficiently thin, the scattered wave can be described by the PGA

$$\psi\left(\vec{R}\right) = e^{i\sigma\int_{t} V\left(\vec{R}, z\right) \mathrm{d}z}, \qquad (3.66)$$

<sup>&</sup>lt;sup>15</sup>The AEP (AMP) can be regarded as a coarsened (or macroscopic) potential, which depends only on the position of the integration volume  $\Omega$ . By dividing the spatial domain into several subvolumes  $\Omega$ , an arbitrary electrostatic potential  $V(\vec{r})$  can be characterized by position dependent AEPs. If one considers a perfect crystal and chooses one unit cell as the integration volume  $\Omega$ , the AEP becomes a constant measure independent from the center point of  $\Omega$ , which corresponds to the first term in the Fourier series expansion and is usually referred to as Mean Inner Potential (MIP, Bethe (1928)). The investigations in this work concentrate on perfect crystals in order to simplify the notation.

i.e. the wavefront is modulated by the potential  $\int_t V\left(\vec{R}, z\right) dz$  projected along the beam direction z, whereas the amplitude remains unchanged. This approximation is restricted to thin objects because the modulations of wave due to interference of e.g. waves scattered at different atoms are neglected. The zero beam of such a wave reads

$$\frac{1}{S} \int_{S} \psi\left(\vec{R}\right) \mathrm{d}^{2}R$$

$$= \frac{1}{S} \int_{S} e^{i\sigma \int_{t} V\left(\vec{R}, z\right) \mathrm{d}z} \mathrm{d}^{2}R \,.$$
(3.67)

If additionally the object is a weak phase object (3.67), it can further be approximated by a Taylor expansion of the exponential function as

$$\frac{1}{S} \int_{S} e^{i\sigma \int_{\Delta z} V(R,z) dz} d^{2}R$$

$$\approx 1 + \frac{i\sigma}{S} \int_{S} \int_{\Delta z} V\left(\vec{R}, z\right) dz \qquad (3.68)$$

$$\approx e^{i\sigma \overline{V}t}.$$

The same approximation holds, if the projected potential does not depend on  $\vec{R}$  within the region S, i.e. it is homogeneous over the area S of the reconstructed wave:

$$\int V\left(\vec{R}, z\right) dz \approx \int V\left(z\right) dz$$
(3.69)

$$\frac{1}{S} \int_{S} e^{i\sigma \int_{t} V\left(\vec{R}, z\right) \mathrm{d}z} \mathrm{d}^{2}R \approx e^{i\sigma \overline{V}t} \,. \tag{3.70}$$

It is now useful to introduce the quotient  $r_{dyn}$  between the phase of the zero beam and the MIP  $\overline{V}$  multiplied with the interaction constant  $\sigma$  and the thickness t

$$r_{dyn} = \arg\left(\frac{1}{S} \int_{S} e^{i\sigma \int_{t} V\left(\vec{R}, z\right) \mathrm{d}z} d^{2}R\right) / \sigma \overline{V}t \,, \tag{3.71}$$

which measures the deviations of the measured phase from the value expected from the MIP and which is well defined even in the limit of infinitely large integration volumes  $\Omega$ . One can conclude that in thin samples the simple relationship (3.65) is rather well fulfilled ( $r_{dyn} = 1$ ), if the object is either a weak phase object or thick enough to provide a homogeneous projected potential. The latter condition leads, however, to the breakdown of the PGA, because the interference effects introduced by the propagation of the electron wave cannot be ignored anymore. Therefore, thick objects have to be considered in a second category.

2. In a sufficiently thick sample, the PGA is violated, i.e. the propagation of the wave within the sample has to be considered. The equations describing the scattering become more involved (see previous sections), e.g. the Multislice (MS) method consists of slice-wise propagation and modulation by the potential V of the initial wave function  $\psi\left(\vec{R}, z_i\right)$ . The complicated alternating application of transmission and propagation functions along the beam direction z makes an analytical analysis of the deviations of the zero beam phase from the MIP predicted by (3.65) difficult: perturbation theory yields (see App. A.4) that, if a small part of the potential  $V_s$  <sup>16</sup>can be separated from the total scattering potential V, equation (3.65) may possibly hold for  $V_s$ , i.e.

$$\psi\left(\vec{R}\right) = \psi'\left(\vec{R}\right)e^{i\sigma\int_{t}V_{s}\left(\vec{R},z\right)\mathrm{d}z},\qquad(3.72)$$

regardless of its failure for the whole scattering process, i.e.

$$\psi'\left(\vec{R}\right) \neq |\psi'_0| e^{i\sigma \int_t \left(V\left(\vec{R},z\right) - V_s\left(\vec{R},z\right)\right) \mathrm{d}z} .$$
(3.73)

In case of a sufficiently homogeneous  $V_s$  the zero beam of (3.72) reads

$$\psi_0 = e^{i\sigma \int_t \overline{V}_s\left(\vec{R}, z\right) dz} \frac{1}{S} \int_S \psi'\left(\vec{R}\right) d^2 R.$$
(3.74)

This relationship allows the measurement of  $V_s$  under dynamical scattering conditions, i.e. moderate tilt angles with respect to low-index zone axis; therefore it is frequently exploited when investigating materials with functional potentials, like pn-junctions, which are usually much weaker than the electrostatic potentials of the atomic constituents (e.g. the MIP) and homogeneous with respect to the resolution of the microscope (Formanek and Bugiel (2006)). Additionally, a rather rough approximation is proposed, which is applicable to amorphous or sufficiently out-of-zone-axis oriented crystals, i.e. materials with a structure, which appears randomized in

<sup>&</sup>lt;sup>16</sup>That can be either an electrostatic potential or the z-component of the magnetic vector potential.

projection. This approach is based on a configurational average denoted by  $\langle \rangle$  of the reconstructed zero beam over completely randomized lattice configurations, i.e.

$$\frac{1}{S} \int_{S} \Psi\left(\vec{R}, z_{N}\right) d^{2}R$$

$$= \frac{1}{S} \int_{S} \left\langle \prod_{n=1}^{N} \mathrm{pf_{n}} \otimes \mathrm{tf_{n}} \Psi\left(z_{0}\right) \right\rangle d^{2}R$$

$$= \frac{1}{S} \int_{S} \prod_{n=1}^{N} \mathrm{pf_{n}} \otimes \left\langle \mathrm{tf_{n}} \right\rangle \Psi\left(z_{0}\right) d^{2}R$$

$$= \prod_{n=1}^{N} \left\langle \mathrm{tf_{n}} \right\rangle.$$
(3.75)

In the second transformation, a homogeneous distribution of the atom positions (denoted by  $R_m$ ) in slice n

$$\langle \mathrm{tf}_{\mathrm{n}} \rangle = \prod_{m} \int e^{i\sigma \int_{z_{n-1}}^{z_{n}} V_{m} \left(\vec{R} - \vec{R}_{m}, z\right) dz} \mathrm{d}^{2} R_{m}$$

$$= \prod_{m} \int e^{i\sigma \int_{z_{n-1}}^{z_{n}} V\left(\vec{R}_{m}, z\right) dz} \mathrm{d}^{2} R_{m}$$

$$= \prod_{m} \mathrm{tf}_{\mathrm{nm}} \left(\vec{K} = 0\right) ,$$

$$(3.76)$$

was inserted, which reduces the propagation function to a unity transformation, if the initial wave  $\Psi(z_0)$  is a plane wave normalized to 1. The zero beam of the single atom transmission functions  $\text{tf}_{nm}\left(\vec{K}=0\right)$  is equivalent to the medium resolution wave obtained from a single atom (see 3.67). Thus, the total medium resolution wave  $\Psi\left(\vec{K}=0,z_N\right)$  obtained in this random object approximation (ROA) is just the product of all single atom waves as obtained from the PGA, i.e.

$$\Psi\left(\vec{K}=0,z_N\right) = \prod_{n,m} \Psi_{nm}^{PGA}\left(\vec{K}=0\right).$$
(3.77)

Since the whole crystal structure has been randomized, each slice n is identical yielding

$$\Psi\left(\vec{K}=0,z_N\right) = \prod_m \left(\Psi_{nm}^{PGA}\left(\vec{K}=0\right)\right)^N \,. \tag{3.78}$$

This expression provides a considerable simplification to the Multislice formula describing fully dynamic scattering (second line of (3.75)) and can be used to quickly estimate the influence of dynamic scattering in medium resolution holographic MIP measurements if the PGA approximation of single atoms is known. The latter is, however, very easy to calculate and a list of all elements in the periodic table will be given below. It will be demonstrated in Sec. 3.2.5.2 that the ROA provides a sufficiently accurate and convenient way of estimating systematic deviations of the zero beam phase from the MIP as expressed by the initial formula (3.65). The ROA (3.75) predicts for instance a constant increase of the phase with growing thickness t (number of slices N) as observed experimentally, i.e.

$$\Psi\left(\vec{K}=0,z_{N}\right) = \prod_{m} \left(\Psi_{m}^{PGA}\left(\vec{K}=0\right)\right)^{N}$$

$$= \prod_{m} |\Psi_{m}|^{N} e^{i\sigma r_{dyn}\overline{V}N(t)}.$$
(3.79)

The correction factor  $r_{dyn}$  for one slice is obtained by a weighted average of atomic correction factors  $r_{dyn,m}$ 

$$r_{dyn} = \frac{1}{\overline{V}} \sum_{m} \overline{V}_m r_{dyn,m}, \tag{3.80}$$

where  $\overline{V}$  is the MIP of the material under consideration and  $\overline{V}_m$  is the AEP of a single atom within one unit cell. The slope of the phase, however, is, due to the correction factor  $r_{dyn} \leq 1$ , decreased with respect to the MIP, which is in good agreement with experimental findings in particular on heavy elements, where dynamical scattering effects are particularly strong (see Tab. 3.2).

In the following, the above expressions will be solved by numerical integration of expression (3.65) and accurate scattering simulations, based on the MS and the forward scattering algorithm, to quantify the approximations leading to (3.65).

#### 3.2.5.1 Single atom measurements

Since the MIP of a single atom is a function of the averaging volume  $\Omega$  (see 3.63), it approaches zero as  $\Omega$  goes to infinity. Likewise, the phase of the zero beam  $\varphi(\vec{K}=0)$  is approaching 0 according to (3.67), if A tends to infinity. The ratio  $r_{dyn}$  is a finite quantity though (see App. A.5), hence can be used to quantify deviations of the zero beam phase from the MIP. For instance, it has been shown above that  $r_{dyn}$  approaches 1 for weak phase objects.

The forward scattering approximation with predefined integration steps as implemented in the MS algorithm is used to evaluate the scattered waves. In Fig. 3.13 the phase calculated by means of MS of both a single Si and a single Au atom is depicted. Contrary to the silicon case, the gold atom cannot be treated as a weak phase object and both potentials do depend on the  $\vec{R}$  coordinate. Therefore, both approximations (3.68), (3.69) of (3.67) lead to a proportionality between the MIP and the measured zero beam phase hence cannot be applied in case of a single gold atom, and consequently also not for atoms with similar core charges. In Fig. 3.15 the ratio



Figure 3.13: Phase shift of object exit wave as produced by scattering on a single silicon and a single gold atom at a distance of 1 Åbehind the atom. Acceleration voltage: 200 kV, sampling: 16/Å, Weickenmeier and Kohl atomic potentials (Weickenmeier and Kohl (1991)).

 $r_{dyn}$  of the zero beam phase to the MIP as defined by (3.71) of the whole periodic table up to the 6th period is shown. As expected from the increasing violation of the weak phase object approximation, the ratio becomes smaller with growing core charge and decreasing acceleration voltage. The smooth transition is interrupted by jumps due to the shell structure of the electronic shell.



Figure 3.14: Ratio  $r_{dyn}$  of phase of the zero beam to MIP multiplied with  $\sigma$  and t for the periodic table of elements with 1 atom per unit cell. Integration volume  $\Omega$ : (1x1x1 nm), acceleration voltage: 200 kV and 300 kV.

#### 3.2.5.2 Zero beam of arbitrary specimens

The investigation of the general behavior of the zero beam for thicker specimen in face of millions of different crystal structures and orientations is complicated. It is therefore useful to apply two different approaches: The first one, i.e. the PGA, can be extrapolated to arbitrary structures. It does, however, not take into account the Fresnel propagation of the electron wave and is therefore only suited to illustrate the behavior of the zero beam at thicknesses up to a couple of monoatomic layers (thickness  $t \in \mathcal{O}(nm)$ ). The second one is based on fully dynamic scattering calculations, properly incorporating the wave propagation and is therefore valid up to large thicknesses. The drawback is that only particular crystal lattices can be considered. Furthermore, the fully dynamic calculations are compared to the ROA derived above to test its validity.

**Zero beam at moderate thickness** To simulate the increase of the thickness t of an out-of-zone axis oriented specimen, a reference lattice with 1x1xt nm spatial extension and a sampling of 128x128x128 was generated

and filled with an increasing number of the same atom species such that the projected atomic density becomes increasingly homogeneous. The zero beam phase is then calculated by means of the PGA. In Fig. 3.15, the ratio of the zero beam phase to the MIP for an increasing number of atoms in the box, corresponding to an increasing thickness t, is depicted. A single atomic layer maximally violates the homogeneity condition for the



Figure 3.15: Ratio  $r_{dyn}$  of phase of the zero beam at 200 kV to MIP multiplied with  $\sigma$  and t for the periodic table of elements with  $1, 4^2, 8^2, 16^2$  and  $32^2$  atoms per unit cell (1x1x1nm)

projected potential (3.69) hence shows the strongest deviation from the MIP. With an increasing number of projected atoms, the homogeneity is restored and the phase approximates the MIP. This behavior serves as a hand-waving argument that out-of-zone-axis conditions are, by increasing the projected homogeneity, important to ensure proportionality of the MIP and the zero beam phase. For arbitrary but sufficiently thin materials, the outcome of (3.67) and in particular the validity of (3.69) can now be calculated from Fig. 3.15 by selecting the graph with a similar projected atomic density and averaging over all atoms in one stoichiometric unit. The estimation of dynamical corrections  $r_{dyn}$  according to the ROA (3.75) proposed for very thick objects is based on the single atom graph: The correction is, according to (3.75), and (3.80) obtained as the arithmetic average of single atomic correction factors, e.g. 0.9925 in the case of Si, 0.963 in the case of PbS and 0.92 in the case of Au.

Zero beam at moderate and large thicknesses The thickness dependent dynamical scattering on thick objects is calculated for both a weakly scattering material Si  $(Fd\overline{3}m, a = 5.431 \text{ Å}, \overline{V} = 13.9 \text{ Weickenmeier and})$ Kohl (1991)) and a strong scatterer Au ( $Fm\overline{3}m$ , a = 4.078 Å,  $\overline{V} = 29.8$  Weickenmeier and Kohl (1991)) tilted around the rotation axis  $\left[-\frac{1+\sqrt{5}}{2}, 1, 0\right]$  into different orientations away from the zone axis [001] (see Fig. 3.16). The orientation of the tilt axis along the Golden Ratio ("most irrational number") ensures a large distance to other low-index zone axes upon rotation. It is pointed out that the MIP values for Si and Au are derived for an assembly of free atoms, hence do not agree with the exact MIP of the real material (see Tab. 3.2). This difference is, however, not important for the following analysis, since we are only interested in the deviations of the measured phase to the input MIP of the calculation due to dynamic effects rather than to the real MIP itself. If neglecting influences of the microscope, which depend on the position of the optical axis like objective lens aberrations, etc., it is in principle not possible to distinguish between a tilted beam and a tilted specimen. Making use of beam tilt in the calculations, however, has the advantage of preserving the periodicity in the xy-plane (see Fig. 3.16) and facilitates the use of a single unit cell within the framework of dynamical scattering simulations used in the following. The computationally demanding numerical forward integration has the advantage of accepting very large beam tilt angles sufficient for our purposes. The numerical forward integration is thus used in combination with tilting the beam. The major drawback of the method is its incompatibility with a proper treatment of the thermal motion of the atoms, because the separate calculation of different lattice configurations and a subsequent averaging is too time consuming and an analytical averaging could not be incorporated into the numerical solver. To properly treat the thermal motion and to check the results obtained by the forward integration, we therefore additionally apply a standard approach, the MS algorithm. The MS algorithm, however, already fails at moderate beam tilt angles larger than 6° (Chen et al. (1997)), thus requiring a rotation of the whole crystal instead of tilting the beam. The rotation in turn destroys the periodicity within the xy-plane, which is a requirement for the MS method. To still obtain sufficiently accurate results, a supercell geometry was set up (see Fig. 3.16), incorporating the tilted crystal for the MS calculations. Although the violation of the periodicity cannot be completely removed due to the limited extension of the supercell, its influence could be reduced. One additionally has to keep in mind that the considered quantity is the zero beam: The dominating influence on the zero beam is the MIP  $\overline{V}$ , hence, when setting up the supercell, one has to ensure that the MIP of the whole supercell equals the MIP of the bulk material. The modified periodicity now shows up as a secondary effect changing the diffracted beams in particular at the boundary of the unit cell. Both simulations provide thickness dependent information by extracting intermediate results at the desired thickness. Both scatterers exhibit a pronounced transition between zone-axis and completely out-of-zone-axis scattering



Figure 3.16: Scattering geometry of the dynamic calculations. The scattering angle and rotation axis are oriented with respect to the diffraction pattern of Au as given by the crystal coordinate system, i.e. the x and y axis of the microscope point along the a and b axis of the crystal, respectively. The MS method is applied to the crystal tilt (ct) and the numerical forward integration to the beam tilt (bt) geometry. The calculated tilt angles  $\alpha$  are tabulated.

conditions, as predicted by scattering theory. The zone-axis waves show the typical oscillations in both amplitude and phase (Fig. 3.17), heavily violating any monotonous thickness dependence like the one predicted by (3.65).



Figure 3.17: Zero beam phase at 0, 10 and 50 mrad according to numerical forward integration for (a) Si and (b) Au at 200 kV acceleration voltage and scattering factors according to Weickenmeier and Kohl (1991). The dynamical effects decrease with increasing tilt angle.

However, eq. (3.65) serves as an upper boundary for the phase of the zero beam in the transition regime between dynamical scattering in zone-axis conditions and kinematic scattering. This behavior can be explained by the elongated optical path of the scattered beams with respect to the zero beam, leading to a retarded phase, which, after being backscattered into the zero beam, is attenuating the latter (see Fig. 3.12). At small tilt angles (10, 50 mrad), the oscillations become smaller in both materials, while the magnitude of the dynamic effects in gold is always larger than in silicon. The oscillations vanish almost completely at a tilt angle of 10° in both silicon and gold, thus marking these angles as out-of-zone axis conditions, which will be discussed in the following. In the case of Si a systematic attenuation of the MS calculated zero beam phase from the projected MIP is observed (Fig. 3.18(a). The attenuation starts at around 13.76 eV ( $r_{dyn} = 0.99$ ) in the very thin region and goes up to the nominal value of 13.9 eV, before it drops again to a value around 13.76 eV ( $r_{dyn} = 0.99$ ). This is in good agreement with both the correction graph calculated with the help of the PGA in the previous section and the expression derived from the ROA (3.75). In case of a strong scatterer like gold, the scattering behavior becomes more involved (Fig. 3.18(b)). Again, at thin regions the behavior is in good agreement with the correction displayed in Fig. 3.14. However, the subsequent maximum is much less pronounced than in the



Figure 3.18: Retrieved MIP from the zero beam phase at tilt of  $5^{\circ}$  (87.3 mrad) and  $10^{\circ}$  (174.5 mrad) according to numerical forward integration (shown in the subimage) and MS (large graph) for (a) Si and (b) Au at 200 kV acceleration voltage and scattering factors according to Weickenmeier and Kohl (1991). The small differences between numerical forward integration and MS are due to the incorporation of thermal motion in MS leading to a phase damping. The nominal MIP of 13.9 V (ROA of 13.8 V) for Si and 29.8 V (ROA of 27.4 V) for Au is depicted as a green dashed line (black dotted line).

Si case, i.e. the input MIP is not attained. Subsequently, the phase drops again to a value which is predicted by the ROA ( $r_{dyn} = 0.92$ ). The reason for not attaining the nominal MIP value at a moderate thickness is the strong dynamical scattering of Au.

#### 3.2.5.3 Comparison to experimental results

MIP measurements on various specimens are reported in literature. Recently, they have been combined with ab-initio calculations similar to those reported in Chap. 4 in order to relate the measured values to effects stemming from chemical bonding, etc. The experimental results are obtained using different microscopes, sample geometries (thin film, cleaved wedge, etc.) prepared by various preparation methods and hence a certain scatter in the reported values is understandable. From the incomplete comparison of reported measurements to ab-initio calculations in Table 3.2, a trend towards underestimating the actual MIP (the ab-initio value), which

mat	$\operatorname{MIP}_{\exp}\left[V\right]$	$\mathrm{MIP_{theo}}\left[\mathrm{V}\right]$	$\Delta V_{dyn}[V]$
C	$10.7^1$ , $8.8^2$	$11.4^{3}$	
Si	$12.5^{4}$	$12.57^{4}$	$0.18^4$
MgO	$13^{5}$		$0.26^{5}$
Ge	$14.3^{6}$	$14.67^{4}$	$0.14^{6}$
GaAs	$14.5^5, 14^7$	$14.19^{14}$	$0.51^{5}$
PbS	$17.2^{5}$		$0.98^{5}$
Cu	$21.2^{8}$	$24.35^{9}$	
Au	$22^{10}, 21.4^{11}$	$30.26^{12}$	

Table 3.2: Extract of experimental and theoretical MIP values. The differences in the dynamical corrections  $\Delta V_{dyn}$  can occur due to different calculation methods (MS, Blochwaves), zone axis, acceleration voltages, etc. <sup>1</sup>Harscher and Lichte (1998), <sup>2</sup>Shindo et al. (2005), <sup>3</sup>Schowalter et al. (2005), <sup>4</sup>Kruse et al. (2006), <sup>5</sup>Gajdardziska-Josifovska et al. (1993), <sup>6</sup>Li et al. (1999), <sup>7</sup>Suk Chung and McCartney (2007), <sup>8</sup>Wang (2003), <sup>9</sup>Rez et al. (1994), <sup>10</sup>Ichikawa et al. (2002), <sup>11</sup>Goswami and Lisgarten (1982), <sup>12</sup>Schowalter et al. (2006).

increases towards stronger scatterers, can be extracted. The reported dynamical corrections  $\Delta V_{dyn}$  calculated by means of the MS or Bloch wave algorithm support this attenuation in the phase and agree well with the approximate correction formula (3.71) derived by configurational averaging.

#### **3.2.6** Other approximations

The scattering formalism presented above is sufficiently accurate and computationally feasible, hence provides the necessary framework to treat the elastic scattering problems occurring within TEM and especially EH. Under more strict circumstances, other approximations, however, are equivalently applicable or even more appropriate. They furthermore provide additional insight to the physics of the scattering problem. Therefore, the first order Born approximation and the semiclassical approximation are briefly mentioned in the following.

- 1. The 1st order Born approximation (FOB) consists of terminating the von-Neumann series expansion of the stationary scattering equation after the first term. It is applicable, if the scattering potential is sufficiently weak in that the higher order terms become small. This criterion is well fulfilled for light atoms, however for heavy atoms and an ensemble of atoms, higher order terms, visible as large amplitudes in the diffracted beams (Kasper and Hawkes (1995)), can be very large. In this sense, one can say that the FOB is applicable, if the object is a weak phase object in the Phase Grating Approximation, i.e.  $\psi = \exp(i\sigma V_{proj}) \approx 1 + i\sigma V_{proj}$ . Electron scattering fulfilling the FOB is referred to as kinematical scattering, whereas all scattering phenomena beyond the FOB are called dynamical scattering (this terminus has already been occasionally used above). It is applied to analyze the scattering on a large class of light materials within TEM in close analogy to XRD, where the FOB is rather well fulfilled for the dipole excitation of the resonant X-ray field coupled to the electron gas (e.g. Landau and Lifshitz (1984)).
- 2. The semiclassical or Wentzel-Kramers-Brillouin (WKB) approximation consists of a series expansion in the exponent of the wave function and is usually terminated at the second order, yielding a first order differential equation for the amplitude and the phase of the wave. The differential equation for the amplitude can be solved with the method of characteristics which are equivalent to the classical particle trajectories. The phase is obtained by integrating the action along the paths. In the words of the Feynman path integral formalism, this would correspond to a reduction of the number of paths to the classically allowed ones. The WKB approximation works well, if the scattering potential change is small on a length scale of one wave length. The condition is met for the electromagnetic fields generated by lenses and deflectors within the microscope, however, it is violated for atomic scattering potentials (Kasper and Hawkes (1995)).

## 3.2.7 Thermal Motion of Lattice

Waves, which have been scattered on an atomic quantity (electrostatic potential V in the case of electrons or electron density  $\rho$  in the case of X-rays) arranged on a thermally oscillating crystal lattice, are not sufficiently described by scattering simulations on a static lattice. The influence of the thermal motion of the atoms must not be neglected, which seems reasonable when keeping in mind that the mean oscillation amplitudes are in the order of pm at room temperature, which is comparable to the extension of the atomic scattering potential (Fig. 3.4). The thermal motion destroys the periodicity of the crystal lattice, historically leading to the fear that lattice reflexions cannot be recorded by means of X-ray diffraction (XRD, see for instance Kittel (1996)). Soon after the successful recording of the first diffraction patterns, P. Debye (Debye (1913)) and I. Waller (Waller (1923)) established a way to treat the effect within the FOB valid for XRD, leading for instance to an exponential damping of the reflexions. In spite of the violation of the FOB in TEM electron scattering, the results obtained within the FOB give a qualitatively correct picture of the occurring effects and will be therefore discussed in Sec. 3.2.7.1. The shortcomings of the FOB are one of the reasons for extensive research activities on the influence of the thermal motion under TEM imaging conditions. The implications of the thermal vibrations on Convergent Beam Electron Diffraction (CBED), e.g. the thermal diffuse background or intensity between Bragg spots uniquely occurring under diffraction conditions, are the topic of the work of Loane et al. (Loane et al. (1991)), installing the frozen lattice formulation. This approximation exploits the large velocity difference between relativistic beam electrons and specimen constituents, virtually "freezing" the lattice vibrations during the passage time of one electron. Consequently, the final image can be calculated by superimposing single electron images elastically scattered on different snapshots of a frozen lattice. It was also shown that correlated thermal motion, i.e. phonons, are responsible for some contrast features, particularly in the so called thermal diffuse background, observed under diffraction conditions (Muller et al. (2001)). The influence of thermal motion in elastic TEM imaging was among others investigated by Cowley and Pogany (Cowley and Pogany (1968)) introducing an absorption potential removing intensities from Bragg beams. G. Möbus and T. Gemming (Möbus et al. (1998); Gemming and Möbus (1999)) conducted an extended frozen lattice study in HREM and Electron Diffraction. The second major research field evolved around the inelastic electron-phonon scattering and its implications on imaging (e.g. (Hall and Hirsch, 1965; Rossouw and Bursill, 1985; Rez, 1993; Omoto et al., 2002; Dinges et al., 1995), see also Sec. 3.3). However, one must not mix up purely elastic scattering on a distributed frozen lattice configurations and inelastic electron-core scattering or phonon excitation due to the coherence loss produced by entanglement with the scatterer states in the case of inelastic scattering (see Sec. 3.3). A realistic electron scattering calculation should incorporate both influences.

The influence of imaging conditions on thermal averaging can be illustrated by a simple example: a pure phase object, e.g. electrons scattered at one atom with interaction constant  $\sigma$  and projected potential  $V_{\text{proj}}$  statistically situated at two different positions  $\vec{R}_1$  and  $\vec{R}_2$  with equal probability. Neglecting any other influences, e.g. aberrations, the following waves would ideally emerge within the PGA

$$\psi_{\{1,2\}}\left(\vec{R}\right) = \frac{1}{\sqrt{2}} \exp\left(i\sigma V_{\text{proj}}\left(\vec{R} - \vec{R}_{\{1,2\}}\right)\right) \,. \tag{3.81}$$

The statistical superposition can be carried out within a density matrix framework

$$\hat{\rho} = \sum_{n=1}^{2} |\psi_n\rangle \langle\psi_n| , \qquad (3.82)$$

with the recorded intensity being the trace of the density matrix  $\hat{\rho}$ . Consequently, the signals recorded in conventional imaging and diffraction read

$$\frac{\left|\psi_{1}\left(\vec{R}\right)\right|^{2} + \left|\psi_{2}\left(\vec{R}\right)\right|^{2}}{2} = 1$$
(3.83)

and

$$\frac{\left|\tilde{\psi}_{1}\left(\vec{K}\right)\right|^{2}+\left|\tilde{\psi}_{2}\left(\vec{K}\right)\right|^{2}}{2}\neq\mathcal{F}\left\{\frac{\left|\psi_{1}\left(\vec{R}\right)\right|^{2}+\left|\psi_{2}\left(\vec{R}\right)\right|^{2}}{2}\right\},$$
(3.84)

respectively. The last inequality illustrates that the non-linear character of the detection leads to different implications of thermal motion. As will be shown subsequently, the by means of off-axis holography (this includes a superposition with a coherent reference plane wave) reconstructed wave can be calculated as

$$\frac{\psi_1\left(\vec{R}\right) + \psi_2\left(\vec{R}\right)}{2} \,. \tag{3.85}$$

The average (3.85) is a complex valued function, with an amplitude lower or equal to 1, in particular in regions  $\vec{R}$ , where the potential is large, i.e.  $V_{\text{proj}}\left(\vec{R}-\vec{R}_{\{1,2\}}\right) \gg 0$ , showing that the impact of heavy atoms on the averaging will be particularly large. The three examples demonstrate that the average over a moving crystal lattice changes according to the imaging conditions prevailing in the experiment.

#### 3.2.7.1 First order Born approximation

The Debye-Waller averaging is obtained within the FOB for elastic semiclassical photon scattering (X-ray scattering) or elastic electron scattering, when the signal is recorded in Fourierspace (diffraction analysis). The recorded intensity  $I\left(\vec{k}\right)$  is proportional to  $|\mathcal{F} \{p(\vec{r})\}|^2$ , with  $p(\vec{r})$  being either the electron density  $\rho(\vec{r})$  in case of X-ray diffraction or the electrostatic potential  $V(\vec{r})$  in the case of electron diffraction.  $p(\vec{r})$  can be written as a superposition of N single atom densities or potentials, i.e.

$$p(\vec{r}) = \sum_{a=1}^{N} p_a \left( \vec{r} - \vec{u}_a \right) \,. \tag{3.86}$$

The oscillations around the atomic equilibrium position is denoted by  $\vec{u}_a$ . Inserting this expression into  $I\left(\vec{k}\right)$  yields

$$I\left(\vec{k}\right) \propto \sum_{a=1}^{N} \sum_{a'=1}^{N} \int \int dr^3 dr'^3 p_a\left(\vec{r}\right) p_{a'}\left(\vec{r'}\right) e^{i\vec{k}\left(\vec{r}-\vec{r'}\right)}.$$
(3.87)

Now, the thermal averaging over different lattices generated by the thermal motions  $\vec{u}_a$  of N atoms is carried out, i.e.

$$\overline{I}\left(\vec{k}\right) \propto \int \mathrm{d}u^{3N} I\left(\vec{k}, \vec{u}_1, ..., \vec{u}_N\right) f\left(\vec{u}_1, ..., \vec{u}_N\right) \,, \tag{3.88}$$

with  $f(\vec{u}_1, ..., \vec{u}_N)$  being the position density of the lattice. The integration of the position density over all but the *i*th and *j*th atomic oscillations

$$\int f(\vec{u}_1, ..., \vec{u}_N) \, du^{3N-6} = f(\vec{u}_i, \vec{u}_j) \tag{3.89}$$

defines the two particle density  $f(\vec{u}_i, \vec{u}_j)$ . By inserting this definition into the equation describing the recorded signal (3.88), one obtains

$$\overline{I}\left(\vec{k}\right) \propto \sum_{a=1}^{N} \sum_{\substack{a'=1\\a'\neq a}}^{N} \int \int dr^{3} dr'^{3} \int \int du_{a}^{3} du_{a'}^{3} f\left(\vec{u}_{a},\vec{u}_{a'}\right) p_{a}\left(\vec{r}-\vec{u}_{a}\right) p_{a'}\left(\vec{r}'-\vec{u}_{a'}\right) e^{i\vec{k}\left(\vec{r}-\vec{r'}\right)} \quad (3.90)$$

$$+ \sum_{a=1}^{N} \int \int dr^{3} dr'^{3} \int du_{a}^{3} f\left(\vec{u}_{a}\right) p_{a}\left(\vec{r}-\vec{u}_{a}\right) p_{a}\left(\vec{r}'-\vec{u}_{a}\right) e^{i\vec{k}\left(\vec{r}-\vec{r'}\right)}.$$
Outside a certain correlation radius  $r_c$  around each atom a, the pair correlation function  $f(\vec{u}_a, \vec{u}_{a'})$  can be safely approximated with  $f(\vec{u}_a, \vec{u}_{a'}) = f(\vec{u}_a) f(\vec{u}_{a'})$ . The collapse of the two particle densities into single particle densities beyond the correlation radius can be used to rewrite the last equation (see App. A.6)

$$\bar{I}\left(\vec{k}\right) \propto \sum_{a=1}^{N} \sum_{a'=1}^{N} \tilde{\bar{p}}_{a}\left(\vec{k}\right) \tilde{\bar{p}}_{a'}^{*}\left(\vec{k}\right)$$

$$+ \sum_{a=1}^{N} \sum_{\substack{a'=1\\a' \neq a, d(a', a) \leq r_{c}}} \left( \tilde{f}_{a,a'}\left(\vec{k}, \vec{k}\right) - \tilde{f}_{a}\left(\vec{k}\right) \tilde{f}_{a'}^{*}\left(\vec{k}\right) \right) \tilde{p}_{a}\left(\vec{k}\right) \tilde{p}_{a'}^{*}\left(\vec{k}\right)$$

$$+ \sum_{a=1}^{N} \left( 1 - \left| \tilde{f}_{a}\left(\vec{k}\right) \right|^{2} \right) \left| \tilde{p}_{a}\left(\vec{k}\right) \right|^{2}.$$
(3.91)

The equations become considerably easier, if the translational symmetry in a periodic crystal lattice  $(N \to \infty)$  can be exploited. Now, the first double sum in (3.91) can be rewritten as (j and j' count the atoms in one unit cell, n and n' count the unit cells)

$$\sum_{n} e^{-i\vec{k}\vec{r}_{n}} \sum_{n'} e^{i\vec{k}\vec{r}_{n'}} \sum_{j} \sum_{j'} \bar{p}_{j}\left(\vec{k}\right) \bar{p}_{j'}^{*}\left(\vec{k}\right) = \sum_{j,j'} \left|\bar{p}\left(\vec{g}\right)\right|^{2} , \qquad (3.92)$$

which is the Debye-Waller averaging, i.e., the recorded signal shows the characteristic  $\delta$ -peaks at reciprocal lattice vectors  $\vec{g}$ , which are dampened due to the thermal averaging. The second sum can be rewritten in a similar manner, yielding

$$\sum_{n} e^{-i\vec{k}\vec{r}_{n}} \sum_{j} \sum_{a' \neq a_{j}, d(a', a_{j}) \leq r_{c}} \left( f_{j,a'}\left(\vec{k}, \vec{k}\right) - f_{j}\left(\vec{k}\right) f_{a'}^{*}\left(\vec{k}\right) \right) p_{j}\left(\vec{k}\right) p_{a'}^{*}\left(\vec{k}\right)$$

$$= \sum_{j} \sum_{a' \neq a_{j}, d(a', a_{j}) \leq r_{c}} \left( f_{j,a'}\left(\vec{g}, \vec{g}\right) - f_{j}\left(\vec{g}\right) f_{a'}^{*}\left(\vec{g}\right) \right) p_{j}\left(\vec{g}\right) p_{a'}^{*}\left(\vec{g}\right)$$

$$(3.93)$$

i.e. it consists again of  $\delta$ -peaks at reciprocal lattice vectors. The third sum

$$\sum_{a} \left( 1 - \left| f_a\left(\vec{k}\right) \right|^2 \right) \left| p_a\left(\vec{k}\right) \right|^2 \tag{3.94}$$

is usually referred to as thermal diffuse scattering (TDS), because it is non-zero at the whole reciprocal space instead of isolated reciprocal lattice vectors. It is centered around the origin of the reciprocal space (zero scattering angle at the experiment). Furthermore, the third term is not dampened exponentially towards large scattering angles and scales with the single atomic scattering power  $|p_a(\vec{k})|^2$  independent from the crystal structure. Thus, large scattering angle measurements such as HAADF always contain the thermal diffuse background as part of the measured signal.<sup>17</sup>An exemplary XRD measurements on a single TiO<sub>2</sub> rutil crystal has been performed to illustrate the shape of the diffuse background (see Fig. 3.19). The XRD measurement was performed at ambient conditions (T = 303 K) using a STADI4 diffraction systemmanual (1997) with Mo-K $\alpha$  radiation ( $\lambda$ Mo-K $\alpha$  = 0.71069 Å) and the rotation axis was chosen such that systematic reflections were avoided. To avoid damage of the detector, the zero beam was blocked by an aperture. The recorded diffraction intensities are depicted in Fig. 3.19. One can readily observe the characteristic attenuation at small scattering angles, which corresponds to the first factor  $\left(1 - \left|f_a(\vec{k})\right|^2\right)$  in (3.94). The atomic form factor  $p_a(\vec{k})$  has a large extension in Fourier space, which correlates to the strong localization of the atomic electron density with

respect to typical thermal displacements at ambient conditions in position space. Thus, the atomic form factor determines the diffraction intensities at large scattering angles  $\theta$ .

Similar results are obtained from electron diffraction measurements, although deviations occur due to the violated FOB and the difference between XRD and electron diffraction atomic form factors. A more accurate consideration of the influence of thermal motion in TEM is achieved by incorporating oscillating atom positions in the MS algorithm derived in Sec. 3.2.4.

### 3.2.7.2 Multislice with thermal motion

To consider the statistical averaging of the actually recorded signal, equation (2.5) has to be evaluated in detail: The electron density is subject to different object structures denoted by p, which in the case of off-axis Electron

 $<sup>1^{7}</sup>$  It is wrong to claim that this background is due to inelastic scattering, since it was calculated from elastic scattering equations. Nevertheless, it will be shown in Sec. 3.3.1 that a very similar behavior at large angles will be produced by a part of the inelastic scattering. The difference between both effects is clearly visible at small scattering angles, where the TDS is dampened towards zero and the inelastic part has a maximum.



Figure 3.19: XRD measurement on a single rutile crystal and fit function to the elastic TDS background. The measurement was performed by T. Leisegang (TU Dresden).

Holography is calculated through

$$\rho\left(\vec{R}, p\right) = 1 + \left|\psi\left(\vec{R}, p\right)\right|^2 + \psi\left(\vec{R}, p\right) e^{-i\vec{K}_0\vec{R}} + \psi^*\left(\vec{R}, p\right) e^{i\vec{K}_0\vec{R}}.$$
(3.95)

The reference wave  $e^{i\vec{K}_0\vec{R}}$  stays unaffected since, being a zero beam, the lattice vibrations are not "seen" by a wave traveling through vacuum. The single electron signals  $\rho\left(\vec{R},p\right)$  are summed up or integrated incoherently over time, i.e. it is the intensities that are summed up, since the electrons do not interfere mutually. The averaging reads (see also 2.5)

$$\overline{\rho}\left(\vec{R}\right) = \int f\left(p\right)\rho\left(\vec{R},p\right)dp \qquad (3.96)$$

$$= 1 + \int f\left(p\right)\left|\psi\left(\vec{R},p\right)\right|^{2}dp$$

$$+ e^{-i\vec{K}_{0}\vec{R}}\int f\left(p\right)\psi\left(\vec{R},p\right)dp + e^{i\vec{K}_{0}\vec{R}}\int f\left(p\right)\psi^{*}\left(\vec{R},p\right)dp,$$

where f(p) is the probability density of the lattice p to occur during exposure time. The averaging process in the conventional image term (second term in the sum) differs substantially from that in the third and fourth term used for reconstructing the wave. From the third term, an averaged wave

$$\overline{\psi}\left(\vec{R}\right) = \int f\left(p\right)\psi\left(\vec{R},p\right)dp \tag{3.97}$$

can be reconstructed, whereas the second term represents an averaged electron density.

In order to perform the averaging over the frozen lattices explicitly, some approximations are introduced to get a handy description. First, it is assumed that the electron shell of one atom is fixed to the nucleus and not separately affected by the thermal motion. Therefore, the parameters to be averaged are the 3D positions of the atoms, i.e.  $p = (\vec{r_1}, \vec{r_2}, ..., \vec{r_n})$ . Since the number of atoms in the investigated specimen area is at least of the order of several ten thousand, an analytical or numerical averaging is not yet routinely applicable. Consequently, the many body distribution  $f(p) = f(\vec{r_1}, \vec{r_2}, ..., \vec{r_n})$  has to be truncated appropriately. In the case of real space imaging, one can assume mutually independent thermal motions of atoms with mutually independent probability densities for each atom position  $f(\vec{r_n})$ , thus neglecting correlated motions like phonons. Then the many body distribution  $f(p) = f(\vec{r_1}, \vec{r_2}, ..., \vec{r_n})$  can be written as a product of single body distributions by  $f(\vec{r_1}, \vec{r_2}, ..., \vec{r_n}) = \prod f(\vec{r_n})$ . In the case of diffraction imaging, however, significant contrast is produced by correlated motion (Muller et al. (2001)), hence a series expansion of  $f(\vec{r_1}, \vec{r_2}, ..., \vec{r_n})$  should stop at two or higher many body distributions, i.e.  $f(\vec{r_1}, \vec{r_2}, ..., \vec{r_n}) = \prod_{i,j \neq i} f(\vec{r_{i,j}})$ . In the following the single body distributions is utilized, although higher order expansions can be readily incorporated. The averaging over the atom positions in the case of the conventional image reads<sup>18</sup>

$$\overline{\rho}\left(\vec{K}\right) = \int \prod_{n} f\left(\vec{r}_{n}\right) \left|\psi\left(\vec{R}, \vec{r}_{1}, ..., \vec{r}_{n}\right)\right|^{2} \mathrm{d}\vec{r}_{n}.$$
(3.98)

<sup>&</sup>lt;sup>18</sup>The corresponding expression for electron diffraction analysis is obtained by replacing the position space coordinate  $\vec{R}$  with the reciprocal space coordinate  $\vec{K}$ .

$$\overline{\psi}\left(\vec{R}\right) = \int \prod_{n} f\left(\vec{r}_{n}\right) \psi\left(\vec{R}, \vec{r}_{1}, ..., \vec{r}_{n}\right) \mathrm{d}\vec{r}_{n} \,. \tag{3.99}$$

The special form of the distribution function  $f(\vec{r}_n)$  has to be determined through calculation of lattice dynamics, e.g. molecular dynamics. In the following it will be shown that the thermal averaging given by (3.98) and (3.99) can be incorporated in the MS algorithm for the calculation of electron scattering. Due to the difference in intensity and reconstructed wave averaging, two substantially different MS algorithms will emerge.

Electron imaging simulations are more complicated in the case of the conventional imaging because the averaging suffers from quadratic terms in (3.98). Consequently, the formalism for the reconstructed wave will be considered first and the extension of it to conventional imaging follows afterward. A convenient description is possible by combining the MS algorithm with the averaging in formula (3.99). The same approach was already followed by J. Cowley (Cowley (1988)), however, the truncation of a series expansion of the exponential function used therein is not sufficient and will therefore be omitted in the following.

One step of the MS algorithm for the approximated Klein-Gordon equation reads (see (3.62))

$$\psi(\vec{R}, z + \Delta z) = \mathcal{F}^{-1}$$

$$\left\{ \exp\left(i / \left(2c\hbar^2 k_0\right) c^2 \hbar^2 \vec{K}^2 \Delta z\right) \right\}$$

$$\mathcal{F}\left\{ \exp\left(i\sigma \int V\left(\vec{R}, z'\right) dz'\right) \Psi(\vec{R}, z) \right\} \right\}.$$
(3.100)

The reconstructed wave averaging is applied to (3.100), i.e.  $\overline{\psi}\left(\vec{R}\right) = \int \prod_{n} f\left(\vec{r}_{n}\right) \psi\left(\vec{R}, \vec{r}_{1}, ..., \vec{r}_{n}\right) dr_{n}$ . Since the only part in expression (3.100) depending on the atom positions is the transmission function of one slice

$$\operatorname{tf}\left(\vec{R}\right) = \exp\left(i\sigma \int V\left(\vec{R}, z'\right) \mathrm{d}z'\right), \qquad (3.101)$$

the averaging is restricted to this part. The transmission function can be written as a product of atomic transmission functions

$$\operatorname{tf}\left(\vec{R}\right) = \prod_{n} \operatorname{tf}_{n}\left(\vec{R}\right) = \prod_{n} \exp\left(i\sigma \int V_{n}\left(\vec{R} - \vec{r}_{n}, z'\right) \mathrm{d}z'\right) \,.$$

Consequently, each of the single atom distributions  $f(\vec{r}_n)$  applies only to one atomic transmission function  $\operatorname{tf}_n\left(\vec{R}\right)$ . This renders an incorporation of the thermal motion of the atoms into electron imaging simulations possible. In a first step, all the necessary atomic transmission functions are calculated and independently averaged by means of

$$\overline{\operatorname{tf}_n\left(\vec{R}\right)} = \int f\left(\vec{r}_n\right) \operatorname{tf}_n\left(\vec{R}\right) \mathrm{d}\vec{r}_n \,. \tag{3.102}$$

Next, all the averaged atomic transmission functions  $\text{tf}_n\left(\vec{R}\right)$  belonging to one slice are multiplied, yielding an averaged transmission function of each slice, which is subsequently used in (3.100). Concerning the thermal motion of the atoms, this represents a MS algorithm for averaged reconstructed wave functions.

However, when describing conventional imaging, the basic object to be considered would be the density matrix  $\hat{\rho}\left(\vec{R},\vec{R'}\right) = \psi\left(\vec{R}\right)\psi^*\left(\vec{R'}\right)$ , providing a convenient way to describe the averaging in the intensity as an averaging over the trace of  $\hat{\rho}$  (see also Wang (1998)). The propagation of the density matrix is calculated exactly along the same lines as the simple wave function, i.e.

$$\hat{\rho}(\vec{R}, \vec{R}', z + \Delta z) = \mathcal{F}^{-1} \left\{ \operatorname{pf}\left(\vec{K}\right) \operatorname{pf}^{*}\left(\vec{K}'\right) \mathcal{F} \left\{ \operatorname{tf}\left(\vec{R}\right) \operatorname{tf}^{*}\left(\vec{R}'\right) \hat{\rho}(\vec{R}, \vec{R}', z) \right\} \right\}.$$
(3.103)

In the image plane only the trace, i.e. diagonal terms  $\vec{R} = \vec{R'}$ , is recorded. Rewriting (3.98) in terms of the density matrix yields

$$\overline{\rho} = \int \prod_{n} f\left(\vec{r}_{n}\right) \hat{\rho}(\tilde{\mathbf{r}}_{n}) \,\mathrm{d}\vec{r}_{n},\tag{3.104}$$

i.e. the averaging is performed in the intensity. The atomic transmission function to be averaged reads

$$\operatorname{tf}_{n}\left(\vec{R}\right)\operatorname{tf}_{n}^{*}\left(\vec{R}'\right) = \exp\left(i\sigma\int V_{n}\left(\vec{R}-\vec{r}_{n},z'\right)\mathrm{d}z'\right)$$

$$\cdot \exp\left(-i\sigma\int V_{n}\left(\vec{R}'-\vec{r}_{n},z'\right)\mathrm{d}z'\right).$$

$$(3.105)$$

Consequently, the averaging for one atomic transmission function will be

$$\overline{\operatorname{tf}_{n}\left(\vec{R}\right)\operatorname{tf}_{n}^{*}\left(\vec{R}'\right)} = \int f\left(\vec{r}_{n}\right)\operatorname{tf}_{n}\left(\vec{R}\right)\operatorname{tf}_{n}^{*}\left(\vec{R}'\right)\mathrm{d}r_{n}.$$
(3.106)

This averaged transmission function can not be separated in two factors anymore, hence has to be multiplied with the density matrix. This demonstrates the crucial point in intensity averaging: It is, like in the case of aberrations not sufficient to average the wave or one atomic transmission function, with subsequently calculating the squared modulus, because

$$\int \int f\left(\vec{r}_{n}\right) f\left(\vec{r}_{n}\right) \operatorname{tf}_{n}\left(\vec{R},\vec{r}_{n}\right) \operatorname{tf}_{n}^{*}\left(\vec{R}',\vec{r}_{n}\right) \mathrm{d}\vec{r}_{n} \mathrm{d}\vec{r}_{n} \neq \int f\left(\vec{r}_{n}\right) \operatorname{tf}_{n}\left(\vec{R},\vec{r}_{n}\right) \operatorname{tf}_{n}^{*}\left(\vec{R}',\vec{r}_{n}\right) \mathrm{d}r_{n} \,. \tag{3.107}$$

Next, numerical calculations based on (3.103) with (3.106) and (3.100) with (3.102) will be presented.

In a first step, the results of molecular dynamics simulations of B2-NiAl at 300 K were taken to describe the thermal motion of the atoms accurately (Gumbsch and Finnis (1996); Ludwig and Gumbsch (1995)). For the imaging simulations, 70 snapshots of a  $4.9 \times 5.1 \times 10 \text{ nm}^3$  supercell were taken (Möbus et al. (1998)). The molecular dynamics simulation includes correlated motion of (adjacent) atoms, i.e. phonons, therefore going beyond the independent atom simplification utilized previously; the influence of the neglecting of the correlation will be discussed subsequently.

In a second step, independent electrostatic atomic potentials according to Doyle and Turner (1968) are placed on the different atom positions according to the snapshots, and MS simulations without thermal averaging are performed for each frozen lattice. The acceleration voltage was 300 kV and the electron beam was oriented to the [110]-direction. Thereafter, the different scattering results of each frozen lattice are averaged in the object exit plane according to the equations (3.98-intensity averaging) and (3.99-reconstructed wave averaging) to measure the influence of different imaging conditions. Results of that "brute force" averaging are depicted in Fig. 3.20 and are subsequently referred to as frozen phonon averages. They serve as reference for the results obtained by the analytical averaging incorporated into the MS algorithm from the previous chapter. The mean vibrational amplitudes used for the analytical averaging were consistently determined from the MD simulations to 7.6 pm for Ni and 7.1 pm for Al at 300 K (Gumbsch and Finnis (1996); Ludwig and Gumbsch (1995)). To separate the influence of the aberrations, they were treated independently, i.e. envelopes and phase plate in the case of reconstructed wave function averaging, and TCC in the case of intensity averaging in real space, are applied only after the averaging over the thermal motion in the object exit plane. One error source is the generally low sampling rate chosen for the unit cell in the simulations that is limited by the large amount of memory used to store the density matrix in the intensity simulations. This is a drawback of the new averaging method, especially when dealing with large supercells. However, convergence tests with respect to the sampling rate for the less critical reconstructed wave simulations show that the sampling rates chosen for the density matrix simulations are sufficiently high.



Figure 3.20: Averaged intensity according to equation 3.98 (a) and squared amplitude of averaged reconstructed wave according to equation 3.99 (b) resulting from averaging over 70 different frozen lattices

To compare the results from different imaging conditions quantitatively, the squared amplitude of the averaged reconstructed wave was calculated (Fig. 3.20 (b)) and compared to the averaged intensity (Fig. 3.20 (a)). The averaged intensity is slightly brighter than the absolute square of the reconstructed averaged wave, this effect, however, is barely visible in the real space image. To get a quantitative measure, the amplitudes of certain reflections in the Fourier-transform of the images are compared in Fig. 3.21. There is a difference in the value of the zero reflection, whereas the other reflections show similar values. The ratio of a reflection to the zero reflection is usually referred to as contrast and it is obvious that this measure is in the case of the averaged intensity lower by a factor of 10% than in the case of the averaged reconstructed wave function. Consequently, electron waves reconstructed from off-axis electron holograms show a slightly higher contrast than conventionally recorded images in the case of B2-NiAl. It will be shown subsequently that with substances consisting of heavier atoms with a higher scattering power, the difference increases as indicated in the introduction.



Figure 3.21: Selected reflections in the Fourier spectra of frozen phonon averaged reconstructed wave function (equation 3.99) and intensity (equation 3.98).

The results of the scattering simulations incorporating an analytical averaging as developed above are now compared with the frozen phonon simulations, i.e. the "brute force" averaging of separately calculated images. In Fig. 3.22(a), the amplitude of an averaged transmission function used in the reconstructed wave calculation of one unit cell B2-NiAl is depicted.



Figure 3.22: Amplitude of averaged transmission functions of one unit cell of B2-NiAl used as one slice for (a) the reconstructed wave MS algorithm (equation 3.102) and (b) scattering simulations removing inelastically scattered electrons.

Due to the averaging, it is not a pure phase object, i.e.  $\exp(i\sigma V_{\text{proj}})$ , anymore. There is a damping in the vicinity of the atoms, producing the attenuation of the zero reflection in Fig. 3.21(a). Although being reminiscent to absorption potentials introduced to remove inelastically scattered electrons (i.e. Fig. 3.22(b) according to Weickenmeier and Kohl (1989)), the damping visible in Fig. 3.22(a) must not be compared to or misunderstood as such an absorption potential. The damping, depicted in Fig. 3.22(a), occurs only in waves reconstructed by means of off-axis Electron Holography due to the thermal motion, it will not show up in averaged intensities (since no electrons are removed due to thermal averaging). Furthermore, it deviates significantly from inelastic absorption potentials in amplitude (see Fig. 3.22(b)) and phase. The smearing out introduced in the phase of the transmission function is reminiscent of the Debye-Waller damping, but quantitatively different. Concerning the resulting reconstructed wave function and recorded intensity, the deviations from the frozen phonon averages are small (see Fig. 3.23), proving the validity of the new Multislice algorithm.

The remaining differences, especially at the [06]-reflections, can presumably be ascribed to the insufficient number of frozen lattice snapshots, the low sampling rate and the deviations from an uncorrelated motion of the atoms present in the molecular dynamics simulations. Both the intensity averaging and the reconstructed wave



Figure 3.23: Selected reflections in the Fourier spectra of frozen phonon and simulated averages for reconstructed waves (a) and intensities (b) in real space imaging

averaging differ substantially from a pure Debye-Waller damping. In Fig. 3.24 the influence of the incorporation of aberrations is depicted, showing that the difference between the averages stays unaltered.



Figure 3.24: Selected reflections in the Fourier spectra of frozen phonon averaged reconstructed wave function and intensity in real space imaging under the influence of aberrations

The new MS formalism for thermal averaging is now applied to investigate the difference between reconstructed wave simulation and conventional intensity simulation, when scattering at substances consisting of heavier atoms. To show the influence, imaging simulations have been conducted for fcc silver and fcc gold. To highlight the difference to the analytic result obtained with the FOB, the result of a diffraction analysis after 5 and 30 gold unit cells is shown in Fig. 3.25. In the thin region (t = 5 u.c.) one can observe a diffuse background referred to as Thermal Diffuse Scattering (TDS), which is qualitatively similar to the FOB case (see Fig. 3.19). However, with increasing thickness (t = 30 u.c.) the difference increases and a structure, the famous Kikuchi lines, develops within the TDS. The appearance of such lines within elastic scattering theory is astonishing at first sight since, obviously, no localized incoherent sources of electron waves due to inelastic scattering are present. A. Rosenauer et. al (Rosenauer et al. (2008)), however, showed that the frozen lattice formalism for electron diffraction can be approximated by a sum of mutually incoherent wave propagations, where the origin of those waves are localized at atomic positions. Consequently, this approximation gives an explanation for the appearance of Kikuchi lines. The connection to the density matrix formalism is discussed further below. In Fig. 3.26 the averaged intensity and the absolute square of the reconstructed averaged wave after 20 gold unit cells oriented in [100]-direction are depicted. Contrary to weak scatterers like B2-NiAl (Fig. 3.20), the two results differ completely. To show the difference quantitatively, the amplitudes of several reflections are again investigated. Fig. 3.27 displays the results for gold, whereas Fig. 3.28 displays those of silver. Besides the



Figure 3.25: By means of density matrix MS simulated diffraction images of gold supercell containing 2x2x5 (left) and 2x2x30 (right) unit cells oriented in [001]-direction. Acc. voltage: 300 kV, sampling: 64x64. Note that the contrast in the two images is scaled differently.





damping in the zero reflection, the other reflections are now altered as well according to the two different kinds of averaging in the image plane.

The [02]-reflections chosen as an example show that the contrast, i.e. the ratio of the [02]- to the [00]beam, of the Debye-Waller damping is generally too large in the thin specimen regions, whereas the contrast of the averaged intensity can be larger or smaller than that of the averaged reconstructed wave function. Other reflections, being quantitatively different, show qualitatively a similar behavior in this respect.

One can conclude that the most prominent factor influencing the deviation between the two types of averaging is the atomic weight. When scattering on materials consisting of light atoms (e.g. NiAl, Si), the only mismatch between reconstructed waves and intensity images occurs in the zero beam and amounts up to several 10 percent according to the specimen thickness. Materials consisting of semi-heavy (like Ag) or heavy (like Au) atoms additionally show a severe mismatch in all other reflections, eventually reaching a factor two- to three hundred percent in the contrast (see Fig. 3.27), which grows with thickness and atomic weight. The mismatch varies from reflection to reflection hence cannot be classified generally. Several authors describe such high mismatches between simulated and recorded images (e.g. Hytch and Stobbs (1994), Boothroyd (1997), Howie (2004)). One important factor contributing to this mismatch is consequently the wrong averaging, i.e. Debye-Waller averaging or reconstructed wave averaging for intensity images. However, due to the strong influence of the atomic weight, contrast mismatches of several hundred percent observed in light materials like Si (Boothroyd (2002)) cannot be ascribed solely to the averaging method.



Figure 3.27: Selected reflections ([0,0] in (a) and [0,2] in (b)) in the Fourier spectra of different simulated averages as a function of increasing thickness of a gold sample oriented in [100]-direction.



Figure 3.28: Selected reflections ([0,0] in (a), and [0,2] in (b)) in the Fourier spectra of different simulated averages as a function of increasing thickness of a silver sample oriented in [100]-direction

### 3.2.7.3 Medium resolution holography with thermal motion

It is now possible to resume the discussion of Sec. 3.2.5 and investigate properties of the zero beam amplitude  $|\Psi_0|$ , which is reported to be attenuated by scattering into non-zero scattering angles as well as inelastic scattering. For the effect of inelastic interaction, M. McCartney et al. (McCartney and Gajdardziska-Josifovska (1994)) introduced the following expression

$$|\Psi_0| = e^{-t/(2\lambda_{in})} \tag{3.108}$$

relating the damping of the reconstructed normalized amplitude to the inelastic mean free path  $\lambda_{in}$  introduced in Sec. 3.1. Significant corrections to this exponential damping (3.108) of the zero beam amplitude due to inelastic scattering (3.108) arise, however, from the configurational average of the reconstructed wave over the lattice vibrations (Rother et al. (2009)). The configurational average for a reconstructed wave scattered at a single atom with a position distribution  $f\left(\vec{R}_m\right)$  reads according to the PGA (3.66)

$$\Psi\left(\vec{R}\right) = \int f\left(\vec{R}_m\right) e^{i\sigma \int_{z_{n-1}}^{z_n} V_m\left(\vec{R} - \vec{R}_m, z\right) dz} \mathrm{d}^2 R_m \tag{3.109}$$

and contains position dependent amplitudes  $|\Psi(\vec{R})|$  smaller than one, i.e. the reconstructed wave is dampened by a statistical decoherence introduced by the moving lattice. The magnitude of the damping strongly depends on the magnitude of the projected potential of the atom, as it has been discussed in the previous section. To illustrate the behavior of the zero beam amplitude  $|\Psi_0|$ , it is useful to make a comparison to the total intensity I found in the sideband (i.e. the over all scattering angles integrated intensity). If the zero beam amplitude is



Figure 3.29: Total intensity (I) damping in the sideband due to thermal motion and zero beam amplitude damping at 10° tilt angle as calculated by MS (200 kV) for (a) Si and (b) Au. The difference between the total intensity damping and the zero beam amplitude damping stems from intensity scattered into non-zero angles.

decreased by scattering into non-zero angles, the total intensity remains unchanged. Interestingly, the zero beam amplitude is decreasing with increasing thickness in both materials with a magnitude, which cannot be explained by scattering outside the zero beam aperture. In fact, the attenuation of the amplitude is an effect arising from the thermal motion of the atoms, leading to an absorption term in the transmission function tf used in the reconstructed wave simulation (Rother et al. (2009)), which shows up as an overall damping of the total intensity I in the sideband (Fig. 3.29). The decrease of the zero beam amplitude is dominated by the thermal motion and much larger in the Au case, due to the larger scattering potential (Fig. 3.29). Experimental determinations of the exponential damping constant of the reconstructed amplitude and systematic comparison to inelastic mean free path lengths obtained by Energy Electron Loss Spectroscopy (EELS) methods are unfortunately still rare. The investigations summed up in Tab. 3.3 compare the holographically obtained values with theoretic calculations valid for EELS. Although the holographic values seem to be systematically smaller than the EELS values, the database is too small to validate the additional amplitude damping due to thermal motion derived from theory. Furthermore, the magnitude of the deviations found for light materials like C and MgO is too large to be solely explained by the influence of thermal motion.

material	$\lambda_{in,exp} [\mathrm{nm}]$	$\lambda_{in,theo} [\mathrm{nm}]$
С	$51.5^{1}$	$70^{2}$
Si	$92^{3}$	$90^{3}$
MgO	$71^{3}$	$98^{3}$
Cu	$96^{4}$	$111^{4}$

Table 3.3: Extract of experimental and theoretical inelastic mean free path  $\lambda_{in}$  values. The investigations have been performed at different acceleration voltages. <sup>1</sup>Harscher and Lichte (1998), <sup>2</sup>Burge (1973), <sup>3</sup>McCartney and Gajdardziska-Josifovska (1994), <sup>4</sup>Wang (2003).

The incorporation of thermal motion within Multislice by making use of the density matrix, unfortunately requires a large amount of memory when performing realistic scattering simulations. This is a major drawback of the method, making further approximations of the formalism desirable. An interesting approach in this respect was recently presented by A. Rosenauer et al. (Rosenauer et al. (2008)). The basic idea of this approach is to separate the total signal into the absolute square of the averaged wave, which can be computed very conveniently (see above), and a remainder, which is calculated within a reasonable approximation, i.e.

$$I_{tot} = |\psi|^2 + I_{rem} \,. \tag{3.110}$$

The approximation used for  $I_{rem}$  makes use of the conservation of total intensity, which is not fulfilled by  $|\psi|^2$ , i.e. on every atom the "missing intensity" introduced by  $|\overline{tf}|^2$  is computed. Each missing intensity is subsequently transferred separately by means of Multislice, then multiplied with the absolute square of the wave and incoherently added to the signal. In this way the use of the density matrix is avoided, a wave like transfer of different parts of the total signal is achieved instead, which decreases computational requirements vastly. In the following, a direct deduction of this approach from the general density matrix formalism is outlined to justify and clarify the approach and the assumptions behind. The density matrix transfer of one slice without propagation reads

$$\hat{\rho}(\vec{R}, \vec{R}', z + \Delta z) = \int f(\vec{r}_n) \operatorname{tf}_n\left(\vec{R}\right) \operatorname{tf}_n^*\left(\vec{R}'\right) \mathrm{d}r_n \hat{\rho}(\vec{R}, \vec{R}', z) \,.$$
(3.111)

Separating the absolute square of the mean wave yields

$$\hat{\rho}(\vec{R},\vec{R}',z+\Delta z) = \left\{ \overline{\mathrm{tf}}\left(\vec{R}\right)\overline{\mathrm{tf}^*}\left(\vec{R}'\right) + \int f\left(\vec{r}_n\right)\left(\mathrm{tf}_n\left(\vec{R}\right) - \overline{\mathrm{tf}}\left(\vec{R}\right)\right)\left(\mathrm{tf}_n^*\left(\vec{R}'\right) - \overline{\mathrm{tf}^*}\left(\vec{R}'\right)\right)\mathrm{d}r_n \right\} \hat{\rho}(\vec{R},\vec{R}',z).$$
(3.112)

The first term is the absolute square of the mean wave and the second term is the remainder. Using the following definition for the deviation  $\delta$  of the transmission function from its thermal average

$$\mathrm{tf}_n\left(\vec{R}\right) - \overline{\mathrm{tf}}\left(\vec{R}\right) = \delta \mathrm{tf}_n\left(\vec{R}\right) \tag{3.113}$$

and neglecting product terms between deviations  $\delta$ ,<sup>19</sup> one gets

$$\hat{\rho}(\vec{R},\vec{R}',z+\Delta z) \approx \left\{ \overline{\mathrm{tf}}\left(\vec{R}\right) \overline{\mathrm{tf}^*}\left(\vec{R}'\right) + \overline{\mathrm{tf}}\left(\vec{R}\right) \overline{\delta \mathrm{tf}^*}\left(\vec{R}'\right) + \overline{\mathrm{tf}^*}\left(\vec{R}'\right) \overline{\delta \mathrm{tf}}\left(\vec{R}\right) \right\} \hat{\rho}(\vec{R},\vec{R}',z) \,. \tag{3.114}$$

The second and third summand in the bracket reintroduces the "missing amplitude" produced by the complex wave average  $\left|\overline{tf}\right|^2$ , i.e. the contribution of one slice to the missing intensity

$$I_{rem}\left(\vec{R}, z + \Delta z\right) = 2\Re\left(\overline{\mathrm{tf}}\left(\vec{R}\right)\overline{\delta\mathrm{tf}^*}\left(\vec{R}\right)\right)\rho\left(\vec{R}, z\right) \,. \tag{3.115}$$

It turns out that the particular shape of the transmission function of one atom indeed leads to positive real parts of the above product and consequently the intensity  $I_{rem}$  is positive. This can be exploited in a last step, which consists of defining the following "missing" wave function

$$\psi_{rem}\left(\vec{R},z\right) = \sqrt{I_{rem}\left(\vec{R},z\right)},\qquad(3.116)$$

which facilitates a wave-like propagation of the missing intensity through the crystal. Accordingly, the propagation of the density matrix through the crystal can be restricted to an "average" wave propagation combined with additional mutually incoherent waves  $\psi_{rem}$  occurring at every slice. The error introduced by doing so is limited to the off-diagonal elements of the density matrix at the respective slice, which eventually mix with the diagonal elements when propagating through the crystal towards the exit face.

## 3.3 Inelastic scattering theory

As mentioned in the introduction of this chapter, the investigations on inelastic scattering will be focused on effects influencing off-axis Electron Holography. Consequently, inelastic scattering events with a large transition probability, i.e. low-loss excitations (see Fig. 3.2), are of special interest. The analysis is based on two different and mutually complementing formalisms: The famous diagram technique based upon time-dependent perturbation theory and the two-particle scattering method based on coupled differential equations. The following inelastic scattering events in TEM will be discussed:

- 1. Electron-electron scattering (see Fig. 3.30). The exchange term can be neglected in the energy regime prevailing in TEM (Greiner and Reinhardt (1984)). The difference to a non-relativistic treatment lies in the retardation of the virtual photon mediating the coupling between both electrons incorporating scalar and vector potential coupling and the electron spin.
- 2. Electron-ion scattering (see Fig. 3.31). The core is treated as a single particle, since form factors stemming from the internal structure of the core can be neglected in the energy regime explored with a TEM. Since the atom core is much heavier than the electron, the scattering is mostly quasistatic, i.e. only small amounts of energy (with however large momentums) are exchanged with a significant probability.
- 3. Bremsstrahlung (see Fig. 3.32). Here, both the direct term and the exchange term are equally important. A wide range of energy in the low-loss regime is covered. The coupling to the external potential, deflecting the electron and thereby producing the Bremsstrahlung will be treated in second order. A related phenomenon is the Cerenkov radiation, which already occurs at the one-vertex level because the simultaneous energy and momentum conservation is fulfilled by the dielectric function of the material. The total cross-section of this inelastic transition severely hampers the experimental determination of band gaps and other low-loss transitions (Stöger-Pollach et al. (2006)).

<sup>&</sup>lt;sup>19</sup>In statistical physics, this approach is referred to as mean field approximation.



Figure 3.30: (a) direct term and (b) exchange term Feynman diagram of electron-electron (Möller) scattering. The arrows denote the initial and final wave functions, which occur in the inelastic interaction mediated by an exchange of a virtual photon (wavy line), which couples to the wave function at the two vertices (black dot).



Figure 3.31: Feynman diagram of electron-core scattering. The core is treated as single particle.

4. Quasiparticle scattering. In spite of the significantly increased complexity of the process of exciting cooperate phenomena like electron density oscillations (plasmons) or cooperate ion motions (phonons), these excitations can approximately be cast into a picture very similar to the single particle excitations described above. The key is an approximate treatment of the multi-particle phenomena as harmonic oscillations or eigenmodes, which are in agreement to the eigenmodes of other physical fields (electromagnetic, etc.) called quasiparticles. Similarly to their free field counterparts, they can be characterized by a (quasi)momentum, which is related to the energy by a possibly very complicated energy dispersion relation. As the energy of phonons is in the range between 0 - 60 meV and plasmon energy is usually found between 0 - 20 eV, they contribute to the low-loss regime, which is the dominating part of the inelastic scattering (see Fig. 3.2).

### **3.3.1** Electron-electron / -ion scattering

The matrix element for the Feynman graph (Fig. 3.30) with the Photon propagator used in the Feynman gauge reads

$$\mathbf{T}_{fi} = e^2 \int d^4 r d^4 r' \frac{d^4 q}{(2\pi)^4} \left[ \mathbf{\Psi}_f^{\dagger}(r) \left( -i \boldsymbol{\gamma}_{\mu} \right) \mathbf{\Psi}_i(r) \right] \frac{-i4\pi e^{-iq(r-r')}}{q^2 + i0} \left[ \mathbf{\Phi}_f^{\dagger}(r') \left( -i \boldsymbol{\gamma}^{\mu} \right) \mathbf{\Phi}_i(r') \right], \quad (3.117)$$

where the fraction between the squared brackets is the virtual photon propagator, which couples to the initial and final states via the vertices in the curvy brackets. The difficulties related to the evaluation (3.117) are the complex initial and final states. Both the specimen states  $\Phi$  and the beam states  $\Psi$  usually deviate from simple plane waves in case of inelastic excitations considered in TEM. The specimen states are solutions of many-particle problems, typically approximated by Hartree-Fock or Density Functional schemes. Within these approximations ground state wave functions can be calculated very accurately, whereas the excited outgoing states can only be approximated (e.g. Eschrig et al. (2004)). Some of the difficulties with the excited states can be resolved by applying core-hole corrections, GW methods, time-dependent DFT and so on. The beam electron states are modified due to elastic scattering preceding or following the inelastic scattering, which unfortunately does not fit into a FOB approximation scheme. Instead of treating inelastic and elastic effects on the same footing, it is therefore necessary to calculate all initial and final beam electron states a priori by the methods outlined in Sec. 3.2.

In the following, the evaluation of (3.117) for the situation prevailing in Energy Electron Loss Spectroscopy (EELS) is schematically outlined to give a description of fully relativistic inelastic scattering and to draw the connection to the non-relativistic and scalar relativistic formulations typically used in literature (e.g. Egerton



Figure 3.32: Feynman diagram of Bremsstrahlung. The exchange term is not illustrated.



Figure 3.33: Feynman diagram of electron-quasiparticle scattering. The quasiparticle is illustrated by the double line.

(1996)). The signal evaluated in a typical EELS experimental setup is the double differential cross-section (A.57). The beam electron part can be written as a sum of Bloch waves (see Sec. 3.2.2)

$$\Psi = \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} \sqrt{\frac{m}{E_i}} \mathbf{u}_i \sum_{\vec{k}} \tilde{\Psi}\left(\vec{k}\right) e^{i\vec{k}\vec{r}} = \sum_j \epsilon_j e^{i\vec{\gamma}_j\vec{r}} \sum_{\vec{g}} \tilde{\Psi}_j\left(\vec{g}\right) e^{i\vec{g}\vec{r}}, \qquad (3.118)$$

where the spin-orbit coupling of the beam electron was neglected (see Sec. 3.2). It is again pointed out that the number of Bloch waves, which is required to describe the abrupt change of the elastic wave function at the sharp atomic potentials, is usually too large to describe the elastic state accurately. Inserting (A.45) into (3.117) yields (see A.10)

$$\mathbf{T}_{fi} = \frac{2i\sqrt{\frac{m^2}{E_f E_i}}e^2 (2\pi)^2 \,\delta \left(E_i - E_f - \Delta E\right) \left[\mathbf{u}_f^{\dagger} \boldsymbol{\gamma}_{\mu} \mathbf{u}_i\right] \cdot}{\sum_{j,j'} \epsilon_j \epsilon_{j'} \sum_{\vec{g}, \vec{g}'} \frac{1}{\left(\vec{g}' - \vec{g} + \vec{\gamma}_j - \vec{\gamma}_{j'}\right)^2 - \Delta E^2} \tilde{\Psi}_{f,j}^* \left(\vec{g}\right) \tilde{\Psi}_{i,j'} \left(\vec{g}'\right) \int d^3y \left[\Phi_f^{\dagger} \left(\vec{r}'\right) e^{-i\left(\vec{g}' - \vec{g} + \vec{\gamma}_j - \vec{\gamma}_{j'}\right)\vec{r}'} \boldsymbol{\gamma}^{\mu} \Phi_i \left(\vec{r}'\right)\right]}$$
(3.119)

The lengthy expression of the absolute square of  $\mathbf{T}_{fi}$  is abbreviated by the defining

$$X_{f,i}^{j,j',\vec{g},\vec{g}'} = \sum_{j,j'} \epsilon_j \epsilon_{j'} \sum_{\vec{g},\vec{g}'} \frac{1}{\left(\vec{g}' - \vec{g} + \vec{\gamma}_j - \vec{\gamma}_j'\right)^2 - \Delta E^2} \Psi_{f,j}^*\left(\vec{g}\right) \Psi_{i,j'}\left(\vec{g}'\right)$$
(3.120)

and the mixed dynamic form factor (Kohl and Rose (1985))

$$\mathrm{MDFF}_{\mu,\nu} = \left\langle \Phi_{f}^{\dagger}\left(\vec{r}'\right) \left| e^{-i\left(\vec{g}' - \vec{g} + \vec{\gamma}_{j} - \vec{\gamma}_{j'}\right)\vec{r}'} \boldsymbol{\gamma}^{\mu} \right| \Phi_{i}\left(\vec{r}'\right) \right\rangle \left\langle \Phi_{f}^{\dagger}\left(\vec{r}'\right) \left| e^{-i\left(\vec{h}' - \vec{h} + \vec{\gamma}_{l} - \vec{\gamma}_{l'}\right)\vec{r}'} \boldsymbol{\gamma}^{\nu} \right| \Phi_{i}\left(\vec{r}'\right) \right\rangle^{*} .$$
(3.121)

The mixed dynamic form factor as originally introduced in the field of TEM scattering is an extension to the concept of the dynamic form factor (van Hove (1955)), i.e.

$$DFF_{\mu,\nu}\left(\vec{q}\right) \stackrel{\vec{q}=\vec{g}'-\vec{g}+\vec{\gamma}_{j}-\vec{\gamma}_{j'}}{=} MDFF_{\mu,\nu}\left(\vec{q},\vec{q}\right) \propto \left|\mathbf{T}_{fi}\right|^{2}.$$
(3.122)

The absolute square of the transition matrix, which determines the double differential scattering cross-section



Figure 3.34: Illustration of energy and momentum conservation in a single inelastic scattering event, where both the initial and the final state of the scattered particle are momentum eigenstates denoted by their respective wave vectors  $\vec{k}_i$  and  $\vec{k}_f$ . If the scattering mate is also in a momentum eigenstate, momentum and energy conservation lead to characteristic momentum transfers  $\vec{q}$  at a certain energy loss. ZOLZ refers to the Zero Order Laue Zone in diffraction space.

(see (A.61)), now reads

$$|\mathbf{T}_{fi}|^{2} = 4e^{4} (2\pi)^{5} \frac{m^{2}}{E_{f}E_{i}} T \sum_{\substack{\mu, j, j', \vec{g}, \vec{g} \\ \nu, l, l', \vec{h}, \vec{h}'}} \left[ \mathbf{u}_{f}^{\dagger} \boldsymbol{\gamma}_{\mu} \mathbf{u}_{i} \right] X_{f,i}^{j,j',\vec{g},\vec{g}'} \left[ \mathbf{u}_{f}^{\dagger} \boldsymbol{\gamma}_{\nu} \mathbf{u}_{i} \right]^{*} X_{f,i}^{*l,l',\vec{h},\vec{h}'}$$
(3.123)  

$$\cdot \text{ MDFF}_{\mu,\nu} \left( \vec{q}, \vec{q}' \right) \delta \left( E_{i} - E_{f} - \Delta E \right) .$$

This is the fully relativistic version of the non-relativistic expression<sup>20</sup>

$$|\mathbf{T}_{fi}|^{2} = e^{4} 4 (2\pi)^{4} \sum_{j,j'} \epsilon_{j} \epsilon_{j'} \sum_{g,g'} \frac{1}{\left(\vec{g'} - \vec{g} + \vec{\gamma}_{j} - \vec{\gamma}_{j}'\right)^{2}} \text{MDFF}\delta\left(E_{i} - E_{f} - \Delta E\right)$$
(3.124)

used in literature (e.g. Rusz et al. (2007b)). The main difference between the fully relativistic and non-relativistic expression is the retardation of the electromagnetic interaction (expressed by  $\Delta E^2$  in (3.120)) and the combined electric and magnetic coupling (expressed by the  $\gamma_{\mu}$ -matrices). The evaluation of (3.124) remains a formidable task though, since one has to calculate multidimensional quantities like the MDFF and sum them up over all incoming / outgoing states with the appropriate energy loss and spin state. Nevertheless, non-relativistic (or partly relativistic) program packages have been developed (e.g. Rusz et al. (2007b), Blaha et al. (2001)) and used to successfully determine EELS in general and Electron Energy Loss Near Edge Spectra (ELNES) or EMCD signals in particular. The cumbersome summations can be drastically simplified by exploiting sum rules available for spin, angular momentum summation, etc. (e.g. Rusz et al. (2007a)).

An alternative simplification is provided by the method based on the coupled differential equation scheme outlined in the introduction of this chapter. The coupled system of equations can be solved directly, when restricting the number of contributing states or assuming that the matrix element (3.14) is small (e.g. Yoshioka (1957); Wang (1995)). If we insert at this point the following starting conditions

$$\psi_0 = \psi_i \tag{3.125}$$
  
$$\psi_{m \neq 0} = 0$$

at the entrance plane of the crystal at z = 0, which are an extension of the forward scattering approximation in elastic scattering, we get the following perturbation series to solve

$$\left( \hat{\mathbf{H}}_{e} - E_{m} + \mathbf{H}_{mm} \right) |\psi_{m}\rangle \approx \begin{array}{c} 0 & m = 0 \\ -\mathbf{H}_{m0} |\psi_{0}\rangle & m \neq 0 \end{array}$$

$$(3.126)$$

The advantage of this scheme is that the differential equation can be solved very fast by utilizing efficient solving algorithms developed for this type of equations, in particular the Multislice algorithm. One approach followed by Stallknecht and Kohl (1996) uses the integral formulation of (3.126)

$$\Psi_{m\neq0} \approx \hat{G}_m \mathbf{H}_{m0} \left| \psi_0 \right\rangle \tag{3.127}$$

 $<sup>^{20}</sup>$ In spite of using a non-relativistic scattering matrix, the incoming electron flux is usually calculated relativistically, hence the final expressions for the scattering cross-section contain a relativistic correction factor.

with the homogeneous solution being zero due to the boundary conditions. The Green-operator  $\hat{G}$  can be constructed from the complete set of eigenfunctions of the homogeneous equation, i.e.

$$G_m(\vec{r} - \vec{r}') = \sum_n \frac{\Psi_m(\vec{r}) \Psi_n^*(\vec{r}')}{E_m - E_n} \,.$$
(3.128)

In Stallknecht and Kohl (1996) the Green-function series expansion is truncated keeping only n = m, assuming that the other parts of the sum will not contribute. The following approaches will not build upon that uncertainty. First, (3.126) can be solved directly with a numerical solver (e.g. Runge-Kutta (Hermann (2004))). This is accurate and very time-consuming, therefore can be used as reference solution for the second approach, a modified Multislice algorithm.

The relativistic Multislice algorithm incorporating inelastic scattering is now derived along the same lines as the elastic version (see Sec. 3.2.4): From the wave function  $\psi_m$  the fast forward traveling part is separated, i.e.  $\psi_m = \varphi_m e^{ik_{0z}z}$  and the small angle scattering approximation is applied, i.e.

$$\frac{\partial}{\partial z}\varphi_m(\vec{R},z) + \frac{-i\left[E_m V + \Delta_{\vec{R}}\right]}{2c^2\hbar^2 k_{0z}}\varphi_m(\vec{R},z) = \mathbf{H}_{m0}(\vec{R},z)e^{i\left(k_{0z}^0 - k_{0z}^m\right)z}\varphi_0(\vec{R},z)\,. \tag{3.129}$$

The formal solution of (3.126) as a first order inhomogeneous differential equation with respect to the zcoordinate reads

$$\varphi_m\left(\vec{R}, z\right) = e^{-\int_0^z p\left(\vec{R}, z'\right) dz'} \left(\int_0^z e^{\int_0^{z'} p\left(\vec{R}, z''\right) dz''} r\left(R, z'\right) dz' + \varphi_m\left(\vec{R}, 0\right)\right)$$
(3.130)

with the homogeneous prefactor

$$p\left(\vec{R},z\right) = \frac{-i\left[E_m V + \Delta_{\vec{R}}\right]}{2c^2\hbar^2 k_{0z}}$$
(3.131)

and the inhomogeneous term

$$\mathbf{r}\left(\vec{R},z\right) = \mathbf{H}_{m0}(\vec{R},z)e^{i\left(k_{0z}^{0}-k_{0z}^{m}\right)z}\varphi_{0}(\vec{R},z).$$
(3.132)

When predefining the integration steps, assuming periodic boundary conditions in the  $\vec{R}$ -plane and  $\int p(\vec{R}, z) dz \ll 1$ , the exponentials can be approximated by  $e^{-\int p(\vec{R}, z) dz} \approx pf \otimes tf$ , with the well-known transmission

$$\mathrm{tf} = \exp\left(\frac{i\int EV\mathrm{d}z'}{2c^2\hbar^2k_0}\right) \tag{3.133}$$

and propagator

$$pf = -\frac{ik_0}{2\pi z} \exp\left(\frac{ik_0 \vec{R}^2}{2z}\right)$$
(3.134)

functions (see Sec. 3.2.4). In the regions where the inhomogeneous part is zero (far away from the inelastic interaction), the algorithm is exactly equivalent to the elastic MS, whereas in the inelastic interaction region excited waves are created by the inhomogeneous part, i.e. the excited wave  $\psi_m$  being zero at the entrance takes non-zero values in the interaction region and then travels like an elastic wave through the rest of the crystal.

The calculation of the z-integral in the bracket on the right hand side of (3.130) can now be further simplified by the following argument: Due to the sharply peaked scattering potential and the per definition fixed position of the atom at the surface of the slice, the transmission function tf can be dragged out of the z'-integral, i.e.

$$\int_{0}^{z} e^{\int_{0}^{z'} p\left(\vec{R}, z''\right) dz''} r\left(R, z'\right) dz' = \int_{0}^{z} \int pf^{*}\left(\vec{R} - \vec{R}', z'\right) tf^{*}\left(\vec{R}', z\right) r\left(R', z'\right) dz' d^{2}R'.$$
(3.135)

Accordingly, each z' plane of the inhomogeneous term is multiplied with the conjugated transmission function and backpropagated to the entrance face, then subsequently summed up with all z' planes and finally propagated to the exit plane to give the contribution of the inelastic scattering. This procedure accounts partially for the z-dependence of the inelastic interaction Hamiltonian and the elastically scattered wave. For small integration (propagation) steps z the propagator function can be furthermore approximated with a  $\delta$ -function

$$pf \approx \delta(0), \qquad (3.136)$$

yielding

$$\varphi_m\left(\vec{R},z\right) = \left(\int_0^z \mathbf{H}_{m0} e^{i\left(k_{0z}^0 - k_{0z}^m\right)z'} \varphi_0\left(R,z'\right) \mathrm{d}z' + \mathrm{tf} \cdot \varphi_m\left(\vec{R},z=0\right)\right), \qquad (3.137)$$

when inserting the simplified z-integral into (3.130). Several authors have derived and successfully used the last expression for calculating both elastically and inelastically scattered electrons (e.g. Dwver (2005), Verbeeck et al. (2009)). The difference of (3.137) to the original formula (3.130) consists in neglecting the modification of the initial and final beam electron state,  $\psi_0$  and  $\psi_m$ , due to the elastic propagation within the inelastic interaction volume. Within this approximation, the inelastic interaction matrix elements  $\mathbf{H}_{m0}$  are multiplied with a phase function and the initial wave function and simply projected, which can be seen as a inhomogeneous (or inelastic) grating approximation (IGA) in close analogy to the phase grating approximation (PGA) incorporating the projected static electromagnetic potentials. However, the IGA can significantly deviate from more accurate results, if the range of the inelastic interaction volume is large or elastic modification of the initial beam electron state within the interaction volume lead to strong modifications of the z' integrals, e.g., if considering dipole excitations in  $SrTiO_3$  (see Sec. 3.3.1.2). With respect to the accurate incorporation of the on-site elastic scattering of the initial and final electron state, the inelastic multislice formalism (3.130) is similar to the Bloch wave method outlined above. The advantage of the multislice method, however, lies in the treatment of nonperiodic specimen, the incorporation of the sharp change of the wave function at the atomic potential (see Sec. 3.2.4) and the clear interpretation of the inelastic scattering as inhomogeneous part in the high energy approximation of the scattering equation. The numerical most demanding part of the above described procedure is the calculation of the  $\mathbf{H}_{m0}$  matrix elements. The key to the solution of that problem is choosing a proper representation of the wave functions  $\phi$ . A radial representation of the integrand seems most convenient, when dealing with core electron wave functions. Other inelastic processes might require different representations. The following simple examples will be discussed in the following:

- 1. Electron-core scattering with unscreened core potential ( $\epsilon_r = 1$ ).
- 2. Core electron excitations within the dipole approximation.

### 3.3.1.1 Electron-core scattering

Single electron-core scattering is usually referred to as knock-on damage and is experimentally observed as a displacement of single atoms either within the crystal structure causing point defects or at the surface of the crystal sputtering away the atom. It can be calculated very conveniently due to the practically  $\delta$ -like localization of the atom core wave function. The transition matrix element is just a Coulomb potential in this case

$$\mathbf{H}_{m0} \approx \frac{1}{\left|\vec{r} - \vec{r'}\right|} \,. \tag{3.138}$$

Here, the retardation factor was neglected since the energy transfer in this collision processes is usually well below  $10 \, \text{eV}.^{21}$  As a consequence of the large mass difference between the core and the electron, inelastic Electron-ion scattering is to a good approximation proportional to the elastic scattering process on a fixed potential. The important difference, however, is that the coherence of such an inelastically scattered electron to the elastic channel. The by a single O ion, situated in the second unit cell behind the entrance face of a 10 unit cell thick SrTiO<sub>3</sub> crystal, inelastically scattered wave is depicted in Fig. 3.35 as a function of the thickness. One can readily observe that the inelastically scattered wave is only weakly excited in front of the O ion. Since backscattering was forbidden by definition, this effect stems solely from the inelastic interaction potential reaching into the pre-ion space. At the ion position the inelastic wave is maximally excited and localized. Behind the ion, the wave propagates, delocalizes and scatters on the following atoms. In a way, the inelastically scattered wave can be regarded as a point source of electrons within the specimen. The size of the point source determines the convergence angle in that virtual illumination.

<sup>&</sup>lt;sup>21</sup>This limit is derived from typical defect energies introduced by the knock-on damage.



Figure 3.35: Absolute square of a by an O ion in  $\operatorname{SrTiO}_3$  inelastically scattered wave as a function of thickness z, which is measured in lattice constants of  $\operatorname{SrTiO}_3 a = 0.395$  nm. The O ion, where the knock-on damage occurs, is situated at (x, y, z) = (0, 0, 1.5). The simulation was performed with the inelastic Multislice algorithm incorporating a 3D integration of the inelastic interaction according to eq. (3.130) at 200 kV acceleration voltage and a sampling rate of 160x160 of the supercell containing 5x5  $\operatorname{SrTiO}_3$  unit cells.

The above derived formalism facilitates the investigation of the inelastic scattering process with respect to the z-dependence of the initial and final beam electron wave function by comparing the 3D inelastic interaction (3.130) and the projected inelastic interaction (3.137). The results of both approximations are depicted in Fig. 3.36. The difference between both formalisms is particularly large at strong scattering sites (i.e. Sr atoms) and occurs both in the overall strength of the scattering and the shape of the inelastically scattered wave. Regarding the magnitude of the difference, one can conclude that for inelastic knock-on damages the IGA gives rather inaccurate results and the more accurate 3D interaction formalism has to be employed. It will be shown in

the next section that this drawback of the IGA holds also when considering other even more localized inelastic excitations.



Figure 3.36: Absolute square of a by an O ion in  $SrTiO_3$  (a = 0.395 nm) inelastically scattered wave at z = 1.5 a (directly behind the O atom) calculated with a 3D and projected inelastic interaction (IGA). The normalized euclidic distance is obtained by dividing the absolute value of the difference between both images by the image obtained from the 3D inelastic interaction. The simulation was performed with the inelastic Multislice algorithm at 200 kV acceleration voltage and a sampling rate of 160x160 of the supercell containing 5x5 SrTiO<sub>3</sub> unit cells.

### 3.3.1.2 Electron-electron scattering in dipole approximation

To simplify the formalism and to concentrate on the characteristic effects, a simple K-shell excitation within the dipol approximation is considered, i.e.

$$\phi_0(\vec{r}') = u(r')$$
(3.139)
$$\phi_m(\vec{r}') = u'(r') Y_{1m}(\phi, \theta) .$$

The spherical harmonics  $Y_{lm}$  are defined in the following way

$$Y_{1-1}(\phi,\theta) = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi}$$

$$Y_{10}(\phi,\theta) = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{1-1}(\phi,\theta) = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi} .$$

$$(3.140)$$

With the help of the Rayleigh expansion

$$e^{i\vec{q}\vec{r}'} = \sum_{\lambda=0}^{\infty} i^{\lambda} j_{\lambda} \left(qr'\right) \sum_{m''=-\lambda}^{\lambda} Y^{*}_{\lambda m''} \left(\psi, \vartheta\right) Y_{\lambda m''} \left(\phi, \theta\right)$$
(3.141)

the transition matrix element  $\mathbf{H}_{m0}$  can be transformed in the following way

$$\mathbf{H}_{m0} = \langle \phi_m | \frac{e^{i(E_m - E_n) |\vec{r} - \vec{r'}|}}{|\vec{r} - \vec{r'}|} | \phi_0 \rangle \tag{3.142}$$

$$= \int \mathrm{d}^3 q \frac{e^{-i\vec{q}\vec{r}}}{q^2 - \Delta E^2} \int \mathrm{d}^3 r' \phi_m^* (\vec{r'}) e^{i\vec{q}\vec{r'}} \phi_0 (\vec{r'})$$

$$= \int \mathrm{d}^3 q \frac{e^{-i\vec{q}\vec{r}}}{q^2 - \Delta E^2} \int \mathrm{d}^3 r' u (r') \sum_{\lambda=0}^{\infty} i^{\lambda} j_{\lambda} (qr') \sum_{m''=-\lambda}^{\lambda} Y_{\lambda m''}^* (\psi, \vartheta) Y_{\lambda m''} (\phi, \theta) u'^* (r') Y_{1m}^* (\phi, \theta)$$

$$= i \int \mathrm{d}^3 q \frac{e^{-i\vec{q}\vec{r}}}{q^2 - \Delta E^2} \langle j_1 (qr') \rangle Y_{1m} (\psi, \vartheta) .$$

Due to the truncation of the  $\lambda$  sum in the Rayleigh expansion, the last line is also referred to as  $\lambda = 1$  approximation. When furthermore assuming that the integration volume  $\int d^3r'$  is sufficiently small, it is allowed to approximate the radial r' integral of the first order Bessel function as a linear function of q up to a certain cut-off  $q_c$  (Kohl and Rose (1985))

$$\langle j_{\lambda}(qr') \rangle = \int dr' r'^2 j_1(qr') \, u'^*(r') \, u(r') \approx a(E) \, q \Theta(q-q_c) , \qquad (3.143)$$

yielding

$$\begin{aligned} \mathbf{H}_{m0} &\approx ia\left(E\right) \int \mathrm{d}q \mathrm{d}\psi \mathrm{d}\cos\vartheta q^{3} \frac{e^{-i\vec{q}\vec{r}}}{q^{2} - \Delta E^{2}} Y_{1m}\left(\psi,\vartheta\right) \Theta\left(q - q_{c}\right) \\ &= a\left(E\right) \int \mathrm{d}q \mathrm{d}\psi \mathrm{d}\cos\vartheta q^{3} \frac{j_{1}\left(qr\right) \sum_{m'=-1}^{1} Y_{1m'}^{*}\left(\psi,\vartheta\right) Y_{1m'}\left(\phi,\theta\right)}{q^{2} - \Delta E^{2}} Y_{1m}\left(\psi,\vartheta\right) \Theta\left(q - q_{c}\right) \\ &= a\left(E\right) Y_{1m}\left(\phi,\theta\right) \int_{0}^{q_{c}} \mathrm{d}q \frac{j_{1}\left(qr\right) q^{3}}{q^{2} - \Delta E^{2}} \,. \end{aligned}$$
(3.144)

According to Schattschneider et al. (1999) the cut-off  $q_c$  can be approximated by the Bethe ridge

$$q_c = \sqrt{2m\Delta E/\hbar^2}, \qquad (3.145)$$

where scattering on quasi-free electrons close to the Fermi level starts to dominate (Schattschneider (1986)). In case of the oxygen K-shell excitation considered here, it is, however, sufficient to use a considerably smaller  $q_c = 1/a_B$  as larger scattering angles can be neglected.



normalized Euclidic distance

Figure 3.37: Absolute square of an inelastic O K-shell excitation in  $SrTiO_3$  (a = 0.395 nm) at z = 1.5 a (directly behind the O atom) calculated with a 3D and projected inelastic interaction (IGA). The normalized euclidic distance is obtained by dividing the absolute value of the difference between both images by the image obtained from the 3D inelastic interaction. The simulation was performed with the inelastic Multislice algorithm at 200 kV acceleration voltage and a sampling rate of 160x160 of the supercell containing 5x5 SrTiO<sub>3</sub> unit cells.

After numerical evaluation of the remaining radial integral in the last line of (3.144), the transmission matrix element is inserted into (3.129), which is then integrated either directly with the help of a Runge-Kutta-algorithm (see Sec. 3.2) or in the small angle approximation with predefined step size as implemented in the inelastic multislice with (3.137) or without the IGA (3.130). A particular O K-shell excitation within different integration methods of inelastic scattering are depicted in Fig. 3.37. Here, a m = +1 excitation with the dipole oriented in z-direction is considered. Furthermore, the excited O atom is chosen to be in the second SrTiO<sub>3</sub> unit cell below the entrance face of the crystal. Similar to the knock-on damage the more accurate 3D integration method deviates significantly from the projected inelastic potential method (IGA). In Fig. 3.38 a m = +1 transition is contrasted with a m = -1 transition. However, this time the dipole is chosen to point into x-direction. Beside the propagation of the inelastically scattered wave "illuminating" subsequent atoms, one can observe a shift of the atomic column contrast containing the inelastically excited atom, i.e. the shift of the atomic column contrast correlates to the chirality of the dipole transition. This intriguing effect occurs due to the elastic scattering on the cubic crystal lattice in general and the atomic potential of the particular O atom, which breaks the symmetry of the dipole transition and introduces a predominant scattering direction. P. Schattschneider et. al proposed to use z-oriented dipoles and introduce a symmetry break by an aperture placed in the optical system behind the crystal to generate transition dependent shifted column contrasts (Schattschneider et al. (2009)). They furthermore suggested to exploit this mechanism in high-resolution investigation of magnetic materials. Here, particular m = +1 and m = -1 transitions in L-shells are not degenerated anymore and occur with different scattering amplitudes due to partly filled shells. Consequently, a dominant column shift could be expected, which might be detectable provided that the resolution of the TEM is sufficiently large.



Figure 3.38: Absolute square of an inelastic O K-shell excitation in  $SrTiO_3$  as a function of thickness z, which is measured in lattice constants of  $SrTiO_3$  a = 0.395 nm. The O atom, where the K-shell excitation occurs, is situated at (x, y, z) = (0, 0, 1.5). The simulation was performed with the inelastic Multislice algorithm incorporating a 3D integration of the inelastic interaction according to eq. (3.130) at 200 kV acceleration voltage and a sampling rate of 160x160 of the supercell containing 5x5  $SrTiO_3$  unit cells.

### 3.3.2 Bremsstrahlung

The matrix element of Bremsstrahlung reads

$$\mathbf{T}_{fi} = -e^{2} \int d^{4}r d^{4}r' \overline{\Psi}_{f}(x) \left\{ \gamma_{\mu} A^{\mu}(r) \, iS_{F}(r-r') \left( \boldsymbol{\gamma}_{\mu} \right) A^{\prime \mu}(r') + \left( \gamma_{\mu} \right) A^{\prime \mu}(r) \, S_{F}(r-r') \left( \boldsymbol{\gamma}_{\mu} \right) A^{\mu}(r') \right\} \Psi_{i}(r') \,.$$
(3.146)

The photon obeys the transversality relation  $k_{\mu}\epsilon^{\mu} = 0$  and is normalized according to  $\epsilon_{\mu}\epsilon^{\mu} = -1$ . The photon modes are normalized in the following way

$$A^{\mu} = \epsilon^{\mu} \sqrt{\frac{4\pi}{2\omega}} e^{ikr} . \tag{3.147}$$

The elastic scattering of electrons on specimen potentials generates the strongest contrast in TEM. It is therefore natural to examine the Bremsstrahlung produced by the strong elastic deflection. The evaluation of the scattering matrix element (3.146) however is very time consuming due to the summation over all possible initial and final states including the different polarizations and spins. The analytical evaluation of (3.146) for a single Coulomb potential and plane waves as electron states is already a formidable task and leads to the famous Bethe-Heitler formula. The specimen potentials and beam electron wave functions are, however, much more complicated. We will therefore restrict the analysis to the case of soft Bremsstrahlung, i.e., the generation of low energetic photons, which are dominating. In this case (3.146) can be approximated in Fourier space to

$$\mathbf{T}_{fi} = \mathbf{T}_{fi}^{0} \left( \frac{\epsilon \cdot p_f}{k \cdot p_f} - \frac{\epsilon \cdot p_i}{k \cdot p_i} \right)$$
(3.148)

i.e., the matrix element is proportional to the FOB approximation of elastic scattering  $\mathbf{T}_{fi}^{0}$ , referred to as the kinematic solution of the elastic scattering problem. The bracketed term shows that weak Bremsstrahlung depends not on the spin state of the electron but on the polarization and wave vector of the outgoing electromagnetic wave. If the wave vector  $\vec{k}$  would be parallel to  $\vec{p}_i$  and hence approximately to  $\vec{p}_f$ , the polarization vector  $\vec{\epsilon}$  would be almost perpendicular to  $\vec{p}_i$  and  $\vec{p}_f$  and therefore the matrix element would vanish. A differential cross-section can be derived from (3.148), if one sums up over all possible polarization directions, i.e. no polarization dependent measurement is performed (Greiner and Reinhardt (1984)). Then, the Bremsstrahlung cross-section is given by the elastic scattering cross-section multiplied with an additional factor, which depends on the scattering angle  $\theta$ :

$$\frac{\partial\sigma}{\partial\Omega} = \frac{\partial\sigma}{\partial\Omega}^{0} \frac{2\alpha}{\pi} \left(1 - \beta_r^2 \cos\theta\right) \int_0^1 dx \frac{1}{1 - \beta_r^2 + 4\beta_r^2 \sin^2\frac{\theta}{2}x \left(1 - x\right)} \,. \tag{3.149}$$

The angular dependence of the additional factor is plotted in Fig. 3.39. At an angle of 200 mrad 0.1 % of all electrons scattered in this direction will suffer from Bremsstrahlung, showing, that the effect is small. Elastic electron scattering is, however, not accurately described by the FOB, i.e. scattering is much stronger, eventually requiring an infinite series expansion like in the Coulomb problem. A stronger scattering will, however, produce larger Bremsstrahlung amplitudes. The explicit calculations, depicted in Fig. 3.39, therefore can only serve as a lower boundary estimate for the Bremsstrahlung amplitude. Energy loss introduced by Bremsstrahlung is contributing to the background in low energy spectroscopic measurements. The photon emission also destroys coherence with not deflected parts of the wave, i.e. the reference wave in EH. The weak Bremsstrahlung will, however, not affect conventional TEM imaging (i.e. incoherent imaging), since the momentum transfer to the electrons is negligible.



Figure 3.39: Scattering cross-section of weak Bremsstrahlung in FOB approximation.

### 3.3.3 Quasiparticle scattering

The most simple approximation for quasiparticles like phonons or plasmons will be plane wave eigenmode (non-relativistic normalization)

$$\phi_o = \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} e^{i\vec{k}\vec{r}'} \tag{3.150}$$

leading to the following interaction matrix element from Sec. 3.1

$$\mathbf{H}_{m0} = e^2 \left(\frac{1}{2\pi}\right)^3 \frac{4\pi e^{-i(\vec{k}_m - \vec{k}_0)\vec{r}}}{\Delta E^2 - \left(\vec{k}_m - \vec{k}_0\right)^2}.$$
(3.151)

In contrast to core-shell excitations, the interaction is completely delocalized in space. Inserting (3.151) into (3.126) yields

$$\left(\hat{\mathbf{H}}_{e} - E_{e,m}\right)|\psi_{m}\rangle = -e^{2} \left(\frac{1}{2\pi}\right)^{3} \frac{4\pi e^{-i(\vec{k}_{m} - \vec{k}_{0})\vec{r}}}{\Delta E^{2} - \left(\vec{k}_{m} - \vec{k}_{0}\right)^{2}}\psi_{0}.$$
(3.152)

Consequently, a plasmon or phonon excitation comes along with a tilt of the initial elastically scattered wave  $\psi_0$  by  $\vec{k}_m - \vec{k}_0$ . The scattering matrix element (3.117) reads<sup>22</sup>

$$\mathbf{T}_{fi} = i4\pi e^2 \int d^3r \left[ \Psi_f^*\left(\vec{r}\right) \Psi_i\left(\vec{r}\right) \right] \frac{e^{-i\left(\vec{k}_m - \vec{k}_0\right)\vec{r}}}{\Delta E^2 - \left(k_0 - k_m\right)^2} \delta\left(\Delta E - E_f + E_i\right) \,. \tag{3.153}$$

Again, the final state  $\Psi_f^*$  perfectly matches the initial elastic state tilted by a certain angle, i.e.

$$\Psi_{f}(\vec{r}) = \mathbf{T}_{fi}\Psi_{i}(\vec{r}) \qquad (3.154)$$

$$\propto e^{-i(\vec{k}_{m}-\vec{k}_{0})\vec{r}}\Psi_{i}(\vec{r}) .$$

As a consequence, the elastic scattering contrast is perfectly preserved after one inelastic scattering event. The range of the tilt angle is determined by the plasmon or phonon dispersion relation, which determines the momentum transfer possible per energy loss. The dispersion relation for bulk plasmons is roughly a constant (Nolting (2005)), i.e.

$$E_{pl}\left(k\right) \approx E_{pl} \,. \tag{3.155}$$

However, the maximally transferred momentum is limited by the onset of single electron excitations (Bethe ridge). The scattering angles of phonon excitations are thus in the range of  $10 \,\mu$ rad, i.e., electrons which have excited a plasmon are scattered in forward direction. Phonon dispersion relations in a 3D crystal lattice are rather complicated. Under certain restrictions<sup>23</sup>, however, one can derive that the transferred momentum is given by the sum of the phonon spatial frequency and an arbitrary reciprocal lattice vector, i.e. (Nolting (2005))

$$ec{k}_m - ec{k}_0 = ec{q} + ec{g}$$
 .

This can lead to scattering angles comparable to those in elastic scattering. The finally recorded electron density is obtained by incoherently summing over all possible phonon excitations, which is equivalent to an incoherent spread of the elastically scattered waves in reciprocal space. A similar spread of electron beam angles is introduced by finite size of the electron source and was characterized by the semiconvergence angle in Sec. 2.1. If the scattering amplitude for phonon scattering with large momentum transfer is comparable to the semiconvergence angle of the electron gun, a significant influence on the imaging properties of the microscope, in particular if coherent aberrations are present, can be expected.

The systematic overestimation of calculated elastic scattering contrast with respect to experimental values is a long standing issue in TEM imaging referred to as Stobbs factor (e.g. Hytch and Stobbs (1994), Boothroyd (1997), Howie (2004)). Contrary, Lehmann et al. (Lehmann and Lichte (2003)) and A. Thust (Thust (2009)) reported good agreement between simulation and experimental results, when using waves reconstructed by off-axis holography or  $C_s$ -corrected imaging. Both results could be explained by the previously discussed inelastic phonon scattering, i.e.,  $C_s$  corrected imaging is robust against an increased semiconvergence angle and holographically reconstructed waves do barely contain inelastically scattered waves. Bulk plasmon scattering comes with a larger energy transfer and is much more confined to the forward scattering direction, and hence the influence on imaging will be due to the increased energy width. The total scattering power of plasmon excitations is, however, smaller than the phononic one, and hence the effect is expected to be rather small.

The total scattering power is also important, when considering the intriguing effect of inelastic excitations in the formation of interference patterns. As already discussed previously, it is necessary to know the probability



Figure 3.40: Coherence as a function of the distance to the specimen edge recorded at an energy loss of 15 eV. The image was recorded and published by H. Lichte and B. Freitag (Lichte and Freitag (2000)).

of an inelastic excitation at the distance from the edge of the sample, where the reference wave is located. This probability can be estimated from a single IGA (3.137) derived above, i.e.

$$\varphi_m\left(\vec{R}\right) = \int \mathbf{H}_{m0}\left(\vec{R}, z\right) e^{i\left(k_{0z}^0 - k_{0z}^m\right)z} \varphi_0\left(R, z\right) \mathrm{d}z \tag{3.156}$$

is evaluated at positions  $\vec{R}$  in the vacuum. In the following calculation, the specimen edge is assumed to be parallel to the x-direction at y = 0 and the vacuum is in the left half plane (y < 0). It is furthermore assumed that the elastic wave function  $\varphi_0 = 1$  for y < 0, i.e., elastic scattering from the usually very thin specimen into the vacuum region will be neglected. Since the largest scattering cross sections for inelastic scattering are in the low-loss regime and to simplify the notation, the non-relativistic form of inelastic matrix element  $\mathbf{H}_{mn}$  will be used in the following (see (3.21)), i.e.

$$\mathbf{H}_{m0} = e^2 \int \mathrm{d}^3 r' \phi_m^*(\vec{r'}) \phi_0(\vec{r'}) \frac{1}{|\vec{r} - \vec{r''}|} \,. \tag{3.157}$$

After plugging  $\mathbf{H}_{m0}$  into (3.156) one obtains

$$\varphi_{m}\left(\vec{R},z\right) = e^{2} \int \int \phi_{m}^{*}(\vec{r}')\phi_{0}(\vec{r'}) \frac{1}{|\vec{r}-\vec{r'}|} e^{i\left(k_{0z}^{0}-k_{0z}^{m}\right)z} dz d^{3}r' \qquad (3.158)$$

$$= \frac{e^{2}}{4\pi} \int \int \mathcal{F}\left\{\phi_{m}\phi_{0}\right\}\left(\vec{q}\right) \frac{1}{\vec{q}^{2}} e^{i\left(k_{0z}^{0}-k_{0z}^{m}+q_{z}\right)z} e^{i\vec{Q}\vec{R}} dz d^{3}q \\
= \frac{e^{2}}{2} \int \mathcal{F}\left\{\phi_{m}\phi_{0}\right\}\left(\vec{Q},k_{0z}^{m}-k_{0z}^{0}\right) \frac{1}{\vec{Q}^{2}+\left(k_{0z}^{m}-k_{0z}^{0}\right)^{2}} e^{i\vec{Q}\vec{R}} d^{2}Q.$$

The last line is an inverse 2D Fourier transform of a product between a specimen dependent function  $\mathcal{F} \{\phi_m \phi_0\}$ and the Fourier transform of the Coulomb potential. By applying the convolution theorem the last result can be equivalently written as

$$\varphi_m\left(\vec{R}, z\right) = \frac{e^2}{4\pi} \int \phi_m\left(\vec{R}, z'\right) \phi_0\left(\vec{R}, z'\right) e^{-i\left(k_{0z}^m - k_{0z}^0\right)z'} dz' \otimes K_0\left(\left(k_{0z}^m - k_{0z}^0\right)R\right)$$
(3.159)

where  $K_0$  is a modified Bessel function of the second kind (see Abramowitz and Stegun (1964) for the Fourier transformation of the 2D Lorentzian).<sup>24</sup> The 2D range  $\vec{R}$  where an at  $\vec{R'}$  inelastically scattered wave can be detected is consequently related to the effective wave vector  $(k_{0z}^m - k_{0z}^0)$ .<sup>25</sup> If the effective wave vector is small,

 $<sup>^{22}</sup>$ The scalar relativistic transition density has been used here since plasmon are non-relativistic oscillations, i.e., only the  $\gamma_0$  component of the spinor transition current, the density, has to considered.

<sup>&</sup>lt;sup>23</sup>The restrictions mainly refer to the harmonic approximation applied to the beam electron-phonon interaction.

 $<sup>^{24}</sup>$ The frequent appearance of  $K_0$  in the context of inelastic scattering theory can be also explained when considering that  $K_0$  is the projection of the screened Coulomb potential.

 $<sup>^{25}</sup>$ Note that one has to distinguish between the delocalization of the inelastically scattered wave function and the delocalization of the inelastic interaction as the latter is given by the (retarded) electromagnetic potentials.

the delocalization of the inelastically scattered wave function is small, i.e., atomic resolution is possible at large energy transfers, against what small energy transfers are delocalized, even though the specimen states  $\phi$  are well localized. Expression (3.159) can be further simplified if assuming that the specimen is homogeneous in *x*-direction, hence

$$\varphi_m\left(\vec{R},z\right) = \frac{e^2}{2} \int \mathcal{F}\left\{\phi_m\phi_0\right\} \left(q_y, k_{0z}^m - k_{0z}^0\right) \frac{1}{q_y^2 + (k_{0z}^m - k_{0z}^0)^2} e^{iq_y y} \mathrm{d}q_y \qquad (3.160)$$
$$= \frac{e^2}{4\pi} \int \phi_m\left(y,z'\right) \phi_0\left(y,z'\right) e^{-i\left(k_{0z}^m - k_{0z}^0\right)z'} \mathrm{d}z' \otimes e^{-\left|k_{0z}^m - k_{0z}^0\right||y|}.$$

That means that the probability amplitude of inelastic scattering at some distance away from the specimen decays exponentially. This result is important when discussing the influence of inelastic scattering on off-axis EH, since the initial assumption that only the elastic channel is projected out by interference with an empty reference wave fails, if the latter is not an elastic pure state but rather a mixed state containing inelastically scattered waves. If, however, the reference wave is spatially well separated, and hence the amplitude of inelastic states stays small, one can safely neglect their contribution. This is the case in medium-resolution EH, where the reference wave is separated several 100 nm. In high-resolution EH the distance can be as small as several 10 nm, where contributions from bulk inelastic excitations start to contribute more significantly, leading to contrast damping similar to that appearing in conventional imaging.

## 3.4 Summary

The description of the scattering process in TEM can be accurately conducted in the framework of QED. Both elastic and inelastic scattering can be simulated for a wide variety of excitation processes with a resolution and accuracy sufficient for current experimental setups. The elastic channel is affected by the following influences

- electrostatic potential of the scatterer, which is in turn dominated by the strongly peaked screened atomic potentials. The complex scattering on multiple atoms arranged on a crystal grid can be sufficiently well described within the forward scattering approximations in general and the small angle approximation combined with fixed integration steps (Multislice) under almost all practical interesting cases. Under special imaging conditions usually used for medium resolution holography, namely thick specimen tilted out of zone axis, the complicated behavior can be approximated by a simple modified Phase Grating Approximation. Spin-orbit coupling can be safely neglected.
- thermal motion of the atoms, which manifests itself depending on the imaging conditions. Dedicated MS formalisms valid for conventional intensity recording and for waves reconstructed by off-axis holography have been developed. A non-trivial modulation of the recorded intensity and in particular the reconstructed wave is obtained, if the scattering potentials are large (e.g. heavy atoms), leading to different modifications of spatial frequencies. Another consequence is an overall reduction of the reconstructed amplitude, which is not related to inelastic scattering but to decoherence. Thus, inelastic mean-free path measurements by means of Electron Holography have to be reinterpreted. Special attention has to be paid, when comparing complex electron waves reconstructed from images subject to different imaging conditions, for instance off-axis Electron Holography with focal-series reconstruction. The intensities recorded at different foci in the image plane, used for reconstructing the wave during focal series reconstruction, are subject to the condition of intensity averaging and not reconstructed wave averaging. Hence they do not compare to waves reconstructed by off-axis Electron Holography or reconstructed wave averaged image simulations, in particular when heavy atoms are involved in the scattering process. The same argumentation has to be applied to phases obtained from diffraction data by refinement techniques.
- coupling to the inelastic channels, mainly seen as a removal of elastically scattered electrons and small and experimentally not yet measured diffraction effects due to a double virtual photon exchange. Since the occurrence of inelastic scattering is mainly concentrated in the (delocalized) low-loss regime the removal of elastically scattered electrons is equally delocalized and corresponds to a damping factor in the reconstructed amplitude.

The properties of inelastic scattering can be distinguished according to the specimen transition involved.

• Localized specimen states such as core electron wave functions or atom cores can be roughly interpreted as localized and characteristic sources for an incoherently scattered electron situated within the specimen. It was shown that the local modification of the elastic wave due to the strongly peaked atomic potentials leads to significant effects in high-resolution EFTEM images or EELS. Both forward scattering and the MS algorithm were generalized to accurately include the local modification of the wave function.

- Delocalized states like photons (Bremsstrahlung), plasmons or phonons act as an amplifier for semiconvergence angles in the beam. The latter can lead to a significant contrast damping, contributing to the Stobbs factor in non-aberration free microscopes.
- The intriguing effect of interference fringes formed by inelastically scattered electrons has a rather small influence in the usual medium-resolution off-axis holographic setup. A significant influence might be detectable in high-resolution EH, leading to a small decrease in contrast.

## Chapter 4

# Ferroic solid state properties

According to Chap. 2, signal resolution is limited by noise and depends on the spatial homogeneity of the image, i.e., high signal resolution can be achieved at medium resolution TEM, whereas the signal resolution is lower at high spatial resolution, when large spatial contrasts like in HRTEM prevail. According to Chap. 3, ion potentials exercise the strongest influence on the beam electron wave, electronic potentials are weaker and often have to be investigated under dedicated imaging conditions. Furthermore, a direct interpretation of TEM data in terms of specimen properties is complicated and often needs support from scattering simulations to gain a better understanding. The determination of the following solid state properties will be considered, emphasizing the quantitative evaluation of which by means of TEM:

- 1. Structural properties: HRTEM gives access to atomic column positions, hence lattice constants, distortions, strain, defect structures like domain boundaries, etc. As will be discussed below, the structural information can be related to electric properties like the polarization, etc.
- 2. Microscopic electric fields such as produced by atoms with different core charges Z. Consequently, different atomic species can be identified according to the atomic electrostatic potential.
- 3. Macroscopic electric fields: medium resolution images give access to information about medium scale electric fields with a high signal precision. Prominent examples are the detection of electric fields in pn-junctions, averaged electrostatic potentials yielding information about the chemical bonding, and depolarization fields characterizing the stability of domain walls or other types of interfaces in ferroic materials.
- 4. Macroscopic magnetic fields: As discussed in Chap. 3, magnetic fields are generally not directly accessible on a microscopic (atomic) length scale. Macroscopic magnetic fields, for instant generated by magnetic particles, are accessible, though. The calculation of such magnetic fields will not be treated in this work.

(Multi-)ferroic and in particular ferroelectric materials will be the main subject in the following. Ferroelectricity is usually generated by a symmetry break in (hybridized) orbitals (e.g. Jahn-Teller effect). It would be intriguing to measure the modulation of the electrostatic potential thereby produced on an atomic length scale and correlate this directly to the chemical bonding. Unfortunately, this goal is not achievable with current state-of-the-art electron holography as will be shown in the following.

Multiferroic materials are characterized by one or more ordering parameters, such as the spontaneous electric or magnetic polarization  $\vec{P_s}$  or  $\vec{M_s}$ , and attracted large interest throughout the decades due to their fascinating physics and the wide area of applications. The ferroelectric ordering parameter is intimately related to the atomic structure of the material, i.e., the distance between the positive (ionic) and negative (electronic) charge center of gravity of the so-called natural unit cell determines the spontaneous polarization (e.g. Kittel (1996)). Within linear response theory, a direct relationship of the ion positions to the electric polarization can be expressed by the following formula

$$d\vec{P} = \frac{1}{\Omega} \sum_{n} \mathbf{Z}_{n}^{*} d\vec{r}_{n} , \qquad (4.1)$$

where  $\mathbf{Z}^*$  is the so-called Born effective charges tensor defined as the change of polarization  $Z_{ijn}^* = \Omega \partial P_i / \partial x_{jn}$ per displacement  $d\vec{r_n}$  of the nth atom in the unit cell with a volume  $\Omega$ . The total spontaneous polarization is obtained by integrating the change in polarization according to (4.1) along a line connecting a non-polar configuration with the polarized one, i.e.

$$\vec{P}_s = \sum_n \int \mathbf{Z}_n^* d\vec{r}_n \,. \tag{4.2}$$

In a seminal paper R.D. King-Smith and D. Vanderbilt derived an expression for  $\mathbf{Z}_n^*$  based on perturbation theory (Vanderbilt and King-Smith (1993)),<sup>1</sup> which allowed an accurate and convenient ab-initio calculation of spontaneous polarizations and polarization changes. The Born effective charge tensor used in the following is calculated with the help of this formula. If the Born effective charge tensor for the material in question is known, the electric polarization can be determined from HRTEM measurements. The polarization  $\vec{P}$  is related to the other macroscopic electric fields through the relationship

$$\epsilon_0 \vec{E} = \vec{D} - \vec{P} \,. \tag{4.3}$$

The bulk ground state of a ferroelectric material is characterized by a zero electric field  $\vec{E}$ , hence the polarization  $\vec{P}$  generated by the structure of the bulk unit cell is completely screened by the electric displacement  $\vec{D}$  generated by surface charges sitting at the boundary of the bulk material. The equivalence of surface charges and polarization is used to determine bulk polarizations from hysteresis measurement (see e.g. Gonzalo and Jiménez (2005)). Non-ground state configurations such as domain boundaries, externally distorted lattices (piezoelectric effect) and thermally excited lattices (pyroelectric effect) are characterized by a non-zero electric field  $\vec{E}$ , which can lead to potentials  $V = -\int \vec{E} \cdot d\vec{s}$ , possibly detectable by electron holographical measurements. These non-zero electric fields  $\vec{E}$  are referred to as depolarization fields due to the force  $\vec{F} = q\vec{E}$  produced by it, which is acting on the ions and electrons in the material in the opposite direction of the polarization. An upper bound for macroscopic depolarization fields  $\vec{E}$  is generally given by the dielectric strength of the material.

Similar to the atomic displacement  $\Delta \vec{x}_n$ , the depolarization field  $\vec{E}$  can be correlated to the polarization  $\vec{P}$ . Within the linear response approach (e.g. Jackson (2006)) the following relationship introducing the linear susceptibility  $\chi$  is established

$$\vec{P} = \epsilon_0 \chi \vec{E} \,. \tag{4.4}$$

Note that changes in the polarization with respect to the ground state, rather than the polarization itself, occur on the left hand side, otherwise the spontaneous polarization itself would lead to unrealistically large electric fields and potential differences (Lichte et al. (2002), Matsumoto et al. (2008)). The correlation of the magnetization to the structure is usually weaker than in the electric case, i.e., changes in magnetization with respect to atomic displacements are weaker. The relationship of the holographically reconstructed phase to the magnetization on the other hand is straight forward, i.e.

$$\phi = -\frac{e}{\hbar} \int \vec{B} \cdot \vec{n}_A dA = 4\pi \frac{e}{\hbar} \int \vec{M} \cdot \vec{n}_A dA, \qquad (4.5)$$

facilitating a straight forward determination by means of Electron Holography (A is the surface enclosed by beam and reference electron). Thus, EH can contribute to the characterization of such materials in terms of ordering parameters either by directly measuring the depolarization fields or by determining the structure. Both approaches, however, motivate the analysis of physical models of ferroic materials in the following.

In this work, ab-initio methods are applied to calculate structural and electrical properties of several perovskite systems.

## 4.1 Hartree-Fock Theory, Density Functional Theory

### 4.1.1 General formulation

The calculation of solid state properties from first principles, i.e. from the basic laws of quantum mechanics, is based on different approximations to the exact solution of the many-body Dirac equation. If spinor properties are negligible, relativistic effects can be treated within a scalar relativistic approach, i.e. a Klein-Gordon equation. If the potentials are small, both relativistic equations can be approximated to a relativistically corrected Pauli or Schrödinger equation. The latter will be shortly illustrated in the following. Due to the Pauli principle, the many-body wave function  $\Psi(\vec{r_1}, \vec{r_2}, ..., \vec{r_N})$  of fermions has to be odd with respect to a permutation of particles  $\vec{r_i} \leftrightarrow \vec{r_j}$ . Thus, it can be written as a sum of so-called Slater determinants

$$\Psi = \begin{vmatrix} \phi_1(\vec{r}_1) & \cdots & \phi_N(\vec{r}_1) \\ \vdots & \ddots & \vdots \\ \phi_1(\vec{r}_N) & \cdots & \phi_N(\vec{r}_N) \end{vmatrix},$$
(4.6)

which form a basis in the Hilbert space of N-particle wave functions (e.g. Scherz (2005)). By choosing a particular basis, a certain N-particle wave function can always be represented as one single Slater determinant.

<sup>&</sup>lt;sup>1</sup>It turns out that the polarization in this theory is connected to the concept of a Berry phase, hence the approach of R.D. King-Smith and D. Vanderbuilt is sometimes referred to as Berry phase approach.

The second ingredient in the theory is the so-called Hartree-Fock approximation, which neglects any fluctuations around the mean value of the wave function, thereby neglecting any time-dependent processes, excitations, etc. The many-body problem can then be stationarized. The total energy of the system is

$$E = \left\langle \Psi \middle| \hat{\mathcal{H}} \middle| \Psi \right\rangle \,. \tag{4.7}$$

After inserting a single Slater determinant one obtains the following typical total energy

$$E = \sum_{i=1}^{N} \left\langle \phi_i \left| -\frac{1}{2} \Delta + V \right| \phi_i \right\rangle + \frac{1}{2} \sum_{i,j=1}^{N} \left[ \left\langle \phi_i \phi_j \left| \frac{1}{|\vec{r}_i - \vec{r}_j|} \right| \phi_i \phi_j \right\rangle - \left\langle \phi_j \phi_i \left| \frac{1}{|\vec{r}_i - \vec{r}_j|} \right| \phi_i \phi_j \right\rangle \right], \quad (4.8)$$

which contains all important energy contributions, i.e. the kinetic energy and the potential energy in the first sum and the energy resulting from the two-body interaction in the second sum. The canonical approach to find stable solutions for  $\Psi$  would require the vanishing of the variation of the total energy E with respect to the many-body wave function, i.e.

$$\frac{\delta E\left[\Psi\right]}{\delta\Psi} = \frac{E\left[\Psi + \delta\Psi\right] - E\left[\Psi\right]}{\delta\Psi} = 0 \tag{4.9}$$

under the restriction of norm conservation  $\langle \Psi | \Psi \rangle = 1$ . The disappearance of the variation yields the Euler-Lagrange differential equation of the many-body system<sup>2</sup>. Unfortunately, the Hamiltonian  $\hat{H}$  contains manyparticle operators, thus preventing a direct analytical solution of the variation. There are several strategies to find a solution numerically (e.g. Springborg (2000)). A rather direct way is the brute-force numeric evaluation of the integrals occurring in (4.7) by Monte-Carlo integration techniques (e.g. Nightingale and Umrigar (1999)). These techniques are restricted to a small number of degrees of freedom (electrons), but provide very accurate results. The two approaches followed in this work are sketched in the following:

1. One possibility is provided by carrying out the variation in the space of Slater determinants forming a complete orthonormal basis, i.e.

$$\frac{\delta E\left[\Psi\left(x\right)\right]}{\delta\Psi\left(x\right)} = \frac{\delta E\left[\Psi\left(a_{i}\right)\right]}{\delta\Psi\left(a_{i}\right)}.$$
(4.10)

In practice, one would have to restrict the Hilbert space to a finite number of basis functions though, therefore making the choice of basic orthonormal Slater determinants very important. This formalism is called configuration interaction and can be combined with the next approach (Springborg (2000)).

2. The second possibility exploits the chain rule of variational calculus:

$$\frac{\delta E\left[\Psi\right]}{\delta\Psi} = \frac{\delta E\left[\phi_1\right]}{\delta\phi_1}\frac{\partial\phi_1}{\partial\Psi} + \dots + \frac{\delta E\left[\phi_N\right]}{\delta\phi_N}\frac{\partial\phi_N}{\partial\Psi} = 0\,,\tag{4.11}$$

providing one equation for each degree of freedom. The variation of the total wave function  $\Psi$  with respect to the single particle wave functions  $\phi_i$  is given by the point-wise derivative of the Slater determinant (4.6)

$$\frac{\partial \Psi}{\partial \phi_i} = \frac{\partial \Psi_{ij}}{\partial \phi_i} \,. \tag{4.12}$$

If the inverse mapping  $\phi_i(\Psi)$  exists and the latter derivative is unequal to zero, then

$$\frac{\partial \phi_i}{\partial \Psi} = \Psi'^{-1} \,. \tag{4.13}$$

The full evaluation of (4.11) is by definition equivalent to the full problem, hence provides no simplification. Postulating that all  $\frac{\delta E}{\delta \phi_i}$  vanish separately is, however, sufficient for solving (4.11), yielding N separate equations

$$\left[ -\frac{1}{2}\Delta + V + \sum_{i=1}^{N} \left( \int \frac{|\phi_i|^2}{|\vec{r}_i - \vec{r}_k|} d\vec{r}_i - \hat{K}_i \right) \right] \phi_k = \epsilon_k \phi_k \,. \tag{4.14}$$

The prize which has to be paid for this simplification is, however, a limitation of the space of solutions, i.e., when for instance seeking the ground state wave function, one will find a solution which has not the lowest energy possible within the complete space of stationary solutions. The difference of this restricted stationary solution to the general one (including time dependent processes) is usually referred to as correlation and can be reduced by various methods (see above). The system of equations (4.14) is referred to as the Hartree-Fock-Slater equations. They constitute a system of coupled nonlinear integro-differential equations. The major obstacle to their solution is the so-called exchange term

<sup>&</sup>lt;sup>2</sup>Some basic properties of functional derivatives are recapitulated in App. A.7.

$$\hat{\mathbf{K}}_{i}\phi_{k}\left(\vec{r}_{1}\right) = \int \frac{\phi_{i}^{*}\left(\vec{r}_{2}\right)\phi_{k}\left(\vec{r}_{2}\right)\phi_{i}\left(\vec{r}_{1}\right)}{\left|\vec{r}_{2}-\vec{r}_{1}\right|} \mathrm{d}r_{2} \,.$$

$$(4.15)$$

To overcome the difficulties with the exchange term, Slater proposed to approximate the exchange term with the exact solution from a homogeneous free electron gas (e.g. Eschrig (1996)). By inserting this approximation, the equations (4.14) are similar to the so called Kohn-Sham (KS) equations within the Local Density Approximation (LDA), being derived within the framework of density functional theory (DFT) (e.g. Eschrig (1996)). Without going much into details, this derivation of the KS equations is based upon a proof of existence of a unique energy functional of the density for the ground state (1st Hohenberg-Kohn theorem), which is extended to the disappearance of the variation in the ground state (2nd Hohenberg-Kohn theorem) (Eschrig (1996)). The exact form of the functionals, however, remains mysterious. By resorting to the free electron gas one can find an analytical expression for the functionals, which can be used in the general case, if one assumes that the real inhomogeneous electron gas can be locally approximation (LDA). The advantage of the LDA approach is that correlation effects are partly incorporated. It has been shown in numerous examples that the theory allows accurate determination of ground state properties for a large class of materials (for an overview see e.g. Springborg (2000)).

Exchange and correlation effects play an important role in materials containing half-metal elements, especially if the atoms have non-zero magnetic moments. A dedicated extension of DFT within the LDA to treat strongly correlated electrons is used in this work, which is derived from the Hubbard model (e.g. Nolting (2005)), where exchange and correlation effects are restricted to on-site terms, i.e. between wave function situated on a particular atom. Within that model, an energy term U for placing an additional electron within a certain state can be derived (Anisimov and Gunnarsson (1991)). This energy depends on the localization of the surrounding orbitals and their energy, which implies that it plays an important role mainly for d and f orbitals. This energy term can be inserted in the Hamiltonian of those orbitals leading to the LDA+U formalism. The size of the energy term U can be adjusted according to experimental results or determined by restricted ab-initio calculations.

### 4.1.2 Solution of Hartree-Fock-Slater / Kohn-Sham-Equations



Figure 4.1: Simplified scheme for the iterative (self consistent, fix point) solution of the Hartree-Fock (Kohn-Sham) equation.

The Hartree-Fock-Slater equations (4.14) combined with the LDA still possess a mathematically complicated structure and require appropriate boundary conditions in order to find a solution. Periodic boundary conditions are most convenient, although Dirichlet or von Neumann boundary conditions are also conceivable. Particularly in the presence of sufficiently strong macroscopic electric or magnetic fields, periodic boundary conditions are not

applicable. This can be important when considering pyroelectric materials, which exhibit strong electric fields under the influence of pressure (piezoelectricity), temperature (pyroelectricity) and during phase transitions. Those effects are, however, dynamic, in that the electrons or ions move along the field lines eventually screening the original field. As already pointed out in the beginning of this chapter, the stable pyroelectric system possesses only a small or zero macroscopic field, allowing the application of periodic boundary conditions. Providing suitable boundary conditions, equations (4.14) can be iteratively solved by a procedure scotched in Fig. 4.1. If the starting wave function is close enough to a fix point of the mapping (4.14), the iteration cycle eventually converges, yielding a solution. If the mapping possesses several fix points, the starting condition determines which one will be converged at. As each different local ground state represents a fix point of the mapping, the starting conditions together with a rule for filling the one electron orbitals in the Slater determinant determine which state is calculated. As will be shown subsequently, KS equations of ferroelectric systems exhibit, under certain circumstances, different fix points even for the ground state, thus require careful considerations for different starting conditions.

The iterative algorithm displayed in Fig. 4.1, requires a truncation of the infinite dimensional Hilbert space of the N-particle wave function  $\Psi$ . Several finite dimensional basis sets have been developed. Within this work, the following ones have been applied:

- 1. It is possible to directly discretize the spatial coordinates, hence to work with plane waves in reciprocal space, where the functionals are most conveniently calculated. This plane wave approach suffers from a very high number of plane waves necessary to describe core electrons, thus is usually combined with pseudopotentials, which contain the core electrons. The pseudopotentials, being non-local, depend on the respective system under investigation. Fortunately, they can be transferred between similar systems, thus making it possible to test the pseudopotential on a well known system and subsequently transfer it to the system under investigation. A plane-wave basis set is used by the software packages VASP (Kresse and Furthmüller (1996)) and ABINIT (Gonze et al. (2002)), used for large parts of the following calculations.
- 2. Another, physically more ostensive, basis set would consist of a limited number of atomic orbitals. The advantage of this approach is the comparatively low number of basis functions needed. A drawback is a more cumbersome integration scheme. To overcome the problem of the integrals, Gaussian atomic orbitals can be used at the cost of increasing the basis set (e.g. used in the software package Gaussian (Frisch et al. (2009)). Particularly interesting ways to minimize the number of orbitals employs an adjustment of the orbitals in every iteration cycle (software package FPLO, Koepernik and Eschrig (1999)).
- 3. Finally, the methods one and two can be combined using plane waves in the space between atoms and atomic orbitals for regions within a sphere around the atom core. At the surface of the sphere, boundary conditions for the wave function determine the coefficients. This approach is implemented in the software package Wien2k (Blaha et al. (2001)).

Having introduced the basics of Density Functional Theory and the software packages implementing the latter, explicit calculations will be conducted in the next section.

## 4.2 Material systems

### 4.2.1 Bulk BaTiO<sub>3</sub>/PbTiO<sub>3</sub>

Bariumtitanate (BaTi $O_3$ ) is one of the most thoroughly analyzed ferroelectric materials. It possesses a simple perovskite structure, the growth of which can be precisely tailored. The polymorph phase diagram is rather complicated, the most important phase considered in this work is the tetragonal phase at room temperature. Major fields of application are actuators (large piezoelectric constant), ceramic capacitors (large dielectric constant) and thermistors (pyroelectric constant). Since the pioneering work of R.E.Cohen and H. Krakauer (Cohen and Krakauer (1990)) the bulk structure is a standard task for DFT calculations, all phases could be calculated by now, including the correct energetic order. Major breakthroughs in the understanding of the ferroelectric effect, like the distinguishing between the frozen-phonon and the order-disorder type (see Fig. 4.2), or the development of an accurate theoretical model, to alternatively describe polarization through the integration of perturbational currents, have been derived from that material.

Density-functional band-structure calculations (Hohenberg and Kohn (1964); Kohn and Sham (1965)) were employed to obtain the structural and electronic properties of the tetragonal and cubic structures of BaTiO<sub>3</sub> within the LDA. A structure optimization was carried out with the program package ABINIT (Gonze et al. (2002)), employing a plane-wave basis with a cutoff energy of 1333 eV to represent the valence and semi-core electrons (Ba:  $5p^{6}6s^{2}$ , Ti:  $3p^{6}4s^{2}3d^{2}$ , O:  $2s^{2}2p^{4}$ ) and soft-core pseudo-potentials for the atom cores (Goedecker et al. (1996)). For the investigation of tetragonal BaTiO<sub>3</sub>, the c/a ratio was kept fixed at the experimental value of 1.011, obtained by XRD. The optimized tetragonal and cubic structures are almost iso-energetic with



Figure 4.2: Lattice configurations illustrating the frozen-phonon and order-disorder ferroelectric behavior in the perovskite structure. The order-disorder type is here characterized by 8 energetically favorable positions of the blue atom in the center of the unit cell. In the cubic phase of the material, the atom occupies all 8 positions. When reducing the temperature a symmetry break occurs leaving the atom on one side of the highest energy wall between the positions.

the tetragonal one being less than 10 meV lower in energy, which is in an excellent agreement with previous calculations on distorted BaTiO<sub>3</sub> phases (Diéguez et al. (2004)). Optimization of the structural parameters yielded lattice parameters (a = 3.994 Å, c = 4.038 Å) similar to those obtained by XRD (Rother et al. (2006)). The atomic positions, calculated by DFT within the LDA are listed in Tab. 2, and selected lattice planes of the unit cell are schematically shown in Fig. 4.3.

atom	x/a	y/b	z/c
Ba	0	0	0
Ti	0.5	0.5	0.483
01	0.5	0.5	0.027
02	0	0.5	0.513

Table 4.1: Fractional atomic coordinates of tetragonal  $BaTiO_3$  (space group P4mm) obtained by DFT LDA calculations. The error is evaluated to be in the order of 1%.

A more accurate computation of the electron density was performed for the tetragonal phase only, since for this crystalline polymorph modification of  $BaTiO_3$  the XRD measurements have been performed. The electron density was calculated using the all-electron full-potential local-orbital (FPLO, version 4.00-16) calculation scheme (Koepernik and Eschrig (1999)). The calculations were scalar-relativistic (Opahle (2001)). The local orbital basis set (Ba: 5s5p/4f5d6s6p, Ti: 3s3p/3d4s4p, O: -/2s2p3d) of semi-core/valence atomic orbitals was chosen. The electron density shown in Fig. 4.3 has been computed within the LDA and on a 128 x 128 x 128 grid of one unit cell. Additionally the thermal averaging was applied, using an average value for each direction of the mean square displacements listed in Tab. 4.1.

The potential calculated on the basis of the DFT electron densities via the Poisson equation is depicted in Fig. 4.4. The dominant asymmetry can be explained by the shift of the Ti and O atoms, when keeping in mind that their nominal charges are +4 and -2. It can be seen that the redistribution of the valence electrons (e.g. Fig. 4.3) produces a comparably small deformation of the nearly spherical atomic potentials in the vicinity of the atoms, which, to a good approximation, agree with that of free atoms. The deviation of the DFT potential from a potential generated by free atoms consists mainly of overall reduced atomic radii and stays smaller than 10 eV (Fig. 4.4). The electrostatic potential will subsequently serve as an input parameter for dynamical scattering simulations (see Chap. 5) to quantify the effects due to the ferroelectric polarization in the scattered wave and to analyze experimental images in the inverse sense (e.g. determine atom positions from experimental data).



Figure 4.3: A scheme of the section of (010) lattice plane at y = 0 (a) and y = 0.5 (b) according to results of structure optimization by DFT (LDA) calculations are drawn. The atomic distances calculated from structure model (Tab. 4.1) are indicated. ED maps of the corresponding crystal planes obtained by DFT (LDA) calculations are shown in (c) and (d). The contour lines characterizing constant positive ED are drawn at  $\rho = 2^n e/Å^3 n \in \{0,1,...,6\}$ . Again, the shift of the Ti and O atoms along c direction can clearly be seen.



Figure 4.4: Potential maps of the BaTiO<sub>3</sub> (010) crystal planes at (a,b) y/b = 0 and (c,d) y/b = 0.5. DFT potential are depicted in (a) and (c), whereas free atom potential according to Weickenmeier & Kohl are depicted in (b) and (d). The contour lines are drawn at  $U = \{0,5,10,50,100,500,1000\}V$ .

Several applications, such as non-volatile memories, require large spontaneous polarizations, stabilizing the ferroelectric distortion. Due to its moderate spontaneous polarization  $BaTiO_3$  is replaced by e.g.  $PbTiO_3$  in that field (Ishiwara et al. (2004)). Besides the Ti-O hybridization the so-called stereochemically inactive  $6s^2$  electron lone pair is the driving force behind the large polarization. The analysis of  $PbTiO_3$  was carried out analogously to that of  $BaTiO_3$ . The obtained lattice parameters (a = 3.908 Å, c = 4.188 Å) agree well with XRD measurements reported in literature (Mabud and Glazer (1979)). In Tab. 4.2 the structural parameters are summarized.

atom	x/a	y/b	z/c
Pb	0	0	0
Ti	0.5	0.5	0.614
01	0.5	0.5	0.102
02	0	0.5	0.531

Table 4.2: Fractional atomic coordinates of tetragonal  $PbTiO_3$  (space group P4mm) obtained by DFT LDA calculations. The standard deviations are evaluated to be in the order of 1%.





Figure 4.5: Potential maps of the PbTiO<sub>3</sub> (010) crystal planes at (a,b) y/b = 0 and (c,d) y/b = 0.5. DFT potential are depicted in (a) and (c), whereas free atom potential according to Weickenmeier and Kohl are depicted in (b) and (d). The contour lines are drawn at  $U = V \{0.5, 10, 50, 100, 500, 1000\}V$ .

#### 4.2. MATERIAL SYSTEMS

The c/a distortion as well as the displacement of the Ti atom with respect to the center of the unit cell is much larger than in the case of BaTiO<sub>3</sub> yielding a very large ferroelectric polarization of  $\sim 88\mu C/cm^2$  (Sághi-Szabó et al. (1998)), which makes the material attractive for various applications. Recently, there have been efforts to replace PbTiO<sub>3</sub> by other materials possessing a large polarization like the BiFeO<sub>3</sub> investigated in the next section to get rid of the environmental problematic lead. In spite of the stronger distortions and displacements, the comparison of the DFT potential and the free atom potential yields again a small difference below 10 eV (see Fig. 4.5).

### 4.2.2 BiFeO<sub>3</sub> domain walls

Perovskite-structured bismuth ferrite, BiFeO<sub>3</sub>, is the subject of much current research because of its large room temperature ferroelectric polarization and simultaneous (antiferro-)magnetic ordering. Such multiferroic materials show a wealth of complex physical properties caused by their coexisting electrical and magnetic order parameters, which in turn suggest potential applications in novel magnetoelectronic devices: Recent reports of electric-field induced switching of magnetization through exchange bias of ferromagnetic Co to BiFeO<sub>3</sub> are particularly promising (Zhao et al. (2006a); Chu et al. (2008)). In addition, the large ferroelectric polarization (Wang et al. (2003)), driven by the stereochemically active  $Bi^{3+}$  lone pair (Neaton et al. (2005)), is motivating investigation of its purely ferroelectric behavior for possible applications in ferroelectric memories.

The suitability of ferroelectric materials for memory applications is determined not only by the magnitude of their ferroelectric polarization, but also by factors such as switchability, fatigue and loss. These are in turn influenced by the structure of the domains and particularly by the boundaries between them. The detailed structure and formation energies of domain walls in some conventional ferroelectrics are now well established (see for example Stemmer et al. (1995); Floquet and Valot (1999) for experimental studies and Padilla et al. (1996); Meyer and Vanderbilt (2002) for calculations). For BiFeO<sub>3</sub>, however, the first experimental study of domain walls was only recently reported (Seidel et al. (2009)), and a detailed theoretical study is lacking. The additional consideration of the effect of a ferroelectric domain wall on the magnetic degree of freedom makes such a study particularly compelling.



Figure 4.6: Crystal structure of bulk  $BiFeO_3$ . Two simple perovskite unit cells are shown to illustrate that successive oxygen octahedra along the polar [111] axis rotate with opposite sense around [111]. The red arrows on the Fe atoms indicate the orientation of the magnetic moments in the (111) plane.

BiFeO<sub>3</sub> is a rhombohedral perovskite with space group R3c. The ground state structure is reached from the ideal cubic perovskite by imposing two symmetry-adapted lattice modes: (1) a non-polar R-point mode which rotates successive oxygen octahedra in opposite senses around the [111]-direction, and (2) a polar  $\Gamma_4^$ distortion, consisting of polar displacements along the [111]-direction as well as symmetric breathing of adjacent oxygen triangles (Fennie (2008)). The resulting rhombohedral lattice constant is 5.63 Å and the corresponding pseudocubic lattice constant is  $a_0 = 3.89$ . The rhombohedral angle,  $\alpha = 59.35^{\circ}$ , is close to the ideal value of 60° (Kubel and Schmid (1990)). First-principles density functional calculations have been shown to accurately reproduce these values (Neaton et al. (2005)). In addition, density functional calculations using the ideal rhombohedral angle of  $60^{\circ}$  had negligible deviation in energy and electronic properties from those at the fully relaxed coordinates; we will make use of this later in constructing the domain wall supercells.

The ferroelectric polarization is large,  $\sim 90\mu$ C/cm<sup>2</sup> (Wang et al. (2003)), and can point along any of the eight pseudo-cubic (111) directions (Kubel and Schmid (1990)). Simple geometrical considerations therefore suggest angles of  $\pm 71^{\circ}$ ,  $\pm 109^{\circ}$  or 180° between allowed polarization orientations of the ideal rhombohedral system ( $\alpha = 60^{\circ}$ , Streiffer et al. (1998)); the different variants are denoted by that ideal domain boundary angle in the following. Experimentally, such relative domain orientations and re-orientation angles have indeed been observed (Zhao et al. (2006b)). Currently nothing is known about the behavior of the octahedral rotations or the magnetism at the domain boundaries.

In general, the energetically favorable domain wall configurations for a particular symmetry are those orientations which can be free of both stress and space charge. For the rhombohedral symmetry of BiFeO<sub>3</sub>, these conditions lead to the following likely domain wall orientations for  $\pm 71^{\circ}$ ,  $\pm 109^{\circ}$  and  $180^{\circ}$  orientations respectively: {011}, {001} and {011} (in pseudo-cubic coordinates) (Streiffer et al. (1998)). For each of these wall orientations, there is a choice of atomic planes about which the domain wall can be centered (for example around a Bi-O or Fe-O plane in the 109° case). In addition, since the rotations of the oxygen octahedra are uncoupled to the orientation of the polarization, different relative orientations of oxygen octahedra on either side of the domain wall are possible. In order to survey all possibilities the following domain boundaries are investigated:

1. 71°: The domain wall lies in the (011) plane with the electric polarization changing from the [111] direction on one side of the domain wall to [ $\overline{1}11$ ] on the other (Fig. 4.7). Two configurations of the rotations of the oxygen octahedra, which are referred to as either continuous or changing are considered. In the continuous case, the phase of the oxygen octahedral rotations remains unchanged along an integral curve of the polarization vector field; in the changing case the phase reverses at the domain wall. In principle the wall could be centered around either a BiFeO or O<sub>2</sub> plane (or an intermediate plane); it will be shown below, however, that the width of the domain wall in this case does not permit a distinction to be made.



Figure 4.7: (a) 71° domain boundary with continuous oxygen octahedral rotations.

2. 109°: The (001) plane is used for the domain wall, with polarization changing from the [111] to the [ $\overline{111}$ ] direction (Fig. 4.8). Again two configurations of the octahedral rotations are explored, with continuous or changing phase in the [100] projection. In this case domain walls centered on FeO<sub>2</sub> and BiO planes could be separately resolved, since their separation is  $\sqrt{2}$  times that of the BiFeO and O<sub>2</sub> planes in the 71° case.



Figure 4.8: (a) 109° domain boundary with continuous oxygen octahedral rotations.

3. 180°: The (011) plane is used for the domain wall, with polarization changing between [111] and [111] directions (Fig. 4.9). Again two octahedral tilt patterns are investigated, with the phases along the polarization direction either continuous or changing across the boundary. As in the 71° case, the BiFeO-and O<sub>2</sub>-centered domain walls are not distinguished.

center of domain wall



Figure 4.9: 180° domain boundary with continuous oxygen octahedral rotations.

Density functional (DFT) calculations have been performed using the Vienna ab-initio simulation package, VASP (Kresse and Furthmüller (1996)), incorporating the projector augmented wave method (Blöchl (1994); Kresse and Joubert (1999)) with the default VASP PAW potentials including semi-core states in the valence manifold (core states Bi: [Kr], Fe: [Ne3s<sup>2</sup>], O: 1s<sup>2</sup>). Furthermore, the rotationally invariant implementation (Liechtenstein et al. (1995)) of the LSDA+U method (Anisimov et al. (1997)) has been employed to describe the exchange-correlation functional with values of U = 3 eV and J = 1 eV that were shown previously to accurately reproduce the experimentally observed structural and electronic properties of bulk BiFeO<sub>3</sub> (Neaton et al. (2005); Ederer and Spaldin (2005a,b)).

Supercells containing two domains separated by domain walls, with a total of 120 atoms (60 atoms per domain) have been constructed; the width of each domain was then six pseudocubic unit cells. The initial lattice parameters are obtained from calculations for bulk BiFeO<sub>3</sub> (see Neaton et al. (2005)), with a slight change: the rhombohedral angle,  $\alpha$ , was taken to be exactly 60° allowing to incorporate both domains in one supercell. While the electronic structure of bulk BiFeO<sub>3</sub> at  $\alpha = 60^{\circ}$  is indistinguishable from that at the experimental  $\alpha = 59.35^{\circ}$ , it is pointed out that this constraint might influence the strain profile at the domain boundary.

Full structural optimizations of the atomic positions (until the forces on each ion were below 0.03 eV per Å) and cell parameters (until energy differences were below 0.01 eV) were then performed with no symmetry constraints imposed for all of the domain configurations described above. The cell parameter relaxations were necessary, because the interlayer distance in all three domain walls is slightly larger (by around 0.1 Å) than that in the bulk. Several initializations different with respect to the initial spin configuration and ion positions were performed for each configuration to reduce the probability of being trapped in local minima. In the 71° and 180° case a  $5 \times 3 \times 1$  and in the 109° case a  $5 \times 5 \times 1$  k-point sampling and a plane wave energy cut-off of 550 eV were used.

In all cases our supercells relaxed to contain two distinct domains, with the layers in the middle of each domain having similar structure to that of bulk BiFeO<sub>3</sub>; this suggests that the supercells were large enough to minimize interactions between the two domain walls present due to periodic continuation.

71° c	71° d	109° Bc	$109^{\circ} \mathrm{Bd}$	$109^{\circ}$ Fc	109° Fd	180° с
363	436	205	896	492	1811	829

Table 4.3: Domain wall energies in  $mJ/m^2$ , B and F indicate the BiFeO- and FeO<sub>2</sub>-centered planes, c and d label the continuous or discontinuous oxygen octahedral rotations.

In Tab. 4.3 the calculated domain wall energies for all of the configurations described in the previous section are listed. It is clear that, in all cases, the configuration with the least perturbation to the phase of the octahedral rotations is lowest in energy. Indeed, in the  $180^{\circ}$  case it was impossible to obtain a converged solution for the case with reversal of the octahedral rotations at the domain boundary. The large differences between the continuous and discontinuous oxygen octahedra rotations are a peculiarity of the  $BiFeO_3$  structure and indicates the importance of the Fe-O-Fe bonding angles in determining the structural stability. The  $109^{\circ}$ wall is energetically the most stable of the three orientations. It is somewhat surprising that the  $109^{\circ}$  wall is lower in energy that the  $71^{\circ}$  wall; since the change in orientation of the electric polarization vector is smaller in the latter, one would also expect the perturbation to the structure to be smaller (previous calculations for PbTiO<sub>3</sub> found the 90° wall to be lower in energy than the 180° wall, consistent with this argument (Meyer and Vanderbilt (2002))). This reversal is possibly caused by the favorable arrangement of the oxygen octahedra at the  $109^{\circ}$  wall boundary: since the  $109^{\circ}$  wall lies in the  $\{001\}$  plane, it is oriented along the apices of the oxygen octahedra (Fig. 4.8(b) upper panel), whereas the  $71^{\circ}$  and  $180^{\circ}$  {011} walls are oriented along the octahedral edges (Figs. 4.7(a) and 4.9(c) upper panels) giving them less freedom to accommodate the changes in polarization direction. The 109° BiO-centered wall is lower in energy than the FeO<sub>2</sub>-centered wall, consistent with previous studies for other perovskite ferroelectric domain boundaries which also found AO-centered walls to be more stable (Meyer and Vanderbilt (2002)). The  $180^{\circ}$  case has the highest domain wall energy, consistent with its having the largest change in the polarization orientation. Finally, it is noted that the domain wall energies in BiFeO<sub>3</sub> are significantly larger than those calculated for PbTiO<sub>3</sub>, which in turn are larger than the BaTiO<sub>3</sub> values (Tab. 4.4). The large increase from BaTiO<sub>3</sub> to PbTiO<sub>3</sub> suggests a correlation between polarization magnitude and domain wall energy. While changes in polarization would predict somewhat larger domain wall energies for BiFeO<sub>3</sub>, there is a large additional increase which is likely a result of the additional deformations caused by the octahedral rotations (see discussion above). It is also possible that the magnetic energy cost associated with perturbing the Fe-O-Fe bond angles further raises the domain wall energies in BiFeO<sub>3</sub>.

angle	$BaTiO_3$	$PbTiO_3$
90°	N/A	35.2
180°	7.5	132

Table 4.4: Lowest calculated domain wall energies  $(mJ/m^2)$  for 90° and 180° domain walls in BaTiO<sub>3</sub> and PbTiO<sub>3</sub>, from Meyer and Vanderbilt (2002).

In Fig. 4.10 the Fe-O-Fe angles in each layer across the supercells are plotted. Within the central region of the domain the bulk value of  $152.9^{\circ}$  is regained as expected. The angles change by up to  $\sim 4^{\circ}$  in the wall region to accommodate the changes in structure associated with the polarization reorientation. However, the Fe-O-Fe angles remain far from  $180^{\circ}$  in all cases, indicating that the structure within the walls is far from an ideal cubic perovskite structure. It is also clear from Fig. 4.10 that the bulk behavior is recovered within one or two layers from the domain wall boundary, consistent with earlier studies on PbTiO<sub>3</sub> domain walls (Meyer and Vanderbilt (2002)).



Figure 4.10: Fe-O-Fe angles in each layer of the supercell, the bulk value is indicated by the straight line. Note the change in values in the domain wall region.

In order to better understand the change in structure across the domain wall, a layer-by-layer analysis of the local polarization was performed by summing over the displacements of the atoms in each layer from their ideal cubic perovskite positions, multiplied by their Born effective charges (BECs). While there is not a unique way to partition the layers, one finds that the results from different decomposition schemes are similar, and so we use the narrowest possible layer partition in order to optimize the resolution. The BECs are taken from the R3c structure calculated in a previous study (Neaton et al. (2005)) using the same computational parameters as in this study; note that the actual BECs might deviate slightly from these values. This technique was used previously to analyze the polarization evolution across PbTiO<sub>3</sub> domain walls (Meyer and Vanderbilt (2002)). Two details are particularly interesting: First whether the polarization reorientation takes place through a rigid rotation of the local polarization, without a reduction in its local magnitude (analogous to the rotation of a magnetic moment in a Bloch wall in a ferromagnet). And second, whether a change in polarization in the direction perpendicular to the wall develops. This is of particular interest since, as discussed in earlier work (Meyer and Vanderbilt (2002)), it gives rise to a potential step at the boundary which, if screened by a dipole layer in the charge density, could give rise to intriguing effects such as enhanced conductivity at the boundary.

First, Fig. 4.11 shows the magnitudes of the calculated layer-by-layer polarizations for all three wall types. It is clear that in the 71° and 180° walls, the magnitude of the polarization remains approximately constant across the wall, indicating a rigid rotation of the polarization in the manner of a magnetic Bloch wall. (Note that the scatter in the local polarization especially at the 180° results from the fairly high force tolerance of 0.03 eV per Å.) In contrast, the 109° wall has a marked reduction in the local polarization in the wall region; this likely results from the greater structural flexibility provided by the orientation of the 109° wall relative to the corners of the octahedra.


Figure 4.11: Layer-by-layer polarization calculated from the sum of the displacements of the ions from their ideal positions multiplied by the Born effective charges.



Figure 4.12: Parallel and normal components of the polarization,  $P_{\parallel}$  and  $P_{\perp}$ , and the macroscopically and planar averaged electrostatic potential, V for (a) 71° domain boundary with continuous oxygen octahedral rotations, (b) 109° domain boundary with continuous oxygen octahedral rotations centered on the FeO<sub>2</sub> plane and (c) 180° domain boundary with continuous oxygen octahedral rotations. Note that only half of the supercell is shown.

Next the local polarization is analyzed by decomposing it into the components parallel and perpendicular to the planes of the domain walls. (Figs. 4.12(a), (b) and (c) for the 71°, 109° and 180° walls respectively.) The total polarization in the mid-domain regions is  $\sim 90 \,\mu \text{C/cm}^2$  in all cases in good agreement with previously reported bulk values (Neaton et al. (2005)). In all cases the component parallel to the domain wall changes from its full mid-domain value in one orientation to the full value in the other orientation within two or three layers. The magnitude of the change in polarization component perpendicular to the wall, however, depends strongly on the domain wall type. In Figs. 4.12(a), 4.12(b) and 4.12(c) also the planar and macroscopically averaged electrostatic potential (extracted as in Meyer and Vanderbilt (2002)) across the supercell are plotted to illustrate the potential step associated with this change in perpendicular component of the polarization. For the 71° wall the change in perpendicular component and corresponding potential step are small; the magnitude of the potential step is  $\sim 0.02$  eV. In the 109° case, the change in the out-of-plane component is considerable, and the corresponding step is significant (0.15 eV). This behavior is analogous to that reported previously in calculations for 90° domain walls (Meyer and Vanderbilt (2002)). Furthermore, depolarization fields of the same magnitude are reported for interfaces between ferroelectrics and non-ferroelectrics (e.g. Albina et al. (2007), Junquera and Ghosez (2003)). Perhaps surprisingly, the  $180^{\circ}$  boundary shows the largest potential step, of 0.18 eV. (Earlier studies of  $180^{\circ}$  domain boundaries in tetragonal PbTiO<sub>3</sub> (Meyer and Vanderbilt (2002)) included an inversion center at the domain wall and therefore obtained no change in perpendicular component). The following analysis of the evolution of the polarization through successive corners of the pseudocube explains the loss of inversion symmetry and the change in the perpendicular component in the 180° case.

Interestingly, the presence of the large potential steps at the  $109^{\circ}$  and  $180^{\circ}$  walls, and the absence of a step at the  $71^{\circ}$  wall, correlate with an intriguing recent observation of electrical conductivity at the  $109^{\circ}$  and  $180^{\circ}$  walls, and its absence at the  $71^{\circ}$  wall (Seidel et al. (2009)). A possible explanation of the observed conductivity is the generation of a space charge layer in the region of the wall to screen this otherwise energetically unfavorable potential discontinuity.

Finally, to help with visualizing the change in polarization across the domain walls, in Fig. 4.13 the local polarization vectors in each layer of the supercells are indicated as blue arrows showing the magnitude and orientation. In the 71° case one can clearly see that the polarization rotates from one corner of the pseudocubic

unit cell, through the center of the edge to the adjacent corner, accompanied by the small attenuation in magnitude which we saw earlier in Fig. 4.11. As already seen in Fig. 4.12(a), this geometry allows the perpendicular component of polarization to remain constant across the wall. The analogous cartoon for the  $180^{\circ}$  wall (Fig. 4.13(c)) shows that the polarization vector rotates between successive corners of the pseudo-cubic unit cell which are the stable orientations of the polarization in R3c BiFeO<sub>3</sub>. At the layer-by-layer level of resolution one sees a jump of 71° followed by a jump of  $109^{\circ}$ ; both intermediate orientations have small components perpendicular to the domain wall. Note that imposition of an inversion center during the structural relaxation, which might be anticipated for a  $180^{\circ}$  wall, would not have allowed this ground state to develop. In contrast, the change in orientation of the polarization across the  $109^{\circ}$  wall is accompanied by a rather large attenuation of the total polarization (see Fig. 4.11 and Fig. 4.13(b)).



Figure 4.13: Evolution of the local polarization across (a) the  $71^{\circ}$ , (b) the  $109^{\circ}$  and (c) the  $180^{\circ}$  domain wall. The blue arrows represent the magnitude and orientation of the local polarization.

### 4.3 Summary

It has been demonstrated that ab-initio calculations can be usefully employed to obtain quantities directly or indirectly measurable with TEM or EH techniques:

• Structural properties: Lattice constants and atomic column positions, including local deviation (strain), can be calculated with sufficient precision. In combination with the Born effective charge tensor, which can be obtained from the same ab-initio calculation, it is possible to correlate the local lattice structure to the macroscopic polarization  $\vec{P}$ . Consequently, local atomic position analysis provides a unique - and within TEM the only - tool to quantitatively measure the electric polarization on a microscopic level.

- Microscopic electric fields such as produced by atoms with different core charges Z are large enough to be measurable. Potential modifications due to redistribution of electrons forming chemical bonds are comparably weak. Furthermore, it is difficult to relate differences in the potential to useful information about the chemical bonding. Consequently, the imaging of properties of the chemical bonding with EH is restricted to characteristic quantities like the averaged electric potential rather than a high-resolution characterization (see also next chapter).
- Macroscopic electric fields: In ferroelectrics, macroscopic electric fields measurable by EH occur in nonequilibrium conditions (e.g. piezoelectricity) or at lattice configurations disturbing the bulk structure. A particular interesting behavior is the formation of a potential jump at domain boundaries, possibly giving rise to interesting physical effects such as increased conductivity. The possibility of measuring these jumps will be analyzed in the next chapter.
- Although being very accurate with respect to ground state electronic and structural properties, many solid state properties are not attainable by ab-initio models. Besides problems with highly correlated systems as described in this chapter, ab-initio methods are computationally unfeasible for large systems containing several thousands of atoms. In this case, (semi-)empirical models have to be employed, which will, however, not be treated within this work.

# Chapter 5

# Inverse problems

The focus of this chapter is the extraction of physically meaningful quantities like the electrostatic potential of the specimen from the acquired image (or reconstructed wave). Since the wave is scattered by the specimen (e.g.  $V \rightarrow \Psi$ ), one therefore has to invert the causality of scattering (e.g.  $\Psi \rightarrow V$ ), which will be denoted as inverse problem according to the definition given in the introduction of this work. Although most of the properties in this chapter will be extracted from holograms, it is well understood that some inverse problems can be equally or even better solved directly from intensity images (e.g. atomic column positions). The following physical quantities are considered:

- 1. By means of both high- and medium-resolution EH reconstructed phases are evaluated with respect to electric depolarization fields  $\vec{E}_d$  or potentials  $V_d$ , i.e. the possibility of separating  $\phi_d = \sigma \int V_d dz$  from the total phase  $\phi$  produced by elastic scattering on the total scattering potential V. As the magnitude of the depolarization fields is small compared to the total scattering potential (see Chap. 4), an accurate comparison to experimental phase detection limits (see Chap. 2), dynamical scattering effects and other uncertainties of the experiments are mandatory to interpret the experimental findings.
- 2. Structure determination of ferroelectrics by means of high-resolution TEM and EH and subsequent fitting procedures of atomic column positions. Knowing the atomic structure, a derivation of the electric polarization  $\vec{P}$  via the Born effective charge tensor  $Z^*$  is discussed,<sup>1</sup> which opens the way to a high-resolution investigation of the electric properties of domain walls, interfaces and defects in these types of materials.
- 3. Reconstruction of 3D electromagnetic potentials from medium-resolution holographic tomographic tilt series. Several authors report a successful application of the technique (e.g. Twitchett-Harrison et al. (2008), Lai et al. (1994), Wolf et al. (2009)). The investigations in this work focus on the transfer and application of novel reconstruction procedure in the field of tomographic TEM based on a singular value decomposition of the projection matrix. This, from an algebraic point of view, natural characterization of the projection matrix allows a particularly easy interpretation of systematic (e.g. the so-called "missing-wedge" or distortion of the projection by dynamic scattering) and statistical (noise) errors in the reconstruction.

After the removal of influences of the microscope as described in Chap. 2, the acquired image data can be considered as (energy-resolved) beam electron densities or reconstructed waves respectively. The recorded signal suffers from statistical fluctuations introduced by the very nature of the quantum mechanical measuring process, the statistical properties of the microscope, the specimen and the digital image manipulations as described in 2.10, which leads to limitations in the achievable spatial and signal resolution. This has to be considered, when extracting physically meaningful values from the image data. High-resolution characterization of the structure and electric potentials will be performed at the following materials:

- 1. bulk  $BaTiO_3$ : It is one of the best investigated ferroelectric materials, i.e. structural and electric properties are well known. Furthermore,  $BaTiO_3$  is a member of the perovskite family like the other ferroelectric materials investigated in the following. Thus, it is an ideal test case for the analysis of structural and electric properties and the characteristic coupling of both in ferroelectrics.
- layered systems of SrTiO<sub>3</sub>/PbTiO<sub>3</sub>/SrTiO<sub>3</sub> and SrRuO<sub>3</sub>/PbTiO<sub>3</sub>/SrRuO<sub>3</sub>: The ferroelectric properties of thin layers depend strongly on the boundary conditions through the accumulation of polarization charges. Large depolarization fields produced by incomplete screening lead to a reduction of the polarization, which is referred to as finite size effect in small scale ferroelectrics (e.g. Scott and Paz de Araujo (1989);

<sup>&</sup>lt;sup>1</sup>These investigations do not fall strictly under the definition of inverse problems. Since, however, the initial data, i.e. the structure, is inversely obtained, it is natural to discuss it in this chapter.



Figure 5.1: Reconstructed amplitude (a) and phase (b) of BaTiO<sub>3</sub> recorded at a Philips CM30 special Tübingen  $(U = 300 \, kV, C_3 = 623 \, \mu m, C_1 = -42 \, nm)$  from [001]-direction. The contrast jumps in the phase occur at  $2\pi$  phase wraps. Starting from the left side, the thickness is slowly increasing to the right side. A single unit cell is indicated by green (Ba) and blue (Ti) dots. The image was recorded by M. Reibold.

Nakao et al. (2005); Scott (2007); Dawber et al. (2005)). It has been shown in various investigations that conducting electrodes provide better screening than insulating ones, hence reducing the finite size effect (e.g. Watanabe (1998); Junquera and Ghosez (2003)). The two layered systems simulate that situation in as much as  $SrTiO_3$  is an insulator and  $SrRuO_3$  is conducting.

3. BiFeO<sub>3</sub>, and KNbO<sub>3</sub> domain boundaries: In close relationship to characteristic structural distortions, such domain walls show an intriguing electrostatic behavior, which is potentially leading to a changed conduction state as well as other electronic properties (see Chap. 4). Characteristic electrostatic potential changes are predicted to occur on a rather large length scale compared to the inneratomic fields produced by the atoms in one unit cell (see 4.2.2). A direct measurement by electron holography at medium resolution and consequently large signal resolutions is therefore within reach and will be conducted in this chapter.

### 5.1 Bulk BaTiO<sub>3</sub>

A wave recorded and reconstructed by means of the methods in Chap. 2 is presented in Fig. 5.1. One prominent feature of the images are local extrema produced by the scattering on the atomic columns. An intriguing feature thereby is the asymmetry of the phases at the atomic column (see vicinity of indicated unit cell in Fig. 5.1(b)), because it might be correlated to the ferroelectric distortion, which manifests as a displacement of the ion positions and an asymmetric redistribution of the outer electrons (see Chap. 4). To investigate the source of this asymmetry dynamic scattering simulations based on the Multislice method as described in Chap. 3 have been performed. The influences of the microscope (like lens aberrations, camera distortions) have been incorporated according to the transfer theory discussed in Chap. 2. It is found that a slight crystal tilt with respect to the beam direction and below the uncertainty of the alignment procedure (2 mrad) is a possible source of the strong asymmetry (see Fig. 5.2), whereas the intrinsic asymmetry of the scattering potential V is too weak to explain the effect in the reconstructed phase. The crystal tilt implies that atomic columns oriented in [001]-direction are not perfectly projected anymore, and hence the scattered wave "feels" the atomic potentials in one column at different spatial positions  $\vec{R}$ , which finally leads to the characteristic asymmetric phases observed in Fig. 5.1(b). In the language of the column approximation (e.g. van Dyck et al. (1989)) the dipole-like phase contrast corresponds to an increasing p-type character of the scattered wave, which has been introduced by the crystal tilt. It is furthermore interesting to note that the reconstructed amplitude is less sensitive to residual tilt, which is a manifestation of the generally lower sensitivity of the amplitude to the scattering potential. It is concluded that a precise control of the crystal tilt is mandatory for an interpretation of the asymmetry in reconstructed object exit wave from ferroelectrics. In the following, a perfect alignment of



Figure 5.2: Experimental (see also Fig. 5.1) and simulated phase of the image wave with a linescan at the position indicated by the blue and red arrow. The Multislice simulation was performed at a crystal tilt of 1 mrad around the a-axis and a thickness of 22 unit cells (U = 300 kV,  $C_3 = 623 \,\mu\text{m}$ ,  $C_1 = -42 \,\text{nm}$ ,  $\sigma_E = 0.8 \,e\text{V}$ ,  $\sigma_{\theta} = 0.15 \,\text{mrad}$ ).

the zone axis is assumed.

The electrostatic potential as calculated by ab-initio methods experiences the dominating influence from the displacement of the ions (a distortion of the outer contour lines due to the redistribution of shell electrons is small in Fig. 4.4). Indeed, similar to the scattering potential itself, the calculated wave rather reflects the displaced atom positions than the modified electron shell and does not exhibit a pronounced asymmetry at the atom site (Fig. 5.3).



Figure 5.3: With Multislice simulated phase after 20 unit cells of a DFT (a) and free atom (b) BaTiO<sub>3</sub> potential at 200 kV acceleration voltage and  $\sigma_{E_s} = 0.8 \, eV$  energy fluctuation in the beam. Additional aberrations are neglected.

Consequently, scattering simulations performed on free atom potentials (Weickenmeier and Kohl (1991)) placed on the ferroelectric ion positions, deviate only slightly from the simulations based on the ab-initio potential (see Fig. 5.4). Although the effects produced by the rearrangement of outer electrons are resolved with high-resolution electron holography (see phase noise in Fig. 5.1), it is pointed out that the determination of large spatial frequency components of the potential from electron holograms will remain a formidable task due to the notorious quantum noise and the inversion procedure complicated by dynamic scattering.

Depolarization fields extending over several unit cells lead to large spatial frequencies in the phase but



Figure 5.4: Difference between object exit amplitudes (a) and phases (b) obtained by Multislice scattering simulations at thicknesses from 0 to 20 Å using ab-initio and free atom potentials. The main differences amplitude and phase stems from the larger radius of the free atom potentials, which lead eventually to  $2\pi$  phase jumps in the region between the atoms indicated by sharp peaks. Additionally, an asymmetry occurs.

not in the amplitude. They are not detectable (see Fig. 5.1) at small thicknesses as used for high-resolution holography. The magnitude of the depolarization field is ultimately limited by the dielectric strength of the material. Typical values of ferroelectric insulators are in the order of  $10 \text{ V}/\mu\text{m}$  (see Chap. 4). Consequently, within a field of view of 20 nm, potential differences of  $\Delta V = 0.02 \text{ V}$  could be realized without destroying the crystal structure. The corresponding phase difference  $\Delta \phi = \sigma \Delta V t$  of such a field in a 10 nm thick specimen is in the order of  $\mu$ rad, which is well below the phase detection limit in reconstructed waves (see Fig. 5.13 and Sec. 2.10). Measurements of depolarization fields are, however, reported for larger specimen thicknesses used in medium resolution investigations (e.g. McCartney et al. (2000), see Sec. 5.3).

In spite of the difficulties connected with the quantitative evaluation of electrostatic potentials from the reconstructed phase, it is possible to determine accurately atomic column positions from high-resolution data. The reported approaches can be divided into two categories:

- 1. The first consists of a refinement of the dynamic scattering simulations to the experimental, i.e. is aiming at solving the inverse problem in a classical sense. Here, problems arise from the rather large number of free parameters (thickness, 3D coordinates of all atoms, microscope parameters, etc.) and the non-linear character of the inverse mapping (see Chap. 3), hence only a few examples are reported in literature (e.g. Scheerschmidt and Knoll (1994), G. Möbus et al. (1998)).
- 2. The second category contains approaches, where a local model for the signal of the atomic column (or a whole unit cell), e.g. a Gaussian, is refined. Thus, the number of refined parameters is drastically reduced, e.g. to fit a single atomic column with a radial Gaussian and a constant background only three parameters are required. This approach does furthermore not require an evaluation of the scattering equations, thereby reducing computing time. The feasibility of this type of position measurements was demonstrated by several authors (e.g. Ernst et al. (2003); Aert et al. (2005); den Dekker et al. (2005)). Additionally, it has been successfully demonstrated that high resolution EH allows a differentiation between Ga and As atomic columns in GaAs oriented in [011]-direction (Lichte et al. (2007)), i.e. beside the determination of the exact position, the magnitude of the phase maximum could be used to determine the composition of an atomic column. The most severe drawback of the method is the disregard of systematic deviations of amplitude and phase maxima from the true atomic column positions due to dynamic scattering. It is demonstrated in the following that this effect can be particularly strong in ferroelectric materials, where particular atomic columns appear asymmetric in projection (e.g. TiO column from [100]-direction).

In the following the second approach will be extended to model-based fitting of atom positions in both amplitude and phase reconstructed by electron holography. It is in principle possible to obtain accurate fit models for the amplitude and phase reconstructed at atomic columns from scattering simulations or experimental images. Furthermore, general considerations from parameter estimation theory apply to optimize the parameter sets and the fitting procedure. Loosely speaking, one can state that the less free parameters models contain, the more stable is the fitting procedure. In order to fulfill the last rule of thumb, an elliptic Gaussian

$$f(x,y;C,A,\alpha,\sigma_1,\sigma_2,\vec{p}) = C + A \exp\left(\frac{1}{2} \begin{pmatrix} x & -p_x \\ y & -p_y \end{pmatrix}^{\dagger} \mathbf{M} \begin{pmatrix} x & -p_x \\ y & -p_y \end{pmatrix}\right)$$
(5.1)

with the bilinear form

$$\frac{1}{2} \begin{pmatrix} x & p_x \\ y & p_y \end{pmatrix}^{\dagger} \mathbf{M} \begin{pmatrix} x & p_x \\ y & p_y \end{pmatrix} = \frac{1}{2} \begin{pmatrix} x & p_x \\ y & p_y \end{pmatrix}^{\dagger} \mathbf{R}^{\dagger} \begin{pmatrix} \sigma_1^2 & 0 \\ 0 & \sigma_2^2 \end{pmatrix} \mathbf{R} \begin{pmatrix} x & p_x \\ y & p_y \end{pmatrix}$$
(5.2)

is employed for both amplitude and potential fitting. The coefficients  $\sigma_{1,2}^2$  are inversely proportional to the size of the elliptic fit function in the direction of the corresponding principle axis, and the orthogonal rotation matrices **R** are parametrized by the rotation angle  $\alpha$ . Accordingly, 7 independent parameters are fitted, all of which can be correlated to physical properties. For the structure determination most important are the position vectors  $\vec{p}$  of the atoms. The constant background *C* is related to the total scattering power and the thickness of the sample, and the height *A* of the Gaussian is a measure for the thickness and scattering power of the respective atomic column. The arithmetic average of  $\sigma_{1,2}^2$  indicates mainly the resolution of the microscope as given by the respective transfer functions, whereas the ratio  $\sigma_1^2/\sigma_2^2$  between the two principal axis is measuring the "ellipticity", which often correlates to a residual specimen tilt and/or axial coma or two-fold astigmatism. Finally, depending on the crystal symmetry, one can relate the rotation angle  $\alpha$  to the respective angle of the residual tilt, axial coma or two-fold astigmatism.

It is noted that other fit models might be equally or even better suited than the one above. Especially, the kurtosis of the atomic column signal in the phase is often smaller than the Gaussian one in the cases investigated within this thesis. Therefore, an additional parameter s in

$$f(x,y) = C + A \exp\left(\frac{1}{2} \begin{pmatrix} x & p_x \\ y & p_y \end{pmatrix}^{\dagger} \mathbf{M} \begin{pmatrix} x & p_x \\ y & p_y \end{pmatrix}\right)^{s}$$
(5.3)

was fitted if necessary to improve the accuracy of the fit. If the phase signal is wrapped (and cannot be unwrapped prior to the fitting procedure) the fit function for the phase has additionally to take into account the wrapping of the phase beyond values of  $2\pi$ . Unfortunately, the fit becomes highly non-linear in that case, producing large fit errors and results depending on the initial guess of the fit parameters. Consequently, reconstructed phases of thick specimen with a contrast beyond  $2\pi$ , such as present in Fig. 5.1 cannot be used for the fit procedure.

The fit itself is based on minimizing the root mean square difference

$$rms = \sqrt{\sum_{a} \left(I_a - f_a\left(C, A, \alpha, \sigma_1, \sigma_2\right)\right)^2}$$
(5.4)

between the image data  $I_a$  and the atomic column fit function  $f_a$ . Different minimization algorithms are available and implemented in standard software packages. In this work the Levenberg-Marquardt algorithm (Levenberg (1944); Marquardt (1963)) as implemented in Matlab<sup>TM</sup> was chosen with respect to the non-linearity of the problem.

In spite of the automatically calculated goodness-of-fit measure (root mean square rms), the accuracy of the determined atomic column positions are difficult to assess. Specimen drift, thermal motion, point spread function of the camera, beam tilt, all sorts of aberrations and dynamical scattering add to the statistical error of the fit procedure and effectively produce a delocalization, i.e. a shift, and an (an)isotropic smearing of the fit function. A strong shift is particularly obscuring the measured values, hence dynamical scattering simulations incorporating the influence of the microscope have to be performed in parallel to check the influences of dynamic scattering. This is illustrated by fitting the position of the Ti-O column in a simulated wave function of BaTiO<sub>3</sub>. The results depicted in Fig. 5.5 show an oscillation of the column position depending on the sample thickness and the type of the signal (amplitude or phase), which is caused by the missing symmetry in *c*-direction and the slight misalignment of Ti and O, when looking in [100]-direction. Consequently, if the sample thickness is not known accurately, a determination of the TiO column position suffers from a systematic error in the range of 0.1 Å. Additionally, asymmetric effects introduced by beam tilt or aberrations have to be considered.

One can conclude that the results of model-based fit of the atomic column positions in bulk  $BaTiO_3$  depend on the type of the original image data (intensity, reconstructed amplitude / phase). In the following, the method has been applied to high-resolution intensity data depicted in Fig. 5.6, where the intensity data preferred to reconstructed waves due to the lower residual beam tilt artifacts and the generally lower signal to noise ratio (see Fig. 5.1). Tetragonal distortions and ferroelectric frozen phonon distortions are now accessible within the accuracy of the the determined column positions. The measured values agree within the large fit error with the predicted bulk values (Fig. 5.6) proving the potential of the method in more elaborate situations such as occurring at defects and boundaries (see Sec. 5.3). A precise knowledge of the atomic positions can be



Figure 5.5: MS simulation of one unit cell  $BaTiO_3$  from [100]-direction at different thickness, 200 kV acc. voltage and 0.8 eV energy spread. The lower panel illustrates the motion of the fitted peak position at the TiO column when increasing the sample thickness.



Figure 5.6: Model-based fit of the atomic positions and composition in bulk  $BaTiO_3$ . The Ba position was set to zero and the Ti position is given relative to the Ba position in relative units (r.u.) of a and c, respectively.

	Ba	Ti	01	O2
$Z^*$	2.74	7.25	-5.71	-2.15

Table 5.1: Born effective charges  $Z^*$  for BaTiO<sub>3</sub> (Ghosez et al. (1998)).

furthermore translated into magnitude of the local electric polarization according to (see Chap. 4)

$$\vec{P} \approx \frac{1}{\Omega} \sum_{n} \mathbf{Z}_{n}^{*} \Delta \vec{r}_{n}$$

$$= \frac{1}{\Omega} \sum_{n} Z_{n}^{*} \Delta r_{np} ,$$
(5.5)

where  $\Omega$  denotes the volume of the unit cell and the index *n* runs over all atoms in the unit cell. The transformation in the second line is valid if the displacements  $\Delta \vec{r_n}$  point into the direction of polarization, e.g.,  $\mathbf{Z}^*$  reduces to

$$\mathbf{Z}^{*} = \begin{pmatrix} Z_{xx} & Z_{xy} & 0\\ Z_{xy} & Z_{yy} & 0\\ 0 & 0 & Z^{*} \end{pmatrix}$$
(5.6)

if the z-axis of the coordinate system is parallel to the polarization axis (c in tetragonal systems). A direct evaluation of (5.5) is, however, only possible if all atomic displacements  $\Delta \vec{r_n}$  including those of the oxygen atoms are separately known. This is often not the case, either due to projection effects within one columns (e.g. the TiO column in BaTiO<sub>3</sub>) or due to the generally weak contrast of light elements such as O (see Fig.5.1). Thus, one has to establish an additional relationship between the O displacement and the Ti displacement, either by ab-initio methods or other measurements. When inserting the proportionality between the O and the Ti displacement obtained from the ab-initio calculations in Sec. 4.2.1 (Tab. 4.1) and the Born effective charges displayed in Tab. 5.1 into expression (5.5) one obtains the following polarization

$$P \approx 7.25e \cdot 0.05 \,\mathrm{nm} - 2 \cdot 2.15e \cdot 0.04 \,\mathrm{nm} - 5.71e \cdot 0.08 \,\mathrm{nm}$$

$$\approx 17.1 \,\mu\mathrm{C/cm^2} \,,$$
(5.7)

which agrees roughly (within the error of the method) with the experimental value of  $26.3 \,\mu\text{C/cm}^2$  (Wieder (1955)). One can conclude that the method has proved to be a valuable tool to investigate electric polarization with nm resolution, which, to the best knowledge of the author, cannot be achieved by any other experimental method. Furthermore, the large error bar of the method with respect to measuring  $\vec{P}$ , is not important, when asking for the extension of volumes, where originally non-polar materials are polarized due to adjacent polar layers. Such systems are investigated in the next section.

# 5.2 $SrTiO_3/PbTiO_3/SrTiO_3$ and $SrRuO_3/PbTiO_3/SrRuO_3$ layered systems

Layered systems of metals, ferroelectrics and insulators allow the investigation of the role of depolarization fields and surface charges on small ferroelectric systems. As already mentioned above, the small size effects describing the reduction of the electric polarization of small ferroelectric systems and thereby limiting the application of ferroelectric layers as memory devices mainly depend on the properties of the interface of the ferroelectric material to the surrounding material. In bulk ferroelectrics the polarization field  $\vec{P}$  is screened by the surface charges. When shrinking the system and thereby reducing the distance between the surfaces, they eventually couple and effectively reduce the polarization in between. The coupling depends on the properties of the surfaces, which are defined by the materials involved. Surface layer widths down to 4 Å are reported for ferroelectric-metal interfaces, where a large number of screening electrons is provided by the metal in a sharply localized plane (Sai et al. (2005)). Comparatively large extensions can occur at ferroelectric-insulator interfaces, where the charge density at the surface is restricted by the small number of free charges. It has to be noted, however, that there are effects, which allow a large surface charge density also in insulators, i.e. charged ionic sites (e.g. oxygen vacancies Ishibashi and Okuyama (2005)) or 2D electron gases in the conduction band (e.g. in LaAlO<sub>3</sub>-SrTiO<sub>3</sub> interfaces (Basletic et al. (2008/08//print))).

In the following, two exemplary systems are investigated, which contain both ferroelectric-metal and insulatormetal interfaces:  $SrTiO_3/PbTiO_3/SrTiO_3$  and  $SrRuO_3/PbTiO_3/SrRuO_3$ . The samples have been provided by K. Honda (Fujitsu Laboratories Ltd., Device and Materials Lab, Atsugi, Japan). The ferroelectric PbTiO\_3 and its properties have been described in the previous chapter.  $SrRuO_3$  (space group *Pbnm*) and  $SrTiO_3$  (space group  $Pm\overline{3}m$ ) are also from the perovskite family. The lattice constant of bulk  $SrTiO_3$  is with 3.95 Å (Geiss



Figure 5.7: Reconstructed amplitude (phase) and lattice plane analysis of  $SrTiO_3/PbTiO_3/SrTiO_3$  ( $SrRuO_3/PbTiO_3/SrRuO_3$ ). The holographic image acquisition and reconstruction was performed by M. Linck.

et al. (1990)) slightly smaller than the PbTiO<sub>3</sub> parameters, thus introducing strain at the interface, which in turn can also change the electric properties (Umeno et al. (2006)). The  $SrRuO_3/PbTiO_3$  interface is strained as well, since the orthorhombic lattice of  $SrRuO_3$  does not fit to the tetragonal PbTiO<sub>3</sub>.

Reconstructed amplitudes and phases of the layered systems are depicted in Fig. 5.7. In the first case, the localization of the atomic columns was better in the amplitude, furthermore, the phase suffered from phase wraps leading to a failing fit procedure. The second sample was thinned sufficiently to avoid phase wrapping effects, hence could be analyzed in both amplitude and phase. After determining the column positions, an additional processing step was introduced to accurately determine the positions of and the distances between the lattice planes: each atomic column has been assigned to a particular lattice plane and the distances of the planes are obtained by subtracting the average positions of the columns within one plane. The errorbars depicted in Fig. 5.7 are obtained by

$$\sigma_{dist} = \sqrt{\sigma_{n-1}^2 + \sigma_n^2} \,, \tag{5.8}$$

assuming that the statistics within one plane is independent from its neighbor.

It is now useful to characterize the lattice plane distances by two measures (see Fig. 5.7): the lattice parameter, i.e. the distance between every second lattice plane for the perovskite structures considered here, and the relative position of the Ti center atom plane in the unit cell. The latter is 0.5 for the non-polarized perovskite structure (Ti atom is exactly in the middle of the unit cell). Any deviations from this position can be translated into a local electric polarization via  $Z^*$ . Both layered systems exhibit only a slight change in the lattice constant perpendicular to the interfaces (the parallel components are clamped). Besides, a strong scatter in the obtained lattice constants is observed. Interestingly, the scatter reduces in case of the Ti column position.

	Sr	Ti	01	O2
$Z^*$	2.55	7.56	-5.92	-2.12

Table 5.2: Born effective charges  $Z^*$  for SrTiO<sub>3</sub> (LaSota et al. (1997))...

A clear displacement (and thus polarization) profile is obtained across the interfaces. The first 3 SrTiO<sub>3</sub> layers at the interfaces are polarized, whereas an ionic displacement extending over 2 unit cells could be measured in the SrRuO<sub>3</sub>. The shorter screening length  $l_s$  in the metallic SrRuO<sub>3</sub> is a consequence of the large electron density at the Fermi level. The all in all short screening lengths are in good agreement with previous experimental and theoretical studies on ferroelectric - nonferroelectric interfaces (e.g. Albina et al. (2007), Junquera et al. (2003)). A small attenuation of the polarization is also observed in the first 2-3 layers within the PbTiO<sub>3</sub>, i.e. a finite size effect on a length scale of 1 - 2 nm is observed for this particular system. In the middle of the ferroelectric PbTiO<sub>3</sub> layer the Ti column displacement of 0.08 is slightly below the bulk value of 0.11 given in Tab. 4.2, i.e. the polarization is slightly smaller than the bulk value ( $\vec{P} = 81.2 \,\mu\text{C/cm}^2 \approx 5 \cdot 10^{14} \,e/\text{cm}^2$ ). In both systems a well of the polarization in the middle of the layer can be observed, the origin of which remains unclear at this stage. It is furthermore interesting to note that the polarization of the PbTiO<sub>3</sub> is equivalently obtained by calculating the polarization charges in the interface from the polarization in the adjacent SrTiO<sub>3</sub> layer with the help of linear response theory ( $\epsilon_{SrTiO_3} = 277$ , Geiss et al. (1990)), i.e.

$$\vec{D} = \frac{\epsilon_{SrTiO_3}}{\epsilon_{SrTiO_3} - 1} \vec{P} \approx \vec{P}$$
(5.9)

 $\operatorname{and}$ 

$$\operatorname{div}\vec{D} = \rho = \frac{\rho_A}{l_s} \,. \tag{5.10}$$

In the last expression, the 3D charge density was replaced by the 2D charge density  $\rho_A = \int_0^{l_s} \rho dl$  divided by the screening length  $l_s$  at the boundary. Again, the Born effective charges obtained from ab-initio calculations (Tab. 5.2) and an O displacement directly proportional to the measured Ti displacement have been used to calculate the polarization  $\vec{P}$  within SrTiO<sub>3</sub>. Finally, by inserting  $l_s = 12$  Å and  $\vec{P}$  into (5.10),  $\rho_A \approx 1 \cdot 10^{14} e/cm^2$  is obtained, which is again below the bulk value of PbTiO<sub>3</sub> and slightly smaller than the polarization obtained from the Ti displacements within the PbTiO<sub>3</sub> layer.

### 5.3 BiFeO<sub>3</sub> and KNbO<sub>3</sub> domain boundaries

The structural and electronic properties of BiFe $O_3$  domain walls as predicted by DFT calculations exhibit two fingerprint quantities potentially accessible through EH in a directly invertible way: the structural distortions of atomic columns at the wall and the electrostatic potential jump due to the polarization fluctuations. In Fig. 5.8 a HRTEM image of a 109° domain wall is analyzed with respect to the atomic column positions of Bi and Fe. The polarization vector is following a rather rigid rotation in agreement with the findings from the DFT calculations (Fig. 4.12). The width of the domain wall, however, is considerably larger in the experiment, indicating a considerably larger domain wall energy. The origin of this behavior could be a temperature effect (thermal oscillation of the atoms in a rather shallow energy landscape), a screening of the potential jump with free charges, the formation of a space charge region and the existence of structural faults at the boundary like oxygen vacancies.

The specimen used for the HRTEM image depicted in Fig. 5.8 has a rather small thickness below 10 nm, which is required in order to preserve a large particle flux in the scattering angles recorded in HRTEM for strong scatterers like BiFeO<sub>3</sub>. It is particularly difficult to record medium resolution EH at large thicknesses, which are required if small potential details have to be separated from the background. The potential jump at the domain wall as predicted by DFT is not larger than 0.2 eV, i.e. two orders of magnitude smaller than typical MIP values. A dedicated experimental setup aiming at measuring this potential difference has to incorporate a thickness interval, where the reconstructed amplitude hence signal resolution is large enough to separate the projected potential jump from other contribution, in particular thickness fluctuations, amorphous surface layers and dynamical scattering effects. As the upper limit is given by the required signal resolution (reconstructed amplitude), it is advisable to use a weak scatterer with a large potential jump for a proof of concept.  $KNbO_3$ fulfills both requirements, i.e. the MIP equals 19 eV and the electric polarization of  $30 \mu C/cm^2$  is large enough to generate large potential jumps at domain walls. The unit cell of  $KNbO_3$  is depicted in Fig. 5.9. Due to its large nonlinear optical coefficient the material finds application in the manufacturing of laser. The orthorhombic symmetry facilitates  $60^{\circ}$ ,  $90^{\circ}$ ,  $120^{\circ}$  and  $180^{\circ}$  domain walls. The experimental observation of the potential jump at the domain wall is severely hampered by the small magnitude of the related phase jump compared to the background phase signal. As in the case of dopant profiling in p-n junctions (Rau et al. (1999)), the



Figure 5.8: High resolution TEM image of a 109° domain wall in bismuth ferrite; B) extracted lattice parameter across the domain wall; C) extracted Fe ion displacement across the domain wall; D) actual Fe ion displacement across the wall versus rigid P rotation (projection on (001)) indicating a strong decrease of polarization. The image was acquired and analyzed in the National Center for Electron Microscopy, Lawrence Berkeley National Laboratory and is published by Seidel et al. (Seidel et al. (2009)).



Figure 5.9: Orthorhombic unit cell of KNbO<sub>3</sub>. The 3 oxygen positions are not related by symmetry.

	$\varphi\!\left(\vec{R}\right) = \sigma \cdot V_{proj}\left(\vec{R}\right)$	
Potential jump at domain w	all	Signal
$P\cong 30~\mu C/cm2 \rightarrow \Delta V\approx 0.1~V$		$\phi_{100nm} = 0.09\text{rad}$
		$\phi_{200nm} = 0.18\text{rad}$
Error source		Magnitude of error
• Surface roughness MIP <sub>KNbO3</sub> ≅ 19 V		$\delta \varphi_{unit  cell} = 0.05  \mathrm{rad}$
• Dynamical scattering and of domain wall (not exact)	$\delta \varphi_{dyn} \simeq 0.1$ rad	
Statistical error		$\delta \varphi_{\scriptscriptstyle stat} = 0.05  \mathrm{rad}$
	t > 250 nm	

Figure 5.10: Optimum thickness estimate for off-axis holographic determination of potential jump at domain boundary in ferroelectric KNbO<sub>3</sub> according to error sources of the measurement. The influence of the surface roughness is estimated with the help of the averaged potential of one unit cell (MIP, see Sec. 3.2.5). Multislice scattering simulations on domain boundaries by F. Röder (personal communication) and the experimental misalignment error of 2 mrad predict the depicted dynamical error. The statistical error was determined from the recorded image. Acc. Voltage U = 200 kV,  $\sigma = 0.00729 \text{ rad}/(\text{Vnm})$ .

measurement is only possible within a special thickness interval of the specimen, which has to be determined in advance through theoretical estimates or by measurements: The achievable signal resolution determined by the noise background and systematic errors have to be small compared to the signal from the potential jump. The noise consists of the general phase noise, which is roughly proportional to the inverse of the reconstructed amplitude (see Sec. 2.10), which is in turn attenuated by large angle scattering, inelastic scattering and thermal motion of atoms. The systematic errors include thickness variations, which can be especially large at the boundary due to preferential etching and dynamic scattering effects due to the loss of symmetry at the domain wall. The latter can be minimized by imaging in out-of-zone-axis conditions (see 3.2.5). The situation is sketched in Fig. 5.10. The estimate is based on several uncertainties like surface roughness and nonlinear dynamical effects. Summing all errors one therefore obtains but a rough measure the required thickness t > 250 nm.



dynamic BF image of 90° domain wall

single reconstructed phase

Figure 5.11: Left: Zone axis bright field image of  $90^{\circ}$  domain boundary in KNbO<sub>3</sub>. Right: Reconstructed phase obtained from a single hologram at kinematic conditions.

A KNbO<sub>3</sub> crystal containing 90° domain boundaries was prepared and investigated by K.Tsuda, Inst. Mul-



dynamic BF image of 90° domain wall

averaged reconstructed phase

Figure 5.12: Left: Zone axis bright field image of  $90^{\circ}$  domain boundary in KNbO<sub>3</sub>. Right: By F. Röder (TU Dresden) reconstructed phase and corresponding linescans. The linescan over the same region of the reconstructed amplitude shows a slight modification at the domain boundary indicating dynamic scattering contrast.



Figure 5.13: The magnitudes of the standard deviation of both amplitude and phase as calculated from the vacuum regions are in good agreement with the theoretically predicted values (see Sec. 2.10).

tidisc. Research: Adv. Materials, Tohoku University, Sendai. Unfortunately, a sample thickness above 160 nm and therefore the necessary thickness could not be prepared, leading to some ambiguities in the obtained results. The holograms have been acquired in Lorentz mode at our Philips CM200 TEM equipped with a 1024k Gatan Multiscan camera (model 794). A reconstructed phase from a single off-axis hologram is depicted in Fig. 5.11. To decrease the large statistical noise, it was necessary to record a series of holograms and average the reconstructed waves after proper alignment and phase offset correction (the details of the method as developed by F. Röder et. al will be reported elsewhere). The phase as obtained by averaging 10 reconstructed waves is depicted in Fig. 5.12. A phase jump at the domain wall can be clearly distinguished, which corresponds to 0.1 eV after dividing the phase difference by the thickness t and the interaction constant  $\sigma$ . In spite of its significance it is not possible to rule out dynamic effects as the source of this effect at the specimen thickness used in the experiment. Further studies at larger thicknesses (and hence larger hologram series) are under preparation and will clarify this remaining uncertainty. As a side product statistical properties of the reconstructed wave are available and depicted in Fig. 5.13. The comparison to the formalism for describing the noise in reconstructed waves derived within Sec. 2.10 yields a very good agreement in contrast to the by F. Lenz derived formulas neglecting the influence of the scintillator. The Gatan Multiscan camera (model 794) used for this analysis has a thick scintillator with a large PSF and particular small DQE. This corresponds to camera (a) discussed in Sec. 2.10, which decreases the shot noise by smearing out the signal and introduces only a comparable small noise by the path statistics in the scintillator.

### 5.4 Holographic Tomography

As it was pointed out in Sec. 3.2.5, medium resolution EH investigations suffer from the undetermined thickness profile. Ferroelectric domains (and domain walls) such as discussed previously can assume rather complicated 3D patterns, which cannot be determined in projection. A rather natural remedy to these problems is to record

and reconstruct a series of holograms each with a different tilt angle  $\alpha$  of the specimen (Fig. 5.14).



Figure 5.14: Principle of Holographic Tomography.

This method is referred to as electron tomography and renders the reconstruction of volume data possible, if the following requirements are fulfilled: The projection of the volume data must be an invertible operation. This condition is fulfilled, if the projection is an injective mapping. From general functional analysis it is known, that the respective form of the inverse mapping, i.e. the reconstruction, can be very complicated, even if the projections are well behaved, i.e. they are linear and continuous. Indeed, the equations describing the scattering, i.e. the Klein-Gordon equation in our case, do not allow a general inversion with respect to the potential. One therefore uses dedicated imaging conditions, i.e. out-of-zone axis imaging, to restrict the problem to the most simple linear or more generally linearizable hence invertible mapping. In this case it was shown in Sec. 3.2.5 that the wave function  $\Psi$  follows an exponential relationship

$$\Psi = e^{\int_t 1/2\lambda'(\vec{r})dz} e^{i\sigma\int_t V'(\vec{r})dz} e^{-i/\hbar \int A_z(\vec{r})dz}$$
(5.11)

in both amplitude and phase. The primed quantities  $\lambda'$  and V' are proportional to the inelastic mean free path  $\lambda_{in}$  and the electrostatic potential V as discussed in Sec. 3.2.5. Without other corrections from dynamical scattering, the relationship between the reconstructed phase and the electrostatic potential is linear, thus well suited for tomographic reconstruction. In order to reconstruct the modified mean free path  $\lambda'_{in}$  or electrostatic potential, one has to linearize the problem first, i.e.

$$\ln |\Psi| = \int_{t} 1/2\lambda'_{in}(\vec{r}) dz \qquad (5.12)$$
  
$$\arctan \Psi = \sigma \int_{t} V'(\vec{r}) dz - 1/\hbar \int_{t} A_{z}(\vec{r}) dz.$$

If the vector potential  $\overline{A}$  is zero, these equations are continuous linear mappings as required for a tomographic reconstruction of scalar fields as discussed in the next 2 sections. The reconstruction of all 3 components of a vector field from longitudinal projections such as occurring in 5.12 is more complicated and will be considered in Sec. 5.4.3. It has to be emphasized that similar projective relationships between the recorded signal and specimen properties hold also for other than EH imaging techniques, namely electron diffraction and energy filtered TEM, however, only electron holography provides direct quantitative access to the static electromagnetic fields of the sample. A limited number of experimental results obtained with the holographic tomographic methods are reported in literature (e.g. Wolf et al. (2009), Lai et al. (1994), Friedrich (1994), Twitchett-Harrison et al. (2008)).

A general hurdle for the application of tomographic methods in TEM is the restricted tilt range for the projections, which arises from limited capabilities of the specimen holder. Only a tilt range of  $70^{\circ} - 80^{\circ}$  can be projected, which leads to characteristic artifacts in the reconstruction referred to as missing-wedge artifacts (e.g. Frank (1992)). Particular considerations are necessary to reduce these artifacts in the reconstruction process discussed in the following.



Figure 5.15: Projection geometry and coordinate systems. The 2D reconstruction of scalar fields is conducted in the yz-plane. A particular point in the reconstruction domain D is characterized by its Cartesian (y, z) or polar  $(r, \varphi)$  coordinates, respectively. The boundary  $\partial D$  of the domain D can be a square, a circle or more generally be adapted to the shape of the specimen. The 3D reconstruction of vector fields additionally requires a reconstruction in the xz-plane (in that case the x-coordinate has to be mirrored, i.e.  $x \to -x$  to form a right handed coordinate system with y and z).

#### 5.4.1 Radon transformation and projection geometry

Expressions (5.12) can be reformulated as an integral along the direction s

$$\hat{f}(p,\alpha) = \iint f(y,z) \,\delta\left(z - (n+mx)\right) dydz$$

$$= \iint f(y,z) \,\delta\left(p - y\cos\alpha - z\sin\alpha\right) dydz$$

$$= \int_0^\infty \int_0^{2\pi} f\left(r,\varphi\right) \delta\left(p - r\cos\left(\alpha - \varphi\right)\right) r dr d\varphi.$$
(5.13)

The projection geometry together with the coordinate systems and variables used are illustrated in Fig. 5.15. The projection can be alternatively expressed with the help of the Fourier transformation and the Fourier slice theorem (e.g. Gaskill (1978))

$$\hat{f}(p,\alpha) = \mathcal{F}^{-1} \left\{ \mathcal{F} \left\{ f(y,z) \right\} \delta\left( k_y \sin \alpha - k_z \cos \alpha \right) \right\}.$$
(5.14)

Accordingly, each projection can be seen as one tilted slice through the origin in Fourier space. The projection operation along continuous tilt angles is invertible, if the function f(y, z) is continuous and vanishes outside the bounded reconstruction domain D (e.g. Helgason (1984); Deans (1983)). The inverse transformation can be formulated as

$$f(y,z) = \int_0^\pi \int \mathcal{F}_p\left\{\hat{f}(p,\alpha)\right\} |k| \, e^{i2\pi k(y\cos\alpha + z\sin\alpha)} dk d\alpha \,, \tag{5.15}$$

where the |k|-filter in Fourier space stems from the integral measure of the Fourier transform in polar coordinates. The pair of forward and backward transformation is called Radon transformation (Radon (1917)). It is furthermore useful to define the filtered data  $\hat{f}^*(p, \alpha)$  as the inverse Fourier transform of  $\tilde{f}(k, \alpha) |k|$ , i.e.

$$\hat{f}^*(p,\alpha) = \int \tilde{f}(k,\alpha) \left|k\right| e^{i2\pi kp} dk$$
(5.16)

in order to obtain the following expression for the inverse Radon transformation in polar coordinates

$$f(r,\varphi) = \int_0^\pi \hat{f}^* \left( r \cos\left(\alpha - \varphi\right), \alpha \right) d\alpha \,. \tag{5.17}$$

Indeed, polar coordinates r and  $\varphi$  provide a more natural coordinate system for the original data f since the projections  $\hat{f}$  are recorded in a polar coordinate system  $(p, \alpha)$  as well.<sup>2</sup> Consequently, the Radon transformation

<sup>&</sup>lt;sup>2</sup>The polar coordinates p and  $\alpha$  slightly deviate from the canonical definition in that the radial coordinate p runs from  $-\infty$  to  $\infty$  and the angular coordinate is accordingly restricted to 0 to  $\pi$ . The canonical form is obtained by shifting all  $(p < 0, \alpha)$  to  $(p > 0, \alpha + \pi)$ .

pair in radial coordinates can be reformulated in a particular symmetric way by using the series expansion of both the data  $f(r, \varphi)$  and the projected data  $\tilde{f}(k, \alpha)$  into circular harmonics, i.e.

$$f(r,\varphi) = \sum_{n=-\infty}^{\infty} f_n(r) e^{in\varphi}$$

$$\tilde{f}(k,\alpha) = \sum_{n=-\infty}^{\infty} \tilde{f}_n(k) e^{in\alpha},$$
(5.18)

where the coefficients of the expansion are obtained by the integrals

$$f_n(r) = \frac{1}{2\pi} \int_0^{2\pi} f(r,\varphi) e^{-in\varphi} d\varphi$$

$$f_n(k) = \frac{1}{2\pi} \int_0^{2\pi} \tilde{f}(k,\alpha) e^{-in\alpha} d\varphi.$$
(5.19)

It has been shown by various authors that in this case the coefficients form a symmetric Hankel transformation pair (e.g. Klug et al. (1958); Cormack (1963), see also App. A.9)

$$\tilde{f}_{n}(k) = 2\pi i^{-n} \int_{0}^{\infty} r J_{n}(kr) f_{n}(r) dr$$

$$f_{n}(r) = 2\pi i^{n} \int_{0}^{\infty} k J_{n}(kr) \tilde{f}_{n}(k) dk.$$
(5.20)

A further characterization of the Radon transformation can now be obtained by a spectral analysis of the Hankel transformation. From such an analysis follows that the eigenvalues decrease with growing "circular momentum" n (Karoui and Moumn (2009)). It is possible to directly exploit this behavior by an inversion formula based on the circular harmonic decomposition (Frank (1992); Chapman and Cary (1986)). Even more insight into the properties of the Radon transformation and its inverse is obtained by a Singular Value Decomposition of the Radon transformation, which can be also performed analytically (e.g. Natterer (1986)). It will be demonstrated below, that this provides the means to characterize the inverse Radon transformation with respect to reconstruction accuracy and error robustness. It turns out that the reconstruction stability decreases with the order of certain radial polynomials which are also limiting the reconstructed "circular moments" (see Natterer (1986)).

In order to reconstruct volume data from projections, one additionally has to consider the effects of sampling, noise and erroneous input data on the reconstruction algorithms. It turns out that different reconstruction methods produce different results, i.e., they are more or less stable with respect to these influences. For instance, the discretized formulation of the Fourier method (5.15), which is referred to as weighted back projection in literature, suffers from some artifacts introduced by sampling of the not band limited |k|- filter, such as aliasing. Thus, the volume data have to be band limited to suppress aliasing. Some of the artifacts can be minimized by applying the method iteratively, i.e. calculating the root mean square difference between the data obtained by another projection (Wolf et al. (2009)). The inversion based on the circular harmonic decomposition does not incorporate Fourier transformation, hence aliasing effects are also suppressed.

In the following, the previous analytic considerations will be used to characterize and apply yet another approach to the tomographic reconstruction. As it is possible to discretize the projection integral exactly by calculating the weight of each path analytically, it is possible to obtain an algebraic formulation of the reconstruction, which is also robust against aliasing artifacts and which allows the application of effective algebraic inversion techniques.

#### 5.4.2 Algebraic formulation

The algebraic formulation of the Radon transformation is

$$\hat{R}f(y,z) = \hat{f}(p,\alpha) , \qquad (5.21)$$

where  $\hat{R}$  denotes the integral operation along the lines parametrized by p and  $\alpha$ . After sampling the reconstruction domain D by a finite number of pixels denoted by n and the Radon space spanned by p and  $\alpha$  by m pixels (see Fig. 5.16), the operator algebra (5.21) transforms into a linear matrix equation

$$R_{mn}f_n = \hat{f}_m \,. \tag{5.22}$$

The discretization introduces no artifacts but a loss in resolution. The Radon matrix  $R_{mn}$  contains the weights



Figure 5.16: Sampling scheme of the reconstruction domain D and the projected data.



Figure 5.17: Projection matrices of (a) Cartesian and (b) radial reconstruction coordinates. The diagonal character of the radial coordinates is clearly visible. Sampling of the data:  $10 \times 10$ , increment of projection angles:  $15^{\circ}$ , missing projection angle:  $30^{\circ}$ , sampling of p is different in Cartesian and polar coordinates.

of a pixel in the reconstructed area in a projection beam and can in principle be calculated analytically. However, it turns out, that it is sufficient and more convenient to use a fast approximate solution to determine the weights, which is based on the projection formula (5.13) in Cartesian or polar coordinates

$$p = y \cos \alpha + z \sin \alpha$$

$$p = r \cos (\varphi - \alpha) .$$
(5.23)

The numerical algorithm consists of two steps. First, a deliberately fine grid of the reconstruction volume is generated by dividing the original grid (either in Cartesian or radial coordinates) into subpixels. For every point of this new grid it is subsequently determined, which projection coordinate p is hit by a beam of a certain angle  $\alpha$ . The normalized number of subpixels from a particular parent pixel n contributing to a particular projection coordinates are depicted in Fig. 5.17. Both matrices are sparsely populated, which facilitates a particularly economic saving scheme. The Radon matrix of the radial coordinates is roughly symmetric with respect to the diagonal and has almost fully populated lines close to the diagonal.

The natural way to calculate the discrete volume data  $f_n$  from the discrete projection data  $f_m$  is the algebraic inversion of (5.22), i.e.

$$f_n = R_{mn}^{-1} \hat{f}_m \,, \tag{5.24}$$

which is, however, only possible, if the matrix has full rank. That requirement is violated in practice, if the number of points in the reconstructed volume does not match the number of points in projection space, which, however, occurs frequently, when certain projection angles cannot be recorded or analyzed or the reconstructed

	latex sphere	silicon needle
sampling of the tilt series $[p \times y \times \alpha]$	$184 \times 130 \times 66$	$256{\times}215{\times}60$
sampling of the reconstructed volume $[x \times y \times z]$	$77 \times 130 \times 77$	$87 \times 215 \times 87$
memory requirement by inverse matrix [Gbyte]	2.1	3.5
time for the reconstruction on single core [h]	50h	60h

Table 5.3: Computational requirement for typical sampling values.

domain is Cartesian. Additionally, it even turns out to be disadvantageous to use the exact inverse (if determined) because of the rather large amplification of input errors. The error amplification is proportional to the condition number C of the Radon matrix  $R_{mn}$ , which is computed by dividing the largest by the smallest non-zero singular value  $C = \sigma_{max}/\sigma_{min}$  (e.g. Bau III and Trefethen (1997)). Thus, if  $\sigma_{min} \ll 1$ , input errors are strongly amplified and obscure the reconstructed data. In that case, one says that the problem is ill-conditioned. Consequently, it is advantageous to use an inversion scheme, which can treat rectangular matrices and minimizes the error amplification. The inverse of rectangular matrices are not defined, however, by additionally requiring a minimized Euclidean distance

$$\left\| R_{mn}f_n - \hat{f}_m \right\| \to \min,$$
 (5.25)

between the projected reconstructed data and the original data, the so-called general, pseudo- or Moore-Penrose inverse  $\mathbf{R}^+$  and  $f_n = R_{nm}^+ f_m$  is found. The calculation of the pseudoinverse can be accomplished by a Singular Value Decomposition (SVD, e.g. Zurmühl and Falk (1986), see also App. A.8), which furthermore facilitates a control of the error amplification upon inversion (Zurmühl and Falk (1986)). If  $\mathbf{R} = \mathbf{V} \mathbf{\Sigma} \mathbf{U}^{\dagger}$  is the singular value decomposition of **R**, the Moore-Penrose inverse writes  $\mathbf{R}^+ = \mathbf{U} \boldsymbol{\Sigma}^+ \mathbf{V}^{\dagger}$ .  $\boldsymbol{\Sigma}^+$  is calculated by inverting the positive entries of the diagonal matrix  $\Sigma$ . One can now control the condition number C by setting the smallest singular values in  $\Sigma$  to zero. In a certain algebraic sense, this procedure is optimal to reduce the influence of the input error, e.g. produced by dynamic scattering (Eckart-Young theorem, Stewart (1993)). Furthermore, the Radon matrix  $\mathbf{R}$  can be regularized by using the proper grid for the reconstructed domain D: As the Radon matrix for polar coordinates is already close to a diagonal form (see Fig. 5.17), the SVD works particularly fast and the singular values itself are larger than their Cartesian counterparts. Indeed, the hierarchy of singular values is closely related to the circular harmonic decomposition (see Sec. 5.4.1). The reconstruction domain eigenfunctions (columns of  $\mathbf{V}$ ) of the six largest singular values of the Cartesian Radon matrix as depicted in Fig. 5.18 clearly exhibit an increasingly multipole character. Consequently, the damping of the condition number by setting small singular values to zero is equivalent to neglecting high-order multipoles in the reconstruction. Vice versa, one can precondition the input data (projections) by applying a low-pass filter in the Fourier domain of the angular space (see 5.19). This type of smoothing can be furthermore considered as an optimum smoothing procedure due to the multipole hierarchy of the Radon transformation and can be used for arbitrary reconstruction schemes.

It is particularly interesting to note that the ordering of multipoles with respect to reconstruction stability changes if a missing-wedge is present in the input data (see Fig. 5.18(b)).<sup>3</sup> This leads to typical stripe-like artifacts in the SVD based reconstruction (Fig. 5.19), which, however, differ from the artifacts known from other non-algebraic reconstruction techniques (e.g. Frank (1992)). If all singular values are used, the SVD based ART can even fully suppress these missing-wedge artifacts, which is not reported for other reconstruction techniques.

Moreover, the Radon matrix can be modified to incorporate restrictions on the reconstruction domain and dynamic effects as calculated in Sec. 3.2.5 on the phase of the zero beam. This can be achieved in an iterative manner, i.e. reconstructed potentials including their boundaries serve as input for dynamic scattering calculations based on semiclassic or more general Multislice simulations, which in turn yield dynamical correction factors used in the same iteration of the reconstruction. Another advantage of the ART reconstruction is that only small modifications are required to reconstruct vector potentials, which will be exploited in Sec. 5.4.3.

The drawback of the method is its large computational cost (both memory and time). Both the projection matrix and the inverse matrix have to be kept in memory; furthermore the SVD is comparatively slow compared to other matrix inversion methods. The memory cost is reduced by the sparse filling of the projection matrix (around 5%), unfortunately this property is not transferred to the inversion matrix. The large memory requirement and the long reconstruction time were the major hurdle for a detailed investigation and comparison of experimental tomographic reconstructions of the ART with other methods (e.g. Sequential Iterative Reconstruction Method). The requirements for tomographic reconstructions performed below are listed in Table 5.3. Recent developments in computer technique and fast SVD algorithms, made the problem however solvable on work stations. Furthermore, the reconstruction of test potentials showed a large increase of the SVD speed

 $<sup>^{3}</sup>$ Strictly speaking, the multipole ordering itself becomes obsolete. However, if the missing-wedge is small, the present statement holds perturbatively.



Figure 5.18: Reconstruction domain eigenfunction of the 6 largest singular values without missing-wedge (a-f) and with a missing-wedge of  $30^{\circ}$  (g-l). m denotes the order of the radial polynomial and it can be seen that  $l \leq m$  and m + l is even, which can be derived analytically (Natterer (1986)). Furthermore, b and c as well as d-f are degenerated with respect to the circular momentum l. If a missing-wedge is present the Singular value Decomposition cannot be classified with the help of radial and circular polynomials. However, at a missing-wedge of  $30^{\circ}$ , the relationship between g-l and a-g is still visible and one observes a directional dependent reordering of the polynomial and circular orders, i.e. one direction is better reconstructed than the other. The tilt increment of the series is  $5^{\circ}$  and Cartesian coordinates are used for the reconstruction domain.



Figure 5.19: Typical stripe-like missing-wedge artifacts occurring in the SVD based ART using (a) 100 %, (b) 70 % and (c) 60 % singular values.

#### 5.4. HOLOGRAPHIC TOMOGRAPHY

if using polar coordinates, which is due to the natural diagonal like structure of the projection matrix. The potential of the ART based on a SVD will be further discussed at one theoretical and two experimental examples:

- 1. Point and disk shaped homogeneous potentials.
- 2. A latex sphere coated with small gold particles. This specimen combines materials with very large and very small scattering potentials, sharp edges and homogeneous volumes and is therefore an ideal test sample.
- 3. A pn-junction embedded in a Si needle prepared with a Focused Ion Beam (FIB). Here, the dynamic scattering effects play a much larger role. Additionally, the contrast is low due to the increased scattering power. The reconstructed 3D pn-junction can be used to derive doping profiles.

#### 5.4.2.1 Point

An arbitrary potential can be decomposed into  $\delta$ -functions according to

$$f(y,z) = \int \delta(y-y',z-z') f(y',z') \, dy' dz' \,. \tag{5.26}$$

The reconstruction  $f_{\delta}(x-y, x'-y')$  of a projection from a  $\delta(y-y', z-z')$ -object is therefore useful to characterize the properties of the reconstruction of arbitrary objects. After one experimental projection-reconstruction cycle, the  $\delta$ -object is smeared out due to the finite sampling, missing-wedge, etc. This reconstructed function  $f_{\delta}$ is referred to as point-spread function (Frank (1992)), since it transforms the original object to the reconstructed object according to

$$f(y,z) = \int f_{\delta}(x-y,x'-y') f(y',z') \, dy' dz' \,. \tag{5.27}$$

In the following, an off-center point  $\delta(x, y - 4)$  is projected and reconstructed with the SVD based ART algorithms in Cartesian and polar coordinates and a SART algorithm.



Figure 5.20: Reconstructions from projected  $\delta(x, y - 4)$  object with (a,c) Cartesian or (b,d) polar SVD based ART and (a,b) 100% singular values or (c,d) 50% singular values. The result from the SART algorithm after 500 iterations is depicted in (e).



Figure 5.21: Euclidic distance of projected reconstructed data to original projections (a) and reconstructed data to original data (b) of SVD based ART and SART algorithm.

Due to the off-centering, the multipole expansion of the point is infinite, and hence all stability scales are present in the reconstruction. The results of the reconstructions are depicted in Fig. 5.20. If 100% singular values are used, the point is almost perfectly recovered independent from the coordinate system used. At 50%the height of the point is drastically reduced in Cartesian as well as polar coordinates. Additionally, a smearing of the point in the Cartesian algorithm can be observed. Finally, the SART algorithm produces a point spread function comparable to the SVD based ART at 50% singular values. One usually determines the quality of the reconstruction by measuring the Euclidic distance between the projections of the reconstructed data and the originally recorded projections (Fig. 5.21). This measure decreases sharply at the first iteration steps of the SART algorithm, however, only little progress is achieved, when proceeding with the iteration. The SVD based algorithms on the other hand show a more or less linear decrease of the Euclidic distance with growing number of singular values. The polar version surmounts the Cartesian one at 50% singular values and both are better than the SART algorithm, when using 80% singular values. It is, however, important to note that the Euclidic distance in the projected data is not equivalent to the error in the reconstructed data. Unfortunately, the latter is not accessible in the experiment, since the original data are not known. Within this numerical experiment, however, the original data, i.e. the  $\delta$ -object is known, hence the distance between the original data and the reconstructed data can be determined as depicted in Fig. 5.21(b). This measure reveals a rather poor point spread function of the SART algorithm ( $rms \approx 0.4$ ), which corresponds to the quality of the SVD based algorithms at 80% singular values.

To illustrate the connection between the order of multipoles contained in the volume data and the quality and convergence of the reconstruction, a centered disk containing a smaller number of multipoles than the off-center point<sup>4</sup> is reconstructed in the following (Fig. 5.22). Similar to the point, the disk is almost perfectly recovered at 100% singular values and the SART result is comparable to the SVD based ART at 80% singular values.



Figure 5.22: Reconstructions from projected disk object with SVD based ART and (a) 100% singular values or (b) 50% singular values. The result from the SART algorithm after 500 iterations is depicted in (c).

 $<sup>^{4}</sup>$  The centered disk itself is just a monopole, however, the missing-wedge present in the reconstruction introduces additional multipoles.



Figure 5.23: Euclidic distance of projected reconstructed data to original projections (a) and reconstructed data to original data (b) of SVD based ART and SART algorithm.

However, the error in the projected values (Fig. 5.23(a)) as well as the reconstructed values (Fig. 5.23(b)) is much smaller than the corresponding point object reconstructions due to the reduced number of multipoles. One can conclude, that the numerical experiments support the multipole hierarchy of the reconstruction. This observation can be used to design a multipole filter stabilizing the reconstruction independent from the actual reconstruction scheme used. Furthermore, the SVD based ART has the potential to produce an almost artifact free reconstruction, which is particularly weakly affected by the missing-wedge. Unfortunately, the number of singular values used for the reconstruction of an experimental tilt series is restricted due to the rather large amount of input errors such as noise, dynamical effects, etc.

#### 5.4.2.2 Latex sphere



Figure 5.24: Single potential slice as reconstructed with SVD based ART (80% singular values) of a Latex sphere with gold markers on top. The linescans indicate an averaged electrostatic potential around 10 eV within Latex and around 28 eV within a gold nanoparticle, where both values are in excellent agreement with theory (see Sec. 3.2.5).

The TEM specimens of latex spheres were prepared by putting a drop of suspension (diluted 10 times by distilled water) on a copper grid with holey carbon film (S147-3 by Plano GmbH, Germany). After solvent evaporation, spheres were found distributed across the carbon film. Subsequently, small gold particles have been precipitated on top of the latex spheres and the carbon film. For several reasons, the combination of latex spheres with small gold particles is an ideal test sample for holographic tomography: The shape and the potential of the reconstructed gold particles is a measure for the resolution of the reconstruction, whereas long-range variations in homogeneous averaged electrostatic potential of the latex sphere characterize the reconstruction artifacts

as for instance introduced by the missing-wedge. Furthermore, the geometry of the specimen is well defined (no modified layers due to FIB preparation), and the dynamical diffraction of the Latex sphere is very small. The tomographic tilt series was recorded and holographically reconstructed by D. Wolf using his tomographic recording and reconstruction software package THOMAS (Wolf et al. (2009)).

It is found that a SVD based ART reconstruction employing 80% singular values is a good compromise between minimizing the Euclidic distance of the projection of the reconstructed object to the experimental tilt series and reducing the reconstruction error amplification (see Fig. 5.3). Both the shape and homogeneity of the Latex sphere as well as the sharply peaked gold potentials are visible and the mean inner potential obtained for the gold particles is in good agreement to the values predicted by dynamical scattering theory (see Sec. 3.2.5). It is furthermore pointed out that the sampling of the reconstructed volume was limited by computational restrictions (restricted memory), i.e., a further improvement in the resolution is expected if using state-of-the-art work stations. Nevertheless, the results show that the SVD based ART provides an alternative to the iterative algorithms (SIRT, SART) also in an experimental environment.

#### 5.4.2.3 Si pn-junction

Silicon pn-junctions have been investigated in numerous holography studies, which facilitate a unique determination of the electrically active dopant profiles (e.g. Lenk et al. (2004); Lichte et al. (2007); Cooper et al. (2006); Rau et al. (1999)). Holographic tomography proved very useful in determining 3D built-in potentials and investigating the formation and extension of so-called dead layers introduces by Focussed Ion Beam (FIB) preparation (e.g. Twitchett-Harrison et al. (2008, 2007); Wolf et al. (2009, 2008)).

The silicon specimen used for the tomographic reconstruction was prepared by combination of the lift-out technique and FIB needle preparation developed by A. Lenk (Lenk (2008)) in order to facilitate large tilt angles in the tomographic series acquisition. The sampling of the reconstructed volume was again limited due to computational restrictions and the tomographic recording and holographic reconstruction was done by D. Wolf (TU Dresden). Similar to the Latex sphere, SVD based ART reconstruction is capable of retrieving the correct mean inner potential even though dynamical scattering effects are much larger than in the Latex case (see Fig. 5.25). However, the missing edge effect shows up much stronger, i.e., a characteristic stripe contrast is observable.



Figure 5.25: Single potential slice within Si needle reconstructed with ART stopped at (a) 70% (b) 80% and (c) 90% of singular values. The horizontal stripes indicated by linescans along the blue arrow (d) are missing-wedge artifacts, i.e. they are reduced upon singular value increase, and split if smaller singular values are incorporated into the reconstruction. One slice of the original projection data (sinogram) is depicted in (e), where the dark stripes observed at particular projection angles correspond the dynamical scattering conditions.

#### 5.4.3 Magnetic vector field tomography

The influence of magnetic fields on the scattering process is small compared to its electrostatic counterpart (see Sec. 3.2). It can be treated within a semiclassical approach, which for the thickness of the specimen used within TEM breaks down the phase integrals along straight lines. This magnetic modulation of the wave front can be visualized by various techniques such as Lorentz imaging or holography (see Fig. 5.26), which provides



Figure 5.26: Holographic analysis of magnetic domains in martensitic Ni50Mn30Ga20 (specimen by Dr. S. Roth, IFW Dresden). Left: Colour-coded phase gradient showing the direction of magnetization in the domains. Right: Lorentz image showing domain walls at the twin boundaries (TB) and within the twin-bands. The hologram was acquired by K. Vogel (TU Dresden) within a broad twin-band (position of hologram acquisition is indicated by the box).

quantitative information on magnetic fields on the length scale of several tens of nanometers such as present for instance in magnetic memory applications. Contrary to the scalar electrostatic potential, however, the three components of a vector potential cannot be tomographically reconstructed from one tilt series. Indeed, one tilt series is sufficient to reconstruct one component of the magnetic field with no additional assumptions about the boundary conditions. The recording of three perpendicular tilt series, which would yield all 3 components, is experimentally unfeasible; even two perpendicular tilt series are already difficult to record, if one keeps in mind the missing-wedge problem, the mechanics of the sample holders and the geometry of the sample. The following section contains a derivation for a reconstruction of all 3 components from 2 tilt series around 2 perpendicular tilt axes without assumptions on the boundary conditions, since the information on them is contained in the data. The treatment is a generalization to the case of vanishing fields at the boundary treated in the literature (Lade et al. (2005), Phatak et al. (2008)). The generalization is, however, necessary if long-range components of the magnetic field leak out of the reconstructed volume given by the hologram width.<sup>5</sup> It is furthermore assumed that the phase shift of the electric potential has been already subtracted, which can be accomplished by recording  $360^{\circ}$  instead of  $180^{\circ}$  tilt series and subtracting projections with  $180^{\circ}$  rotation angle difference. This procedure cancels the electrostatic field which is symmetric under this symmetry operation (time inversion symmetry), whereas the magnetic field is doubled since it is antisymmetric.

#### 5.4.3.1 2D Helmholtz representation

The starting point of the derivation is the Helmholtz expansion (e.g. Arfken and Weber (2005)) of a 2D vector field defined on the reconstruction domain D in a divergence-free (solenoidal) part  $\vec{A}_{W_0}$ , a curl-free (irrotational) part  $\vec{A}_{Q_0}$  and a harmonic part  $\vec{A}_H$ , with the first two being subject to homogeneous boundary conditions, i.e.

$$\vec{A} = \vec{A}_{W_0} + \vec{A}_{Q_0} + \vec{A}_H$$
(5.28)  

$$\vec{\nabla} \cdot \vec{A}_{W_0} = 0, \ \vec{A}_{W_0} \cdot \vec{n}_{\sigma} = 0$$

$$\vec{\nabla} \times \vec{A}_{Q_0} = 0, \ \vec{A}_{Q_0} \times \vec{n}_{\sigma} = 0$$

$$\Delta \vec{A}_H = 0.$$

Here,  $\vec{n}_{\sigma}$  denotes the surface normal of the reconstruction volume. Consequently, the harmonic part is determined by the non-homogeneous boundary conditions of the 2D vector potential on the surface  $\partial D$ . Since the 2D vector potential is the projection of the 3D vector potential onto the 2D reconstruction domain D a Coulomb gauge  $\vec{\nabla} \cdot \vec{A}$  of the 3D potential is not sufficient for a disappearance of the 2D divergence. By inserting the

 $<sup>^{5}</sup>$ Such a generalization, however, removes but one drawback of the previous methods, since potentials outside of the reconstructed volume are still neglected in the projection integrals. To remedy this problem, one could think of an iterative algorithm, which uses the boundary values of the reconstructed volume to calculate the potential in the region outside of the reconstruction volume, which is later-on incorporated into the projection.



Figure 5.27: 3D reconstruction geometry

Helmholtz expansion into the longitudinal projection of the vector potential (5.12) one obtains

$$f(x,y) = \int (A_{W_0,z} + A_{Q_0,z} + A_{H,z}) dz$$

$$= \int (A_{W_0,z} + A_{H,z}) dz$$
(5.29)

i.e. the rotation free part is not contributing to the projection. The missing part  $\vec{A}_{Q_0}$  is responsible for the most of the difficulties occurring in the reconstruction of magnetic vector potentials as will be shown subsequently.

#### 5.4.3.2 2D algebraic reconstruction

The longitudinal projection of the vector potential  $\vec{A}$  can be similarly to the scalar case formulated as an algebraic equation

$$\hat{R}\vec{A} = \hat{f}\left(p,\alpha\right)\,,\tag{5.30}$$

which after writing out the scalar product in (5.29) reads

$$\begin{pmatrix} -\sin\alpha\hat{R},\cos\alpha & \hat{R} \end{pmatrix} \begin{pmatrix} A_y \\ A_z \end{pmatrix} = \hat{f}(p,\alpha) .$$
 (5.31)

The algebraic inversion of the discretized form of this expression is analog to the scalar case (5.24) except that the number of columns on the left hand side has doubled (two components of the vector potential are reconstructed in one step). This is reducing the stability of the inversion. An advantage of the algebraic inversion for vector potentials is that both the divergence-free part and the harmonic part are obtained.

#### 5.4.3.3 3D reconstruction

The complete 3D reconstruction consists of a repetition of the above described process for a large number of slices along the tilt axis and the recording of a second tilt series around a perpendicular tilt axis (e.g. axis 1: [010],axis 2: [100]), i.e.

$$A^{1R} = \bar{A}^{xz}_{W_0} + \bar{A}^{xz}_H$$

$$A^{2R} = \bar{A}^{yz}_{W_0} + \bar{A}^{yz}_H .$$
(5.32)

It yields two datasets containing 2D vector fields, where the respective curl free part is not appearing in the reconstruction. In the following, it will be demonstrated that this is sufficient to obtain all 3 components of the 3D magnetic field  $\vec{B}$ :

The magnetic field  $\vec{B}$  is determined by

$$\vec{\nabla} \times \vec{A} = \begin{pmatrix} \frac{\partial}{\partial y} A_z - \frac{\partial}{\partial z} A_y \\ \frac{\partial}{\partial z} A_x - \frac{\partial}{\partial x} A_z \\ \frac{\partial}{\partial x} A_y - \frac{\partial}{\partial y} A_x \end{pmatrix} = \begin{pmatrix} B_x \\ B_y \\ \frac{\partial}{\partial x} A_y^{2R} - \frac{\partial}{\partial y} A_x^{1R} - \left(\frac{\partial}{\partial y} A_{Q_0x}^1 - \frac{\partial}{\partial x} A_{Q_0y}^2\right) \end{pmatrix}.$$
(5.33)

In the first (second) line the 2D quantity from the second (first) tilt series is inserted and it is made use of the fact that the 2D rotation of the missing part  $\vec{A}_{Q_0}$  is by definition zero. The bracket on the third line, however,

contains the missing rotation free potential  $\vec{A}_{Q_0}$ , which will be replaced with the help of the third Maxwell equation

$$\vec{\nabla} \cdot \vec{B} = \frac{\partial}{\partial x} B_x + \frac{\partial}{\partial y} B_y + \frac{\partial}{\partial z} B_z = 0.$$
(5.34)

A direct z-integration is impossible, because the unknown boundary condition of  $B_z$  in z-direction is unknown. However, the x-derivative of the x-component of  $\vec{B}$  (see (5.34)) can be written as

$$\frac{\partial}{\partial x}B_x = \frac{\partial}{\partial x}\left(\frac{\partial}{\partial y}\left(A_z^{1R} + A_{Q_0z}^1\right) - \frac{\partial}{\partial z}\left(A_y^{2R} + A_{Q_0y}^2\right)\right).$$
(5.35)

Inserting the following equality from the Helmholtz decomposition (5.28)

$$\frac{\partial}{\partial x}A^{1}_{Q_{0}z} = \frac{\partial}{\partial z}A^{1}_{Q_{0}x}$$
(5.36)

yields

$$\frac{\partial}{\partial x} \left( B_x - \frac{\partial}{\partial y} A_z^{1R} + \frac{\partial}{\partial z} A_y^{2R} \right) = \frac{\partial}{\partial z} \left( \frac{\partial}{\partial y} A_{Q_0 x}^1 - \frac{\partial}{\partial x} A_{Q_0 y}^2 \right) \,. \tag{5.37}$$

This is a first order differential equation for the unknown bracket in the right hand side of the third line in (5.33). The integration within deliberate z boundaries reads

$$\left(\frac{\partial}{\partial y}A^{1}_{Q_{0}x} - \frac{\partial}{\partial x}A^{2}_{Q_{0}y}\right) = \int_{z_{0}}^{z} \frac{\partial}{\partial x} \left(B_{x} - \frac{\partial}{\partial y}A^{1R}_{z} + \frac{\partial}{\partial z}A^{2R}_{y}\right) dz + \left(\frac{\partial}{\partial y}A^{1}_{Q_{0}x} - \frac{\partial}{\partial x}A^{2}_{Q_{0}y}\right)_{z=z_{0}}.$$
 (5.38)

The tangential components of  $A_{Q_0}$  at the boundary vanish by definition (see (5.28)), hence, if the z-coordinate  $z_0$  of the lower boundary of the reconstruction volume is independent from x and y, i.e. the reconstructed volume is limited in z-direction by a plane, the last bracket in the previous expression is zero yielding a formula for the missing bracket:

$$\begin{pmatrix} \frac{\partial}{\partial y} A^{1}_{Q_{0}x} - \frac{\partial}{\partial x} A^{2}_{Q_{0}y} \end{pmatrix} = \int_{z_{0}}^{z} \frac{\partial}{\partial x} \left( B_{x} - \frac{\partial}{\partial y} A^{1R}_{z} + \frac{\partial}{\partial z} A^{2R}_{y} \right) dz'$$

$$= \int_{z_{0}}^{z} \frac{\partial^{2}}{\partial x \partial y} \left( A^{2R}_{z} - A^{1R}_{z} \right) dz' .$$

$$(5.39)$$

Inserting this result into the curl of  $\vec{A}$  (5.33) finally yields the z-component of the magnetic field  $\vec{B}$ 

$$B_z = \frac{\partial}{\partial x} A_y^{2R} - \frac{\partial}{\partial y} A_x^{1R} - \int_{z_0}^z \frac{\partial^2}{\partial x \partial y} \left( A_z^{2R} - A_z^{1R} \right) dz' \,. \tag{5.40}$$

The last bracket disappears if  $A_z^{2R} = A_z^{1R}$  due to rotational symmetry or if the vector potentials drop to zero on the boundaries of the reconstruction volume. In the latter case the harmonic parts  $\vec{A}_H$  vanish, consequently

$$\int_{z_0}^{z} \frac{\partial}{\partial x} A_z^{1R} dz' = \int_{z_0}^{z} \frac{\partial}{\partial x} A_{W_0 z}^{1R} dz' = -\int_{z_0}^{z} \frac{\partial}{\partial z} A_{W_0 x}^{1R} dz' = 0$$
(5.41)

 $\operatorname{and}$ 

$$\int_{z_0}^{z} \frac{\partial^2}{\partial x \partial y} \left( A_z^{2R} - A_z^{1R} \right) dz' = 0.$$
(5.42)

One can conclude the following for the case that a magnetic field is to be tomographically reconstructed, which is rotationally asymmetric with respect to the optical axis and assumes large values on the boundary of the reconstruction volume. Then the complete expression (5.40) has to be evaluated and the reconstruction volume has to be limited by a planar surface in z-direction. The reconstruction of real magnetic fields remains a future task due to the missing possibility of recording a tilt series around two perpendicular axis in this work. A detailed analysis of the particular properties of the ART for vector fields is postponed for the same reasons.

### 5.5 Summary

The determination physical quantities by means of EH can be split into the direct determination of static electromagnetic fields by means of the reconstructed phase and more complex indirect methods, where the reconstructed waves are related to models containing the desired physical quantities as parameters.

- The reconstructed phases are currently either too noisy or too obscured by dynamical scattering effects to uniquely determine electric depolarization fields on a nm length scale such as occurring at ferroelectric domain boundaries. Nevertheless, dedicated experimental conditions, such as optimum specimen properties in terms of scattering power and thickness and improvements in both the quantitative evaluation of the signal to noise ratio itself could be derived to facilitate a unique determination in the future.
- The structure determination of ferroelectrics by means of high-resolution TEM and EH imaging and subsequent fitting procedures of atomic column positions is a powerful tool, which is able to remedy some of the drawbacks encountered at the direct determination of electric fields from the reconstructed phase in ferroelectrics. This method was applied to measure screening lengths of 8 12 Å at ferroelectric-nonferroelectric interfaces. High-resolution investigations of electric properties of domain walls and interfaces are possible by calculating the electric polarization  $\vec{P}$  via the Born effective charges, which correlate the measured atomic column positions to the polarization. The measured polarizations indicate a finite size effect at the investigated layered structures, which is stronger for the ferroelectric-insulator interface and decreases at interfaces of ferroelectric to conducting materials.
- Holographic tomographic tilt series reconstruction facilitates the quantitative investigation of 3D electromagnetic fields. A review of the reconstruction process suggests the use of projection geometry adapted to polar coordinates for sampling the reconstructed volume. Algebraic reconstruction routines based on singular value decompositions proved to be robust against artifacts such as the missing-wedge and provide a straight forward mechanism to control the error of the reconstruction. Furthermore, the vector field reconstruction formalism has been extended to facilitate the reconstruction of magnetic fields leaking out of the reconstruction volume. Further developments of the technique are necessary for successful applications in the field of weak electrostatic depolarization fields and magnetic fields.

# Chapter 6

# Summary and Outlook

The goal of this work was to investigate and advance the limits of electron holography as a truly quantitative microscopic technique. In the light of ever faster development and in particular shrinking of dimensions of functional materials and solid state technology, it is an urgent task for TEM techniques to deliver quantitative information about specimen properties down to sub-Å length scales. State-of-the-art microscopes facilitate aberration corrected imaging within a large resolution interval. Furthermore, the imaging theory is well developed to describe most of the remaining artifacts introduced by the microscope in a quantitative manner. Electron holography (EH) has the capability to overcome severe limitations of the conventional TEM imaging process which is intrinsically connected to the reconstruction of the image wave in both amplitude and phase, or more generally to the reconstruction of certain off-diagonal elements of the image density matrix. Since the beam electron wave is the fundamental quantity interacting with the specimen according to the basic laws of quantum electrodynamics, EH offers a rather straight forward approach to specimen properties. In order to exploit this advantage, it is, however, indispensable to consider the whole holographic experiment including both the physics of the microscope, the electron-specimen interaction and the specimen itself. Only a combination of all three areas promises a successful quantitative measurement of minute electromagnetic fields and structure distortions as required for the understanding of modern functional materials like (multi-)ferroic ceramics. Historically, such a holistic approach was put back due to more urgent experimental issues connected with reliable electron holographic measurements and the ongoing efforts to efficiently simulate electron-specimen and imaging as well as solid state properties. The achievements made until now, however, changed the situation, facilitating the combined approach outlined above towards fully quantitative off-axis EH.

A truly quantitative interpretation of the reconstructed wave relies all the more on a precise description of the electron holographical imaging and reconstruction process, which can be split into two parts, the image acquisition and the reconstruction process. In spite of the in large parts similar optical setup of the microscope the properties of the interference terms produced by the biprism differ fundamentally from the conventional image. The Möllenstedt biprism introduces two additional electron optical effects, which have to be considered, when reconstructing holograms. Firstly, diffraction at the sharp edge of the filament leads to Fresnel fringes in the image plane. It was shown in this work that the effects can be removed by calculating the missing terms analytically and adding them to the interference pattern. Secondly, the illumination angle dependent modulation of path lengths in the tilted beams behind the biprism produces a shift of the interference pattern. which yields a contrast damping, when summed over the convergence angle of the illumination. It was shown in this work that the aberrations of the objective lens have to be incorporated in that summation yielding a modified form of the previously considered spatial envelope. Furthermore, it has been not discussed which improvements could be achieved by changing the optical setup of the microscope itself. For instance, optimized positions of the biprism or the use of multiple biprisms could drastically reduce or remove the influence of Fresnel fringes as well as the contrast damping. The statistical superposition (or trace of the density operator) leads to reconstructed wave averages instead of intensity averages, hence amplitude (or contrast) damping due to destructive decoherence. Consequently, the averaging over lens aberrations produces chromatic and spatial envelope functions; a directional damping function is introduced by specimen drift. The interference terms can be analyzed with respect to the spatial distortions introduced mainly by the hardware  $C_s$ -corrector, the biprism, the projective system and the fiber optics of the camera. Based on accurate distortion measurements a digital distortion removal as part of the standard reconstruction process has been proposed, which removes the drawbacks of the usual division with a parallely reconstructed noisy empty wave. Similar considerations apply to the investigation of the holographic reconstruction process. It was shown that the numerical filtering of the sideband with a sinc mask corresponds to a local fit, i.e. a least-square fit, of a rectangular patch of the hologram to a cosinoidal interference pattern. This mask is therefore optimal with respect to minimizing delocalization effects due to the reconstruction, i.e. the resolution is maximally preserved. The noise figures of reconstructed amplitude and phase are mainly determined by shot noise smeared and amplified by the scintillator. Accurate

amplitude and phase detection limits have been derived, which consider both shot noise and scintillator noise and differ substantially from the previously used amplitude and phase detection limits based on shot noise only. However, significant noise level reductions are preferably achieved by developing new experimental techniques. That involves the use of scintillator free (direct) detectors, brighter electron sources, more stable microscopes, and multiple hologram acquisition and reconstruction. Further improvement of quantitative reconstruction methods and implementation into software packages accessible to the scientific community remain an open task for the future. It is furthermore pointed out that other holographic techniques, like inline holography, exist, which might be advantageous in terms of noise or other important experimental parameters. Thus, a thorough comparison of different electron holographic approaches would be a worthwhile endeavor.

Theoretical considerations on both the scattering process and the probed solid state properties are growing ever more to indispensable tools for EH. Although the basics of electron scattering on solids, i.e. the laws of quantum electrodynamics, have been developed together with the first electron microscopes (or even before) and remained valid since then, efficient and accurate scattering computation schemes are still under development. The elastic channel of electron-specimen scattering mainly depends on the electrostatic potential of the scatterer, which is in turn dominated by the strongly peaked screened atomic potentials. The complex scattering on multiple atoms arranged on a crystal grid can be sufficiently well described within the forward scattering approximations in general and the small-angle approximation combined with fixed integration steps (Multislice) in almost all cases interesting for EH. It was shown that under special imaging conditions usually used for medium resolution holography, namely thick specimen tilted out-of-zone axis, the complicated dynamic scattering behavior can be approximated by a simple modified Phase Grating Approximation. Special emphasis was put on the influence of relativistic effects within elastic scattering and it was found that spin-orbit coupling of the beam electron is negligible. One of the most important factors for elastic scattering is the treatment of the thermal motion of the atoms, which manifests itself depending on the imaging conditions. Dedicated Multislice formalisms valid for conventional intensity recording and for waves reconstructed by off-axis holography have been developed. A non-trivial modulation of the recorded intensity and in particular of the reconstructed wave is obtained if the scattering potentials are large (e.g. heavy atoms), leading to different modifications of spatial frequencies. Another consequence is an overall reduction of the reconstructed amplitude, which is not related to inelastic scattering but to decoherence introduced by oszillating lattice configurations. Thus, inelastic mean-free path measurements by means of amplitudes reconstructed from off-axis EH have to be reinterpreted. Special attention has to be paid, when comparing complex electron waves reconstructed from images subject to different imaging conditions, for instance off-axis EH with Inline Holography. There, the intensities recorded at different foci in the image plane, used for reconstructing the wave, are subject to the condition of intensity averaging and not reconstructed wave averaging. Hence, they do not compare to waves reconstructed by off-axis Electron Holography or reconstructed wave averaged image simulations, in particular when heavy atoms are involved in the scattering process. The same argumentation has to be applied to phases obtained from diffraction data by refinement techniques. Additionally, a particularly fast approximation has been derived to compute forwardly scattered waves from very thick objects such as used in medium-resolution investigations. Some remaining open points of the elastic scattering theory, which have still been insufficiently discussed in the field of EH, are the effects of correlations in the thermal atomic motion (phonons) and the magnitude of virtual inelastic scattering mediated by a parallel exchange of two virtual photons between the scatterer and the electron, which is expected to produce additional phase information. The theory of inelastic electron scattering is far more complicated than the elastic one. The particularly large elastic scattering cross-sections require furthermore that elastic scattering before and after the inelastic excitation have to be considered. This combination leads to intriguing effects like atomic column contrasts depending on specific core-loss excitations or an effective enhancement of the illumination semiconvergence angle through electron-phonon scattering, discussed in this work. The latter can lead to a significant contrast damping, contributing to the Stobbs factor in non-aberration free microscopes. For off-axis EH core electron excitations play a minor role though. The dominant inelastic excitations are in the low-loss regime, e.g. phonons or plasmons. Their dominant influence on off-axis holographic measurements is a contrast reduction, as they do not interfere with the elastically scattered reference wave. If the reference wave, however, is itself scattered inelastically, interference terms occur, which influence the total contrast. To quantify the aforementioned inelastic effects, an accurate and fast scattering formalism has been developed, which facilitates a combined calculation of elastically and inelastically scattered electrons both in the low-loss and core-loss regime. The incorporation of fully relativistic scattering based on the Dirac equation is still under development as well as the incorporation of ab-initio specimen wave functions.

Ab-initio modeling of solid state properties enhances the possibilities of EH techniques by providing correlations between the measured quantities, e.g. the atomic structure and electromagnetic fields, and other physical quantities of interest like the electric polarization or band occupations. The present work's main target in that field was the computation of electrostatic fields in perovskite ferroelectric (hetero-)structures by Density Functional Theory (DFT) in order to interpret EH measurements. Bulk ferroelectrics of the perovskite class exhibit a shift of the central atom with respect to the non-ferroelectric phase. This ionic displacement in turn leads to a deformation of the total electrostatic potential, which is visible as a shift of atomic column signals in EH. Thus, a truly quantitative polarization measurement on a nm length scale is possible by combining the shift signal with the linear relationship between displacement and polarization, which is given by the Born effective charge tensor and can be calculated by DFT methods. Changes of the potential in the interstitial region between the atoms turned out to be rather weak and furthermore difficult to interpret in terms of electric polarization. A quantitative EH determination and interpretation of interstitial bulk potentials in ferroelectrics is therefore currently beyond reach. Ferroelectric heterostructures lend their intriguing properties, like the formation and response of the material to depolarization fields. A depolarization field magnitude in the order of 0.1 V/nm was predicted to occur in BiFeO<sub>3</sub> domain walls. All three possible domain wall configurations (71°, 109° and 180°) in BiFeO<sub>3</sub> have been calculated and an increase of the potential jumps correlating with increased domain wall conductivity could be observed. A comprehensive ab-initio modeling of the magnetic properties of the domain wall remains an open task for the future.

A direct holographical reconstruction of the previously mentioned depolarization fields is currently hampered by the low signal to noise ratios and spurious effects from dynamical scattering, specimen preparation and systematic errors of the microscope. A unique experimental proof of depolarization fields at domain walls could therefore not be obtained. However, the combination of EH at a weak scatterer  $(KNbO_3)$  with a large thickness and improved recording and reconstruction methods proved that such a measurement is in principle possible. Future advances of equipment and reconstruction schemes are therefore expected to finally remove the remaining ambiguities and extend to applicability of the method to arbitrary materials. The combination of ab-initio calculations with very precise structure measurements offers a complementary way for the determination of local polarizations and depolarization fields. To this end an atomic position refinement algorithm has been developed, which, depending on the quality of the experimental results, yields positions with a precision in the range of 10 pm. Application of the technique to SrTiO<sub>3</sub>/PbTiO<sub>3</sub>/SrRuO<sub>3</sub> heterostructures allowed a determination of finite size effects, depolarization charges and screening lengths. For instance, the extension of the  $PbTiO_3/SrRuO_3$  interface into  $SrRuO_3$  was determined to be approximately 8Å and thus 4Å thinner than the corresponding SrTiO<sub>3</sub>/PbTiO<sub>3</sub> interface. This behavior can be explained by the larger charge carrier density in metallic SrRuO<sub>3</sub> compared to the non-metallic SrTiO<sub>3</sub>. Other interesting material structures like the "2D electron gas system"  $LaAlO_3/SrTiO_3$  are currently successfully investigated by holographic atomic position analysis.

One of the current frontiers in EH is the elucidation of 3D structures and electromagnetic potentials at nm resolution by means of electron holographic tomography (EHT). The prospects of a successful implementation of that measurement are manifold. Atomic displacements could be analyzed in 3D, complex 3D electromagnetic fields such as occurring in domain structures could be investigated, etc. An integrated part of that development is an advanced reconstruction algorithm for both scalar and vector potentials. As experimental limitations with respect to noise and erroneous or incomplete data are especially severe in EH, special emphasis has to be put on the stability and accuracy of reconstruction algorithms. Thus, the well-known singular value decomposition of the Radon transform has been successfully applied on EHT data and analyzed with respect to different grid representations and regularizations. Future development aims at improving the currently low reconstruction speed, applying the method to vector potentials and transfer the knowledge gained about different regularization schemes to other frequently used reconstruction algorithms.

One can conclude that the quantification of results obtained by means of EH offers unique possibilities for determining structures and electromagnetic potentials, for instance in the field of ferroelectric materials. Detecting atomic displacements or potentials of ever weaker magnitudes, however, requires advances in the field of image acquisition, holographic and tomographic reconstruction as well as the combination with suitable solid state physical models as provided for instance by ab-initio methods. This journey still continues and promises to establish EH as a standard tool for quantitative solid state characterization.

"There is a lot of things to do, but let us begin" - H. Lichte

# Appendix A

# Mathematical supplement

## A.1 Fresnel integral

The complex Fresnel integral

$$F(x) = \sqrt{\frac{2}{\pi}} \int_{0}^{x} e^{it^{2}} dt$$

$$= C_{1}(x) + iS_{1}(x)$$
(A.1)

is defined with the help of the normalized Fresnel integrals

$$C_1(x) = \sqrt{\frac{2}{\pi}} \int_0^x \cos t^2 dt \tag{A.2}$$

 $\operatorname{and}$ 

$$S_1(x) = \sqrt{\frac{2}{\pi}} \int_0^x \sin t^2 dt$$
 (A.3)

The definition of the complementary Fresnel integral

$$Fc(x) = \sqrt{\frac{2}{\pi}} \int_{x}^{\infty} e^{it^{2}} dt \qquad (A.4)$$
$$= \sqrt{\frac{2}{\pi}} \int_{-\infty}^{-x} e^{it^{2}} dt$$
$$= \frac{1+i}{2} - F(x)$$

is equivalent to that of the complementary error function erfc (see Abramowitz and Stegun (1964)).

## A.2 Covariance of the detector

Similarly to the to mean intensity the spatial covariance  $Cov\left(\vec{R},\vec{R}'\right)$  of the signal is calculated according to

$$Cov\left(\vec{R},\vec{R}'\right) = \int dS_{\varrho} dQ\left(\vec{R}''''\right) dR''''$$

$$+ \left(\int \delta_{\varrho''''}\left(\vec{R}''-\vec{R}''''\right) pf_s\left(\vec{R}-\vec{R}''\right) dR''\right) \left(\int \delta_{\varrho''''}\left(\vec{R}''-\vec{R}''''\right) pf_s\left(\vec{R}'-\vec{R}''\right) dR''\right)$$

$$+ \overline{\rho}\left(\vec{R}\right) \overline{\rho}\left(\vec{R}'\right) .$$

$$(A.5)$$

In the next step the outermost brackets are multiplied by introducing another dummy coordinate  $\vec{R}^{\prime\prime\prime}$ 

$$Cov\left(\vec{R}, \vec{R}'\right) = \int dS_{\varrho} dQ\left(\vec{R}'''\right) dR'' dR''' dR''''$$

$$\cdot \quad \delta_{\varrho''''}\left(\vec{R}'' - \vec{R}'''\right) pf_s\left(\vec{R} - \vec{R}''\right) \delta_{\varrho''''}\left(\vec{R}''' - \vec{R}'''\right) pf_s\left(\vec{R}' - \vec{R}'''\right)$$

$$- \quad \overline{\rho}\left(\vec{R}\right) \overline{\rho}\left(\vec{R}'\right) .$$
(A.6)

Now, it is useful to define the following quantity

$$nsf_{\varrho}\left(\vec{R} - \vec{R}'', \vec{R}' - \vec{R}'''\right) = \int pf_{s}\left(\vec{R} - \vec{R}''\right) pf_{s}\left(\vec{R}' - \vec{R}'''\right) dS_{\varrho}$$

$$= Cov_{sz\varrho}\left(\vec{R} - \vec{R}'', \vec{R}' - \vec{R}'''\right) + psf\left(\vec{R} - \vec{R}''\right) psf\left(\vec{R}' - \vec{R}'''\right) \\ = \frac{1}{\varrho}Cov_{sz1}\left(\vec{R} - \vec{R}'', \vec{R}' - \vec{R}''\right) \delta\left(\vec{R}'' - \vec{R}'''\right) + psf\left(\vec{R} - \vec{R}''\right) psf\left(\vec{R}' - \vec{R}'''\right)$$
(A.7)

as the noise spread function of the scintillator.<sup>1</sup>In the second and third line, the covariance of the scintillator spread as defined in (2.79), (2.78) and (2.75) is inserted. Together with the covariance of the shot noise (2.72), the following expression is obtained

$$Cov\left(\vec{R}, \vec{R}'\right) = \int dQ\left(\vec{R}'''\right) dR'' dR''' dR'''' \delta_{\varrho}\left(\vec{R}'' - \vec{R}'''\right) \delta_{\varrho}\left(\vec{R}''' - \vec{R}'''\right) nsf_{\varrho}\left(\vec{R} - \vec{R}'', \vec{R}' - \vec{R}'''\right) - \overline{\rho}\left(\vec{R}\right) \overline{\rho}\left(\vec{R}'\right) = \int dQ\left(\vec{R}''''\right) dR'' dR''' dR'''' \left(\delta_{\varrho}\left(\vec{R}'' - \vec{R}'''\right)\right) \delta_{\varrho}\left(\vec{R}''' - \vec{R}'''\right)\right) Cov_{sz\varrho}\left(\vec{R} - \vec{R}'', \vec{R}' - \vec{R}'''\right) + \int dQ\left(\vec{R}''''\right) dR'' dR''' dR'''' \cdot \left(\delta_{\varrho}\left(\vec{R}'' - \vec{R}'''\right)\right) \delta_{\varrho}\left(\vec{R}''' - \vec{R}''''\right)\right) dQ\left(\vec{R}''''\right) psf\left(\vec{R} - \vec{R}''\right) psf\left(\vec{R}' - \vec{R}'''\right) - \overline{\rho}\left(\vec{R}\right) \overline{\rho}\left(\vec{R}'\right) = \int dQ\left(\vec{R}''''\right) dR'' dR''' dR'''' \cdot \left(\delta_{\varrho}\left(\vec{R}'' - \vec{R}'''\right)\right) \delta_{\varrho}\left(\vec{R}''' - \vec{R}''''\right) Cov_{sz\varrho}\left(\vec{R} - \vec{R}'', \vec{R}' - \vec{R}'''\right) + \int \delta\left(\vec{R}'' - \vec{R}'''\right) \sigma_{in}^{2}\left(\vec{R}''\right) psf\left(\vec{R} - \vec{R}''\right) psf\left(\vec{R}' - \vec{R}'''\right) dR'' dR''''.$$

Finally, after integrating over the  $\delta$ -functions the covariance assumes the following form

$$Cov\left(\vec{R},\vec{R}'\right) = \int \overline{\rho}_{in}\left(\vec{R}''\right)Cov_{sz1}\left(\vec{R}-\vec{R}'',\vec{R}'-\vec{R}''\right)dR''$$

$$+ \int \sigma_{in}^{2}\left(\vec{R}''\right)psf\left(\vec{R}-\vec{R}''\right)psf\left(\vec{R}'-\vec{R}''\right)dR'' .$$
(A.9)

# A.3 Power spectrum of the detector

The power spectrum of an arbitrary image reads

$$\int \left| \mathcal{F}\left\{ \rho\left(\vec{R}\right) \right\} \right|^2 \mathrm{d}S_{\varrho} \mathrm{d}Q = \mathcal{F}\left\{ \int \rho\left(\vec{R}\right) \rho\left(\vec{R} + \vec{R}'\right) \mathrm{d}S_{\varrho} \mathrm{d}Q \mathrm{d}R \right\} \,. \tag{A.10}$$

Inserting the expressions for the electron density from (2.80) yields

$$\int \int \left| \mathcal{F}\left\{\rho\left(\vec{R}\right)\right\} \right|^2 \mathrm{d}S_{\varrho} \mathrm{d}Q = \mathcal{F}\left\{\int \mathrm{d}R'' \mathrm{d}R''' \mathrm{d}S_{\varrho} \mathrm{d}Q\left(\vec{R}'''\right) \mathrm{d}R \\ \cdot \quad \delta_{\varrho}\left(\vec{R}'' - \vec{R}'''\right) pf_s\left(\vec{R} - \vec{R}''\right) \delta_{\varrho}\left(\vec{R}''' - \vec{R}''''\right) pf_s\left(\vec{R} + \vec{R}' - \vec{R}'''\right) (A.11)$$

 $<sup>^{1}</sup>$  The name noise spread function is somewhat misleading, since it does not describe the spread of the noise in terms of a transfer theory.
which can be simplified by inserting the expressions for the nsf and covariance of the quantum noise:

$$\begin{split} \int \int \left| \mathcal{F}\left\{\rho\left(\vec{R}\right)\right\} \right|^{2} dS_{\varrho} \mathrm{d}Q &= \mathcal{F}\left\{\mathrm{d}R'' \mathrm{d}R''' \mathrm{d}Q\left(\vec{R}'''\right) \mathrm{d}R \\ &\cdot \left(\operatorname{Cov}_{in}\left(\vec{R}'', \vec{R}'''\right) + \rho_{in}\left(\vec{R}''\right)\rho_{in}\left(\vec{R}'''\right)\right) nsf_{\varrho,\varrho'}\left(\vec{R} - \vec{R}'', \vec{R} + \vec{R}' - \vec{R}'''\right) \right\} \\ &= \mathcal{F}\left\{\int \rho_{in}\left(\vec{R}''\right) \operatorname{Cov}_{sz1}\left(\vec{R} - \vec{R}'', \vec{R} + \vec{R}' - \vec{R}''\right) \mathrm{d}R'' \mathrm{d}R\right\} \\ &+ \mathcal{F}\left\{\int \sigma_{in}^{2}\left(\vec{R}''\right) \operatorname{psf}\left(\vec{R} - \vec{R}''\right) \operatorname{psf}\left(\vec{R} + \vec{R}' - \vec{R}''\right) \mathrm{d}R'' \mathrm{d}R\right\} \\ &+ \mathcal{F}\left\{\int \overline{\rho}_{in}\left(\vec{R}\right) \overline{\rho}_{in}\left(\vec{R} + \vec{R}'\right) \mathrm{d}R\right\} \,. \end{split}$$

If the incoming signal is white noise the last term becomes constant and can be subtracted from the power spectrum, leaving after some transformations

$$\int \int \left| \mathcal{F} \left\{ \rho \left( \vec{R} \right) - \overline{\rho}_{in} \right\} \right|^2 dS_{\varrho} dQ = \rho_{in} \mathcal{F} \left\{ \int Cov_{sz1} \left( \vec{R}, \vec{R} + \vec{R}' \right) dR \right\}$$

$$+ \sigma_{in}^2 \mathcal{F} \left\{ \int psf \left( \vec{R} \right) psf \left( \vec{R} + \vec{R}' \right) dR \right\}$$

$$= \mathcal{F} \left\{ Cov \left( \vec{0}, \vec{R}' \right) \right\}.$$
(A.13)

Again, the integral of the single spread covariance instead of the covariance itself is determined.

### A.4 Perturbation expansion for small potentials

The small angle approximation reads

$$\frac{\partial}{\partial z}\Psi(\vec{R},z) = \frac{i\left[EV + c^2\hbar^2\Delta_{\vec{R}}\right]}{2c^2\hbar^2k_{0z}}\Psi(\vec{R},z)\,. \tag{A.14}$$

The formal solution

$$\Psi(\vec{R}, z_f) = e^{i \int \frac{\left[EV + c^2 \hbar^2 \Delta_{\vec{R}}\right]}{2c^2 \hbar^2 k_{0z}} dz} \Psi(\vec{R}, z_i)$$
(A.15)

is now expanded with respect to a perturbation parameter  $\lambda$  as occurring in a series expansion of the electrostatic potential  $V = \sum_{n} \lambda^{n} V_{n}$ . The zero order term  $\Psi_{0}$  is

$$\Psi_0(\vec{R}, z_f) = e^{i \int \frac{\left[EV_0 + c^2 \hbar^2 \Delta_{\vec{R}}\right]}{2c^2 \hbar^2 k_{0z}} dz} \Psi(\vec{R}, z_i) \,. \tag{A.16}$$

The first order term is  $\Psi_1$ 

$$\Psi_{1}(\vec{R}, z_{f}) = e^{i \int \frac{\left[EV_{0} + \lambda EV_{1} + e^{2\hbar^{2}\Delta_{\vec{R}}}\right]}{2e^{2\hbar^{2}k_{0z}}} dz} \Psi(\vec{R}, z_{i})$$

$$\approx e^{i \int \frac{\lambda EV_{1}}{2e^{2\hbar^{2}k_{0z}}} dz} \Psi_{0}(\vec{R}, z_{i}).$$
(A.17)

In the last transformation the Baker-Campbell-Haussdorf formula was inserted.

# A.5 The dynamical correction factor

The dynamical correction factor  $r_{dyn}$  as defined in (3.71) approaches 1 for weak phase objects (see (3.68)). Here we demonstrate that  $r_{dyn}$  is finite and becomes independent of the integration volume  $\Omega$  in the limit  $\Omega/\Omega_{V\neq 0} \gg 1$ 

$$\begin{aligned} r_{dyn} &= \frac{\arg\left(\int_{A} e^{i\sigma \int_{L} V(\vec{R},z)dz} d^{2}R\right)}{i\frac{\sigma}{A} \int_{\Omega} V(\vec{R},z)dz} r} \\ &= \frac{\arg\left(\int_{A(V\neq 0)} e^{i\sigma \int_{L} V(\vec{R},z)dz} d^{2}R + \int_{A(V=0)} dR\right)}{i\frac{\sigma}{A} \int_{\Omega} V(\vec{R},z)dz} r} \\ &= \frac{\operatorname{atan}\left(\frac{\Im\left\{\int_{A(V\neq 0)} e^{i\sigma \int_{L} V(\vec{R},z)dz} d^{2}R\right\}}{\Re\left\{\int_{A(V\neq 0)} e^{i\sigma \int_{L} V(\vec{R},z)dz} d^{2}R\right\}} + \int_{A(V=0)} dR\right)}{\frac{\sigma}{A} \int_{\Omega} V(\vec{R},z)d^{3}r} \\ &\leq \frac{A\Im\left\{\int_{A(V\neq 0)} e^{i\sigma \int_{L} V(\vec{R},z)dz} d^{2}R\right\}}{\sigma \int_{\Omega} V(\vec{R},z)d^{3}r \left(\Re\left\{\int_{A(V\neq 0)} e^{i\sigma \int_{L} V(\vec{R},z)dz} d^{2}R\right\} + \int_{A(V=0)} dR\right)} \right)}. \end{aligned}$$
(A.18)

The last expression is now used to obtain the limes  $\Omega/\Omega_{V\neq 0} \to \infty$ , i.e.

$$\lim_{\Omega/\Omega_{V\neq0}\to\infty} r_{dyn} \le \frac{\Im\left\{\int_{A(V\neq0)} e^{i\sigma\int_t V\left(\vec{R},z\right)dz}d^2R\right\}}{\sigma\int_{\Omega(V\neq0)} V\left(\vec{R},z\right)d^3r} \,. \tag{A.19}$$

The result shows that  $r_{dyn}$  becomes independent from the integration volume, since the remaining integrals depend only on the size of  $\Omega \ (V \neq 0)$ , which is a constant value. It is furthermore important to note that the smallest integration volumes  $\Omega$  considered in this work are unit cells of crystalline materials. They have an extension in the range of several Å, hence are one order of magnitude larger than the extension of typical atomic potentials. Consequently,  $\Omega/\Omega_{V\neq 0} \gg 1$  is approximately fulfilled and the correction factors  $r_{dyn}$  calculated for single atoms become independent from the integration volume  $\Omega$  (unit cell volume) used in the calculation.

#### A.6 Thermal averaging in first order Born Approximation

The starting point of the averaging is the intensity in reciprocal space  $\overline{I}\left(\vec{k}\right)$ 

$$\overline{I}\left(\vec{k}\right) \propto \sum_{a} \sum_{a' \neq a} \int \int dr^3 dr'^3 \int \int du_a^3 du_{a'}^3 f\left(\vec{u_a}, \vec{u_{a'}}\right) p_a\left(\vec{r} - \vec{u_a}\right) p_{a'}\left(\vec{r'} - \vec{u_{a'}}\right) e^{i\vec{k}\left(\vec{r} - \vec{r'}\right)} \quad (A.20)$$

$$+ \sum_{a} \int \int dr^3 dr'^3 \int du_a^3 f\left(\vec{u_a}\right) p_a\left(\vec{r} - \vec{u_a}\right) p_a\left(\vec{r'} - \vec{u_a}\right) e^{i\vec{k}\left(\vec{r} - \vec{r'}\right)}.$$

Outside a certain correlation radius  $r_c$  around each atom a, the pair correlation function  $f(\vec{u}_a, \vec{u}_{a'})$  can be safely approximated with  $f(\vec{u}_a, \vec{u}_{a'}) = f(\vec{u}_a) f(\vec{u}_{a'})$ . The collapse of the two particle densities into single particle densities beyond the correlation radius can be used to rewrite the last equation

$$\begin{split} \overline{I}\left(\vec{k}\right) &\propto \sum_{a} \sum_{a' \neq a, d(a',a) \leq r_c} \int \int dr^3 dr'^3 \int \int du_a^3 du_{a'}^3 f\left(\vec{u_a}, \vec{u_{a'}}\right) p_a\left(\vec{r} - \vec{u_a}\right) p_{a'}\left(\vec{r'} - \vec{u_{a'}}\right) e^{i\vec{k}\left(\vec{r} - \vec{r'}\right)} (A.21) \\ &+ \sum_{a} \sum_{d(a',a) > r_c} \int \int dr^3 dr'^3 \int \int du_a^3 du_{a'}^3 f\left(\vec{u_a}\right) f\left(\vec{u_a}\right) p_a\left(\vec{r} - \vec{u_a}\right) p_{a'}\left(\vec{r'} - \vec{u_{a'}}\right) e^{i\vec{k}\left(\vec{r} - \vec{r'}\right)} \\ &+ \sum_{a} \int \int dr^3 dr'^3 \int du_a^3 f\left(\vec{u_a}\right) p_a\left(\vec{r} - \vec{u_a}\right) p_a\left(\vec{r'} - \vec{u_{a'}}\right) e^{i\vec{k}\left(\vec{r} - \vec{r'}\right)}, \end{split}$$

or equivalently

$$\overline{I}\left(\vec{k}\right) \propto \sum_{a} \sum_{a' \neq a, d(a',a) \leq r_{c}} \tilde{f}_{a,a'}\left(\vec{k},\vec{k}\right) \tilde{p}_{a}\left(\vec{k}\right) \tilde{p}_{a'}^{*}\left(\vec{k}\right) 
+ \sum_{a} \sum_{d(a',a) > r_{c}} \tilde{\bar{p}}_{a}\left(\vec{k}\right) \tilde{\bar{p}}_{a'}^{*}\left(\vec{k}\right) 
+ \sum_{a} \int du_{a}^{3} f\left(\vec{u}_{a}\right) \tilde{p}_{a}\left(\vec{k}\right) e^{i\vec{k}\vec{u}_{a}} \tilde{p}_{a}^{*}\left(\vec{k}\right) e^{-i\vec{k}\vec{u}_{a}} 
= \sum_{a} \sum_{a'} \tilde{\bar{p}}_{a}\left(\vec{k}\right) \tilde{\bar{p}}_{a'}^{*}\left(\vec{k}\right) 
+ \sum_{a} \sum_{a' \neq a, d(a',a) \leq r_{c}} \left(\tilde{f}_{a,a'}\left(\vec{k},\vec{k}\right) - \tilde{f}_{a}\left(\vec{k}\right) \tilde{f}_{a'}^{*}\left(\vec{k}\right)\right) \tilde{p}_{a}\left(\vec{k}\right) \tilde{p}_{a'}^{*}\left(\vec{k}\right) 
+ \sum_{a} \left(1 - \left|\tilde{f}_{a}\left(\vec{k}\right)\right|^{2}\right) \left|\tilde{p}_{a}\left(\vec{k}\right)\right|^{2}.$$
(A.22)

In the last transformation step, the first double sum was completed with the a = a' terms and the the a' terms beyond the correlation radius. These terms have in turn been subtracted from the second and third sum.

# A.7 Functional derivative

In the following, some definitions and rules for functional derivatives are listed. The functional derivative is defined with the help of the following linear functional

$$\delta E\left[\Psi\right] = \int \mathrm{d}y \frac{\delta E\left[\Psi\right]}{\delta \Psi\left(y\right)} \delta \Psi\left(y\right) \,, \tag{A.23}$$

which leads to the following limes

$$\frac{\delta E\left[\Psi\right]}{\delta \Psi\left(y\right)} = \lim_{\epsilon \to 0} \frac{E\left[\Psi + \epsilon \delta\left(x - y\right)\right] - E\left[\Psi\right]}{\epsilon} \tag{A.24}$$

when considering point-wise perturbations of the function. Those two definitions translate to the following derivation rules:

$$\frac{\delta\Psi(x)}{\delta\Psi(y)} = \delta(x-y) \tag{A.25}$$

$$\frac{\delta E\left(\Psi\left(x\right)\right)}{\delta\Psi\left(y\right)} = \frac{\partial E\left(\Psi\right)}{\partial\Psi\left(y\right)}\delta\left(x-y\right) \tag{A.26}$$

$$\frac{\delta E\left[\Psi\right]}{\delta \Psi\left(y\right)} = \sum_{i=1}^{N} \int \frac{\delta E\left[\Psi\right]}{\delta \Phi_{i}\left(x\right)} \frac{\delta \Phi_{i}\left(\Psi\left(x\right)\right)}{\delta \Psi\left(y\right)} dx$$

$$= \sum_{i=1}^{N} \frac{\delta E\left[\Psi\right]}{\delta \Phi_{i}\left(y\right)} \frac{\partial \Phi_{i}\left(\Psi\left(y\right)\right)}{\partial \Psi\left(y\right)}.$$
(A.27)

## A.8 Moore-Penrose Inverse and Singular Value Decomposition

3.7

The Moore-Penrose Inverse is a generalization of the usual matrix inverse, which is well defined even if the usual matrix inverse does not exist, i.e. the matrix is not regular. The Moore-Penrose inverse occurs naturally in the context of linear least-square fitting problems, where

$$|\mathbf{A}x - y| \to \min$$
 (A.28)

for a given set of parameters x and experimental data y. Equation (A.28) requires all derivatives of the left hand side with respect to each  $x_i$  to vanish independently, yielding the so-called normal equation

$$\mathbf{A}^T \mathbf{A} x = \mathbf{A}^T y \,. \tag{A.29}$$

The algebraic solution of (A.29)

$$x = \left(\mathbf{A}^T \mathbf{A}\right)^{-1} \mathbf{A}^T y = \mathbf{A}^+ y \tag{A.30}$$

defines the Moore-Penrose inverse  $\mathbf{A}^+$  with the following properties

$$\mathbf{A}\mathbf{A}^{+}\mathbf{A} = \mathbf{A}^{+}$$
$$\mathbf{A}^{+}\mathbf{A}\mathbf{A}^{+} = \mathbf{A}$$
$$(\mathbf{A}^{+}\mathbf{A})^{\dagger} = \mathbf{A}^{+}\mathbf{A}$$
$$(\mathbf{A}.31)$$
$$(\mathbf{A}\mathbf{A}^{+})^{\dagger} = \mathbf{A}\mathbf{A}^{+}.$$

The calculation of  $\mathbf{A}^+$  is very conveniently by applying the Cholesky decomposition to find  $(\mathbf{A}^T \mathbf{A})^{-1}$ , if the Hermitian normal equations matrix  $\mathbf{A}^T \mathbf{A}$  is not just positive semidefinite but positive definite. Besides treating not the general case, this solution suffers from large input error amplification, if the matrix  $\mathbf{A}^T \mathbf{A}$  is ill-conditioned, i.e. the quotient between its largest and smallest singular value  $\sigma$  is large

$$\frac{\sigma_{max}}{\sigma_{min}} \gg 1. \tag{A.32}$$

The error amplification can be suppressed by calculating  $\mathbf{A}^+$  with the help of the Singular Value Decomposition  $(\mathbf{U}, \mathbf{V} \text{ unitary}, \boldsymbol{\Sigma} \text{ diagonal})$ 

$$\mathbf{A} = \mathbf{U} \mathbf{\Sigma} \mathbf{V}^T \,, \tag{A.33}$$

i.e.

$$\mathbf{A}^{+} = \mathbf{U}^{T} \mathbf{\Sigma}^{+} \mathbf{V} \,, \tag{A.34}$$

where  $\Sigma^+$  is generated by inverting the non-zero diagonal entries of  $\Sigma$ . The non-zero diagonal elements of  $\Sigma$  are the singular values  $\sigma$  of  $\mathbf{A}$ , hence by truncating  $\Sigma$  through setting all  $\sigma$  below a certain threshold to zero, the condition number of  $\mathbf{A}$  can be reduced. The prize of this truncation is an imperfect minimization of the Euclidic distance (A.28), which can be, however, less severe than the error amplification.

# A.9 Hankel transformation and Radon Transformation

The 2D Fourier transformation in radial coordinates reads

$$\tilde{f}(k,\alpha) = \int_0^\infty \int_0^{2\pi} f(r,\varphi) \, e^{-ikr\cos(\varphi-\alpha)} r \mathrm{d}\varphi \mathrm{d}r \,. \tag{A.35}$$

If inserting the circular series expansions

$$f(r,\varphi) = \sum_{n} f_{n}(r) e^{in\varphi}$$

$$\tilde{f}(k,\alpha) = \sum_{n} \tilde{f}_{n}(k) e^{in\alpha}$$
(A.36)

and the following definition for the Bessel function

$$J_n(kr) = \frac{i^{-n}}{2\pi} \int_0^{2\pi} e^{in\varphi} e^{ikr\cos\varphi} \mathrm{d}\varphi \,, \tag{A.37}$$

one obtains

$$\sum_{n} \tilde{f}_{n}(k) e^{in\alpha} = \int_{0}^{\infty} \int_{0}^{2\pi} \sum_{n} f_{n}(r) e^{in\varphi} e^{-ikr\cos(\varphi-\alpha)} r d\varphi dr$$

$$= \sum_{n} \int_{0}^{\infty} r f_{n}(r) \int_{0}^{2\pi} e^{in\varphi} e^{-ikr\cos(\varphi-\alpha)} d\varphi dr$$

$$= 2\pi \sum_{n} i^{-n} e^{in\alpha} \int_{0}^{\infty} r f_{n}(r) J_{n}(kr) dr.$$
(A.38)

The coefficients of the circular expansion therefore must be related by the Hankel transformation pair

$$\hat{\tilde{f}}_{n}(k) = 2\pi i^{-n} \int_{0}^{\infty} r f_{n}(r) J_{n}(kr) dr$$

$$f_{n}(r) = 2\pi i^{n} \int_{0}^{\infty} k J_{n}(kr) \hat{\tilde{f}}_{n}(k) dk.$$
(A.39)

In the last formula the Fourier slice theorem from Sec. 5.4 stating that each tomographic projection corresponds to a the Fourier back-transform of a specific slice in Fourier space.

#### A.10 Double-differential cross-section

The scattering matrix for particle-particle scattering within second order QED perturbation reads (see (3.117))

$$\mathbf{S}_{fi} = e^2 \int d^4 r d^4 r' \frac{d^4 q}{(2\pi)^4} \left[ \mathbf{\Psi}_f^{\dagger}(r) \left( -i\gamma_{\mu} \right) \mathbf{\Psi}_i(r) \right] \frac{-i4\pi e^{-iq(r-r')}}{q^2 + i0} \left[ \mathbf{\Phi}_f^{\dagger}(r') \left( -i\gamma^{\mu} \right) \mathbf{\Phi}_i(r') \right].$$
(A.40)

After collecting i and splitting the integration in a spatial and time part, one obtains

$$\mathbf{S}_{fi} = ie^{2} \int d^{3}r dr^{0} d^{3}r' dr'^{0} \frac{d^{3}q dq^{0}}{(2\pi)^{4}}$$

$$(A.41)$$

$$\cdot e^{iE_{f}r^{0}} \left[ \Psi_{f}^{\dagger}(\vec{r}) \gamma_{\mu} \Psi_{i}(\vec{r}) \right] e^{-iE_{i}r^{0}} \frac{4\pi e^{i\left(\vec{q}(\vec{r}-\vec{y})-q^{0}\left(r^{0}-r'^{0}\right)\right)}}{\vec{q}^{2}-(q^{0})^{2}+i0} e^{iE_{f}'r'^{0}} \left[ \Phi_{f}^{\dagger}(\vec{r}') \gamma^{\mu} \Phi_{i}(\vec{r}') \right] e^{-iE_{i}'r'^{0}}.$$

Now the  $x_0, y_0$  and  $q_0$  integration is performed by using (3.3) and the energy difference  $\Delta E = E'_f - E'_i$  is introduced yielding

$$\mathbf{S}_{fi} = ie^2 \int d^3r d^3r' \frac{d^3q}{(2\pi)^2} \left[ \mathbf{\Psi}_f^{\dagger}(\vec{r}) \gamma_{\mu} \mathbf{\Psi}_i(\vec{r}) \right] \frac{4\pi e^{i\vec{q}(\vec{r}-\vec{r}')}}{\vec{q}^2 - E^2} \left[ \mathbf{\Phi}_f^{\dagger}(r') \gamma^{\mu} \mathbf{\Phi}_i(r') \right] \delta\left( E_i - E_f - \Delta E \right) .$$
(A.42)

Since spin orbit coupling of the beam electron is negligible (see section 3.2), the beam electron wave function can be separated in a constant spinor and a spatial dependent scalar, i.e., inserting

$$\Psi_{f,i} \quad (\vec{x}) = \quad \mathbf{u}_{f,i} \Psi_{f,i} \left( \vec{r} \right) \tag{A.43}$$

into (A.42) gives

$$\mathbf{S}_{fi} = i \sqrt{\frac{m_0^2}{E_f E_i}} e^2 \left[ \overline{\mathbf{u}}_f \gamma_\mu \mathbf{u}_i \right] \int \mathrm{d}^3 r \mathrm{d}^3 y \frac{\mathrm{d}^3 q}{(2\pi)^2} \Psi_f^* \left( \vec{r} \right) \Psi_i \left( \vec{r} \right) \frac{4\pi e^{i\vec{q}\left( \vec{r} - \vec{r}' \right)}}{\vec{q}^2 - E^2} \left[ \mathbf{\Phi}_f^\dagger \left( \vec{r}' \right) \gamma^\mu \mathbf{\Phi}_i \left( \vec{r}' \right) \right] \delta \left( E_i - E_f - \Delta E \right)$$
(A.44)

The spatial dependent scalar  $\Psi_{f,i}$  can be written as a sum of Bloch waves

$$\Psi\left(\vec{r}\right) = \sum_{\vec{k}} \tilde{\Psi}\left(\vec{k}\right) e^{i\vec{k}\vec{r}} = \sum_{j} \epsilon_{j} e^{i\vec{\gamma}_{j}\vec{r}} \sum_{\vec{g}} \tilde{\Psi}_{j}\left(\vec{g}\right) e^{i\vec{g}\vec{r}}, \qquad (A.45)$$

which leads to

$$\mathbf{S}_{fi} = -i\sqrt{\frac{m_0^2}{E_f E_i}}e^2\delta\left(E_i - E_f - \Delta E\right)$$

$$\cdot \left[\overline{\mathbf{u}}_f \gamma_{\mu} \mathbf{u}_i\right] \int d^3r d^3r' \frac{d^3q}{(2\pi)^2} \sum_{\vec{k}, \vec{k}'} \Psi_f^*\left(\vec{k}'\right) \Psi_i\left(\vec{k}\right) e^{i\left(\vec{k} - \vec{k}' + \vec{q}\right)\vec{r}} \frac{4\pi e^{-i\vec{q}\vec{y}}}{\vec{q}^2 - E^2} \left[\Phi_f^{\dagger}\left(\vec{r}'\right)\gamma^{\mu}\Phi_i\left(\vec{r}'\right)\right]$$
(A.46)

Now, the spatial  $\vec{x}$ -integration yields again a  $\delta$ -expression

$$\mathbf{S}_{fi} = 2i\sqrt{\frac{m_0^2}{E_f E_i}}e^2 (2\pi)^2 \,\delta\left(E_i - E_f - \Delta E\right) \tag{A.47}$$

$$\cdot \left[\overline{\mathbf{u}}_f \gamma_\mu \mathbf{u}_i\right] \int \mathrm{d}^3 q \frac{1}{\vec{q}^2 - \Delta E^2} \sum_{\vec{k}, \vec{k}'} \Psi_f^*\left(\vec{k}'\right) \Psi_i\left(\vec{k}\right) \delta\left(\vec{k} - \vec{k}' + \vec{q}\right) \int d^3 r' \left[\mathbf{\Phi}_f^{\dagger}\left(\vec{r}'\right) e^{-i\vec{q}\vec{r}'} \gamma^{\mu} \mathbf{\Phi}_i\left(\vec{r}'\right)\right],$$

which reduces the spatial  $\vec{q}$ -integration to

$$\mathbf{S}_{fi} = 2i \sqrt{\frac{m_0^2}{E_f E_i}} e^2 (2\pi)^2 \,\delta \left(E_i - E_f - \Delta E\right) \\ \cdot \left[\overline{\mathbf{u}}_f \gamma_\mu \mathbf{u}_i\right] \sum_{\vec{k}, \vec{k}'} \frac{1}{\left(\vec{k}' - \vec{k}\right)^2 - \Delta E^2} \Psi_f^* \left(\vec{k}'\right) \Psi_i \left(\vec{k}\right) \int d^3 r' \left[ \Phi_f^{\dagger} \left(\vec{r}'\right) e^{-i\left(\vec{k}' - \vec{k}\right)\vec{r}'} \gamma^\mu \Phi_i \left(\vec{r}'\right) \right] \delta \left(E_i - E_f - \Delta E\right)$$

When using the Bloch wave decomposition instead of the Fourier series expansion, one obtains

$$\mathbf{S}_{fi} = 2i\sqrt{\frac{m_0^2}{E_f E_i}}e^2 (2\pi)^2 \,\delta \left(E_i - E_f - \Delta E\right) \left[\overline{\mathbf{u}}_f \gamma_\mu \mathbf{u}_i\right]$$

$$\cdot \sum_{j,j'} \epsilon_j \epsilon_{j'} \sum_{\vec{g},\vec{g}'} \frac{1}{\left(\vec{g}' - \vec{g} + \vec{\gamma}_j - \vec{\gamma}_{j'}\right)^2 - \Delta E^2} \Psi_{f,j}^* \left(\vec{g}\right) \Psi_{i,j'} \left(\vec{g}'\right) \int d^3y \left[\mathbf{\Phi}_f^{\dagger} \left(\vec{r}'\right) e^{-i\left(\vec{g}' - \vec{g} + \vec{\gamma}_j - \vec{\gamma}_{j'}\right)\vec{r}'} \gamma^\mu \Phi_i \left(\vec{r}'\right)\right]$$
(A.48)

The matrix element can be further simplified if the specimen wave function can be separated in the same manner like the beam wave function, i.e.

$$\mathbf{\Phi}_{f,i} = \mathbf{u}_{f,i}' \Phi_{f,i} \tag{A.49}$$

This holds, unfortunately, not generally, as spin-orbit coupling can be significant in magnetic materials and the spatial dependence of the small part of the spinor  $\Phi_i$  can differ from the big part in heavy materials. The scattering matrix now reads

$$\mathbf{S}_{fi} = 2i\sqrt{\frac{m_0^2}{E_f E_i}}e^2 (2\pi)^2 \,\delta \left(E_i - E_f - \Delta E\right) \left[\overline{\mathbf{u}}_f \gamma_\mu \mathbf{u}_i\right] \left[\overline{\mathbf{u}}_f' \gamma^\mu \mathbf{u}_i'\right]$$

$$\cdot \sum_{j,j'} \epsilon_j \epsilon_{j'} \sum_{\vec{g},\vec{g}'} \frac{1}{\left(\vec{g}' - \vec{g} + \vec{\gamma}_j - \vec{\gamma}_{j'}\right)^2 - E^2} \Psi_{f,j}^* \left(\vec{g}\right) \Psi_{i,j'} \left(\vec{g}'\right) \int d^3y \left[\Phi_f^* \left(\vec{r}'\right) e^{-i\left(\vec{g}' - \vec{g} + \vec{\gamma}_j - \vec{\gamma}_{j'}\right)\vec{r}'} \Phi_i \left(\vec{r}'\right)\right] \,.$$
(A.50)

After having derived the fully relativistic matrix elements, a short overview on the connections of the standard non-relativistic formalism via the scalar relativistic one is given. The scalar relativistic electronelectron scattering matrix element, which incorporates vector potential coupling and retardation but neglects the electron spin, reads

$$\mathbf{S}_{fi} = e^2 \int \mathrm{d}^4 r \mathrm{d}^4 r' \Psi_f^*(r) \overleftrightarrow{\partial}_{\mu} \Psi_i(r) \left( i \mathbf{D}_F(r-r') \right) \Phi_f^*(r') \overleftrightarrow{\partial}^{\mu} \Phi_i(r') , \qquad (A.51)$$

with

$$\Psi_{f}^{*}(r)\overleftrightarrow{\partial}_{\mu}\Psi_{i}(r) = \Psi_{f}^{*}(r)\partial_{\mu}\Psi_{i}(r) - \Psi_{f}(r)\partial_{\mu}\Psi_{f}(r) .$$
(A.52)

Inserting the Fourier transform of the photon propagator, (A.51) reads

$$\mathbf{S}_{fi} = e^2 \int \mathrm{d}^4 r \mathrm{d}^4 r' \frac{\mathrm{d}^4 q}{\left(2\pi\right)^4} \Psi_f^*\left(r\right) \overleftrightarrow{\partial}_{\mu} \Psi_i\left(r\right) \frac{-i4\pi e^{-iq\left(r-r'\right)}}{q^2 + i0} \Phi_f^*\left(r'\right) \overleftrightarrow{\partial}^{\mu} \Phi_i\left(r'\right) \,. \tag{A.53}$$

Introducing plane waves  $\Psi$  and carrying out the x and q integration, one gets

$$\mathbf{S}_{fi} = 2ie^2 \int d^4y \frac{-i4\pi e^{i(p_{f,\mu}-p_{i,\mu})r'}}{(p_{f,\mu}-p_{i,\mu})^2 + i0} \Phi_f^*(r') (p_{f,\mu}+p_{i,\mu}) \overleftrightarrow{\partial}^{\mu} \Phi_i(r') .$$
(A.54)

By approximating the derivatives  $p_{f,\mu} = p_{i,\mu} = (E_{\Psi}, \vec{p}) \Psi_i$ ,  $\partial_{\mu} \Phi_f = \partial_{\mu} \Phi_i = (E_{\Phi}, \partial_m) \Phi_i$ , one ends up with an expression very similar to those in Schattschneider et al. (2005), which resolved the magic angle problem

$$\mathbf{S}_{fi} = 2ie^2 \int d^4y \frac{-i4\pi e^{i(p_{f,\mu}-p_{i,\mu})r'}}{(p_{f,\mu}-p_{i,\mu})^2 + i0} \Phi_f^*(r') \left(E_{\Psi}E_{\Phi} - p^m\partial_m\right) \Phi_i(r') .$$
(A.55)

This result indicates that both the retardation of the potential as well as the incorporation of vector potential exchange play an important role in electron-electron scattering.

# A.11 Cross section, form factor and mixed dynamic form factor

The cross section  $\sigma$  is defined as the quotient of the rate R of scattering events per time and the incoming particle flux  $j_i$  measured in the laboratory frame, i.e.

$$\sigma = \frac{R}{j_i} \,. \tag{A.56}$$

A TEM equipped with some sort of energy filter allows a differentiation between energy loss and scattering solid angle  $\Omega$  reflected by the so-called double-differential cross section defined as

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} = \frac{\partial^2 R}{j_i \partial E \partial \Omega} \,. \tag{A.57}$$

The incident current density  $j_i$  can be expressed by the initial electron velocity  $\vec{v}_i$  and the infinitesimal volume dV

$$j_i = \frac{1}{\mathrm{d}V} \left| \vec{v}_i \right| \,. \tag{A.58}$$

The transition rate R, on the other hand, is given the sum of the probability  $|\mathbf{S}_{fi}|^2$  of a transition from the initial state i to the final state f over the number of the respective final states, i.e.

$$R = \sum_{f} \left| \mathbf{S}_{fi} \right|^2 \,. \tag{A.59}$$

 $\mathbf{S}_{fi}$  is the scattering matrix, which is characteristic for a particular scattering event. Finally, by combining (A.59), (A.58) and (A.56) or (A.57), one obtains the following expression for the cross section

$$\sigma = \frac{1}{j_i} \sum_{f} |\mathbf{S}_{fi}|^2 \tag{A.60}$$

and the double-differential cross-section

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} = \frac{\mathrm{d} \left( \sum_f |\mathbf{S}_{fi}|^2 \right)}{j_i \mathrm{d} E \mathrm{d} \Omega} \,. \tag{A.61}$$

$$\left|\mathbf{S}_{fi}\right|^{2} \propto \mathrm{DFF}_{\mu,\nu}\left(\vec{q}\right) \stackrel{\vec{q}=\vec{g}'-\vec{g}+\vec{\gamma}_{j}-\vec{\gamma}_{j'}}{=} \mathrm{MDFF}_{\mu,\nu}\left(\vec{q},\vec{q}\right).$$
(A.62)

The MDFF can be reformulated in the following way

$$MDFF = \left\langle \Phi_{f}^{*}(\vec{r}') e^{-i\left(\vec{g}' - \vec{g} + \vec{\gamma}_{j} - \vec{\gamma}_{j'}\right)\vec{r}'} \Phi_{i}(\vec{r}') \right\rangle \left\langle \Phi_{f}^{*}(\vec{r}') e^{-i\left(\vec{h}' - \vec{h} + \vec{\gamma}_{l} - \vec{\gamma}_{l'}\right)\vec{r}'} \Phi_{i}(\vec{r}') \right\rangle^{*} .$$
(A.63)

The summation of all possible final states m can be further simplified by noting, that

$$\sum_{m} \text{MDFF} = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} dt e^{-i\Delta E/\hbar t} \left\langle \rho\left(\vec{q}\right) \rho\left(-\vec{q'},t\right) \right\rangle \,. \tag{A.64}$$

This relationship between the MDFF and the density-density correlation function is very useful for it replaces the cumbersome sum on the left hand side of the last formula with a calculation of a two-particle Greens function or generalized susceptibility, which is related to the density-density correlation through the spectral theorem

$$\int_{-\infty}^{\infty} \mathrm{d}t e^{-i\Delta E/\hbar t} \left\langle \rho\left(\vec{q}\right)\rho\left(-\vec{q}',t\right)\right\rangle = \frac{2\pi}{\hbar} Im\chi\left(\vec{q},\vec{q}',\Delta E\right) \,. \tag{A.65}$$

It is furthermore important to note that trace of this susceptibility can be expressed by the complex dielectric function, i.e.

$$\epsilon\left(\vec{q},E\right) = 1 + \frac{4\pi}{Vq^2}\chi\left(\vec{q},\Delta E\right) \,. \tag{A.66}$$

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